

Solvent Extraction of Mn(II), Ni(II) and Zn(II) by Cyanex 272: Equilibrium and Kinetic Studies



A Dissertation

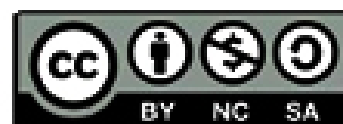
*Submitted to the University of Rajshahi, Bangladesh in Partial
Fulfillment of the Requirements for the Degree of Doctor of Philosophy
in Applied Chemistry & Chemical Engineering*

MD. SAIDUR RAHMAN

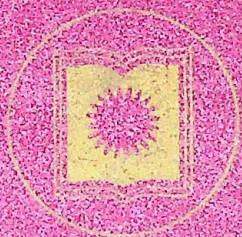
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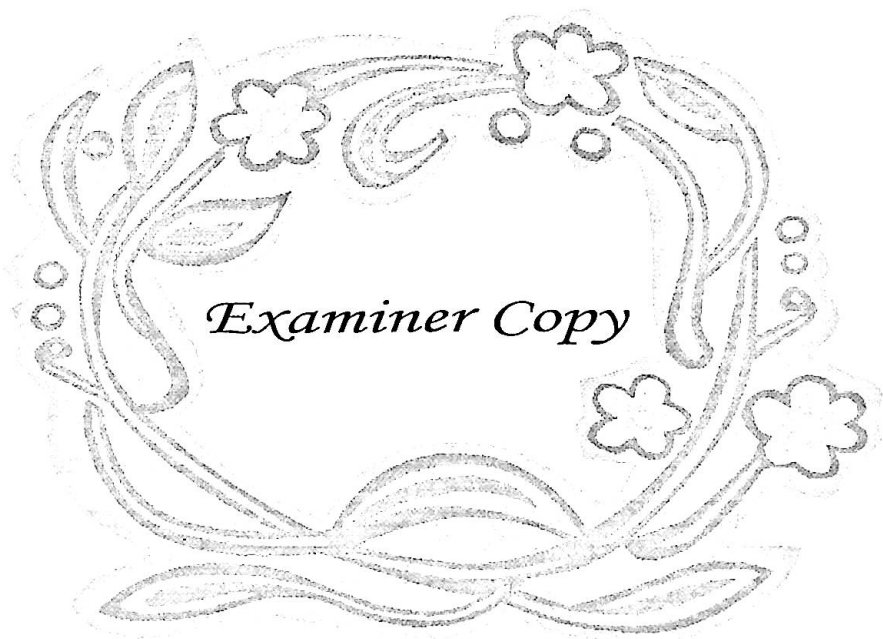
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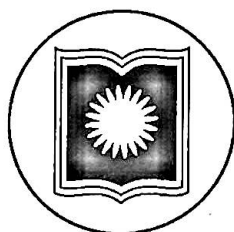
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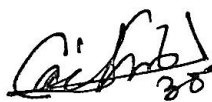
My Beloved Wife

Salma Akhter/luna



DECLARATION CERTIFICATE

I hereby declare that the entire thesis is made on the basis of my own insight and investigation and this thesis has not been submitted or placed anywhere for any award or degree or any profitable purpose.



28.06.2010

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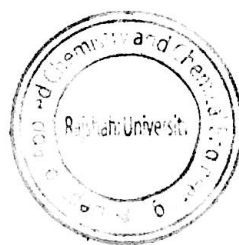
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DECLARATION CERTIFICATE

The undersigned certifies that all the research works presented in this dissertation are the original work of **Md. Saidur Rahman**, B. Sc. (Hons), M. Sc. who carried out his laboratory works in this Department. No part of this work has been used before by any body for other degree.

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30.6.10

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ABSTRACT

The solvent extraction systems: $\text{Mn(II)}\text{-SO}_4^{2-}\text{-Ac}^-$ - Cyanex 272-kerosene, $\text{Ni(II)}\text{-SO}_4^{2-}\text{-Ac}^-$ - Cyanex 272-kerosene and $\text{Zn(II)}\text{-SO}_4^{2-}$ - Cyanex 272-kerosene have been thoroughly investigated from equilibrium and kinetic point of views. From the dependence of extraction ratio (at constant equilibrium values of other parameters) on various parametric concentrations, the equations for extraction ratios have been derived at 303 K as:

$$\log {}^cD_{\text{Mn}} = -6.17 + 2 \text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 1.9 [\text{SO}_4^{2-}])$$

$$\log {}^cD_{\text{Ni}} = -11.16 + 2 \text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 6.92 [\text{SO}_4^{2-}]) - \log [\text{Ac}^-]; \text{ at } [\text{H}_2\text{A}_2]_{(\text{o,eq})} < 0.05 \text{ kmol/m}^3$$

$$\log {}^cD_{\text{Ni}} = -11.56 + 2 \text{pH}_{(\text{eq})} + 3 \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 6.92 [\text{SO}_4^{2-}]) - \log [\text{Ac}^-]; \text{ at } [\text{H}_2\text{A}_2]_{(\text{o,eq})} > 0.10 \text{ kmol/m}^3$$

$$\log {}^cD_{\text{Zn}} = -3.11 + 2 \text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 2 [\text{SO}_4^{2-}]); \text{ at } [\text{H}_2\text{A}_2]_{(\text{o,eq})} < 0.05 \text{ kmol/m}^3$$

$$\log {}^cD_{\text{Zn}} = -2.08 + 2 \text{pH}_{(\text{eq})} + 2 \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 2 [\text{SO}_4^{2-}]); \text{ at } [\text{H}_2\text{A}_2]_{(\text{o,eq})} > 0.10 \text{ kmol/m}^3$$

where, the first terms on the right hand sides represent the logarithmic values of extraction equilibrium constants (K_{ex}). The equilibrium extraction reactions in low concentration regions of extractant are suggested as $\text{M(II)} + \text{H}_2\text{A}_{2(\text{o})} \rightleftharpoons [\text{MA}_2]_{(\text{o})} + 2 \text{H}^+$; but disolvated and monosolvated species are extracted in the cases of Ni(II) and Zn(II), respectively, at high concentration regions of Cyanex 272 (H_2A_2). The extraction processes are found to be endothermic. The maximum loading capacities of the extractant are found to be 9.52 g Mn(II), 21.28 g Ni(II) and 11.5 g Zn(II) per 100 g extractant. The extracted species are strippable by dilute H_2SO_4 , HNO_3 and HCl solutions.

In kinetics of forward extractions of the selected divalent metal ions by Cyanex 272, the rates have been measured the single falling drop technique at various extraction parametric concentrations in order to determine the orders of reaction with respect to various concentration terms and also to evaluate the $\log k_f$ values. Rates have measured at various temperatures to determine E_a , $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values at various parametric conditions for all systems under consideration. The rates of forward extractions of Mn(II), Ni(II) and Zn(II) at 303 K can be expressed respectively as:

$$\log F_f = -3.6 + \log [\text{Mn(II)}] + 0.5 \log [\text{H}_2\text{A}_2]_{(\text{o})} - \log (1 + 10^{4.5} [\text{H}^+]) - \log (1 + 1.58 [\text{SO}_4^{2-}])$$

$$\log F_f = -3.7 + \log [\text{Ni(II)}] + 0.5 \log [\text{H}_2\text{A}_2]_{(\text{o})} - \log (1 + 10^{6.35} [\text{H}^+]) - \log (1 + 6.3 [\text{SO}_4^{2-}]) - \log (1 + 0.55 [\text{Ac}^-])$$

$$\log F_f = -8.4 + \log [\text{Zn(II)}] - \log [\text{H}^+]_{(\text{int})} + 0.5 \log [\text{H}_2\text{A}_2]_{(\text{o})} + \log (1 + 1.07 [\text{H}_2\text{A}_2]_{(\text{o})}^{1/2})$$

where, F_f represents flux of metal transfer from one phase to another and defined as rate per unit interfacial area. From the rate equations, the mechanisms of extractions are given.

Invariably in all cases under investigation, the attachment of the first monomeric anion of the extractant (A^-) to the metal ion is the rate controlling ($M^{2+} + A^- \xrightarrow{\text{slow}} [MA]^+$); which has been supported by high activation energy (>48 kJ/mol). However, in certain parametric conditions diffusions rather the chemical reaction stated become rate controlling, which is supported by low activation energy. In case of Ni(II) extraction, at high concentration region of extractant, the reaction: $Ni^{2+} + HA_2_{(int)}^- \rightarrow [NiHA_2]$ becomes rate controlling. The highly negative $\Delta S^\ddagger$ values in all cases suggest the chemical rate determining step occurs via S_N2 mechanism.

The kinetics of stripping of metal ions from highly metal ion loaded organic phases by sulphuric acid solutions have been investigated by the single falling drop technique to derive respective stripping rate equations at 303 K. The stripping rate equations derived for stripping of Mn(II), Ni(II) and Zn(II), respectively, are:

$$\log F_b = -4.88 + \log [MnA_2]_{(o)} - 0.5 \log (1 + 0.002 [H^+]^{-1}) + \log (1 + 5.129 [SO_4^{2-}])$$

$$\log F_b = -4.35 + \log [Ni-H_2A_2 \text{ complex}]_{(o)} - \log (1 + 10^{-3.42} [H^+]^{-1}) - \log ([H_2A_2]_{(o)}^{1/2} + 2.5 [H_2A_2]_{(o)}) + \log (1 + 6 [SO_4^{2-}]) + \log (1 + 3.2 [Ac^-])$$

$$\log F_b = -5.24 + \log [Zn-H_2A_2 \text{ complex}]_{(o)} + \log [H^+] - 0.5 \log [H_2A_2]_{(o)} + \log (1 + 1.5 \log [SO_4^{2-}])$$

The rate equations have been analyzed to give stripping mechanisms. It is found that the dissociation of second anion ligand from $[MA_2]_{(o)}$ is rate determining which occurs in the bulk aqueous phase ($MA^+ \xrightarrow{\text{slow}} M^{2+} + A^-$), which is, supported by high E_a values. This mechanism is valid for Mn(II) and Zn(II) covering all concentration region of free extractant in the organic phase; and also for Ni(II) in low concentration region of extractant, but at its high concentration region, the dissociation of dimeric anion (HA_2^-) from $[Ni(HA_2)_2 \cdot H_2A_2]_{(o)}$ appears as rate determining. However, low E_a value suggests this step occurs via S_N2 mechanism.

The extraction equilibrium constants (K_{ex}) for Mn(II) and Zn(II) derived from equilibrium studies are matchable to those from respective kinetic studies ($K_{ex} = k_f/k_b$). But in the case of Ni(II), a deviation by a factor of 10 is obtained, which may be attributed to the loss buffer action resulting the change of interfacial pH. The possibilities of separations of the metal ions under consideration from their mixtures by Cyanex 272 have been theoretically evaluated and it has been shown that the mutual almost complete separation of this metal ion by single or by at least two stage extractions by Cyanex 272 solution in kerosene is possible.

CHAPTER I

INTRODUCTION

a) Solvent extraction:

Solvent Extraction is a unit operation (process!) used in hydrometallurgy for the separation, purification and recovery of metals from solutions. In general, the extraction is a term in which a soluble constituent, present either as a solid or liquid in a solid or liquid medium is removed by the use of a solvent. The solvent is no longer limited to water. When the solute constituent (either solid or liquid) present in a liquid medium is removed by the use of a solvent, then the term applied is liquid-liquid extraction (commonly termed as solvent extraction in hydrometallurgy). Thus the solvent extraction in hydrometallurgy is a technique in which a solution (generally an aqueous phase containing metal ions) is brought into contact with a second solvent (usually an organic phase containing an extractant) essentially immiscible with the first, in order to bring about a transfer of one or more solutes (metal ions) into the second solvent.

The extractant reacts preferentially with a metal ion to form an organic-metal complex, ion pair or solvated ion pair soluble in the organic phase. Impurities normally do not react with the extractant and remain in the aqueous phase. The organic phase containing the metallic species separated from the aqueous phase is stripped to recover by an acidic or basic aqueous phase on reversing the chemical reaction. Solvent extraction was first applied to the high value metals such as uranium, thorium etc but now due to availability of new extractants with improved selectivity, faster kinetics and phase disengagement times, and recent developments in efficient equipment with less area and reagent inventory, the technology is now applicable to many low value metals. Separation depends solely on selectivity of the extractant used towards the metal ions existing in the aqueous solution (usually leached solution).

The distribution of which takes part during equilibration is called distribuend. The solvent is capable of dissolving the distribuend to some extent. The extractant and diluent together act as a solvent. Sometimes a higher liquid alcohol ($C_6 - C_{12}$, known as modifier) is used up to 5% to constitute a solvent to facilitate phase separation. An extractant is a substance, which is either a liquid or a solid when pure, and is used as a solution. The extractant reacts with the distribuend through solvation, chelation, ion-pairing,

ion-exchange etc. to extract it from the aqueous phase. A suitable diluent is used to dissolve the extractant and improve its physical properties. The diluent has no extraction capability.

Peligot [1] was the first person to observe that the organic solvents can extract metal ions (uranyl nitrate can be extracted by diethyl ether) and proposed to use this property for separating uranium from other constituents of pitchblende. Another example is the extraction of iron(III) from hydrochloric acid solution with diethyl ether [2, 3]. Nevertheless, the wide spread application of the solvent extraction technique has been started since the start of the Second World War for the production of uranium, thorium, lanthanides and actinides of high purity from their respective lean ores; whilst. The equipments such as mixer-settlers [4], baffle-cup plate tower [5], sieve-plate tower [6], spray tower [7] etc used industrially to carry out the technique have been developed in early sixties of the last century. But stoppered separatory funnels or reagent bottles of handy sizes are always used in the laboratory scale.

On the other hand, the following techniques or cells have been used to study the solvent extraction kinetics:

- i) Shake out method [8-14]
- ii) The static constant interfacial area cell: Hahn cell [15-18]
- iii) The stirred constant interfacial area cell: Lewis cell [16,17,19-22]
- iv) The stirred tank: AKUFVE apparatus [23, 24]
- v) The laminar jet [25]
- vi) The rotating diffusion cell: RDC [26-30]
- vii) The single drop technique: rising and falling [31-37]

Every technique exhibits different hydrodynamics relating to the metal transfer from one phase to another. Furthermore, the above-listed techniques except the RDC have many demerits in rate determinations, such as:

- i) Relatively very high time consumption for the rate determination in the static constant interfacial area (Hahn) cell,
- ii) An imperfect interface in the stirred constant interfacial area (Lewis) cell,
- iii) Fully unknown interfacial area in the stirred (AKUFVE) tank and shake-out technique,
- iv) Very short time of contact in the laminar jet and

- v) Unknown hydrodynamics in single drop apparatus owing to the internal circulation and the presence of oscillations and wakes [38].

b) The theoretical principles of solvent extraction

The theoretical principles of solvent extraction involving chelation have been outlined by Calvin [39]. If the overall reaction involved in transfer of a metal ion (M^{n+}) from the aqueous to organic phase by an acidic extractant ($\overline{HA}$) is represented by



where, M^{n+} = metal ion of oxidation state 'n' in the aqueous phase, $\overline{HA}$ = organic chelating acid and species under bars represent organic species; then, the equilibrium constant, K_{ex} for M^{n+} extraction with $\overline{HA}$ may be defined as follows:

$$K_{ex} = \frac{[\overline{MA_n}] [H^+]^n}{[M^{n+}] [\overline{HA}]^n} = \frac{D_M^o [H^+]^n}{[\overline{HA}]^n} \quad (2)$$

where, D_M^o represents the distribution or extraction ratio of the metal ion (ratio of concentration of metal ion in the organic phase to that in the aqueous phase). Thus, for any given, $M^{n+}/\overline{HA}$ system, the distribution ratio is given by:

$$D_M^o = \frac{K_{ex} [\overline{HA}]^n}{[H^+]^n} \quad (3)$$

Since the value of K_{ex} is different for different metal ions [40], it is clear how such a system may be used for the separation of metal ions.

The Eq. (2) is valid for the extraction of non-hydrolyzed metal ions. Kolthoff and Sandell [41] have described a modified form of the equation for distribution ratio taking into account the hydrolysis of the metal ion in the aqueous phase. If hydrolysis occurs, it is seen that the dependence of distribution ratio on $[\overline{HA}]$ is not affected but the exponent of $[H^+]$ in Eq. (3) is decreased and in the extreme case involving the complete hydrolyzed metal ion, D_M^o is independent of pH. Thus, when hydrolysis occurs, Eq. (3) should be rewritten as:

$$D_M^o = \frac{K_{ex} [\overline{HA}]^n}{[H^+]^m} \quad (4)$$

where, $n - m$ = number of hydroxyl group attached to the metal ion in the aqueous phase prior to extraction. The approximate equation developed above for the distribution ratio, D_M^o for the solvent extraction of a metal chelate, offers a valuable method for studying the composition of the chelate, the nature of the metal ion in solution and then the overall extraction equilibrium reaction i.e., mechanism.

The method of solvent extraction has also been applied in the study of hydrolysis of the metal ion and in the determination of the stability constant of various species present in the system.

c) Application of solvent extraction

Solvent extraction is now well established in hydrometallurgy. The following few paragraphs narrate some of the established applications of solvent extraction processes:

- i) The American Potash and Chemical Corporation have developed a process for boron recovery from lake water using solvent extraction by polyols [42].
- ii) The extraction of cesium from radioactive reactor waste solution by a substituted phenol has been developed by Oak Ridge National Laboratory (ORNL, USA) [43].
- iii) The extraction of copper in commercial scale is done at Blue Bird Randers Company in Miami, Arizona using the extractant LIX 64 N [44].
- iv) Gold and silver leached by cyanide solution containing $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$, are industrially extracted by amines, e. g., tri-octylamine [45].
- v) Cobalt has been recovered since 1979 in South Africa by extraction with di(2-ethylhexyl)phosphoric acid (D2EHPA) from the electrolyte of a Nickel refinery [46]. Nippon Mining in Japan has implemented this process in a commercial plant, but there the extractant is mono-(2-ethylhexyl)2-ethylhexyl phosphonic acid (EHEHPA) because of its higher separation factor [47]. Very recently, Cyanex 272 has been used in commercial scales.
- vi) D2EHPA is also used commercially in the USA for beryllium recovery from a beryllium ore leach solution and for the extraction of gallium. In addition, it is employed in the separation of rare earths in the USA, Norway, Japan, Canada and China [48]. Yttrium and rare earths recovery plants are being operated in Japan, Canada, Norway and France [49].

- vii) Indium is recovered in Japan using D2EHPA and tributylphosphate (TBP) as extractants [50]. Molybdenum is recovered in Finland from a copper shaft furnace residue by solvent extraction using D2EHPA as extractant and 1-dodecanol as phase modifier [51]. D2EHPA has been used in the USA to purify crude strontium-90.
- viii) Uranium is recovered from wet process phosphoric acid using D2EHPA - tri-(n-octyl) phosphine oxide (TOPO) mixed extractant [52]. Plants are currently operating in the USA, Sweden and reportedly also in Iraq [47, 53]. D2EHPA is also used to recover uranium from tailings from a copper refinery in the USA. D2EHPA has also been used with dibutyl butyl phosphonate (DBBP) as coextractant in the recovery of uranium from wet process phosphoric acid in Taiwan [51]. D2EHPA - tributyl phosphate (TBP) mixed extractant has been used in the commercial recovery of uranium from its ore (DAPEX process); where vanadium is recovered as a by-product [54].
- ix) Plants in Portugal and Spain use D2EHPA in the second cycle of a zinc recovery process [55]. A company in Japan removes zinc with D2EHPA prior to separating cobalt and nickel. D2EHPA has also been used in the recovery of zinc from the effluent of a rayon plant in Sweden and spent galvanizing baths in South Africa [56].
- x) Iron has been separated from a cobalt and nickel-containing stream in a US plant by extraction with D2EHPA [57]. The US Bureau of Mines has proposed similar iron removal technique during cobalt recovery from copper leach solutions [58]. Nihon Solex in Japan has developed a process involving D2EHPA extraction – $\text{NH}_4\text{OH}/\text{HF}$ stripping to recover a high purity iron from waste acids of steel pickling with an aim to recover acid. A plant in Japan uses this technology [59].
- xi) Suphuric acid leach solution of monazite sand contains rare earths, thorium and uranium. The Eldorado Mining and Refining Company at Port Hope, Ontario has developed a process for separation of these metals by selective extraction on varying pH, adding complexing agent and choosing selective extractant. Another example is the treatment of a concentrate consisting mainly of fine hydroxides of uranium, copper, cobalt and nickel. After being leached the solid with dilute H_2SO_4 ; uranium is first extracted by a tertiary amine and then copper by a mixer

of LIX63 and D2EHPA. Finally, after pH adjustment cobalt is extracted, while the nickel remaining in solution is recovered by precipitation. Besides this, separation of copper-nickel, hafnium-zirconium, niobium-tantalum, plutonium-uranium-fission products, scandium-uranium, vanadium, Fe(III)-Cr(III)- Mn(II)-Ti(IV) etc. can be carried out by solvent extraction [60-66].

d) Extractants

The classification of extractant can be done in a wide variety of ways considering both the extraction mechanism and the physico-chemical properties of the extractant. Consequently, various classifications have been proposed and they are described in very great detail in specialized textbooks dealing with the thermodynamics of solvent extraction [67, 68]. Such classifications inevitably are arbitrary to a certain degree since they require a schematization of the extraction mechanism (solvation, chelation, ion-exchange etc.) and of the properties of the extracting reagent (basic, acidic, ionic and inert etc.). In fact, the macroscopic physico-chemical properties of extractants do vary continuously and often can be looked upon simultaneously from different points of view. Thus any newly chosen criterion of classification cannot be expected to further clarify the situation, even if the kinetic behavior, instead of the equilibrium properties, is considered. Therefore, in order not to add further confusion to the matter, it is better to adopt an already established classification scheme of the extractant reagents. This scheme is based on the functional group present. According to this classification scheme, the extracting reagents will be divided into three classes:

- i) Acidic extractants,
- ii) Basic extractants and
- iii) Neutral extractants.

i) Acidic extractants

These are organic reagents characterized by the presence of a donor group having a dissociating proton such as, the phenolic or enolic hydroxyl group (-OH), carboxylic group (-COOH), phosphoric acid group ($R_2O_2 PO(OH)$), phosphorus acid group ($R, RO=P(OH)$) or phosphinic acid group ($-R_2PO(OH)$) etc. The dissociation of this group forms a conjugate base by the release of a proton H^+ . This can be facilitated by the replacement with a positively charged metal ion initially present in the aqueous phase. Of course a sufficient number of anionic species must combine with the metal cation to form uncharged species

wherever necessary. In addition to the acidic group, acidic extractants may possess another donor group which does not contain a dissociating proton. These second types of donor groups may be, for example, $-C=O$, $-P=O$ etc. Some acidic extractants are listed below:

- i) Stearic acid,
- ii) Naphthenic acid,
- iii) Di (2-ethylhexyl) phosphoric acid (D2EHPA, DAPA),
- iv) Dodecylphosphoric acid (DDPA),
- v) Octylpyro-phosphoric acid (OPPA),
- vi) Dialkylphosphinic acid (Cyanex 272),
- vii) Dialkyl thiophosphinic acid (Cyanex 302),
- viii) Dialkyl dithiophosphinic acid (Cyanex 301),
- ix) polyol,
- x) o-phenyl phenol,
- xi) 8-hydroxyquinoline (oxine) and its derivatives,
- xii) β -diketones (acetylacetone, benzyleacetone, thenoyltrifluoroacetone, hexafluoroacetylacetone etc),
- xiii) Hydroxyoximes (LIX-reagents)
- xiv) Ethyl hexyl phosphonic acid monoethylhexyl ester (HEHEHP, PC 88A).

ii) Basic extractants

These are organic reagents, which can easily form a salt when in contact with an aqueous acid solution. The only basic extractants studied in some detail from the point of view of the equilibrium and kinetics of extraction are high molecular weight amines. Since the extraction of metals occurs with long-chain amines which have been previously converted into alkylammonium salts, the interactions between the extractable metals and the organic reagent are mainly electrostatic. This fact means that extraction can take place through the formation of an ion-pair and for this reason; these extractants have been also called "Liquid anion exchangers". Some examples are listed below:

- i) Tri-laurylammonium chloride,
- ii) Di-trimethylhexylammonium chloride,
- iii) Tri-n-octylamine (TOA),
- iv) Tri-iso-octylamine (TIOA)
- v) Trilaurylamine (TLA),
- vi) Primen JMT,

- vii) Amberlite LA-1,
- viii) Armeen,
- ix) Tridodecylamine,
- x) Tribenzylamine etc.

iii) Neutral extractants:

These are organic reagents possessing only donor groups that do not contain dissociating protons. Since no anionic or cationic groups are available in the reagent molecule, the metal species are extracted from the water phase as neutral complexes. The neutralizing ions are water soluble coexisting inorganic anionic ligands. The extraction takes place by solvation in the organic phase of the neutral metal salt by means of the uncharged organic reagent. Water molecules co-ordinately bound to the cation can be substituted with the donor group of the extracting reagent. The extracted solvated metal species can then be regarded as a mixed complex since it is co-ordinated with two different types of ligands, i.e., a water soluble anion and an organic-soluble electron-donating function. The donor group is usually an oxygen atom. Some examples of neutral extractants are listed below:

- i) Tributyl phosphate (TBP),
- ii) Tri-n-octylphosphine oxide (TOPO),
- iii) Di-benzo-18-crown-6 (DBC),
- iv) Methyl-iso-butyl ketone (MIBK),
- v) Dithizone,
- vi) Cupferron,
- vii) Alizarin,
- viii) Morin,
- ix) Nitrosonaphthols etc.

e) Cyanex 272 [bis (2,4,4- trimethyl)pentyl phosphinic acid] as an extractant

A large number of extractants are available now. There are about 50 reagents, which are offered as proprietary reagents excluding several dozens, which are used every day. The alkylphosphoric acids, alkylamines and neutral organophosphates are all familiar extractants, which are all in use in variety of processes (nuclear and non-nuclear). Carboxylic acids originally proposed as cheap alternative to the more expensive alkylphosphoric acids for use in non-ferrous non-nuclear hydrometallurgy, have never achieved widespread commercial

use because of their unselective nature and poor pH functionality. Although, the acid chelating reagents like LIX, Kelex and Cyanex extractants have shown widespread applications in the selective extractions of copper, cobalt and nickel only; they have not shown great promise in the extraction of other metal ions.

Acidic organophosphorus compounds extract metals by a cation exchange reaction between one or two acidic hydrogen of the extractant and the extractable metal ion. Unlike the other acidic extractants, which dissociate ionically in the aqueous phase and do not associate molecularly in the organic phase, organophosphorus acids have a very pronounced tendency toward association into dimers and larger aggregates. Another complicating phenomenon is that the solvation of the metal-extractant complex by additional one or more extractant molecules may occur. But both the extent of polymerization and degree of solvation of the metal species are rather usually sensitive to various experimental parameters. These include the nature of diluent (enhanced aggregation in aliphatic hydrocarbons), the concentration of the extractant and the metal loading of the organic phase (saturation results in lowering the solvation of the complex and even deaggregation of the extractant).

Among the various types of organophosphorus compounds, di(2-ethyl hexyl) phosphoric acid (D2EHPA) and tributyl phosphate (TBP) have been widely used by various solvent extraction chemists [68-69] for their desirable properties and costs. However during the last two decades, phosphinic acid derivatives (Cyanex compounds) have been used for separation of metal ions, particularly for the separation of Co(II) from Ni(II) [70-82].

Cyanex 272 extractant is a proprietary but technical grade item of Cytec Canada Inc. (Garner Road, P.O. Box 240, Niagara Falls, Ontario, Canada L2E 6T4). The particulars of this extractant as supplied are noted below:

Product name: Cyanex 272

Synonyms: Bis-(2,4,4-trimethylpentyl) phosphinic acid

Chemical family: Dialkylphosphinic acid

Molecular formula: $C_{16}H_{35}O_2P$

Molecular weight: 290

Purity: 83-87%

Impurity: Trialkylphosphine oxide

Flash point: $> 108^{\circ}C$

Boiling point: $> 300^{\circ}\text{C}$

Melting point: $< -32^{\circ}\text{C}$

Specific Gravity: 0.92 at 20°C

Volatility: 0%

Solubility in water: 16 mg/dm^3 at 20°C

Appearance and odor: Slightly amber colored viscous liquid

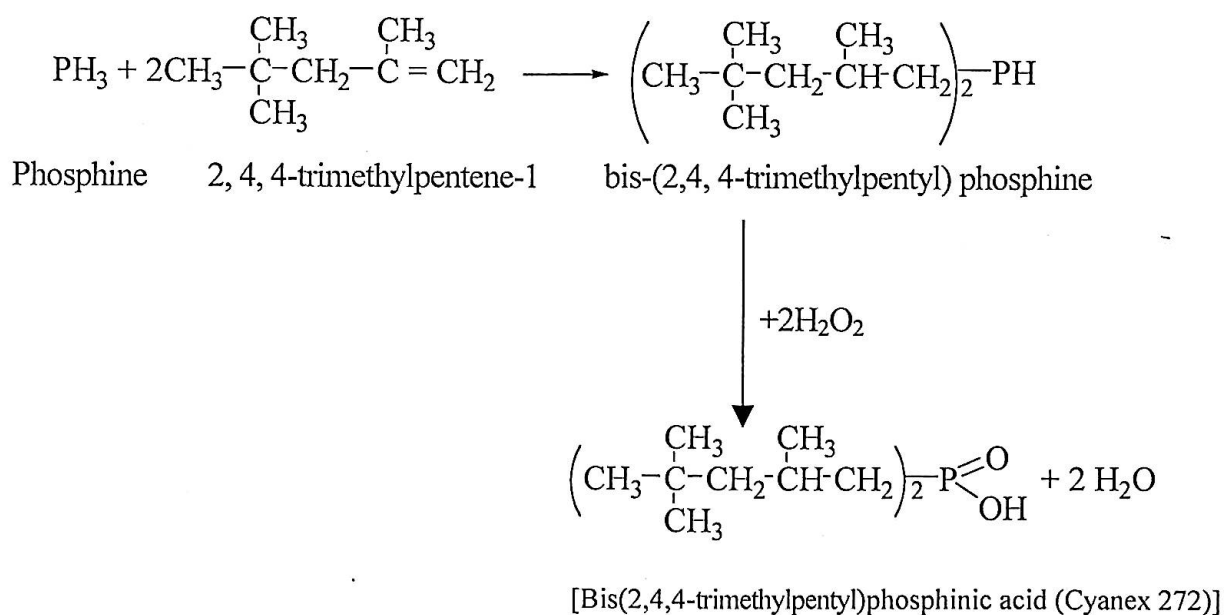
Hazard ness: Causes eye and skin irritation on direct contact

Stability: Stable; does not polymerize

COD: 195000 ppm

Octanol- H_2O partition coefficient: $> 10^{2.65}$

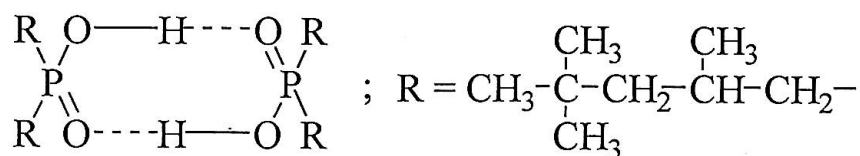
Cyanex 272 extractant is manufactured by reacting phosphine (PH_3) with 2,4,4-trimethylpentene-1 and then oxidizing the intermediate with hydrogen peroxide as shown below [77]:



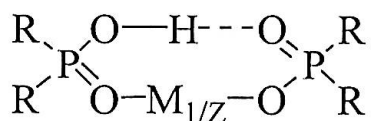
During this synthesis, tris-(2,4,4-trimethylpentyl)phosphine oxide (TOPO) is also formed to an extent of 10-17%. Sole and Hiskey [83] have found by ^{31}P -NMR and GC-MS that the extractant supplied by Cyanamide Canada Inc. contains 87-88% BTMPPA, 10% TOPO and 2% unknown compounds. Paatero *et al.* [84] have shown that the existence of TOPO in BTMPPA increases the extractibility towards copper(II). This means that as received Cyanex 272 is a better reagent for Cu^{2+} than purified Cyanex 272 (BTMPPA). So many researchers use as received Cyanex 272 in metal extraction studies as TOPO in BTMPPA exhibits synergism. But in order to investigate on the mechanism of a metal

extraction by Cyanex 272, from equilibrium and kinetic point of views, at least 99% BTMPPA should be used. It is therefore desirable to purify Cyanex 272 prior to its use in mechanistic investigations.

The purification method for Cyanex 272 together with D2EHPA (di-2-ethylhexylphosphoric acid) and HEHEHP (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) by copper salt precipitation and crystallization has been used for a long time when extraction mechanism and other fundamental studies have been carried out using these extractants [85]. This method is time consuming and costly, consuming large quantities of acetone and ether. Zhengshui *et. al.*, [86] have developed a new purification method for dialkyl phosphoric / phosphonic / phosphinic acid extractants based on the formation a middle microemulsion phase. The later method of purification is easier and cheaper. Like carboxylic, phosphoric and phosphonic acid derivatives; Cyanex 272, also exists in dimeric form in a non-polar solvent as shown below [87]:



If one of the acidic hydrogen atoms of this is removed by ionization, the resulting singly charged anion should be capable of chelating with a positively charged metallic ion, on the assumption that the remaining hydrogen bond is not broken. This may be shown schematically for metal ion, M^{z+} as follows:



It may be noted from the above postulated structure of the dimer, two phosphorus tetrahedrals are joined at two corners by O-H...O bridges, so that they are effectively joined edge to edge. In some cases, particularly at high metal loadings monomer of Cyanex 272 from the chelate with metal ion concerned after monomerization and ionization.

CHAPTER II

REVIEWS OF LITERATURE

In the last eight decades, a considerable progress has been made towards the elucidation of powerful method for separation of metal ions by organic solvents from the aqueous phase. Now the extension of researches has allowed the extraction study practically for all the metal ions throughout the entire Periodic Table. A substantial amount of these investigations is related to the mechanism of extraction and ultimately to a model for the extraction system. The following summarizes the up-to-date reports on:

- (A) The physico-chemical properties of BTMPPA / Cyanex 272
- (B) The use of Cyanex 272 as an extractant for different metal ions
- (C) Solvent extraction chemistry of Mn(II), Zn(II) and Ni(II) by different extractants
- (D) Kinetics of metal-ion extraction by various extractants using various techniques and
- (E) Kinetics of Mn(II), Zn(II) and Ni(II) extraction by various extractants using various techniques.

A) The physico-chemical properties of BTMPPA / Cyanex 272 Extractant

As pointed out in the introduction section, BTMPPA - the active component of Cyanex 272 exists mainly as the dimer like D2EHPA in most organic diluents of low polarity i.e. diluents not forming strong hydrogen bonds with BTMPPA. The various states of BTMPPA in both organic and aqueous phases can be expressed by the dimerization (K_2), distribution (K_d) or partition (p) and acid dissociation (K_a) constants and these constants can be determined by the phase distribution data of BTMPPA. As a rule, the distribution data can be obtained by the analysis of BTMPPA content in the aqueous phase. In the case of di-2-ethylhexylphosphoric acid (D2EHPA), it is observed [88-93] that the anion present in the aqueous phase as well as the diluent used to constitute the organic phase and measurement technique affect the values of K_2 , K_d and K_a . Therefore, for BTMPPA also, the values of K_2 , K_d and K_a depend on the aqueous condition and the diluent used in the organic phase. A very few reports on the values of K_2 , K_d and K_a for BTMPPA could be found in the literature.

Ke-an *et al.* [94] have reported the equilibrium constants of organophosphorous extractants including BTMPPA (Cyanex 272) by inductively coupled plasma-atomic emission spectroscopy (ICP-AAS). The 213.618 nm first order atomic emission line of

phosphorous has been monitored to determine the equilibrium constants. For sulfate-acetate / chloroform-BTMPPA system at 298 K, they have reported the values of K_d , K_2 and K_a as 43.8 ± 1.8 , $184.3 \pm 16.1 \text{ dm}^3/\text{mol}$ and $(6.6 \pm 0.7) \times 10^{-4} \text{ mol/dm}^3$ ($\text{pK}_a = 3.18$), respectively.

The dissociation equilibria of BTMPPA together with three other phosphorous acids have been studied in ethanol-water mixtures by potentiometric titration at 25°C [95]. Data have been analyzed both graphically and numerically using the program LETAGROP-ZETA. The obtained pK_a values have been correlated with the corresponding values in water, determined both indirectly by means of extraction measurements and by estimation using the suitable Hammett equation. They have reported that the pK_a values of BTMPPA are 5.42, 5.44 ± 0.02 , 3.38 and 3.51 ± 0.05 as obtained by graphical, LETAGROP-ZETA, Hammett equation and distribution measurements, respectively.

A technique consisting of digestion of BTMPPA sample by mixture of 70% HNO_3 – 70% HClO_4 (2:1) to convert phosphinic acids into orthophosphate has been reported by Biswas *et al.* [96]. The orthophosphate which is produced quantitatively can be estimated by the molybdenum blue colorimetric method at 830 nm. The method is sensitive with a molar extinction coefficient of 2.6×10^4 and reproducible within $\pm 2 \%$. Applying this technique of analysis, the values of K_2 , K_d and K_a of the purified BTMPPA have been estimated to be 190, 53 and 5.52×10^{-4} , respectively.

Using vapor pressure osmometry (VPO), Paatero *et al.* [84] have shown that the mean self-association number, $\bar{n}$ for BTMPPA in chloroform at 25°C is about 2.1 in the concentration range of 0.01 – 0.13 mol/dm^3 .

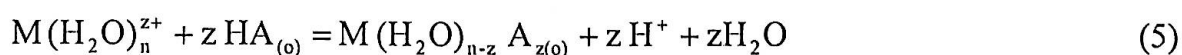
It is now well recognized that almost all hydrometallurgical liquid-liquid extraction reagents can behave as surface-active agents. The interfacial activity of these extractants is a result of their amphipathic nature, i.e., the presence of both hydrophobic and hydrophilic groups in the same molecule. The hydrophobicity is contributed by the hydrocarbon radicals, which may be straight or branched alkyl chains, or alkylaryl groups involving benzene or naphthalene rings. The polar functional groups such as:

Functional Group	Compound
$\begin{array}{c} \text{—C=O} \\ \\ \text{OH} \end{array}$	Carboxylic acids
$\begin{array}{c} >\text{P=O} \\ \\ \text{OH} \end{array}$	Derivatives of Phosphoric, Phosphonic and phosphinic acids,
$\text{—SO}_2\text{—OH}$	Sulfonic acid
$\begin{array}{c} \text{—CH—C—} \\ \quad \\ \text{OH} \quad \text{N—OH} \end{array}$	Hydroxyoximes
$\begin{array}{c} =\text{C—C—N=} \\ \\ \text{OH} \end{array}$	Oxines
$\text{—NH}_2, >\text{NH} \text{ and } \equiv \text{N}$	1°, 2° and 3° amines
$\equiv \text{NR}^+ \text{X}^-$	Quaternary ammonium salts

are responsible for the hydrophilic nature. The amphipathic characteristic is necessitated by the fact that an extractant must be able to interact with aqueous phase species while still maintaining preferential organic phase solubility. The hydrophilic groups provide the functional groups, which form the metal-ligand bonds while the organic radicals ensure the desired organic phase solubility.

In spite of the growing recognition of the surfactant properties of solvent extraction reagents, it cannot be said that there is complete agreement concerning the significance of interfacial phenomena in extraction processes. In a plenary lecture presented during ISEC'80, Freiser [97] was insisted on that interfacial effects were of little importance in metal extraction. On the other hand, in another plenary lecture at the same conference, Hanson [98] has suggested that reaction occurs in "a narrow zone in the aqueous phase immediately adjacent to the interfaces but with a significant (and possibly sometimes dominating) diffusional resistance in a zone (likely to be of greater thickness) on the organic side of the interface".

Liquid-liquid extraction involves ligand exchange processes whereby metal-organic ligand bonds substitute for the metal-oxygen bonds present in the hydrated aqueous species:



In general, extractant molecules possess extremely low aqueous solubilities. For example, according to Foakes *et al.* [99], the aqueous solubility of commercial hydroxyoxime copper extractants can be as low as 10^{-6} mol/dm³. Thus, it is not unreasonable to expect the locale of the extraction reaction to be near the two phase boundary. However, the tendency in the literature to appeal to indirect evidence (e.g., mathematical models of metal extraction rates, measurements of bulk phase metal distribution) as support for the significance or insignificance of interfacial phenomena in metal extraction processes is clearly unacceptable. More direct experimental evidences derived from the interfacial and the bulk phase physico-chemical investigations are needed.

In 1967, two pioneering studies appeared in which interfacial tension measurements were used to elucidate metal extraction mechanisms: one by McDowell and Coleman [100] on the uranium-amine sulfate system and other by Scibona *et al.* [101] on the kinetics of the reaction of tetraheptylammonium chloride with bromide ions. However, since then, with the exception of a few investigators such as Danesi *et al.* [102-104], Van Dalen *et al.* [105,106], Flett *et al.* [107,108], Yagodin *et al.* [109,110] and Osseo-Asare *et al.* [111-113], there is little attempt to undertake systematic and extensive investigations focusing on the interfacial region. The BTMPPA-extraction systems have not yet been investigated focusing on the interfacial region excepting the work of Singha [114-115].

Although there are some investigations on the interaction of D2EHPA-diluent in binary or ternary mixtures [90, 116-117], the interaction of BTMPPA- diluent has not been investigated excepting the work of Biswas and Singha [114, 118].

B) The use of Cyanex 272 as an extractant for different metal ions

Since the incipency of Cyanex 272 Extractant by Cyanamide Corporation (USA and Canada) at the beginning of the eighties of the last century, it has been widely used for the separation of cobalt (II) from nickel (II). The solvent extraction characteristics of cobalt and nickel by phosphoric, phosphonic and phosphinic acid derivatives have been reported from nitrate media [119] and from sulfate media [72]. In each case, cobalt is extracted at lower pH values than nickel; under comparable conditions, the cobalt-nickel separations increases in the order di-2-ethylhexylphosphoric acid (D2EHPA) < 2-ethylhexylphosphonic acid mono 2-ethylhexyl ester (EHEHPA) < di-2,4,4-trimethylpentylphosphinic acid (Cyanex 272). Danesi *et al.* [71] have reported the separation of cobalt and nickel by liquid-liquid extraction and supported membranes with bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272).

Fu and Golding [72] have reported the equilibrium and mass transfer (measured by Lewis cell) for the extraction of cobalt and nickel from sulfate solutions into BTMPPA (Cyanex 272). Cobalt extraction is observed to be practically independent of the aqueous phase nickel concentration, but the presence of cobalt in the aqueous phase inhibits nickel extraction. Separation factor is found to be dependent of cobalt loading. The separation of nickel and cobalt from sulfate solution by solvent extraction using Cyanex 272 Extractant has been patented by Chou and Beckstead [120]. Cho and Dai [121] have reported the separation of zinc, cobalt and nickel using solvent extraction technique involving various extractants including Cyanex 272. The cobalt(II) separation from nickel(II) in the laboratory scale has also been investigated by a number of other workers [73, 122-128]. There are also few reports on the cobalt-nickel separation on commercial plants [129-131].

There are considerable reports on the use of Cyanex 272 as extractant for the extractive separations of Co(II) from Cu(II) [132, 133], Cu(II) from Zn(II) [134], Sc(III) from Fe(III) [135] and Th(IV) [74], Zn(II) from Cd(II) [136], from Ca(II) [137] and Fe(II) [138], Al(III) from Ni(II) [139] and from Co(II), Ni(II) and Mg(II) [140], Mn(II) from Co(II) [141] and from Zn(II) [142-145], Ti(IV) from Fe(III) [146], Co(II) from Li(I) [147] and also on the mutual separations of Cu(II)-Ni(II)-Zn(II) [148], Cu(II)-Zn(II)-Co(II)-Ni(II) [149], Fe(III)-Cu(II)-Zn(II)-Ni(II) [150, 151], Fe(III)-Cd(II)-Ni(II) [152], Co(II)-Li(I)-Ni(II) [153], Co(II)-Ni(II)-Cd(II) [154-156], Co(II)-Ni(II)-Mg(II)-Ca(II) [157] etc.

Moreover, there are also some mechanistic (equilibrium) studies on some individual metal ions by Cyanex 272. Among them, the extractions of Ln(III) [75,76,78,158], Mo(VI) [159, 160], Zn(II) [77, 161, 162], Th(IV) [163], V(IV) [164, 165], Ag(I) [79], Al(III) [140, 166], Co(II) [153, 167], Zr(IV) [168], Fe(III) [81, 82, 116], Cu(II) [169, 170], Cd(II) [171], Mn(II) [141], Pb(II) [172], Ni(II) [173], Na(I) [174] etc. Cyanex 272 systems are mentionable.

C) Solvent extraction chemistry of Mn(II), Ni(II) and Zn(II) by different extractants

The solvent extractions of various metal ions studied up to 1976 have been summarized by Sekine and Hasegawa [68]. Some of the works on the extractions of Mn(II), Ni(II) and Zn(II) reported till now are mentioned briefly in the following paragraphs:

i) Solvent extraction of Mn(II): The extraction characteristics of manganese depend on its oxidation states. Manganese exists in its oxidation states from +2 to +7. In General, extraction of its chelate complex is suitable for the lower oxidation states, while extraction of its ion pair is usually encountered in the cases of +6 and +7 valency states.

Furthermore, during the extraction of manganese, the redox reaction may take place. Consequently, the oxidation state of the extracted species is not sometimes reported. Some of the works published so far on the solvent extraction of Mn(II) by different extractants from equilibrium view point are outlined below:

i) Tributyl phosphate, TBP [175-179], ii) Salicylic acid in TBP [180], iii) Thenoyltrifluoroacetone, TTA, with acetone, pyridine, bromate and its derivatives [181-183], iv) Diethyldithiocarbamate and its derivatives [184-186], v) Oxine in chloroform [187], vi) 2-methyl oxine [188], vii) Benzoylacetone in benzene and with dibenzoylmethane in benzene [189], viii) p-methoxybenzothiohydroxamic acid [190], ix) Diphenylcarbazone [191], x) Di-(2-ethylhexyl) phosphoric acid, D2EHPA [172,192-194], xi) Acetylacetone in chloroform or benzene [195], xii) Methyl-iso-butyl ketone, MIBK [196], xiii) Dithizone [197], xiv) 1-phenyl-3-methyl-4-capryl-(or-4-benzoyl)-5-pyrazolone [198], xv) Aminophosphonic acids [199], xvi) Fatty acids [200-202], xvii) PC88A [171, 203], xviii) Tris-(2-ethyl hexyl)phosphate [204], xix) Cyanex 272 [172], xx) N,N'-bis-(2-hydroxyphenylmethyl)-N,N'-bis(2-pyridylmethyl)-1,2 ethanediamine and its derivatives [205], xxi) Trioctylphosphine oxide, TOPO + pyrazolone [206], xxii) 5, 10, 15, 20-tetraphenyl-21H, 23H porphine [207], xxiii) LIX 1104 [208], xxiv) 4, 7-diphenyl-1, 10- phenanthroline [209], xxv) 2-propionyl-1-naphthol oxime [210], xxvi) 1-phenyl 3-methyl-4-aryl-5-pyrazolone [211], xxvii) Thenoyltrifluoroacetone (TTA) plus triethylamine [212], xxviii) Bis-(2-hydroxy-5-octylbenzyl) amine [213], xxix) 8-mercaptoquinoline, 8-quinollinol and their derivatives [214] and xxx) 3-[(dioctylamino) methyl] alizarin [215], xxxi) Alamine 336 [216] etc.

ii) Solvent extraction of Ni(II): In the divalent state nickel forms a very extensive series of compounds. This is the only oxidation state of importance in the aqueous chemistry of nickel and with the few exception of a few special complexes of nickel in other oxidation states, Ni(II) is also the only important oxidation level in its non aqueous chemistry.

The solvent extractions of Ni(II) by different extractants so far published are mentioned below:

i) Tributyl phosphate, TBP [175, 217-220], ii) Carboxylic acids [221-223], iii) Di-2-ethylhexylphosphoric acid, D2EHPA [224-227], iv) Thenoyltrifluoroacetone, TTA [228-232] v) Other Diketones: acetylactone [233, 234], isonitroacetylacetone [235], benzoylacetone [189], dibenzoylmethane [189, 234], trifluoroacetylacetone [235], vi) Dihydrogen methylene biphosphonate [236] vii) 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone [237, 238],

viii) β -isopropyltropolone [239], ix) 8-hydroxyquinoline (oxine) and its derivatives [187,240-245], x) Dioximes: α -furildioxime [246-249], α -benzyldioxime [249, 250], salicyldioxime [251], cyclopentane (or hexane) dionedioxime [246, 252-255], other dioximes [246, 249, 256-260], dimethylglyoxime [249, 261-267], xi) 1-Nitroso-2-naphthol [268] xii) Cupferon [269], xiii) Thio compounds: Thionaphthanic acid [270], Thiodibenzoylmethane [271], thio-TTA [272, 273], and thio-oxine [274], (xiv) Dithizone [275-281], xv) Dithiocarbamates [282-287], xvi) Xanthate [288] xvii) PC 88A (2-ethylhexylphosphoric acid mono-2-ethylhexyl ester) [224, 289], xviii) DP-8R and ACORGA M5640 [290], xix) 5,7-dibromo-8-hydroxyquinoline through ELM [291], xx) Cyanex 301 [292], xxi) Cyanex 272 (70% neutralized) [224], xxii) Quaternary ammonium salts [293, 294], xxiii) Various amines [295-299], xxiv) Cyanex 272 [119, 148, 149, 225, 300, 301], xxv) Aloxime [225], xxvi) LIX reagents: LIX 65N [302], LIX 87QN [303], LIX 84I [304], LIX 64N [305], LIX 84 [306], LIX 860 [307], xxvii) KELEX 100 [308], etc.

iii) Solvent extraction of Zn(II): Zinc is stable in its divalent state. Divalent zinc can form inner complexes on chelation by several ligands to be extracted into an organic phase. The works published so far on the solvent extraction of Zn(II) by various extractants are summarized below:

(i) Tributylphosphate, TBP [309-313] (ii) β -diketones: acetylacetone [314-319], benzoylacetone [188,317], dibenzoylacetone [188, 234, 317], trifluoroacetylacetone [235, 315, 320], hexafluoroacetylacetone [315, 320], thenoyltrifluoroacetone, TTA [320-322], (iii) β -isopropyltropolone [323], (iv) Diethylether + methyl-iso-butyl ketone (MIBK) [324, 325], (v) Fatty acids [326-328], (vi) Naphthenic acid [329, 330], (vii) Salicylic acid [180], (viii) Dinonylnaphthalenesulphonic acid [331], (ix) 8-hydroxyquinoline (Oxine) [186, 332-336], (x) Oxine derivatives [337-339], (xi) Tri-octylphosphine oxide (TOPO) [317, 340], (xii) 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone [341], (xiii) Peroxyacetyl nitrate (PAN) [342, 343], (xiv) Diethyldithiocarbamate [283, 284, 344, 345, 347-350], (xv) Dithizone [279,346-353], (xvi) Oxime [354], (xvii) Thiocompounds: dialkyldithiophosphoric acid [355-357], thio-TTA [272] and thio-oxine [358] (xviii) N-benzoyl-N-phenylhydroxylamine [359], (xix) Amines [313, 360-364], xx) PC 88A [144,365], (xxi) Quaternary ammonium salts [366, 367], (xxii) Di-2-ethylhexylphosphoric acid (D2EHPA) [144, 368-371], (xxiii) Cyanex 921 [313, 366, 372], (xxiv) Cyanex 272 [77, 137, 144, 172, 173, 312], (xxv) 4-ethyl-1-phenyl-1, 3-octadione [373], (xxvi)

Dibutylbutylphosphonate [374], (xxvii) DP 8R [375], (xxviii) Cyanex 302 [137, 312, 313], (xxix) Cyanex 301 [137, 312] etc.

During review of literatures, it is noticed that all three metal ions under investigation have been extracted widely before eighties of the last century by TBP, β -diketones, organic acids, oxines, dithizone, diethyldithiocarbamate, TOPO, PAN, amines etc. whilst in the recent years by LIX-reagents, D2EHPA, Cyanex-reagents etc.

Besides above investigations, one or two of the metal ions considered in this work have been separated from other metal ions by various extractants in recent times. These include-

- i) Separation of Co(II) from Ni(II) by 5, 7-dibromo-8-hydroxyquinoline [20],
- ii) Separation of Zn(II) from Ca(II) by Cyanex -272, -302, -301 [137],
- iii) Separation of Zn(II) from Mn(II) from sulphate medium by D2EHPA, PC 88A and Cyanex 272 [144],
- iv) Separation of Co(II) from Ni(II) by PC 88A [289],
- v) Separation of Co(II) from Ni(II) by DP 8R and ACORGA M5640 in Exxsol D100 [290],
- vi) Separation of Zn(II), Cd(II) and Cr(III) by TBP [311],
- vii) Separation of Zn(II) from iron by TBP, Cyanex 272, -302 and -301; and found TBP and Cyanex 301 as best extractant [312],
- viii) Separation of Zn(II) from Co(III) by supported LMI DP-8R [375],
- ix) Separation of Cu(II), Fe(III), Zn(II) and Ni(II) from nitrate medium by LK-C2 [376],
- x) Separation of Zn(II), Cd(II), Mn(II), Cu(II), Co(II), and Ni(II) by M2EHPA, D2EHPA and TBP [377],
- xi) Separation of Ni(II) from Co(II) by trioctylphosphine sulphide and tri-iso-butylphosphine sulphate in kerosene [378],
- xii) Separation of Zn(II) from Ni(II) by TBP, Cyanex 272 and Cyanex 301 [379],
- xiii) Stripping separation of Cd(II) and Ni(II) from their D2EHPA complexes in organic phase by H_2SO_4 [380] etc.

D) Kinetics of metal-ion extraction by various extractants using various techniques

i) Shake-out Technique:

Most works using this technique appeared during 1960-1980. Sekine *et al.* [9, 10, 381-383] used thenoyltrifluoroacetone (TTA or HTTA) in rate measurements for the extractions of Be^{2+} , Fe^{3+} and Ga^{3+} .

The very slow extraction of Cr^{3+} by HTTA [384] was attributed to the very slow substitution of coordinated water-by-water soluble TTA⁻.

The kinetics of the system Zn^{2+} - ClO_4^- - β -diketones (acac, bzac)- CHCl_3 was investigated [317] and reported that the slow step was the transfer of the neutral complex (formed in the aqueous phase) through the interface.

Di-2-ethylhexylphosphoric acid (D2EHPA, HDEHP) was widely used for extraction kinetic measurements by the shakeout technique. In almost all these works, the rate constants and the reaction orders with respect to concentrations of metal ion, hydrogen ion and D2EHPA were determined; and invariably in all cases, the formation of 1:1 complex in the bulk aqueous phase or at the interface was sorted out for the rate determining step. Islam and Biswas [11-13, 385, 386] reported the forward and backward extraction kinetics of Ti^{4+} , V^{4+} , Fe^{3+} and Cr^{3+} (only forward) from sulfate-acetato media, extractant being dissolved in benzene. In few cases, the rate data have been compared to the equilibrium data.

Kletenic and Patapova [387] investigated on Be^{2+} - $\text{HCl}/\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{SO}_4$ - D2EHPA- benzene/heptane/dibutylether system where the rates were measured at different metal ion concentrations, agitation speed, pH and temperature.

The systems Al^{3+} - D2EHPA, Am^{3+} - ClO_4^- - D2EHPA, Ln^{3+} - [AcH-NaAc-EDTA] -D2EHPA/2-ethylhexylphosphonic acid mono-ethylhexyl ester/ bis (2,2,4-trimethylpentyl)phosphonic acid - n - octane, Ti^{4+} - H_2SO_4 - di-o-tolylphosphate - benzene - isobutanol, Zn^{2+} - ClO_4^- - diphenyldithiocarbazide - CCl_4 and $\text{Zn}^{2+}/\text{Ni}^{2+}/\text{Co}^{2+}$ - dithizone / 2,2'-dimethyldithizone/ di- α -naphthylthiocarbazone - CHCl_3 were investigated by Sato *et al.* [388], Ilozhava and Karpacheva [389], Cao *et al.* [390], Biswas and Ali [391], Honaker and Freiser [392] and McClellan and Frieser [279], respectively using the shake out method.

ii) The Static Constant Interfacial Area Cell Technique:

Initially for studying the kinetics of mineral acid extraction, this method was suggested [388, 393]. The characteristics of this technique is that the interface is flat, stable and of constant surface area. This cell was used by Tarasov *et al.* [394] for studying the kinetics of the system UO_2^{++} - HNO_3 - TOPO (trioctylphosphinoxide) - toluene. Moreover, this technique has been used in the kinetic measurements of some extraction systems such as $\text{Am}^{3+}/\text{Th}^{4+}$ - D2EHPA [395], Cu^{2+} - N-8-quinolyl-p-dodecyl-benzenesulfonamide - toluene [396], VO^{2+} - D2EHPA - toluene [397], Mn^{2+} - D2EHPA - toluene [16], VO-D2EHPA complex - D2EHPA - toluene - H_2SO_4 [17], Mn^{2+} -D2EHPA- toluene - H_2SO_4 [398] etc.

iii) The Stirred Constant Interfacial Area Cell Technique:

This technique of measuring extraction and stripping kinetics had been widely used. Cianette and Danesi [399] investigated on the kinetics of the systems $\text{Ni}^{2+}/\text{Co}^{2+}/\text{Zn}^{2+}$ - H/KNO_3 - D2EHPA- n-dodecane using this technique. Results were explained on the basis of two models: (a) the mass transfer is controlled by slow reversible interfacial reaction and (b) the mass transfer controlled by interfacial film diffusion. Both models were found adequate. The Zn^{2+} - H_2SO_4 -D2EHPA kerosene system was investigated by Huang and Juang [400]. The conclusion drawn from both studies was that the slow step was interfacial. In studying the extraction kinetics of the system, Pu^{4+} - HNO_3 - trioctylammonium nitrate - n-dodecane + octyl alcohol Fomin *et al.* [401] plotted $\ln\{[\text{Pu}] - [\text{Pu}]_{\text{eq}}/[\text{Pu}]_0 - [\text{Pu}]_{\text{eq}}\}$ against t. These plots were characterized by an initial curve part brought the conclusion that a change of regime and mechanism occurred during the progress of the reaction.

Some other systems which were investigated by this technique are (a) UO_2^{2+} - HNO_3 - TBP - n-dodecane [402], (b) V^{5+} - HCl - TBP [403], (c) K^+ - picrate-dibenzo- 18-crown-6- 1,2- dichloroethane [404], (d) Li^+ - LIX54 + TOPO [405], (e) Zn^{2+} - H_2SO_4 - D2EHPA - n-heptane [406], (f) Zn^{2+} - HClO_4 - D2EHPA - ESSO (Isopar-H) [407], (g) La^{3+} - D2EHPA - Shellsol - K [408], (h) Sc^{3+} - HCl - D2EHPA - kerosene [409], (i) Ca^{2+} - HNO_3 - D2EHPA - dodecane [410], (j) Molybdosilicic acid - (Na, H) NO_3 - trioctylamine-toluene/trichloroethane [411], (k) Pu^{4+} - acids -trilaurylammonium salts-aromatic diluents [412], (l) VO^{2+} - D2EHPA - toluene [397], (m) Mn^{2+} - D2EHPA - toluene [16], (n) VO - D2EHPA complex - D2EHPA - toluene - H_2SO_4 [17], (o) Mn - D2EHPA complex - D2EHPA - toluene - H_2SO_4 [398], (p) Zr(IV) - Cl^- - D2EHPA - kerosene [413], (q) Mn(II) - Cl^- - D2EHPA- Kerosene [22], (r) Y(III) - sec - nonylphenoxy acetic acid (CA-100) [414], (s) Y(III) - Cyanex 272 - heptane [415], (t) Y(III) - HCl - Cyanex 272/ P507- heptane [416] and (u) Yb^{3+} - Cyanex 272- n heptane [417] etc.

iv) Technique Involving Stirred Tank (AKUFVE Apparatus):

AKUFVE apparatus (highly stirred tanks) were also used for the kinetic measurements of the following extraction systems: (a) Hf^{4+} - H_2SO_4 - tri-n-octylamine sulfate-xylene [418], (b) La^{3+} - diethylenetriaminepentaacetic acid- carboxylic/ lactic acid – D2EHPA – n-dodecane [419, 420], (c) Ni^{2+} - HNO_3 - α - L-hydroxyoxime + lauric acid - n-hexane [421], (d) Cu^{2+} - H_2SO_4 – LIX-extractants- toluene [422], (e) VO^{2+} – H_2SO_4 – D2EHPA – n – hexane [24] etc. In these works, the authors claimed that their measurements were at the maximum possible stirring speeds. Stirring speeds of 500 – 2500 rpm were used. Chemical reactions in the aqueous film were claimed to be the rate determining.

v) Rotating Diffusion Cell Technique (RDC):

With this best known sophisticated technique, the extraction kinetics of the following system had so far been investigated: (a) VO^{2+} - H_2SO_4 -D2EHPA-n-hexane [29], (b) Mn^{2+} - H_2SO_4 – D2EHPA – n-hexane [30], (c) $\text{Zn}^{2+}/\text{Co}^{2+}/\text{Ni}^{2+}$ - HClO_4 – D2EHPA – n-heptane [28], (d) Cu^{2+} - ACORGA- P50 [27, 423], (e) UO_2^{2+} - HNO_3 – TBP [424], (f) $\text{CO}^{2+}/\text{Ni}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$ - H_2SO_4 – D2EHPA – n-hexane [425] etc. In most of these cases, the experimental results had been fitted to MTWCR (mass transfer with chemical reaction) model [20].

vi) Single Drop Technique:

Several workers applied this technique in the last two decades. A brief description of same of these works are assembled below:

The UO_2^{2+} - NO_3^- - D2EHPA system had been studied by Pen and Wang [426]. Rate was found to be proportional to $[\text{UO}_2^{2+}]$, $[\text{D2EHPA}]^2$ and $[\text{H}^+]^0$. Activation energy of 16 kJ/mol was measured. Formation of an interfacial complex between UO_2^{2+} and D2EHPA was suggested to be the rate controlling.

Biswas *et al.* reported the extraction kinetics of (a) Mn^{2+} - HCl – D2EHPA – kerosene [34, 35], and (b) Ti^{4+} - HCl – D2EHPA- kerosene [427] and (c) Zr(IV) – HCl – D2EHPA – kerosene [36, 37], (d) Cu^{2+} - H_2SO_4 – Cyanex 272 - kerosene [428] using the single drop techniques. The kinetics of Cu^{2+} extraction from sulfate media by LIX-64N in Escaid 100 using this technique has been reported by Hughes *et al.* [429-431]. Atwood *et al.* [432] reported the extraction kinetics of Cu^{2+} by LIX-64N. Rate was found to be proportional to $[\text{Cu}^{2+}]$, $[\text{L-Hydroxybenzophenone component of LIX-64N}]^{1/2}$ and $[\text{hydroxime component of LIX-64N}]^{1/2}$. A surface reaction mechanism was the rate controlling. Activation energy was only 30 kJ/mol.

The other works which had been investigated using this technique are: (a) Sc^{3+} -D2EHPA [409], (b) UO_2^{2+} / Pu^{4+} - HNO_3 - TBP- dodecane [433], (d) Zn^{2+} - pH (4-5.2)-dithizone- CHCl_3 [33], (e) Nb^{5+} - HCl (8- 10 mol dm^{-3}) - di-(3,5,5- trimethylhexyl) ammonium chloride - CHCl_3 / CCl_4 / C_6H_6 [434], (f) UO_2^{2+} - HNO_3 - triphenylphosphate / tricresylphosphate [435, 436], (g) Cu^{2+} - HCl / H_2SO_4 / SME 529 / LIX-64N/ LIX-65N/ LIX-70/ACORGA P 17/ KELEX 100 [437], (h) Cu^{2+} - hydroxyoxime [31], (i) Cu^{2+} - LIX-64N [438], (j) Zn^{2+} - HCl (acetate buffer) - dithizone - CCl_4 [439], (k) V^{4+} - H_2SO_4 - D2EHPA - n-hexane [32] etc.

E) Kinetics of Mn(II), Ni(II) and Zn(II) extraction by various extractants using various techniques

The following summarizes the reports on the kinetics of extraction (and stripping) of Mn(II), Ni(II) and Zn(II) by various extractants using various phase contact techniques:

Kinetics of Mn^{2+} - H_2SO_4 - D2EHPA-kerosene system has been investigated by Lewis and Hann cell techniques has been studied by Biswas *et al.* [16]. In data treatment, pseudo rate constant, q and flux, F methods have been applied. Empirical rate equations have been derived. Results have been compared among themselves and other published works on this system. The rate components obtained from q and F methods differ in magnitude and units and an explanation of this has been given.

The kinetics of stripping of Mn(II)-D2EHPA chelate ($\text{MnA}_2\cdot\text{HA}\cdot\text{H}_2\text{A}_2$) existing in kerosene phase by aqueous sulphuric acid solutions at constant sulphate ion concentration of 0.50 M have been investigated by Biswas *et al.* [398] using the constant interfacial area stirred (Lewis) and non-stirred (Hahn) cells. Both pseudo-rate constant (q) or (rate / area) and flux (F) methods of the rate data treatment have been applied. The empirical rate equations have been derived. Results have been compared among themselves and other published works on Mn(II)-D2EHPA chelate stripping kinetics. Rate constants obtained from (q) or (rate / area) and (F) methods differ in magnitude and units and an explanation of this has been given. An analysis of rate equations obtained from the Lewis cell experimentation ($F_b = 10^{-4.1} [\text{MnA}_2\cdot\text{HA}\cdot\text{H}_2\text{A}_2]_{(o)} (1 + 0.005[\text{H}^+]_{(i)}^{-1})^{-1} (1 + 7.94[\text{H}_2\text{A}_2]_{(o)}^{0.5})^{-1}$) suggests that the process is chemically controlled at lower aqueous acidity and higher free D2EHPA concentration regions; whereas, it is diffusion-controlled at higher aqueous acidity and lower free D2EHPA concentration regions. In the investigated D2EHPA concentration and aqueous acidity regions, majority of data fall in the intermediate controlled region. The

suggested mechanisms are supported by the values of activation energy (E_a). In the kinetic regime, the reaction step: $MnA^+ \rightarrow Mn^{2+} + A^-$ occurring in the bulk aqueous phase is the slowest step which proceeds through S_N2 mechanism as indicated by the comparable higher negative value of $\Delta S^\ddagger$ in the stated condition. In Hahn cell technique, the empirical rate equation is: $F_b = 10^{-5.9} [MnA_2.HA.H_2A_2]_{(o)} (1 + 0.0025[H^+]_{(i)}^{-1})^{-1} (1 + 2.8[H_2A_2]_{(o)}^{0.5})^{-1}$. Analysis of this equation together with the E_a value of 12–42 kJ/mol indicate that the stripping process is completely diffusion controlled in the low pH and extractant concentration region and in other parametric condition, that is intermediate controlled. For both cells, the ratio of (k_f) to (k_b) equals almost to K_{ex} of $10^{-2.44}$ obtained from the distribution study.

The kinetics Mn(II)-extraction from acidic sulphate solution by D2EHPA dissolved in n-hexane have been investigated using RDC by Hughes and Biswas [30]. The -generalized MTWCR of Hughes and Rod has been used to fit the experimental data. A ΔpH tem has been introduced to calculate the interfacial pH, which yields better fitting of the experimental data. The log-log plots of vs. determining chemical reaction step. Low E_a (20 kJ/mol) suggests that the extraction mechanism is mixed chemical with mass transfer control.

The rate of forward extraction of Mn(II) from Cl^- medium by D2EHPA-kerosene has been measured by single rising drop technique. The flux is proportional to $[Mn(II)]$, $[H_2A_2]_{(o)}$ and $[H^+]_{(int)}^{-1}$ k_f is measured to be $10^{-6.35}$ m/s. E_a , $\Delta S^\ddagger$ and $\Delta H^\ddagger$ are calculated to be 7.6 kJ/mol, -224 kJ/mol and 7.6 kJ/mol, respectively at > 303 K and 77 kJ/mol, -15.3 kJ/mol and 77 kJ/mol, respectively at lower temperature. Analysis of rate data suggests that the formation of $[MnHA_2]^+$ at the interface is the rate determining. Negative $\Delta S^\ddagger$ suggests that the rate determining reaction occurs via S_N2 mechanism regions have reported by Biswas *et al.* [34]

The rate of backward extraction of Mn(II) from Mn-D2EHPA complex distribute in kerosene by HCl has been measured by the single rising drop technique and the (F) at $30^\circ C$ is gives as: $J \text{ (kmol/m}^2\text{s)} = 10^{-4.08} [Mn-D2EHPA]_{(o)} (1 + 0.011 [H^+]^{-1})^{-1} (1 + [H_2A_2]_{(o)}^{0.5})^{-1}$. Analysis of this equation suggests that the process is almost chemically controlled at lower aqueous acidity and higher free D2EHPA concentration region; whereas it is almost diffusion control at higher aqueous acidity and lower free D2EHPA concentration regions have reported by Biswas *et al.* [35]

Kinetics of Mn^{2+} -HCl - D2EHPA-kerosene system has been investigated by the Lewis cell technique. The reaction order with respect to Mn^{2+} , D2EHPA and H^+

concentration have been estimated to be + 1, + 1 and -1, respectively. The value of k_f is calculated to be $10^{-6.534}$ m/s at lower pH region, the chemical reaction: $\text{Mn}^{2+} + \text{HR}_2^- \rightarrow [\text{MnHR}_2]^+_{(\text{int})}$ is the slowest at lower temperature region and at the higher temperature region, diffusion of species to the to occur the above reaction is the slowest have reported by Biswas *et al.* [22].

A study on the kinetics of nickel ion extraction by Kelex 100 (7-(4-ethyl-1-methyloctyl)8-hydroxyquinoline) has been presented Hokura *et al.* [440] by stopped flow method. A reaction scheme has been proposed and the kinetics is shown to be controlled by the two parallel initial addition steps.

The extraction of nickel with 2-hydroxy-5-nonylbenzophenone oxime (LIX 65N; HL) has been studied by Akiba and Freiser [302] into chloroform solution. The extracted species has been found to be NiL_2 and its extraction constant of $10^{-5.90}$ is obtained. The rate of extraction of nickel has been found to be first-order in metal and ligand and inverse first-order in hydrogen ion. The apparent rate constant of extraction (k') was $10^{-7.40}$. These results support the hypothesis that the formation of the 1:1 complex in the aqueous phase is the rate-determining step. The rate constant of the formation of this complex was evaluated as $10^{5.90}$.

The interfacial adsorption of (*E*)-2'-hydroxy-5'-nonylacetoophenone oxime and its role in the extraction kinetics of the nickel(II) ion with the oxime have been investigated by Watarai *et al.* [441] in heptane/aqueous phase systems by means of a high-speed stirring apparatus. The interfacial oxime concentration is correlated to the organic phase concentration, obeying the Langmuir isotherm. The interfacial activity of the oxime is also measured by means of interfacial tension measurements. The initial extraction rate of nickel(II) ion is linearly proportional to the interfacial concentration of the oxime (rather than to the bulk-phase concentration), to the nickel-ion concentration, and inversely to the hydrogen-ion concentration. These results have supported the mechanism that the rate-determining step in the extraction is the 1:1 complex formation at the interface

The rate of nickel extraction by α hydroxy oxime/carboxylic acid mixtures are first order with respect to nickel, α hydroxy oxime and carboxylic acid concentrations and inverse first order with respect to the hydrogen ion concentration as reported by Flett *et al.* [107]. The rate dependencies for the reverse reaction are the reciprocal of the extraction reaction. Although it has not proved possible from these data to derive an unambiguous kinetic scheme, the study has highlighted the importance of the interfacial properties of the metal chelate solvent extraction systems.

Kinetics of nickel(II) extraction by 2-ethylhexanal oxime (EHO) has been investigated by Buch *et al.* [442] in a homothetic cell (Rushton cell) from ammonium solutions. The kinetic study has been carried out with a stirring speed fast enough to eliminate the diffusion limitation. The chemical regime can then be assumed and the kinetic result can be used to determine the reaction mechanism. Thus, a kinetic mechanism has been suggested and a limiting step found. Influence of pH and the concentrations of NH_4NO_3 and EHO on rate have been investigated and results suggest that the limiting step is an interfacial reaction between a molecule of EHO monomer (HOx) and the adsorbed complex $\text{Ni}(\text{Ox})(\text{H}_2\text{O})_{5\text{ad}}$.

The extraction kinetics of cobalt and nickel in a mixer-settler have been investigated by Zhou *et al.* [443]. The extraction system comprised an aqueous phase of cobalt and nickel sulphate and an organic phase of 10% EHPNA (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) -kerosene. The experimental results show that the extraction rates of both cobalt and nickel are high and the extraction rate of cobalt is generally higher than that of nickel.

Teresa *et al.* [444] has been studied the kinetics of zinc extraction from sulfate media with bis(2-ethylhexyl)thiophosphoric acid (D2EHTPA). A cell with a constant interfacial area and with vibrational mixing has been used to measure the initial extraction and initial stripping rates under several operating conditions. The results obtained suggest that the extraction process can be described by the reaction mechanism scheme proposed by Ajawin *et al.* [445]. The reaction rate constants have been evaluated by taking into account the nonideality of the aqueous phase. The activity coefficients of the ions in the ZnSO_4 - H_2SO_4 - Na_2SO_4 aqueous system have been calculated by applying the Pitzer model. The thermodynamic kinetic constants for the forward and backward reactions are found to be $3.1 \times 10^{-5} \text{ m sec}^{-1}$ and $1.0 \times 10^{-6} \text{ kmol}^{-0.5} \text{ m}^{2.5} \text{ sec}^{-1}$, respectively, at 293 K. The ratio between these rate constants agrees satisfactorily with the thermodynamic equilibrium constant obtained in a previous study.

Corsi *et al.* [446] have been made on the kinetics of zinc stripping for the $\text{Zn}/\text{H}_2\text{SO}_4/\text{D2EHPA}/n$ -heptane system which is being considered as a Recommended System by the European Federation of Chemical Engineering (EFCE) Working Party on Distillation, Absorption and Extraction. A constant interface cell designed by Hancil has been used to determine chemical rate-controlling parameters and a five-compartment rotating disc contactor (RDC) of 0.152 m diameter has been used with single drops to determine appropriate diffusional mass transfer coefficients.

Maclean and Dreisinger have reported [447] the kinetics of zinc extraction from perchlorate solutions by di(2-ethylhexyl) phosphoric acid in n-heptane when measured using the rotating diffusion cell technique. The extraction of zinc is controlled by the mass transfer of reactants (Zn^{2+} and D2EHPA) to the interface: bulk pH has little effect. It appears that the chemical reaction rate is so fast that it has a negligible effect on the overall extraction rate. A mass transfer mathematical model has been developed which is adequate for predicting the extraction rate under variable conditions of zinc concentration, D2EHPA concentration and pH. The effect of using a partially loaded organic extractant has been investigated and the system has been found to be mass transfer controlled. A second mathematical model has been developed which predicts that the speciation of organic-complexed zinc changes with increasing preload and, at high loadings, the direction of $\text{ZnL}_2\cdot\text{HL}$ and $\text{ZnL}_2\cdot(\text{HL})_2$ flux reverses, with these species providing extractant to the interface. At very high loadings, $\text{ZnL}_2\cdot\text{HL}$ provides almost all the extractant to the interface. Experimental studies of the effect of temperature on the rate of zinc extraction resulted in calculation of an activation energy of 12.4 kJ/mol, which is consistent with a diffusion-controlled mechanism. The extraction rate decreases significantly for a very small filter pore size, while there appears to be little or no effect for larger filter pore sizes. It was therefore concluded that, for the filter pore size used in this study, the filter pores do not pose an additional resistance to mass transfer.

Bart and Rousselle has been investigated [448] the kinetics of zinc extraction for the $\text{ZnSO}_4/\text{D2EHPA}/\text{isododecane}$ system which is being considered as a Recommended Liquid-Liquid Extraction Test System by the European Federation of Chemical Engineering (EFCE) Working Party on Distillation, Absorption and Extraction. A constant interfacial cell has been used to determine the chemical rate-controlling parameters at 25°C.

Jianbing *et al.* [449] have been studied the role of kinetics of extraction in the design of extraction equipment is becoming more important with the move to reduce organic inventories and phase residence times. This paper examines the influence of the kinetics of ZnSO_4 extraction into di-2-ethylhexyl phosphoric acid (D2EHPA) in Shellsol 2046 in a 100 mm diameter, 1 m tall column packed with Super Mini Rings (SMR). Concentrations of zinc along the column in both phases can be simulated to within $\pm 10\%$ using an axial dispersion model with a diffusion-kinetic model incorporated.

The effects of a salt on the extraction kinetics of metal cations Co^{2+} and Zn^{2+} by di(2-ethylhexyl) phosphoric acid (D2EHPA) diluted in *n*-dodecane have been studied by Simonin *et al.* [450] using the rotating membrane cell (RMC) technique. The kinetics have been investigated for tracer amounts of radiolabelled metal ions (2×10^{-8} M Co(II) and 10^{-4} M Zn(II)) and D2EHPA concentration in the range 0.02–0.5 M. A “pre-equilibrated” nitric acid (PENA) solution has been used for some experiments. This solution is prepared by contacting a HNO_3 solution with a 0.2 M D2EHPA organic phase. First, the effect of the nature of the anion (acetate, Cl^- , ClO_4^- , NO_3^-) is investigated at pH 3 and 5. The results are compared with those using the D2EHPA-saturated PENA solution. For Zn(II), the kinetics are fast with all anions.

CHAPTER III

OBJECTIVE OF THE PRESENT INVESTIGATION

In the hydrometallurgical processing of manganiferrous shales, manganese sea nodules, spent catalysts, copper converter slag, dry cells (Zn-C, Ni-Cd etc. batteries), sulphide minerals, etc. the leach liquor contains invariably iron, manganese, copper, cobalt, nickel, cadmium, zinc etc in the acidic leach liquor along with some other impurities. On the other hand, the processing of ammoniacal leach liquors is easier due to minor contamination by iron and manganese. On careful going through the related literature reveals that the purification or separation of these metal ions by solvent extraction plays a vital role. Though the use of solvent extraction in the separation of Mn(II) - Co(II) - Ni(II) - Zn(II) from sulphate solution is stricky, the availability and the use of organophosphorus extractants viz. D2EHPA, PC 88A, Cyanex 272 etc. has made the separation feasible.

Although there are some reports on the separations of binary or multinary metal ion mixtures containing Mn(II), Ni(II) and/or Zn(II) by Cyanex 272, researches on the thermodynamically and kinetic aspects of the extractions of Mn(II), Ni(II) and Zn(II) are lacking. So to gather the theoretical aspects (both thermodynamic and kinetic) of the Mn(II)-SO₄²⁻-Ac⁻-H⁺-Na⁺ - Cyanex 272-kerosene, Ni(II)-SO₄²⁻-Ac⁻-H⁺-Na⁺ - Cyanex 272-kerosene and Zn(II)-SO₄²⁻-Ac⁻-H⁺-Na⁺ - Cyanex 272-kerosene systems, the present investigation has been made. With this view in mind, the investigation has been comprised of the following plans of work:

3.1. Extraction Equilibrium Study

Each of the above mentioned three systems will be investigated with aims to find the extents of variations of extraction ratios (after determining the equilibration times) as functions of (i) metal ion concentration in the aqueous phase, (ii) equilibrium pH of the aqueous phase, (iii) equilibrium extractant (Cyanex 272) concentration in the organic phase, (iv) coexisting sulphate and acetate (if added to buffer the system) ions concentrations in the aqueous phase and (v) temperature. The results obtainable from the above studies will be used to calculate extraction equilibrium constant (K_{ex}), enthalpy change during extraction and propose extraction equilibrium reaction. The loading of Cyanex 272 with the metal ions under consideration will also be investigated. Furthermore, the possibilities of the stripping of metal-loaded organic phases by mineral acids will be examined.

3.2. Kinetics of Forward Extractions

The systems under consideration will be investigated from the kinetic view points using the easy-to-handle single falling drop technique. The kinetic studies will be comprised of the determination of (i) the end effect (time required for drop formation and coalescence), (ii) the reaction order with respect to metal ion concentration through $\log F_f$ vs. $\log [M(II)]$ plots constructions, (iii) the reaction order with respect to H^+ concentration through $\log F_f$ vs pH plots constructions, (iv) the reaction order with respect to H_2A_2 (Cyanex 272) concentration of the organic phase through $\log F_f$ vs. $\log [H_2A_2]_{(o)}$ plots constructions, (v) the reaction orders with respect to sulphate and acetate (of added) ion concentrations through $\log F_f$ vs. $\log [SO_4^{=}]$ or $\log [Ac^-]$ plots constructions, (vi) activation energy (E_a), activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$) through $\log F_f$ vs. $1/T$ and $\log \left(\frac{F_f h}{kT} \right)$ vs. $1/T$ plots constructions. From the intercepts of the above plots (excepting temperature dependence plots), the forward extraction rate constant (k_f) for each system under investigation will be evaluated. Based on the results gathered, the extraction mechanisms for each system under investigation will be proposed.

3.3. Kinetics of backward extraction

The systems under consideration will be investigated from the kinetic view points using the easy-to-handle single falling drop technique. The kinetic studies will be comprised of the determination of (i) the reaction order with respect to metal ion concentration through $\log F_b$ vs. $\log [M(II)]$ -Cyanex 272 complex plots constructions, (ii) the reaction order with respect to H^+ concentration through $\log F_b$ vs $pH_{(ini)}$ plots constructions, (iii) the reaction order with respect to H_2A_2 (Cyanex 272) concentration of the organic phase through $\log F_b$ vs. $\log [H_2A_2]_{(o)}$ plots constructions, (iv) the reaction orders with respect to sulphate and acetate (of added) ion concentrations through $\log F_b$ vs. $\log [SO_4^{=}]$ or $\log [Ac^-]$ plots constructions, (v) activation energy (E_a), activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$) through $\log F_b$ vs. $1/T$ and $\log \left(\frac{F_b h}{kT} \right)$ vs. $1/T$ plots constructions. From the intercepts of the above plots (excepting temperature dependence plots), the backward extraction rate constant (k_b) for each system under investigation will be evaluated. Based on the results gathered, the extraction mechanisms for each system under investigation will be proposed.

3.4. From the values of rate constants for a particular system, the value of ($K_{ex(rate)}$) will be evaluated and matched with that obtained from the equilibrium study. Moreover, possibilities of separation of the metal ions will be predicted.

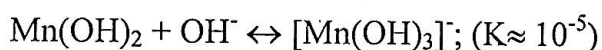
CHAPTER IV

AQUEOUS CHEMISTRY OF Mn(II), Ni(II) AND Zn(II)

4.1. Aqueous Chemistry of Manganese(II)

The most important and stable oxidation state of manganese is +2. In neutral and acid solutions, it exists as the very light pink colored hexaquo ion, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$. Since the reduction potential of $\text{Mn}^{2+}/\text{Mn}^{3+}$ is highly negative ($E^0 = -1.51 \text{ V}$), Mn^{2+} is not easily converted into Mn^{3+} . Therefore, Mn^{2+} is not a good reducing agent. The great stability of Mn^{2+} ion is due to the existence of stable $3d^5$ configurations.

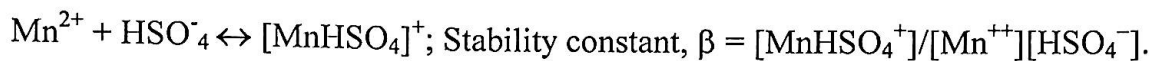
Since the reduction potential of $\text{Mn}^{2+}/\text{MnO}_4^-$ is almost equal to that of $\text{Mn}^{2+}/\text{Mn}^{3+}$, strong oxidizing agents such as KIO_4 , NaBiO_3 etc. can oxidize Mn^{2+} directly to MnO_4^- (Mn^{7+}). On addition of alkali metal hydroxide to Mn^{2+} solution, white gelataneous precipitate of $\text{Mn}(\text{OH})_2$ is formed which darkens rapidly for the oxidation by air. Virtually, Mn(II) can produce hydroxides of numerous compounds. The stability constants (β) at 25°C and zero ionic strength for $\text{Mn}(\text{OH})^+$ ($\beta = [\text{Mn}(\text{OH})^+]/[\text{Mn}^{2+}][\text{OH}^-]$), $\text{Mn}(\text{OH})_2$ ($\beta = [\text{Mn}(\text{OH})_2]/[\text{Mn}^{2+}][\text{OH}^-]^2$), $\text{Mn}_2\text{OH}^{3+}$ ($\beta = [\text{Mn}_2\text{OH}^{3+}]/[\text{Mn}^{2+}]^2[\text{OH}^-]$), $\text{Mn}_2(\text{OH})_3^+$ ($\beta = [\text{Mn}_2(\text{OH})_3^+]/[\text{Mn}^{2+}]^2[\text{OH}^-]^3$) and $\text{Mn}(\text{OH})_4^{2-}$ ($\beta = [\text{Mn}(\text{OH})_4^{2-}]/[\text{Mn}^{2+}][\text{OH}^-]^4$) are $10^{12.8}$, $10^{18.10}$ and $10^{7.70}$ respectively [451(a)]. Stability constant of MnOH^+ at 2.0, 1.0 and 0.1 ionic strength are $10^{3.5}$, $10^{3.0}$ and $10^{2.9}$ respectively at 25°C [451(a)].



Excepting phosphate and carbonates, manganese(II) salts are all soluble in water. Most of them could be crystallized as hydrated salts from their aqueous solutions. The hydrated MnSO_4 salts may have various degrees of water of crystallization. The hepta, penta and tetrahydrated MnSO_4 differ in their stability. The mono hydrated sulfate salt is crystallized out at 27°C and its solubility is decreased with increasing temperature.

Manganese(II) can form many complexes but the equilibrium constants formation in the aqueous solution are not so high compared to those of Fe(II) – Cu(II) for its largest size among them and also for the lack of ligand field stabilization energy. The complexes may be seven (e.g. $[\text{Mn}(\text{OH})_2\text{EDTA}]^{2-}$), six (e.g. $[\text{Mn}(\text{SCN})_6]^{4-}$), five (e.g. $[\text{Mn}(\text{OH})_2\text{CH}_2(\text{CH}_2)\text{NHCH}_2\text{NH}_2]$) and four (e.g. $[\text{Mn}(\text{H}_2\text{O})\text{SO}_4\cdot\text{H}_2\text{O}]$, $[\text{MnCl}_4]^{2-}$ etc.) coordinated. Some time the complexes may be polymerized i.e. Mn(II)-acac complex is trimerized.

In the aqueous solution of manganese sulfate, $[\text{MnHSO}_4]^+$ species may exist due to the following equilibrium.



The stability constants for the formation of the mono-bisulfato and mono-sulphato complexes at 25°C and zero ionic strength are $10^{2.26}$ [451(e)] and $10^{2.28}$ [452(a)] respectively.

Manganese(II) also forms complex with acetate ion (usually mono-acetate complex. The stability constant at 25°C ($\beta = [\text{Mn-Ac}^+]/[\text{Mn}^{2+}][\text{Ac}^-]$) of the Mn(II) acetate complexes are $10^{0.8}$, $10^{0.69}$ and $10^{1.40}$ respectively at ionic strengths of 0.16, 1.0 and 0.0 [453(a)].

Considering the following equilibria

- (i) $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$; $[\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}] = 10^{-14}$ at zero ionic strength
- (ii) $\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^-$; $[\text{HSO}_4^-]/[\text{H}^+][\text{SO}_4^{2-}] = 98.5$ at zero ionic strength
- (iii) $\text{Mn}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{MnSO}_{4(\text{aq})}$; $[\text{MnSO}_4]/[\text{Mn}^{2+}][\text{SO}_4^{2-}] = 190$ at zero ionic strength
- (iv) $\text{Mn}^{2+} + \text{HSO}_4^- \rightleftharpoons \text{MnHSO}_4^+$; $[\text{MnHSO}_4^+]/[\text{Mn}^{2+}][\text{HSO}_4^-] = 181.97$ at zero ionic strength
- (v) $\text{Mn}^{2+} + \text{OH}^- \rightleftharpoons \text{MnOH}^+$; $[\text{MnOH}^+]/[\text{Mn}^{2+}][\text{OH}^-] = 6.27 \times 10^3$ at zero ionic strength
- (vi) $\text{Mn}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Mn}(\text{OH})_2$; $[\text{Mn}(\text{OH})_2]/[\text{Mn}^{2+}][\text{OH}^-]^2 = 6.31 \times 10^{12}$ at zero ionic strength

Mass balance equation:

$$[\text{Mn}]_i = [\text{Mn}^{2+}] + [\text{MnSO}_4] + [\text{MnHSO}_4^+] + [\text{MnOH}^+] + [\text{Mn}(\text{OH})_2] + (V_{\text{org}}/V_{\text{aq}})[\text{MnH}_{2x}\text{A}_{2+2x}]$$

$$[\text{A}]_i = 2[\text{H}_2\text{A}_2] + 2(1+x)[\text{MnH}_{2x}\text{A}_{2+2x}].$$

Charge balance equation:

$$[\text{H}^+] + [\text{MnOH}^+] + 2[\text{Mn}^{2+}] = [\text{OH}^-] + [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}]$$

Sousa Jr *et al.* [454] used some sort of computer programming to the Mn(II) species and $\text{HSO}_4^-/\text{SO}_4^{2-}$ species distributions. The species distributions are depicted in the following two figures (Fig. A and B): The first one shows the distributions of MnHSO_4^+ , Mn^{2+} and MnSO_4 at various pH values when $[\text{Mn}^{2+}]$ (total) is kept at 0.00805 Kmol/m^3 ; whilst the second figure represents the distributions of HSO_4^- , SO_4^{2-} , MnHSO_4^+ and MnSO_4 species at various pH values at the same total manganese(II) concentration in the system.

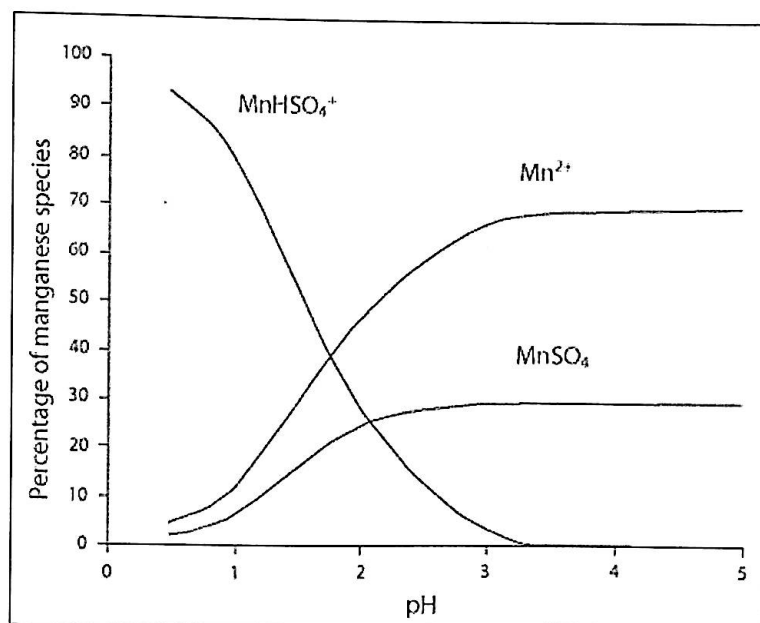


Fig. A. Effect of pH on the manganese distribution $[\text{Mn}]_i = 0.00805 \text{ kmol/m}^3$.

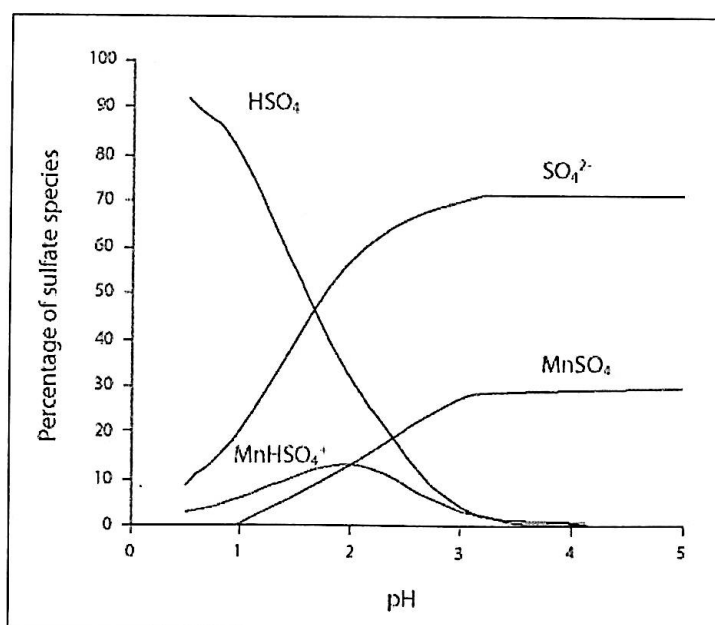


Fig. B. Effect of pH on the distribution of sulfate $[\text{Mn}]_i = 0.00805 \text{ kmol/m}^3$.

4.2. Aqueous Chemistry of Nickel(II)

Nickel(II) sulfate, a blue-colored highly soluble salt is a common source of the Ni^{2+} ion for Ni- electroplating, electrefining and electrowining. Several sulfate salts of nickel(II) are known, all being paramagnetic. X-ray crystallography measurements show that $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ consists of octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ions. These ions in turn are hydrogen bonded to sulfate ions. Dissolution of the salt in water gives solutions containing the ion $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

Aqueous solutions of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and related hydrates react with ammonia to give $[\text{Ni}(\text{NH}_3)_6]\text{SO}_4$ and with ethylenediamine to give $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]\text{SO}_4$. The latter is occasionally used as a calibrant for magnetic susceptibility measurements because it has no tendency to hydrate. Nickel(II) can commonly form four (both square planar and tetrahedral) and six co-ordinated complexes with ligands.

The stability constant ($\beta_{\text{temp.}}^{\text{ionic strength}}$) for the formations of NiHSO_4^+ ($\beta = [\text{NiHSO}_4^+] / [\text{Ni}^{2+}] [\text{HSO}_4^-]$) are $\beta_{25}^0 = 10^{2.32}$, $\beta_{25}^{1.0} = 10^{0.5}$, $\beta_{20}^{2.0} = 10$ and $\beta_{23}^{3.0} = 10^{0.26}$ whilst those of $\text{Ni}(\text{HSO}_4)_2$ ($\beta = [\text{Ni}(\text{HSO}_4)_2] / [\text{Ni}^{2+}] [\text{HSO}_4^-]^2$) is $\beta_{25}^{1.0} = 10^{1.42}$ [451(e)]. The value of $\{[\text{NiSO}_4] / [\text{Ni}^{2+}] [\text{SO}_4^{2-}]\}$ is $10^{2.4}$ at 25°C and zero ionic strength [452(b)]. Ni^{2+} solutions are usually hydrolyzed at higher pH regions. The stability constants of 1:1 $\text{Ni}^{2+}\text{-OH}^-$ species are ($\beta = [\text{NiOH}^+] / [\text{Ni}^{2+}] [\text{OH}^-]$) at 25°C are $10^{4.1}$, $10^{3.7}$ and $10^{3.8}$ at ionic strength of 0.0, 0.5 and 1.0 respectively [451(b)]. This value for 1:2 species ($\beta = [\text{Ni}(\text{OH})_2] / [\text{Ni}^{2+}] [\text{OH}^-]^2$) is 10^8 at 25°C and zero ionic strength [451(b)]. Nickel(II) in aqueous phase is also complexed with acetate (Ac^-) ion. The stability constants ($\beta = [\text{NiAc}^+] / [\text{Ni}^{2+}] [\text{Ac}^-]$) at 25°C have been reported to be $10^{1.43}$, $10^{0.74}$ and $10^{0.83}$ in ionic strengths of 0, 0.5 and 1.0 respectively [453(a)].

4.3. Aqueous Chemistry of zinc(II)

Zinc has the only stable oxidation state of +2. Due to the absence of vacant or partially filled d-orbital, zinc(II) complexes are always tetrahedral due to Sp^3 hybridizations.

The hydroxide $\text{Zn}(\text{OH})_2$ is precipitated from solution of zinc(II) salts by addition of an alkali.

Further $\text{Zn}(\text{OH})_2$ is readily dissolves in an excess of alkali to give zincate ions, probably of the type $\text{ZnO}_2 \cdot 2\text{H}_2\text{O}$. Moreover, $\text{Zn}(\text{OH})_2$ is readily dissolved in an excess of strong NH_3 to form the ammine complexes, for example, $[\text{Zn}(\text{NH}_3)]^{2+}$. In general the species present in an slightly acidic aqueous solutions is $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$.

With bisulphate ion, $\text{Zn}(\text{II})$ forms species of bisulphato complexes. The values of the formation/stability constant for monobisulphato complex ($\beta = [\text{ZnHSO}_4^+]/[\text{Zn}^{2+}][\text{HSO}_4^-]$) are $\beta_{25}^{0.0} = 10^{2.38}$, $\beta_{25}^{0.5} = 10^{0.93}$, $\beta_{25}^{1.0} = 10^{0.89}$, $\beta_{25}^{2.0} = 10^{0.76}$ and $\beta_{25}^{3.0} = 10^{0.70}$; while those for bis-bisulphato complex ($\beta = [\text{Zn}(\text{HSO}_4^-)]/[\text{Zn}^{++}][\text{HSO}_4^-]^2$) are $\beta_{25}^{0.5} = 10^{1.9}$, $\beta_{25}^{1.0} = 10^{1.2}$, $\beta_{25}^{2.0} = 10^{1.2}$ and $\beta_{25}^{3.0} = 10^{0.70}$ [451(f)]. Tris- bisulphato and tetrakis-bisulphato complexes are also formed whose stability constant are also given the book of Smith and Martell [451(f)].

It is also reported that sulphate ion can also form complexes with $\text{Zn}(\text{II})$. Usually mono-sulphato complex is formed whose stability constant at 18°C and zero ionic strength is $\sim 10^{2.3}$ [452(a)].

Depending on aqueous pH (increasing pH), $\text{Zn}(\text{II})$ forms $\text{Zn}_2\text{OH}^{3+}$, $\text{Zn}(\text{OH})^+$, $\text{Zn}(\text{OH})_2$, $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{=}$. The stability constant (25°C) for $\text{Zn}_2(\text{OH})^{3+}$, $\text{Zn}(\text{OH})^+$, $\text{Zn}(\text{OH})_2$, $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{=}$ are $10^{5.0}$, $10^{5.0}$, $10^{11.1}$, $10^{13.6}$ and $10^{14.8}$, respectively at zero ionic strength [451(c)].

Acetate ion can form mono-, di- and tri-acetato complexes with $\text{Zn}(\text{II})$, for mono-acetato complex, the values of stability constants are $\beta_{25}^{0.0} = 10^{1.57}$, $\beta_{25}^{0.1} = 10^{1.1}$, $\beta_{25}^{1.0} = 10^{0.63}$. For bioacetato-complex of $\text{Zn}(\text{II})$, the stability constants are $\beta_{25}^{3.0} = 10^{1.36}$ and $\beta_{25}^{0.1} = 10^{1.9}$; whereas that for triacetato complex is $\beta_{25}^{3.0} = 10^{1.57}$ [453(b)].

CHAPTER V

EXPERIMENTAL

5.1. Chemicals used, their sources and specifications

The chemicals used in this investigation were of reagent grade. The specifications of the used compounds are as follows:

Name of chemical	Producer	Purity
Nickel(II) sulfate hexahydrate	Fluka, Chemika, England	>99%
Zinc(II) sulfate heptahydrate	E. Merck, Germany	>99.99%
Manganese(II) sulfate monohydrate	Loba Chemie, India	98%
Sodium salt of EDTA	Fluka, Chemika	>99%
Ethyl alcohol (Absolute)	Germany	>99.80%
Cyanex 272	CYTEC Canada. Inc., Canada	85-87%
Potassium periodate	Riedel-Dehaen, Germany	99%
Acetic acid	E. Merck, Germany	> 99.50%
Ammonium chloride	E. Merck, Germany	99.99%
Solochrome black (indicator)	George T Gurr. Ltd., London,	-
Oxalic acid dihydrate	E. Merck, Germany	>99%
Nitric acid	E. Merck, Germany	>70%
Ammonium nitrate	E. Merck, Germany	
Sodium carbonate (anhydrous)	E. Merck, Germany	>99.50%
Bromine	Saturated	—
NH ₃ solution (sp.gr.= 0.91)	E. Merck, Germany	25-29%
Sodium acetate trihydrate	BDH, Poole, England	99%
Sulfuric acid	E. Merck, Germany	95-98%
Hydrochloric acid	E. Merck, Germany	36 -37%
Potassium permanganate	BDH, Poole, England	99.50%
Potassium nitrate	Loba Chemie, Mumbai	99%
Octan-1-ol	BDH, England	>99%
n-hexane (analar)	BDH, England	>99%

Carbon tetrachloride	BDH, England	99.8%
Sodium sulfate(anhydrous)	Merck, India	>98%
n-heptane(analar)	BDH, England	>99.5%
Chlorform(analar)	BDH, England	>99.5%
Benzene(analar)	BDH, England	>99%
Toluene(analar)	BDH, England	>99%
1,2-Dichloroethane(analar)	BDH, England	>99.5%
Heptan-1-ol	BDH, England	>99%
Cyclohexane	BDH, England	>99.5%
Kerosene	Local market	Distilled out within 200-270 ⁰ C
Acetone	BDH, England	>99%
Hexan -1-ol	BDH, England	>99%

5.2. List of Symbols and Abbreviations

The following symbolic formulae and abbreviations have been used in this manuscript for the sake of simplicity and in the ease of discussion:

Symbol or abbreviation	Meanings
A	Interfacial area, m ²
a, b, c, d and e	Reaction orders with respect to metal ion, H ⁺ , H ₂ A ₂ , SO ₄ ²⁻ and Ac ⁻ concentration, respectively, in the forward /backward extraction.
a _{Mn(II)}	Amount of Mn(II) transferred from a drop, kmol
a _{Ni(II)}	Amount of Ni(II) transferred from a drop, kmol
a _{Zn(II)}	Amount of Zn(II) transferred from a drop, kmol
^c D	Corrected D at constant equilibrium parametric concentrations
D	Extraction ratio of Mn(II), Zn(II) or Ni(II) partitioned
E _a	Activation energy, kJ/mol
F _b	Flux of backward extraction/stripping, kmol/m ² s
F _f	Flux of forward extraction, kmol/m ² s

$f(R)$	Function of reactants
h	Plancks constant, 6.6252×10^{-37} kJ s
H_2A_2	Dimer of Cyanex 272 molecule
HA	Monomer of Cyanex 272 molecule
k	Boltzmann constant, 1.38×10^{-23} , J/K
$K_{aH_2A_2}$	Acid dissociation constant of dimeric Cyanex 272 at interface, kmol/m ³
K_{aHA}	Acid dissociation constant of monomeric Cyanex 272 in bulk aqueous phase, kmol/m ³
k_b	Backward extraction rate constant
k_f	Forward extraction rate constant
K_2	Dimerization constant of Cyanex 272 in the organic phase, kmol/m ³
K_{ex}	Equilibrium constant from the equilibrium study
$K_{ex(rate)}$	Equilibrium constant from the rate study
Mn-BTMPPA	Complex of Mn(II) with Cyanex 272
Ni-BTMPPA	Complex of Ni(II) with Cyanex 272
P	Partition coefficient
R	Universal gas constant, 8.314 J/deg mol
S_N1	Substitution nucleophilic unimolecular
S_N2	Substitution nucleophilic bimolecular
Zn-BTMPPA	Complex of Zn(II) with Cyanex 272
β	Stability constant/Separation factor
$\Delta S^\pm$	Entropy of activation, J/K mol
$\Delta H^\pm$	Enthalpy of activation, kJ/mol
ΔH	Apparent enthalpy change for extraction, kJ/mol
Suffix "eq"	Equilibrium
Suffix "o"	Organic phase
Suffix "ini"	Initial
Suffix "int"	Interface
Suffix "b"	Backward extraction/stripping
Suffix "f"	Forward extraction

5.3. Definition of terms

The following terms have been used in this dissertation, which are associated with the solvent extraction chemistry:

i) Extraction:

The operation of transferring metal ion of interest from the aqueous phase to the organic phase. The extraction produces a loaded organic phase containing the metal value and an aqueous phase depleted of the metal known as raffinate.

ii) Scrubbing:

The selective removal of impurity metals from the loaded organic phase by treatment with either fresh scrub solution or a bleed of the strip liquor. The spent scrub solution is normally combined with the aqueous Feed. The scrubbed organic phase containing metal of interest is advanced to stripping.

iii) Stripping:

The process of removing metal value from the scrubbed organic phase by reversing the extraction chemical reaction. It is normally conducted under conditions in order to produce strip liquor containing a high concentration of the metal value. The strip liquor is the product of the solvent extraction circuit.

iv) Diluent:

It is the organic solvent in which the extractant is dissolved to form the organic phase. It consists of either aliphatic or aromatic hydrocarbon or halogenated hydrocarbon. It is used in order to improve the physical properties such as viscosity, density etc of the extractant. Even though the diluent may be a single or the major component of the organic phase, the term “solvent” must be avoided as it has a wider meaning in the context of liquid-liquid extractions. The term carrier may be used but it is not recommended as it implies that the diluent is inert.

v) Dispersion:

An unstable emulsion caused by contacting the organic and aqueous phases.

vi) Distribution /Extraction ratio:

It is a measure of the extracting power of the organic phase. It equals the concentration of the metal in the organic phase divided by that in the aqueous phase at equilibrium condition. It is denoted as 'D'.

vii) Emulsion:

It is a stable dispersion of the organic and aqueous phases that require a long time to coalesce and separate.

viii) Extractant:

The active organic component in the organic phase that chemically reacts with the metal to form an organic-metal complex - soluble in the organic phase. Extractant and diluent together act as a solvent.

ix) Loading Capacity:

It is the maximum concentration of a metal in the organic phase under a given set of specified conditions. The loading capacity is defined as the amount of metal content in gram extracted per 100 g of pure extractant. Maximum loading varies widely from one extractant to another. The term, "maximum loading" and "saturation loading" are the synonyms for loading capacity. The organic phase increases in viscosity with increasing metal ion loading.

It is an important factor for the study of mechanism of extraction in addition to also for the industrial evaluation of the extractant. High value of loading capacity is desirable for any particular extractant-metal system for its industrial application.

x) Modifier:

A component added to the organic phase, usually for preventing the formation of a third phase as well as emulsion by increasing the solubility of the organic-metal complex is called a modifier. Generally, higher alcohols ($C_6 - C_{12}$) are used as modifier

xi) Phase ratio (O/A):

It is the ratio of the volume of the organic phase to that of the aqueous phase used in the extraction process.

xii) Percent Extraction:

It is calculated by the following equation:

$\% \text{ Ext'n} = [(O/A) \times D / \{1 + (O/A) \times D\}] \times 100$; where "D" is the distribution or extraction ratio.

xiii) Phase Disengagement:

It is a term used to describe an operation to coalesce and separate two component phases.

xiv) Separation Factor, β :

It is a measure of the selectivity of the organic phase. It is calculated by the following equation:

$SF (\beta) = D(\text{metal}) / D(\text{impurity})$; where "D" is the distribution ratio.

xv) Equilibration:

It is a process whereby a system of two liquid phases is brought to a condition where further changes of concentration of a distributing species with respect to time do not take place in a single stage.

5.4. Experimental Techniques**a. Phase mixing: Shaking machine**

For laboratory scale or preliminary liquid-liquid extraction studies, an electrically driven Zencons' Stuart Flask Shaker with eight arms (220 V, 50 Hz) was used. For phase mixing, the equal aliquots of aqueous and organic phases were taken into 125 cm³ separatory funnels or suitable reagent bottles and agitated for a definite time in a thermostatic water bath. The shaking speed was controlled by a regulator at about ~ 300 strokes/min.

b. Acidity measurement: pH meter

Acidity of the test solutions were measured by a Mettler-Toledo 320 pH meter (England). The pH meter was furnished with a combined glass electrode having an ATC mode (automatic temperature compensator). Before taking each reading, the pH meter was standardized by standard buffers of pH 4 and 7. After standardization of the pH meter, the electrode was rinsed with sufficient distilled water; the residual water present on the surface of the electrode was removed by a piece of filter paper. It was then placed within the test solution and kept in such a way at least 5 min before taking the readings.

c. Balance

A Mettler Toledo (Switzerland) balance (model AB 204-S) was used for all weight-measurements in this investigation. Its maximum capacity was 220 g with a sensitivity of 0.0001 g. The calibration of the balance was checked time-to-time by the standard weights supplied by the Company.

d. The temperature control: Thermostat

Since the value of the extraction equilibrium constant for a particular metal ion extraction depends on the temperature of extraction, a thermostatic water bath was used for the necessary control of temperature during the extractions as well as other measurements wherever necessary. The separatory funnel or reagent bottle containing equal volumes of aqueous and organic phases were shaken in the bath, thermostated at the desired temperature for the definite length of time. Care was taken so that the funnels or bottles were immersed under water at least up to three-fourth portions of the funnels or bottles. When the temperature gradient between the ambient and the experimental temperatures were large (more than 10°C), the empty funnels or bottles were first placed in the thermostatic bath to attain the temperature of the bath. The aqueous and organic solution containing flasks were also placed in the bath for the same.

e. The single drop technique

The principle of single drop technique consists in producing a drop (organic or aqueous phase) at the end of a vertical column being filled with the other phase, the drop then travels along the middle of the tube and during the time of traveling metal extraction takes place across the drop surface. In this technique, the droplets of the aqueous phase are allowed to fall through a continuum of the organic phase taken a column of a definite height and the droplets are collected continuously from the bottom of the column. The time of fall of the drop is equal to the extraction time. The change in the metal ion concentration in the aqueous phase is proportional to the mass transferred.

A schematic diagram of a Single drop (falling) apparatus is shown below:

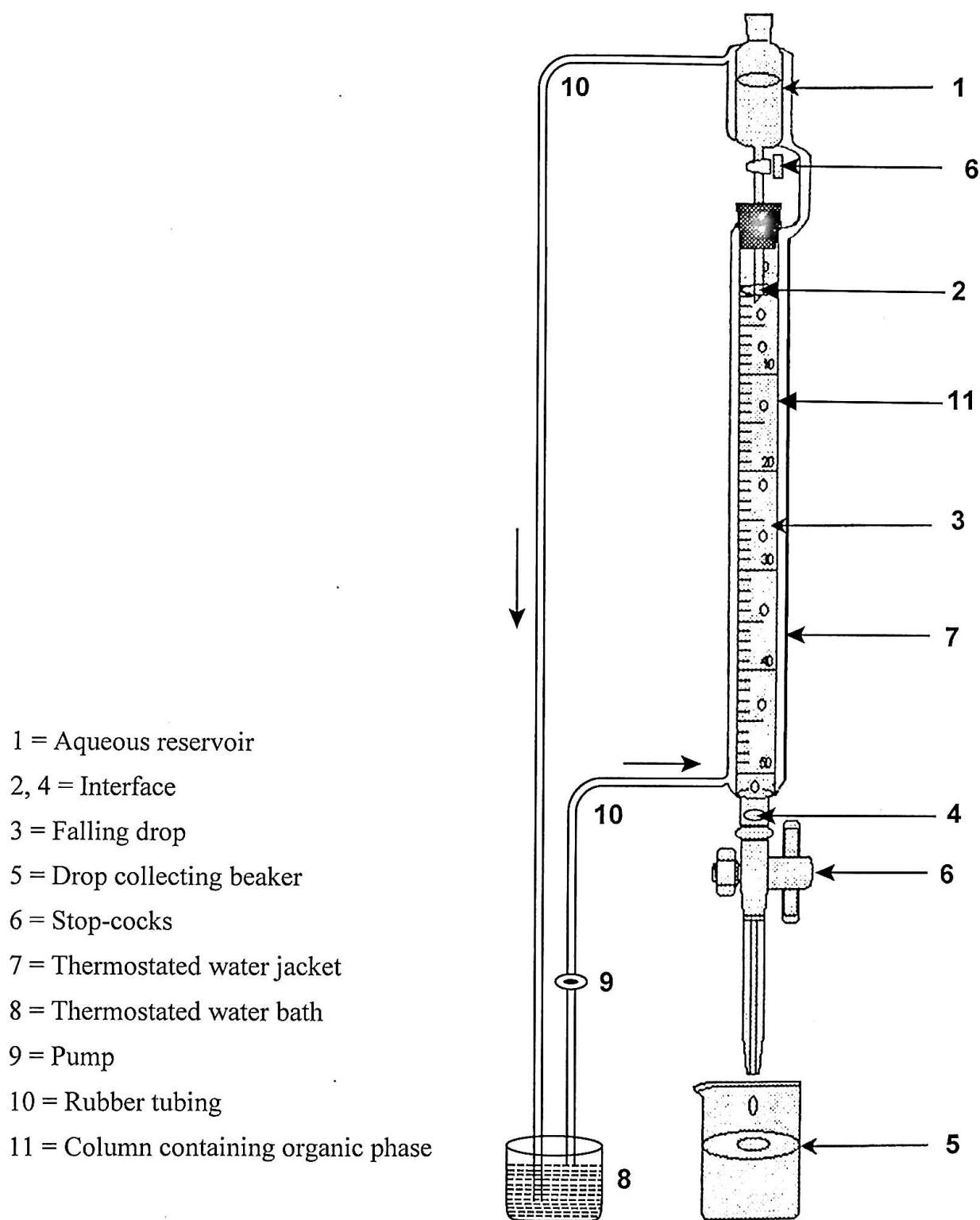


Fig. C. A schematic diagram of a Single Drop (falling) apparatus.

On knowing the average surface or interfacial area of a drop, the time of traveling and concentration of the traveling drops, it is possible to evaluate the rate of extraction or flux of mass transfer. The average surface area of a drop can be obtained from the drop size (may be known from the volume of definite number of drops). This technique can be applied both to drops which move upwards (rising drops) or downwards (falling drops); the choice depends on the higher or lower density of the loaded drop with respect to the continuum liquid filling the column. The interfacial area of a drop is generally calculated by assuming that the drops are perfect spheres.

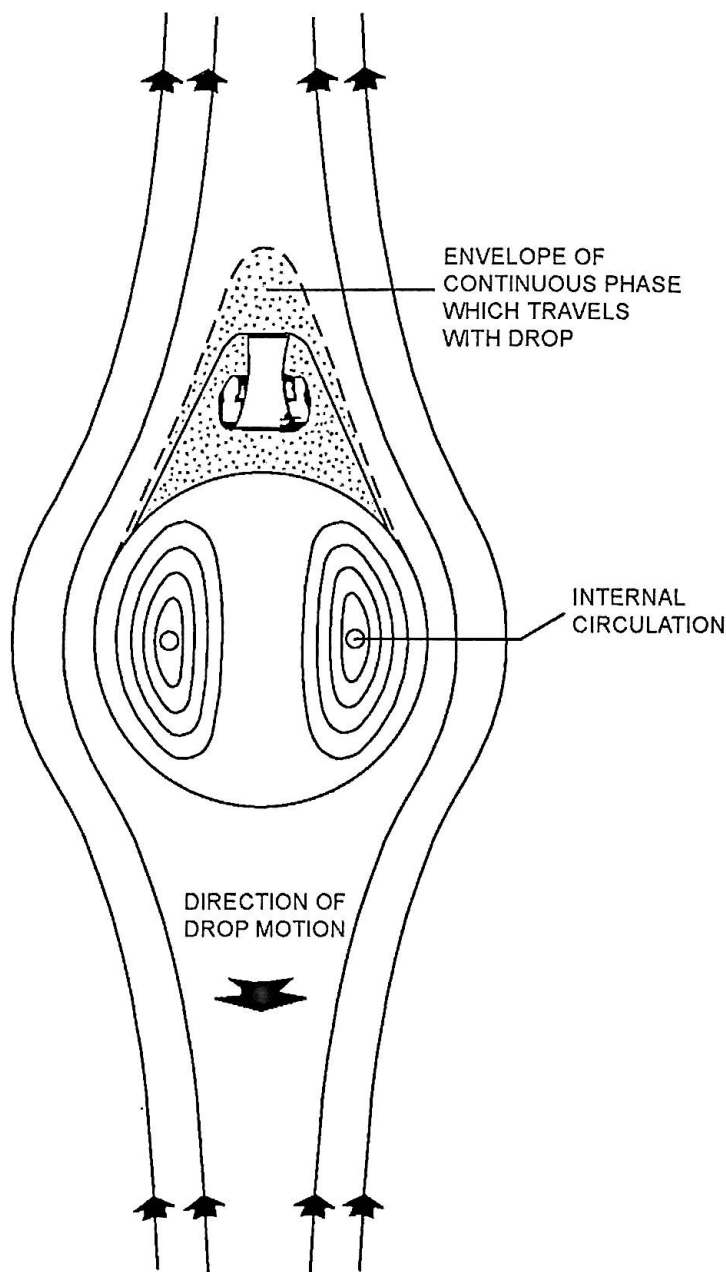


Fig. D. Flow regime for a falling drop.

A detailed description of the various apparatus in use can be found in literature [38, 432, 438, 455, 456]. Figure C shows the design of the experimental apparatus used in this work with some simplified modification of falling drop apparatus. Some modifications of this basic scheme have been proposed in the literature. They concern the substitution of the glass capillary, where the drop is formed with a stainless steel jet [38], the modification of the collection head with a tubing of constant diameter to maintain the level of the interface [438] and in the elimination of stagnant pool of the dispersed phase [432]. Although the technique allows the control of both the drop size and the interfacial area, some disadvantages impose the use of great care both in the treatment of the experimental data and planning of the apparatus. When the extraction kinetics is very rapid, much of the extraction can take place during drop formation and coalescence. Further, extraction can also take place in the stagnant pool, where the drops are collected. The data have to be properly corrected as described earlier [38, 432, 439, 457]. On the other hand, when the extraction kinetics is very slow, very long columns are required to assure long enough drop residence time. Finally, the hydrodynamic control of the single drop is very difficult because of internal circulation and the presence of drop oscillations and wakes [438].

Figure D shows a schematic representation of the flow regime for a falling drop. As described earlier [432, 458-460], the hydrodynamics of the drops can be rather complex and variable according to the experimental conditions, which are used. In general, since the drops are not rigid, a transfer of a momentum can take place through the interface and an internal drop circulation should be promoted. However, when the drops are very small or the extractant is a surfactant, which adsorbs on the drops surface, this internal circulation can be absent. Consequently, the extraction kinetics becomes extremely slow. It is then very difficult to establish whether the degree of turbulence of the two phases which is obtained with the moving drop method can ever be high enough to ensure the measurement of the transfer rate in a kinetic regime or, in the opposite case, is so slow that the mass-transfer rate is always occurring in a diffusional regime (providing extremely slow chemical reactions do not take place). This uncertainty in establishing the type of extraction regime, which occurs when the single moving drop method is used to study the extraction kinetics often introduced difficulties in the interpretation of the data. As an example of this difficulty, it is worth quoting that according to the opinion reported [461], the single drop technique provides best turbulent conditions compared to those can be achieved in an AKUFVE apparatus or in a Lewis cell. On the contrary, according to what was reported [462] on the hydrodynamic that was higher than that achieved in the constant interfacial area cell, operating at 1000 rpm.

Of many practical and theoretical problems in the study of solvent extraction kinetics, the following four problems are citable. These are the cleanliness, end effects, misleading comparison and prejudiced presentations. The uncleaning contaminations may alter the kinetics in several routes, e.g. by altering effective concentrations of reagents in either phase, by interface blocking, by competing with metal-ion for extractant or even by acting as a synergist. So it is suggested to use the clean system as far as possible. End effects are generally associated with single drop apparatus and its treatment is still a matter of controversy [38, 463]. This effect is also present in all kinetic experiments excepting the RDC, involving two phases. For example, in a batch stirred tank, there will have an induction time before true interdispersion is achieved, and the substantial mass transfer occurs during the sampling and coalescence of the dispersion for analysis. A careful consideration must be given to the influence of end effects in each experiments performed and, since end effects are unavoidable except in steady state experiments, methods of elimination must be derived which at the same time minimizes the magnitude of the unwanted mass transfer. Comparisons between commercial products are very difficult and while the fundamental studies should compare extractants at the same molar concentrations, industrial studies are more appropriately concerned with solution of equal cost. Although, it is often attempted to express the experimental results in terms of existing theory and then to encompass any anomalies uncovered by the minor changes of theory, it can be remarkably unrewarding on occasion. A careful consideration must be given to the influence of the end effects and in each experiment; method of elimination must be derived which at the same time minimizes the magnitude of the unwanted mass transfer.

Methods:

The falling drop technique has been applied in the rate measurements for the extraction of Mn(II), Ni(II) and Zn(II) respectively. Organic phase loaded in a column of definite height was vertically held by a column supporter. Another short column having a pointed tip with a regulator containing aqueous phase has been placed at the top interface of the main column. Hundred drops were collected in a beaker whose volume was determined by the weight- density method of collected 100 drops in each experiment. From the number of drops and its volume, the surface area of a drop was determined. The aqueous drop formation in the short column was so regulated that a definite rate of drop falling was obtained. The drop fall time was obtained by dividing T by N ; where T is the cumulative time needed to fall N number of individual drops.

Analytical:

The concentrations of Mn(II), Ni(II) and Zn(II) in the aqueous phases, were analyzed colorimetrically or by atomic absorption spectrophotometer (AA-6800, Shimadzu Corporation, Japan). The pH measurements and adjustments were done using a Mettler Toledo pH meter.

Working formula for flux calculation:

For each forward or backward extraction experiment, flux (F_f or F_b) was calculated as follows:

$$\text{Flux } (F_f \text{ or } F_b) = a_M (\text{kmol})/A (\text{m}^2) \times t (\text{s}) \quad (6)$$

where, a_M = amount of M(II) transferred = $(x \text{ V/NM}) \times 10^{-9} \text{ kmol}$

$$= \frac{\text{Conc. change in aqueous phase } (x, \text{ mg/L}) \times \text{Vol. } (v, \text{ mL}) \text{ of } N = 100 \text{ drops}}{N(100) \times \text{At. wt. of metal, M}} \times 10^{-9} \text{ kmol}$$

$$A = 0.000483567 \times (V/N)^{2/3} \text{ m}^2; \quad \text{as: } V/N = 4/3 \pi r^3; r = (3V/4\pi N)^{1/3} \text{ cm}$$

$$A = 4\pi (3V/4\pi N)^{2/3} \text{ cm}^2 = 4.83567 (V/N)^{2/3} \text{ cm}^2$$

t = drop fall time, s

Considering atomic weight of Mn, Ni and Zn as 54.94, 58.70 and 65.40 respectively

$$\text{or, } (F_f) \text{ or } (F_b) = 3.76 (V/N)^{1/3} (1/t) \times 10^{-8} \text{ kmol/m}^2 \text{ s} \quad (7a) \quad \text{for Mn(II)}$$

$$= 3.52 (V/N)^{1/3} (1/t) \times 10^{-8} \text{ kmol/m}^2 \text{ s} \quad (7b) \quad \text{for Ni(II)}$$

$$= 3.16 (V/N)^{1/3} (1/t) \times 10^{-8} \text{ kmol/m}^2 \text{ s} \quad (7c) \quad \text{for Zn(II)}$$

At a constant temperature,

$$F_f = k_f [M^{2+}]^a [H^+]^b [H_2A_2]_{(o)}^c [SO_4^{2-}]^d [Ac^-]^e \quad (8)$$

Except temperature, there are five other variables. On keeping all other variables constant except one (say, M(II) concentration), if flux values (F_f) are measured at various concentrations of M(II) concentration, then Eq. (8) is applicable:

$$\log F_f = \log \{k_f [H^+]^b [H_2A_2]_{(o)}^c [SO_4^{2-}]^d [Ac^-]^e\} + a \log [M^{2+}] \quad (9)$$

Eq. (9) states that the plots of $\log F_f$ vs. $\log [M^{2+}]$ will be straight line with the slope equalling to “a”, the reaction order with respect to $[M^{2+}]$. Whilst the intercept of the line will be equal to $\log \{k_f [H^+]^b [H_2A_2]_{(o)}^c [SO_4^{2-}]^d [Ac^-]^e\}$ from which the value of k_f can be evaluated after knowing the values of b, c, d and e.

In the similar way, the values of b, c, d and e can be evaluated as the slope of the log F_f vs. log $[H^+]$, log F_f vs. log $[H_2A_2]_{(0)}$, log F_f vs. log $[SO_4^{2-}]$ and log F_f vs. log $[Ac^-]$; plots, respectively. Intercepts of the plots will yield again the value of k_f .

Temperature dependence data of the rate study can be treated by the Arrhenius equation to obtain the value of activation energy (E_a):

$$\log F_f = \log \text{constant} - E_a/2.303 RT \quad (10)$$

The slope of the log F_f vs. $1/T$ plot will be equal to $(-E_a/2.303 R)$ from which the value of E_a can be determined. The temperature dependence rate data can also be treated by the activated complex theory as follows:

$$\log \left(\frac{k_f h}{kT} \right) = \log \left(\frac{F_f h}{kT f(R)} \right) = - \frac{\Delta H^\ddagger}{2.303 RT} + \frac{\Delta S^\ddagger}{2.303 R} \quad (11)$$

$$\text{or, } \log \frac{F_f h}{kT} = \log f(R) - \frac{\Delta H^\ddagger}{2.303 RT} + \frac{\Delta S^\ddagger}{2.303 R} \quad (12)$$

so that the plot of $\log \left(\frac{F_f h}{kT} \right)$ vs. $\frac{1}{T}$ will be a straight line with slope equaling to $-\Delta H^\ddagger/2.303R$ and intercept equaling to $\log f(R) + \Delta S^\ddagger / 2.303$. From the experimental slope value, the value of $\Delta H^\ddagger$; whilst from the experimental intercept value the value of $\Delta S^\ddagger$ can be evaluated at calculating $\log f(R)$ value.

In the similar way, the variations of flux in backward extractions can be treated.

5.5. Analytical Techniques

a. Visible Spectrophotometer

The visible spectrophotometer is used extensively for the determination of optical density or absorbance of the colored test solutions. The principal advantage of spectrophotometric analysis is that they provide the simple, easier and prompt means of determining minute quantities of substances more accurately in comparison to the other methods as gravimetric, volumetric and so on.

The visible spectrophotometric method of concentration determination is based on the Beer-Lambert law:

$$\log \frac{I_0}{I_t} = \epsilon c t \quad (13)$$

where $\log \left(\frac{I_0}{I_t} \right)$ represents optical density or absorbance(A) or extinction, whereas, ϵ , c and t represent the molar extinction co-efficient, concentration in g mol/L and thickness of solution medium (cm) through which light passes, respectively.

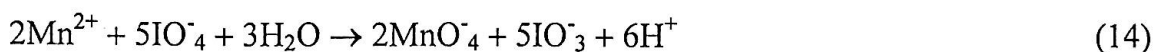
The equation (13) represents that the absorbance is proportional to the concentration, C . Hence by plotting 'A' (as ordinate) against concentration (as abscissa), a straight line passing through the origin is usually obtained. Thus if the absorbances' for a number of solutions of known concentrations are determined with a visible spectrophotometer and a calibration curve is constructed, then the unknown concentration of the same substance can be read off from the calibration curve after measuring its absorbance.

Discrepancies in spectrophotometric analysis are usually found when the colored solute ionizes, dissociates or associates in solution, Discrepancies may also occur when monochromatic light is not used. Throughout the investigations of equilibrium studies of Mn(II) and Ni(II), concentrations were determined with the help of a visible Spectrophotometer, ERMA, AE-300 (Japan).

i. Spectrophotometric Estimation of Mn(II):

Principle:

Minute quantities of Mn(II) can be determined colorimetrically by oxidizing it to permanganic acid [464]. The two oxidizing agents are generally used: i) ammonium persulfate in a phosphoric acid - nitric acid medium in the presence of a little silver nitrate as a catalyst and ii) potassium periodate. The later has been used in this case. In a hot acid solution (HNO_3 or H_2SO_4) periodate oxidizes manganous ion quantitatively to permanganic acid:



The intensity of the color of permanganic acid is proportional to the amount of Mn(II) present.

Construction of calibration curve for Mn(II):

A solution of KMnO_4 having concentration of 0.10 g-eq/L was prepared and standardized by the previously standardized ammonium ferrous sulfate solution. It was then used as the standard solution of Mn(II) in the visible spectrophotometric estimation at 545 nm. The aliquots of the standard solutions were diluted in such a way so that the resultant solutions contained 2-12 mg/L Mn(II). The results were displayed in Fig.1 as absorbance against concentration plot and shown in Table I.

Estimation of Mn(II) in the test solutions:

A definite volume of test solution was taken in a 100 mL volumetric flask and to it 5 mL concentrated HNO_3 and ~ 0.20 g potassium periodate were added [465b]. A slight excess of periodate made the solution more stable. Whereas excess of periodate made the solution cloudy. The solution was diluted and heated up to boiling for 2 min and kept hot about 10 min. Then the solution was diluted to such a volume that the absorbance of the solution fall within the range of the calibration curve. The absorbance of the test solution was measured against a reagent blank solution. The concentration of Mn(II) in the aqueous solution was then estimated from the calibration curve as shown in Fig. 1.

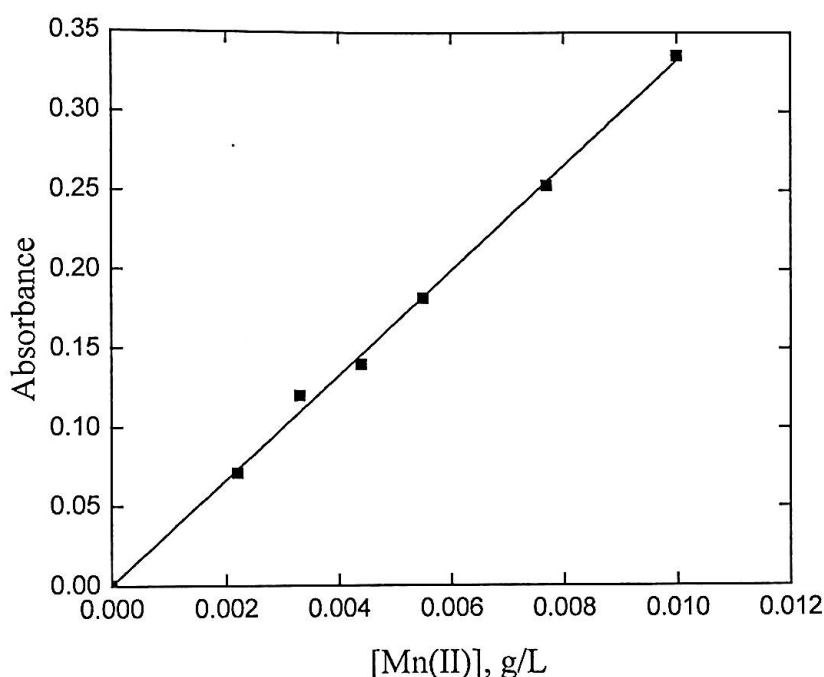
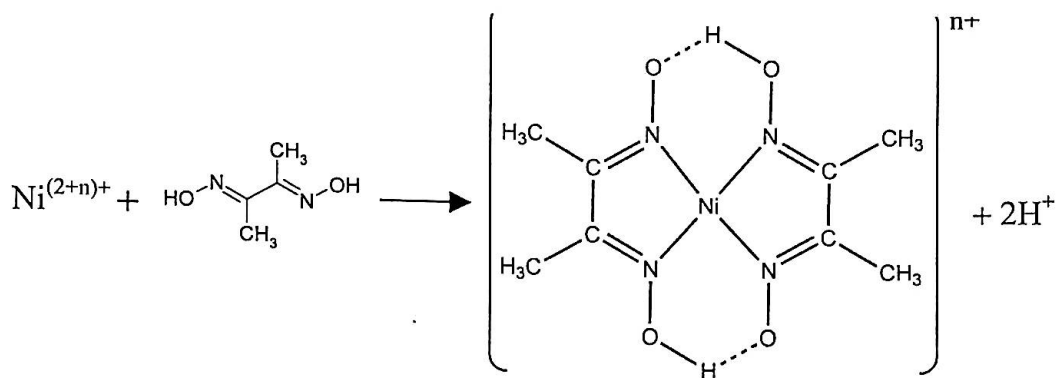


Fig. 1. Calibration curve for the estimation of Mn(II) by visible spectrophotometric techniques at 545 nm (Table I)

ii. Spectrophotometric Estimation of Ni(II):

This method involves the formation of nickelic dimethylglyoxime with dimethyl glyoxime. Interference from various ions has been discussed [466].

When dimethylglyoxime is added to an alkaline solution of nickel salt, which has been treated with an oxidizing agent (such as bromine), a red color is obtained. In this way the formation of dimethylglyoxime complexes of nickel in a valence state higher than two occurs. The following reaction takes place:



Dimethylglyoxime

 $\text{Ni}^{(2+n)+}$ -dimethylglyoxime Complex

Ammoniacal solutions are generally employed.

Construction of calibration curve of Ni(II):

Exactly 2, 4, 6, 8, 10 and 12 mL portion of the standard solution of Ni(II) (1 g/L) were taken in six different 100 mL volumetric flasks. In each flasks 1 mL saturated bromine water was added followed by 2 mL of concentrated NH_3 solution and then 1 mL of 1% dimethylglyoxime solution. Contents were diluted and made up to the mark with distilled water. The blank solution was prepared as usual excepting Ni(II) solution. The absorbance of the samples were measured at 445 nm and the calibration curve was constructed by plotting absorbance vs. Ni(II) concentration as shown in Fig. 2 (data given in table II). From the curve the amount of Ni(II) concentration in unknown solution was calculated after measuring the absorbance.

Estimation of Ni(II) in the test solutions:

The test solution of Ni(II) was taken in a suitable volumetric flask(100/50/25 mL) and to it 1 mL of saturated bromine water followed by 2 mL of concentrated ammonia solution and then 1 mL of 1% dimethylglyoxime were added. Then the solution was diluted and made up to the mark with distilled water. The absorbance of the test solution was measured against a reagent blank solution. The concentration of Ni(II) in the aqueous solution was then be estimated from the calibration curve as shown in Fig. 2.

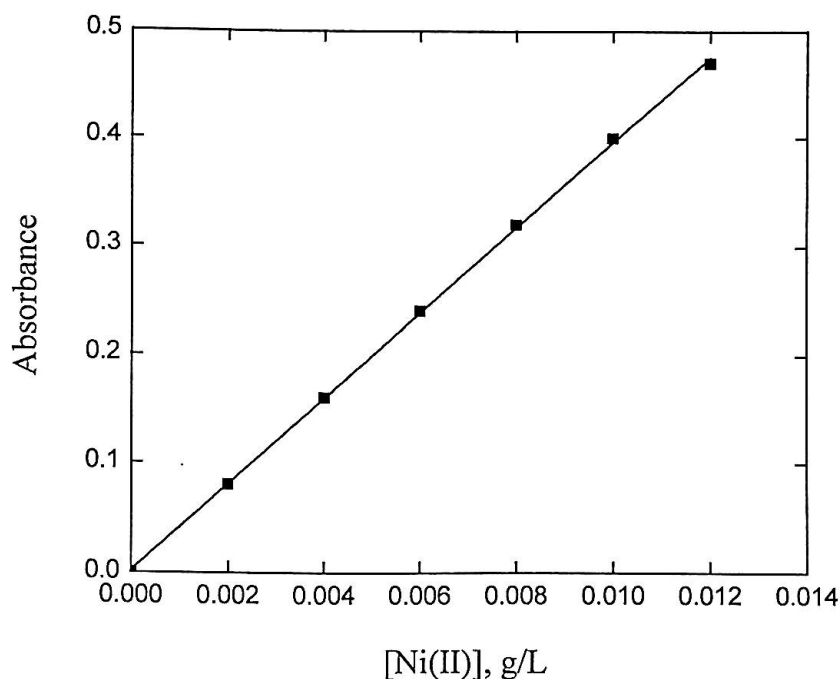


Fig. 2. Calibration curve for the determination of Ni(II) by visible spectrophotometric technique at 445 nm (Table II).

b. Complexometric titration method for Zn(II) by EDTA

Procedure:

Zinc(II) sulfate solution (0.05 M) was made by dissolving 14.378 g of the A.R. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in a 1 L of distilled water and it was standardized by titration with 0.05 mol/L EDTA solution using Solochrome Black as indicator.

Buffer solution (pH 10) was prepared by dissolving exactly 8.0 g A.R. ammonium nitrate in 65 mL of distilled water and adding 35 mL of concentrated ammonia solution (sp.gr. = 0.88).

An aliquot of 25 mL of zinc(II) solution to be estimated for zinc(II)-content was taken into a 250 mL conical flask, diluted to 100 mL with distilled water and then 10 mL buffer solution and 30 - 40 mg of indicator/ KNO_3 mixture were added. The solution was warmed to 40°C and titrated (stirred magnetically) with the standard EDTA solution to obtain a pure blue color [465a]. The procedure was used only in the case of equilibrium study of zinc(II).

In the case of forward and backward extraction studies of Zn(II), Ni(II) and Mn(II) Atomic Absorption Spectrophotometric (AAS) techniques were applied.

c. Principles of Atomic Absorption Spectrophotometry (AAS)

The basic principle of atomic absorption spectrophotometry based on the absorption of light of intrinsic wavelength by atoms. It deals with the excitement of atoms. Atoms are excited in a hot flame. As they fall back to the ground state, photons are emitted. A line source emitting a narrow spectral line of the characteristic energy is used to excite the free atoms formed in the flame. The energy of the line source is decreased (absorption) which is consequently measured.

Two most common line sources are obtained from the “hollow cathode lamp (HCL)” and the “electrodeless discharge lamp (EDL)”. Absorption is proportional to the concentration of free atoms in the flame:

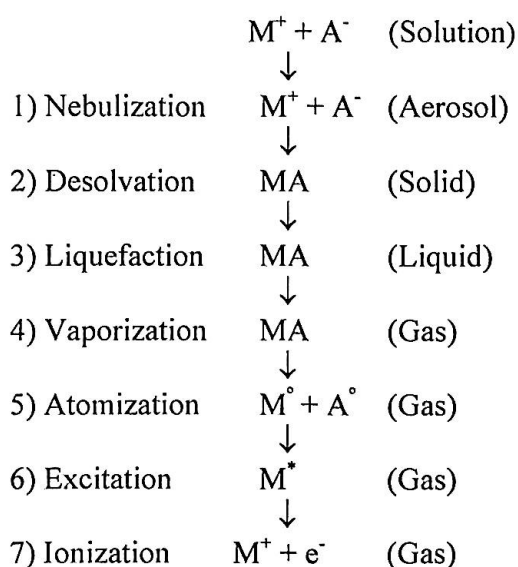
$$\text{Absorbance} = \log_{10} \left(\frac{I_0}{I_1} \right) = K.C.L$$

where, C = concentration of sample (free atoms)

K = constant (can be determined experimentally)

L = path length

The flame process occurring in an Atomic Absorption Spectrophotometer (AAS) is depicted below:



Scheme 1. The flame process. “M⁺” is a metal cation and “A⁻” is the associated anion.

A Shimadzu AA-6800 spectrophotometer was used for the estimations of Mn(II), Ni(II) and Zn(II) using air- acetylene flame. The line sources usable for the estimation of metal ions under consideration are 279.50, 232.00 and 213.90 nm for Mn, Ni and Zn respectively.

i) Construction of calibration curve for Mn(II) estimation by AAS:

Standard 2, 3, 5, 7.5 and 10 ppm solutions of Mn(II) were prepared and absorbance of the solutions were measured by the AAS to construct the following calibration curve (Fig. 3).

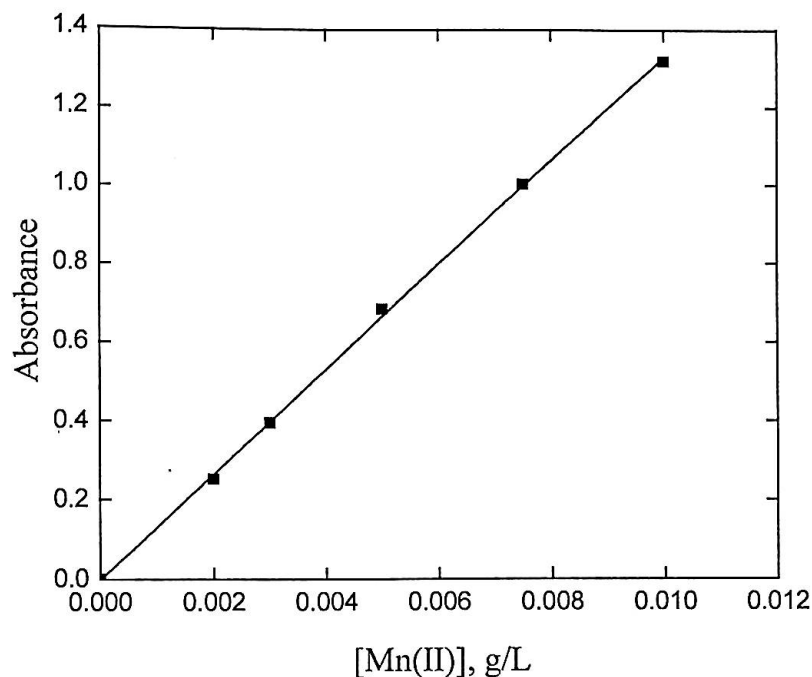


Fig. 3. Calibration curve for the estimation of Mn(II) by atomic absorption spectrophotometric techniques at 279.5 nm (Table III)

ii) Construction of calibration curve for Ni(II) estimation by AAS:

Standard 0.5, 1, 1.5, 2, 3 and 4 ppm solutions of Ni(II) were prepared and absorbances of the solutions were measured by the AAS to construct the following calibration curve (Fig. 4).

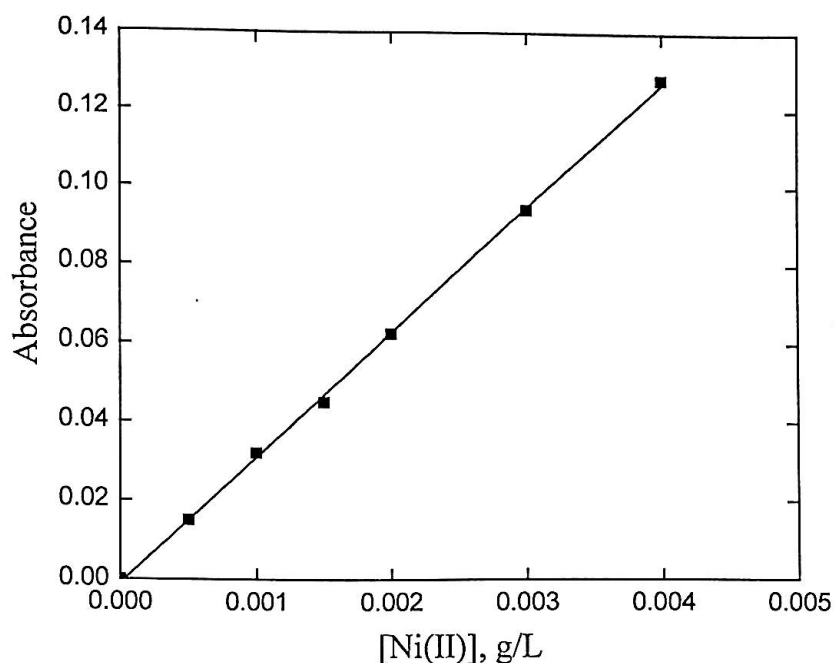


Fig. 4. Construction of calibration curve for the estimation of Ni(II) by atomic absorption spectrophotometric technique at 232 nm (**Table IV**)

iii) Construction of calibration curve for Zn(II) estimation by AAS:

Standard 0.25, 0.50, 0.75, 1 and 1.5 ppm solutions of Zn(II) were prepared and absorbance of the solutions were measured by the AAS to construct the following calibration curve (Fig. 5).

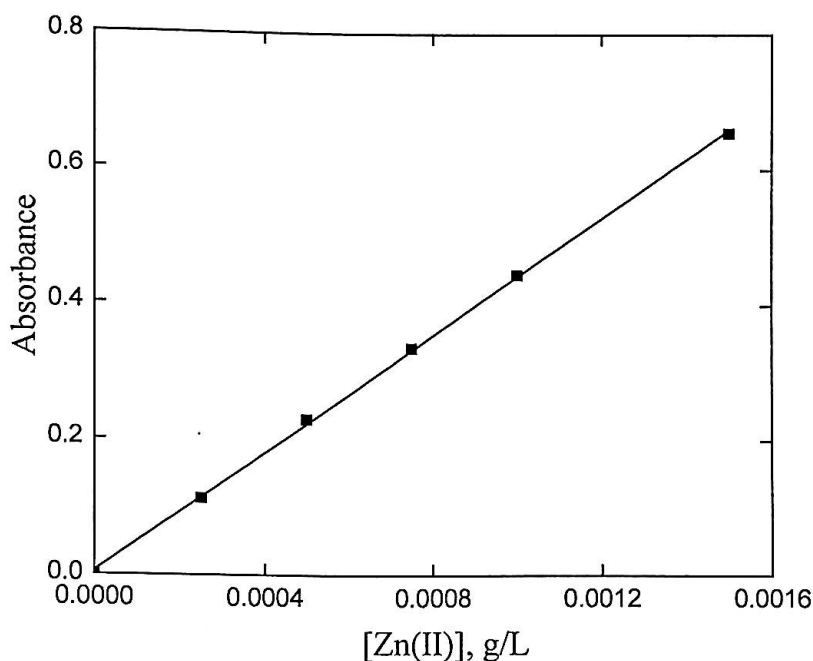


Fig. 5. Calibration curve for the estimation of Zn(II) by atomic absorption spectrophotometric techniques at 213.9 nm (Table V)

5.6. Preparation of Different Solutions

a. Preparation of aqueous solutions

i) Dimethyl glyoxime (1%):

2.50 g dimethylglyoxime crystal was weighed out in a dry 250 mL volumetric flask and made up to the mark with absolute alcohol. The solution was used for the estimation of Ni(II) in spectrophotometric technique.

ii) Nickel(II) Sulfate Solution:

22.39 g $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was weighed out in a dry 1 L volumetric flask and made up to the mark by distilled water. The solution was standardized by EDTA titration. On standardization, the Ni(II) content of the solution was found to be 4.99 g/L. The solution was used throughout the investigations of Ni(II) equilibrium and forward extraction rate studies

iii) Manganese(II) Sulfate Solution:

15.38 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was weighed out in a dry 1 L volumetric flask and made up to the mark by distilled water. The solution was standardized by EDTA titration. On standardization, the Mn(II) content of the solution was found to be 4.98 g/L. The solution was used throughout the investigations of Mn(II) equilibrium and forward extraction rate studies.

iv) Zinc(II) Sulfate Solution:

22.08 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was weighed out in a dry 1 L volumetric flask and made up to the mark by distilled water. The solution was standardized by EDTA titration. On standardization, the Zn(II) content of the solution was found to be 5.01 g/L. The solution was used as stock throughout the investigations of Zn(II) equilibrium and forward extraction rate studies

v) Sodium Sulfate (Na_2SO_4) solution:

284.012 g A. R grade Na_2SO_4 (anhydrous) was weighed out in a 1 L volumetric flask and made up to the mark with distilled water. The solution was 2 mol/L. This solution was used as stock for sulfate ion concentration adjustment of the aqueous phase wherever.

vi) Sodium hydroxide:

About 60 g NaOH was taken in a beaker and washed out thrice with distilled water for removal of carbonate. The washed mass was then dissolved in distilled water taken in a 1 L volumetric flask. The concentration of this solution was estimated by titration with standard oxalic acid solution (1 g eq/L). The strength of the NaOH solution prepared was 1.25 mol/L.

vii) Preparation of oxalic acid solution:

15.75 g of $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was accurately weighed out into a 250 mL volumetric flask. The solid was dissolved in distilled water and made up to the mark and shaken well. The solution (1 N) was used in the standardization of NaOH solutions prepared above.

viii) Sodium carbonate:

53 g anhydrous Na_2CO_3 was weighed out into a 1 L volumetric flask and made up to the mark with distilled water to get 1 g eq/L Na_2CO_3 solution. The solution was standardized by the oxalic acid solution. This solution was used for estimation of acid strength.

ix) Preparation of acetic acid solution:

For the preparation of 1 mol/L acetic acid solution, 58 mL portion of concentrated acetic acid was taken in a 1 L volumetric flask and made up to the mark with distilled water. It was standardized by previously standardized NaOH solution using phenolphthalein as an indicator. This solution was used to constitute the aqueous phase for Mn(II) and Ni(II) throughout the investigations of equilibrium as well as kinetic studies.

x) Preparation of sodium acetate solution:

136 g $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ was weighed out into a 1 L volumetric flask and made up to the mark with distilled water. This solution was used in preparation of aqueous phases during equilibrium and kinetic studies for Mn(II) and Ni(II) , whenever necessary.

xi) Buffer solution (pH = 10):

It was prepared by dissolving 8.00 g A. R. ammonium nitrate in 65 mL de-ionized water and adding 35 mL of concentrated ammonia solution (Sp.gr. = 0.91) to it. This buffer solution was used during the determination of Zn(II) concentration by EDTA titration throughout the equilibrium study.

xii) Solochrome Black (Eriochrome Black T):

The indicator was prepared by grinding 0.10 g of Solochrome Black with 10 g of A. R. potassium nitrate and mixed homogeneously as powder. This indicator was used during the estimation of Zn(II) concentration by EDTA titration method throughout the equilibrium study.

b. Preparation of aqueous solutions for forward extraction and equilibrium studies

The metal ion solutions prepared as described above were used for this purpose. The calculated amount of a particular the stock solution was pipetted out into 100 mL volumetric flasks so that the resultant solution after proper dilutions contained the desired amount of a particular metal ion (Mn(II) , Ni(II) or Zn(II)) considered. Before diluting up to the mark, calculated amounts of sulphuric acid and acetic acid (for Mn(II) and Ni(II) only) solutions were added so that the test solutions contained desired concentrations of sulphate and acetate ions. To prepare Zn(II) test solution, acetic acid solution was not added. In all the cases, anhydrous sodium carbonate was used for adjusting pH. The equilibrium pH was recorded after extraction in all cases.

c. Preparation of organic solutions**i) Kerosene:**

Kerosene was purchased from the local market and distilled to collect the colorless fraction obtained in the range of 473 to 533 K. It was mostly aliphatic in nature. In all cases, distilled kerosene was used as a diluent.

ii) BTMPPA [bis (2,4,4-trimethyl pentyl)phosphinic acid]:

1 mol/L BTMPPA solution was prepared by dissolving exactly 580 g of Cyanex 272 in a dry clean 1 L volumetric flask by distilled kerosene and made up to the mark. Extractant solutions of different concentrations were prepared by proper dilution of this stock solution by distilled kerosene.

iii) Mn-BTMPPA complex:

The stock solution of the organic phase loaded with Mn(II) was made by contacting 500 mL 0.2 mol/L BTMPPA solution with equal volume of aqueous phase containing 2.00 g/L Mn(II) at pH 4.8 for 5 min. After equilibration, the organic phase metal ion concentration was estimated by the method of difference. The loaded organic phase was collected as stock solution for backward extraction rate studies. The Mn(II) content of the loaded organic phase (stock solution) was found to be 1.28 g/L and free BTMPPA was 0.177 mol/L.

iv) Ni-BTMPPA complex:

The stock solution of the organic phase loaded with Ni(II) was prepared by shaking 500 cm³ 0.20 kmol/m³ BTMPPA solution with same volume of aqueous phase containing 4.00 g/L of Ni(II) at pH 6 for 2 min until the equilibrium was reached. After equilibration the organic phase metal ion concentration was estimated by the method of difference. The loaded organic phase was found to contain 2.90 g/L of Ni(II) with 0.1506 mol/L of free BTMPPA.

v) Zn-BTMPPA complex:

The stock solution of the organic phase loaded with Zn(II) was prepared by shaking 500 mL 0.20 mol/L BTMPPA solution with same volume of aqueous phase containing 5.00 g/L of Zn(II) at pH 6 for 5 min until the equilibrium was reached. After equilibration, the organic phase Zn(II) concentrations was estimated by the method of difference. The loaded organic phase was found to contain 3.505 g/L of Zn(II) with 0.1464 mol/L of free BTMPPA.

vi) Preparation of BTMPPA- different diluent mixture:

Aliquots of 2.9 g BTMPPA were taken into ten different 50 mL volumetric flasks and made up to the mark with (carbontetrachloride, 1,1-dichloroethane, benzene, toluene, chloroform, cyclohexane, n-heptane, heptane-1-ol, hexane-1-ol and kerosene). As a result, 0.1 mol/L BTMPPA in different diluents were prepared and used to study the effect of diluents on distribution ratios of Mn(II).

vii) Preparation of organic phase for back extraction rate studies:

The solutions prepared in the above sections (iii), (iv) and (v) were properly diluted after adding calculated amount of free BTMPPA by kerosene to prepare the organic phases containing desired amounts of Mn(II)/Ni(II)/Zn(II)- BTMPPA complex and free BTMPPA.

viii) Preparation of aqueous phase for backward extraction rate studies:

The aqueous phases to be used in the backward extraction rate studies were prepared by proper dissolution of H_2SO_4 / Na_2SO_4 - AcH - AcNa mixture (only H_2SO_4 / Na_2SO_4 in case of Zn(II) - system) and proper adjustment of pH.

5.7. Procedures for the Equilibrium and Rate Measurements**i) Experimental procedure for the equilibrium studies of Mn(II), Ni(II) and Zn(II):**

In all cases of extraction a definite aliquot of an aqueous phase (20 mL) containing definite [Mn(II)] or [Ni(II)] or [Zn(II)], $[\text{SO}_4^{=}]$ and $[\text{Ac}^-]$ (in the case of [Mn(II)] and [Ni(II)]) at a pH was taken in a 125 mL reagent bottle and to it same aliquot of BTMPPA (de-emulsifier, in the case of Ni(II) only) in kerosene of definite concentration was added. The bottle was stoppered properly and shaken in a thermostated water bath for a predetermined time (eg., Mn(II) for 5 min, Zn(II) for 5 min and Ni(II) for 2 min). After equilibration the phases were allowed to settle and disengaged by a separatory funnel. The aqueous phase was subjected for equilibrium pH measurement and the metal ion content as mentioned earlier. The equilibrium organic phase metal ion concentrations were estimated by the method of difference. The distribution or extraction ratio (D) of a metal ion was calculated as the ratio of metal ion concentration [Mn(II) or Zn(II) or Ni(II)] in the organic phase to that in the aqueous phase at equilibrium. In the case of loading studies, the organic phase was repeatedly contacted with fresh equal volume of aqueous solutions until the saturation of the organic phase with the metal was attained. For the stripping studies 25 mL of BTMPPA solution containing [Mn(II) or Ni(II) or Zn(II)] and free BTMPPA of definite concentration was equilibrated for 5 min at (303 ± 0.5) K with an equal volume of a mineral acid (H_2SO_4 , HNO_3 and HCl) solution of definite strength. Stripping ratio (S) was calculated on dividing [Mn(II)] in the aqueous phase to that in the organic phase at equilibrium.

ii) Experimental procedure for the forward extraction rate measurements of Mn(II), Ni(II) and Zn(II) by Single drop techniques:

A single (falling) drop apparatus was used for the investigation on the rate of forward extractions of Mn(II), Ni(II) and Zn(II) by BTMPPA dissolved in kerosene. The main column of the apparatus was filled with the organic phase containing a definite concentration of BTMPPA (in the cases of Ni(II) extraction 3% octan-1-ol by volume was used). The over-head small column was filled (2/3 portion) with the aqueous phase containing definite amounts of metal ion [Mn(II) or Ni(II) or Zn(II)], $[\text{SO}_4^{=}]$ and $[\text{Ac}^-]$ (in the cases of Mn(II) and Ni(II) only) at a definite pH. The cumulative time for falling 10 separate drops (one after another) was determined to get the average fall time (t). It was found that the average drop fall time was dependent of the compositions of aqueous and organic phases. Then, falling 100 drops were to be collected in the actual experiment. The volume of counted 100 collected drops was estimated by the Weight and Density method. The metal content of collected drops in actual experimentation was determined by the atomic absorption spectrophotometric (AAS) method. Using this way, the volume of 1 drop and consequently, the surface area (A) of a drop were calculated. The subtraction of the metal concentration in the collected drops of actual experimentation from the initial concentration of the aqueous phase gave an idea on the mass transferred through the interface of a drop during the falling period of a drop through the continuum of the organic phase.

iii) Experimental procedure for rate measurements in backward extractions of Mn(II), Ni(II) and Zn(II) by Single drop techniques:

In the measurements of the rate of backward extraction of the metal ions under consideration, the same (falling drop) technique as used in the forward extraction rate studies was applied. The main column of the device was filled with the organic phase containing a definite concentrations of Mn(II)-BTMPPA, Ni(II)-BTMPPA or Zn(II)-BTMPPA complex and free BTMPPA. The aqueous phase containing sulfuric acid and acetic acid at a desired pH was used to form drops. The drops of the aqueous solution were allowed to fall through the continuum of the organic phase. During falling, metal ions from the organic phase were transferred to the aqueous phase.

CHAPTER VI

RESULTS AND DISCUSSION

The results and discussion part of this thesis has been presented under the following sub-headings:

1. Studies on the extraction equilibrium of the $\text{Mn(II)-SO}_4^{=}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene system
2. Studies on the extraction equilibrium of the $\text{Ni(II)-SO}_4^{=}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene-octanol system
3. Studies on the extraction equilibrium of the $\text{Zn(II)-SO}_4^{=}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene system
4. Studies on the kinetics of forward extraction of Mn(II) in the $\text{Mn(II)-SO}_4^{=}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene system
5. Studies on the kinetics of forward extraction of Ni(II) in the $\text{Ni(II)-SO}_4^{=}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene system
6. Studies on the kinetics of forward extraction of Zn(II) in the $\text{Zn(II)-SO}_4^{=}\text{-(Na}^+, \text{H}^+)$ - Cyanex 272-kerosene system
7. Studies on the kinetics of backward extraction/stripping of Mn(II) in the Mn(II)- Cyanex 272 complex-free extractant-kerosene - $\text{SO}_4^{=}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ system
8. Studies on the kinetics of backward extraction/stripping of Ni(II) in the Ni(II)- Cyanex 272 complex-free extractant-kerosene - $\text{SO}_4^{=}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ system
9. Studies on the kinetics of backward extraction/stripping of Zn(II) in the Zn(II)- Cyanex 272 complex-free extractant-kerosene - $\text{SO}_4^{=}\text{-(Na}^+, \text{H}^+)$ system and
10. An overall discussion on the correlation of the respective equilibrium data with the kinetic data. Prediction on the separation of Mn(II), Ni(II) and Zn(II) by Cyanex 272 will also be discussed

1. Studies on the extraction equilibrium of the $\text{Mn(II)}\text{-SO}_4^{\text{=}}\text{-Ac}^{\text{=}}(\text{Na}^+, \text{H}^+) - \text{Cyanex 272-kerosene system}$

As pointed out in the 'Objective of Present Investigation' section, the leaching of the manganiferrous ores, deep sea nodules, waste dry cells, sulfide ores, converter slag etc. by sulphuric acid solution yields leached solution containing many metal ions including Mn(II). With an aim in mind to separate Mn(II) from such solution using Cyanex 272 as extractant, this study has been carried out in order to examine its extraction behavior from sulphate medium. As the preliminary experiments showed that the extraction of Mn(II) occurred between pH $\sim$ 3.20 - 4.80, it became necessary to control the aqueous pH which was invariably decreased to a large extent with the progress of extraction as well as with the increase in extractant concentration; and to do this acetate buffer was added to the aqueous solutions.

The title system has been investigated as follows:

i) Effect of phase contact time on extraction of Mn(II)

The effect of phase contact time on the extraction of Mn(II) from an aqueous solution containing 0.40 kg/m^3 Mn(II), 0.008 kmol/m^3 $\text{SO}_4^{\text{=}}$, 0.25 kmol/m^3 $\text{Ac}^{\text{=}}$ at pH 4.6 by kerosene solution of 0.025 kmol/m^3 dimeric Cyanex 272 at 303 K has been investigated. As extraction proceeds, the concentration of Mn(II) in the aqueous solution is decreased gradually whilst that in the organic phase is increased. The experimental results are given in Table VI. The concentration variation of Mn(II) in the aqueous phase is depicted in Fig. 6, as $[\text{Mn(II)}]_{(\text{aq})}$ vs. time plot.

The Fig. 6 also contains a plot representing the variation of the concentration ratio ($[\text{Mn(II)}]_{(\text{o})}/[\text{Mn(II)}]_{(\text{a})}$) with time. It is found that the decrease in the aqueous Mn(II) concentration or the increase in the concentration ratio takes place up to 4 min's of phase contact. After this time neither concentration of Mn(II) in the aqueous phase decreases further nor the concentration ratio increases further. Consequently, it is concluded that the equilibration time for the system is about 4 min. In subsequent experiments, a phase contact time of 5 min has been used in order to ensure equilibration at different experimental parameters. It is noteworthy to cite here that the equilibration time of 10 min has been reported for the extraction of Mn(II) from the sulphate-acetate medium by di-2-ethylhexyl phosphoric acid (D2EHPA) [193].

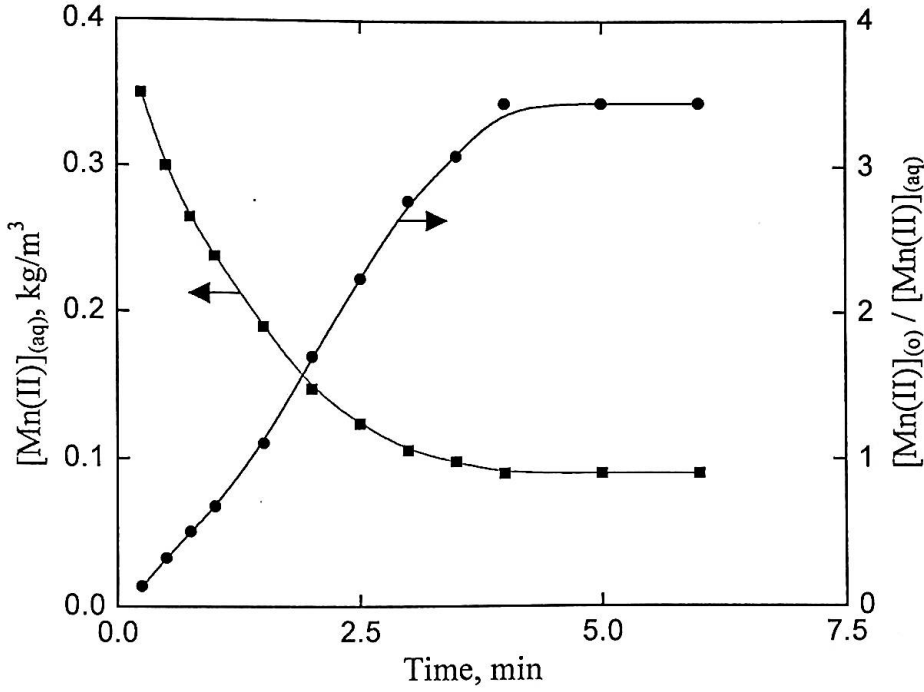
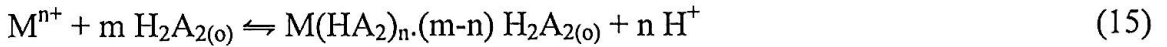


Fig. 6. Effect of time on the extraction of Mn(II) from sulfate - acetato medium by Cyanex 272 in kerosene (*cf.* Table VI). $[\text{Mn(II)}]_{(\text{ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.60$, Temperature = $(303 \pm .50) \text{ K}$, O/A (Phase ratio) = 1

ii) Effect of Mn(II) concentration on extraction ratio of Mn(II)

Cyanex 272 is an acidic extractant. It can extract a metal ion (M^{n+}) by chelation in combination with solvation as shown below.



The equilibrium constant or better to say extraction equilibrium constant (K_{ex}) for Eq. (15) can be expressed as:

$$K_{\text{ex}} = \frac{C_{\text{M}(\text{HA}_2)_n \cdot (m-n) \text{H}_2\text{A}_{2(\text{o})}} C_{\text{H}^+}^n}{C_{\text{M}^{n+}} C_{\text{H}_2\text{A}_{2(\text{o})}}^m} \quad (16)$$

Defining the distribution or extraction ratio (D) as, $\frac{C_{\text{M}(\text{HA}_2)_n \cdot (m-n) \text{H}_2\text{A}_{2(\text{o})}}}{C_{\text{M}^{n+}}}$, the Eq. (16)

can be modified to

$$K_{\text{ex}} = D \cdot \frac{C_{\text{H}^+}^n}{C_{\text{H}_2\text{A}_2(\text{o})}}$$

$$\text{or, } \log D = \log K_{\text{ex}} + n \text{ pH} + m C_{\text{H}_2\text{A}_2(\text{o})} \quad (17)$$

Equation (17) represents the basic equation for a chelate forming solvent extraction system for a metal ion by an acidic extractant. It is mentionable here that the all concentration terms or pH refer to the equilibrium values of the respective species. Consequently, Eq. (17) represents that the value of log D should be independent of initial or equilibrium metal ion concentration at a constant equilibrium pH and equilibrium extractant concentration.

The aqueous phases containing 0.018 kmol/m³ sulfate, 0.025 kmol/m³ acetate and different amounts of Mn(II) ranging from 0.003 kmol/m³ to 0.0356 kmol/m³ at initial pH of 4.6 have been equilibrated with 0.025 kmol/m³ Cyanex 272 solution in kerosene at aqueous to organic phase ratio (O/A) of 1 (A = 25 cm³). The experimental results are shown in Table VII. It is found that the logarithm of extraction ratio (log D) values are decreased (though the equilibrium concentrations of Mn(II) in the organic phase being increased) with increasing the initial manganese concentration in the aqueous phase. It is also noticeable that the equilibrium pH values differ from the initial pH values. This is no doubt due to different extent of H⁺ liberation in the system for different amount of Mn(II) being extracted into the organic phase.

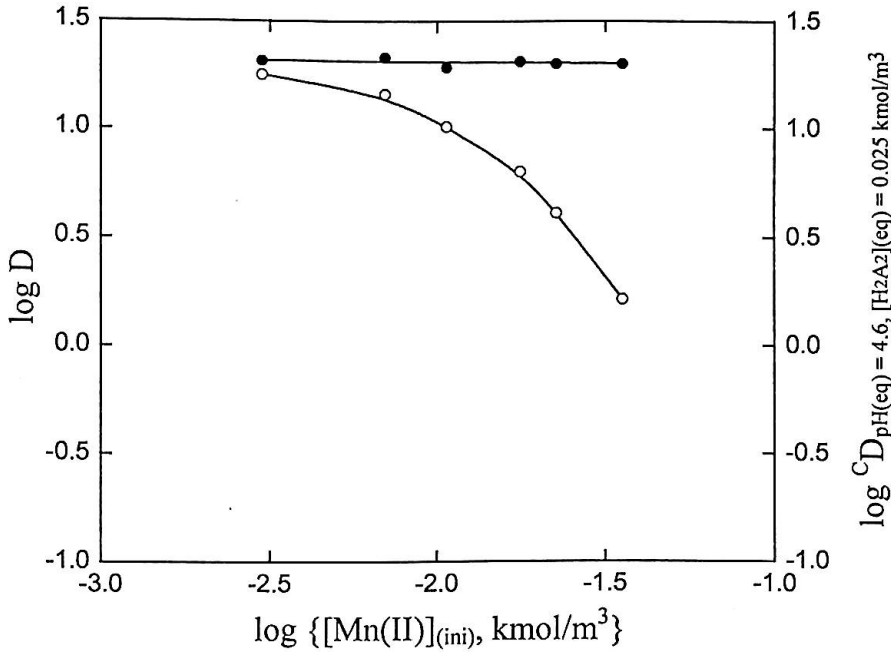


Fig. 7. Effect of metal ion concentration on the extraction of Mn(II) by Cyanex 272 in kerosene (cf. Table VII). $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o},\text{ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.018 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.60$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, $\text{O/A} = 1$.

The $\log D$ vs. $\log ([\text{Mn(II)}]_{(\text{ini})}, \text{kmol/m}^3)$ plot is represented in Fig. 7. According to Eq. (17), the plot should be horizontal but a curve is obtained. The reason for this is obviously the variability of equilibrium pH and free extractant concentration (resulting from various amounts being associated with the extracted species). After determining the pH and extractant dependences, the corrected D values ($\hat{D}$) and subsequently $\log \hat{D}$ values at a chosen constant equilibrium pH and free extractant concentration can be calculated. If the pH and extractant dependences are 2 and 1, respectively, (referred to the following two sections), the equation for calculating $\log \hat{D}$ at $\text{pH}_{(\text{eq})} = 4.6$ (constant) and $[\text{H}_2\text{A}_2]_{(\text{o},\text{eq})} = 0.025 \text{ kmol/m}^3$ (constant) will be as follows:

$$\log \hat{D}_{\text{pH} = 4.6, [\text{H}_2\text{A}_2] = 0.025 \text{ kmol/m}^3} = \log D + 2 (\text{constant pH}_{(\text{eq})} - \text{pH}_{(\text{eq})} \text{ experimental}) + \{ \text{constant} \\ \log [\text{H}_2\text{A}_2]_{(\text{o},\text{eq})} \text{ chosen} - \log ([\text{H}_2\text{A}_2]_{(\text{o},\text{ini})} - [\text{Mn(II)}]_{(\text{o},\text{eq})}) \} \quad (18)$$

where, all concentration terms are in kmol/m^3 . When $\log \hat{D}$ has been plotted against $\log \{[\text{Mn(II)}], \text{kmol/m}^3\}$, a horizontal line is obtained which is in consistent with Eq. (17) or with the fundamental aspect of solvent extraction chemistry. The independence of $\log \hat{D}$ on initial Mn(II) concentration in the aqueous phase indicates that the Mn(II) speciation change does not occur with its concentration change.

iii) Effect of aqueous pH on the extraction ratio of Mn(II)

Equation (17) indicates that the plot of $\log D$ vs. equilibrium pH ($pH_{(eq)}$) should be a straight line with slope equaling to 'n', the number of H^+ liberated from extractant on complexation with a manganese(II) ion; provided the equilibrium extractant concentration remains constant.

The aqueous solutions containing $0.40 \text{ kg/m}^3 \text{ Mn(II)}$, $0.008 \text{ kmol/m}^3 \text{ SO}_4^{2-}$ and $0.025 \text{ kmol/m}^3 \text{ Ac}^-$ at different pH values have been prepared and each solution has been equilibrated with both 0.025 and 0.10 kmol/m^3 Cyanex 272 solutions in kerosene at $O/A = 1$ and 303K . The equilibrium data are given in Table VIII. The fifth column of the table represents experimental $\log D$ values at various equilibrium pH values at constant initial extractant concentrations but not at constant equilibrium extractant concentrations. The logarithm of corrected D values ($\log {}^cD$) at equilibrium extractant concentration have been calculated by the following relations:

$$\log {}^cD_{[H_2A_2]_{(o,eq)} \text{ chosen constant}} = \log D + \{ \log ([H_2A_2]_{(o,eq)} \text{ chosen as constant}) - \log ([H_2A_2]_{(o,ini)} [Mn(II)]_{(o,eq)}) \} \quad (19)$$

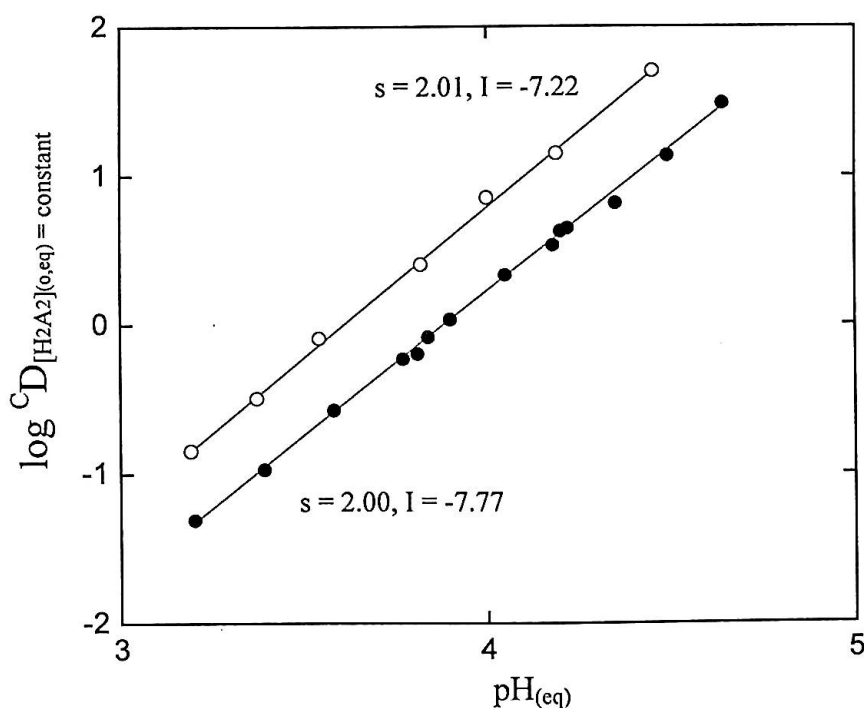


Fig. 8. Effect of equilibrium pH on the extraction of Mn(II) by Cyanex 272 in kerosene (cf. Table VIII). $[Mn(II)]_{(ini)} = 0.40 \text{ kg/m}^3$, $[Ac^-] = 0.25 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.008 \text{ kmol/m}^3$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, $O/A = 1$. (•), $[H_2A_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$, ${}^cD = D$ at constant ($[H_2A_2]_{(o,eq)} = 0.025 \text{ kmol/m}^3$), (O), $[H_2A_2]_{(o,ini)} = 0.10 \text{ kmol/m}^3$, ${}^cD = D$ at constant ($[H_2A_2]_{(o,eq)} = 0.10 \text{ kmol/m}^3$).

These values are given in the last column of the table. The Fig. 8 represents the $\log {}^cD_{[H_2A_2]_{(o,eq)} = \text{constant}}$ vs. $pH_{(eq)}$ plots at constant equilibrium values of 0.025 and 0.10 kmol/m^3 . Straight lines are obtained with slopes of 2.00 and 2.01 for 0.025 and 0.10 kmol/m^3 equilibrium extractant concentrations, respectively. The respective intercepts are -7.77 and -7.22. Therefore, the value of 'n' or the pH dependence in the Mn(II)-Cyanex 272 system is 2. In other words, 2 g ions of H^+ are liberated for complexation of each g ion of Mn(II) by Cyanex 272.

iv) Effect of organic phase extractant (Cyanex 272) concentration on the extraction ratio of Mn(II)

According to Eq. (17), the plot of $\log D$ vs. $\log [H_2A_2]_{(o,eq)}$ at a particular constant equilibrium pH should be a straight line with slope giving the number of moles of Cyanex 272 associated with 1 g ion of Mn(II) to form the extractable species. But it is very difficult to gather $\log D$ values at constant equilibrium pH values. Consequently, corrected $\log D$ values should be evaluated as mentioned above.

Three aqueous solutions each containing 0.40 kg/m^3 Mn(II), 0.008 kmol/m^3 $SO_4^{=}$ and 0.25 kmol/m^3 Ac^- at initial pH values of 3.75, 4.15 and 4.45; and each solution has been equilibrated with Cyanex 272 solutions in kerosene of different concentrations. The experimental data are given in Table IX. The $\log D$ vs. $\log ([H_2A_2]_{(o,ini)}, \text{ kmol/m}^3)$ plots at initial pH values of 3.75, 4.15 and 4.45 are shown in Fig. 9. Straight lines are obtained instead with slopes of 1.03, 1.02 and 1.10 for constant initial pH values of 4.45, 4.15 and 3.75, respectively, with respective intercepts of 2.48, 1.90 and 1.45. Considering extractant dependency of unity, $\log [H_2A_2]_{(o,eq)}$ values have been calculated ($= \log [H_2A_2]_{(o,ini)} - [Mn(II)]_{(o,eq)}$), whilst on considering pH dependency of 2, the values of $\log {}^cD$ have been calculated using the following relationship:

$$\log {}^cD_{pH_{(eq)} = \text{constant}} = \log D + 2 (pH_{(eq)} \text{ chosen as constant} - pH_{(eq)} \text{ experimental}) \quad (20)$$

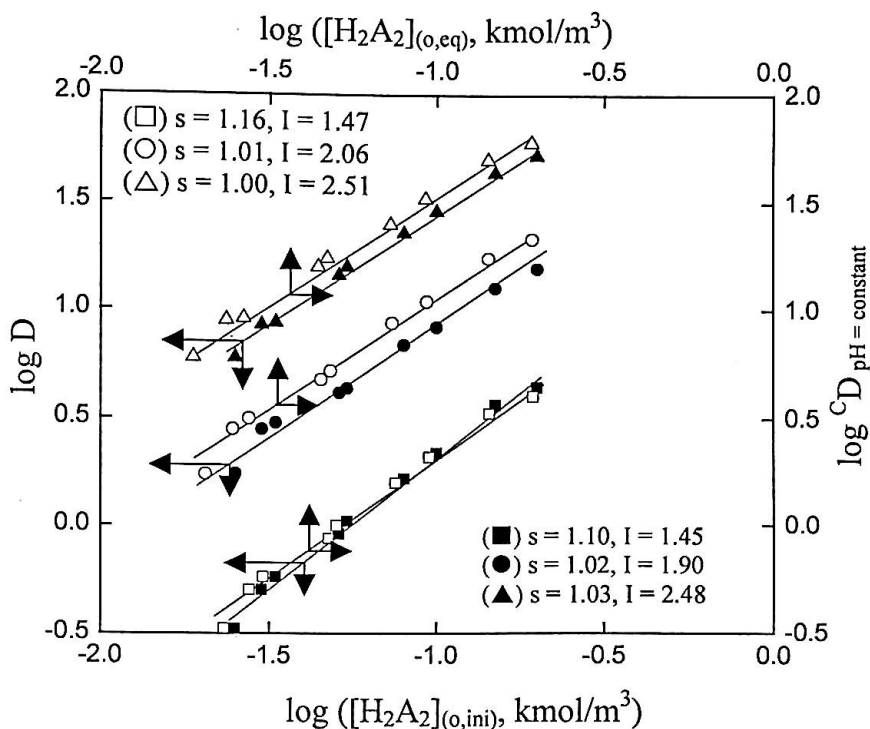


Fig. 9. Effect of extractant (Cyanex 272) concentration on the extraction of Mn(II) from aqueous sulfate - acetato medium (*cf.* Table IX). $[\text{Mn(II)}]_{(\text{ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, $\text{O/A} = 1$, (■, □); $\text{pH}_{(\text{ini})} = 3.75$, $^cD = D$ at constant ($\text{pH}_{(\text{eq})} = 3.74$), (▲, △); $\text{pH}_{(\text{ini})} = 4.45$, $^cD = D$ at constant ($\text{pH}_{(\text{eq})} = 4.35$), (●, ○); $\text{pH}_{(\text{ini})} = 4.15$, $^cD = D$ at constant ($\text{pH}_{(\text{eq})} = 4.13$).

Fig. 9 also shows the $\log ^cD_{\text{pH}(\text{eq}) = \text{constant}}$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o,eq})}$ plots at constant equilibrium pH values of 3.74, 4.13 and 4.35. In all cases, straight lines are obtained with respective slopes of 1.16, 1.01 and 1.00; and intercepts of 1.47, 2.06 and 2.51. It is therefore concluded from this result that the value of 'm' in Eq. (17) or the extractant dependency is 1 i.e. 1 mol of Cyanex 272 is associated with 1 g ion of Mn(II) to form extractable species.

From the foregoing results, the extraction equilibrium reaction for the extraction of Mn(II) by Cyanex 272 (H_2A_2) can be presented as:



v) Effect of temperature on the extraction ratio of Mn(II)

An aqueous phase containing 0.40 kg/m^3 Mn(II), 0.008 kmol/m^3 SO_4^{2-} and 0.25 kmol/m^3 Ac^- at pH 3.8 has been prepared and equal aliquots of this solution (25 cm^3) and either 0.025 or 0.10 kmol/m^3 extractant in kerosene have been equilibrated at 288, 293, 298, 303, 308, 313 and 318 K to find out the values of extraction ratios as usual. A similar

aqueous phase at pH 4.25 has also been prepared and equal portions of this solution have been equilibrated with 0.025 kmol/m³ Cyanex 272 solution at different temperatures for the same purpose. The results obtained from this experimentation have been tabulated (Table X). As it is found that the equilibrium pH values as well the extractant concentration (due to different extent of extractant beings used up to form the extractable species) differ, the log D values at specified constant pH_(eq) and [H₂A₂]_(o,eq) values i.e. the values of log ^cD have been calculated by Eq. (18) and given in the last column of the Table.

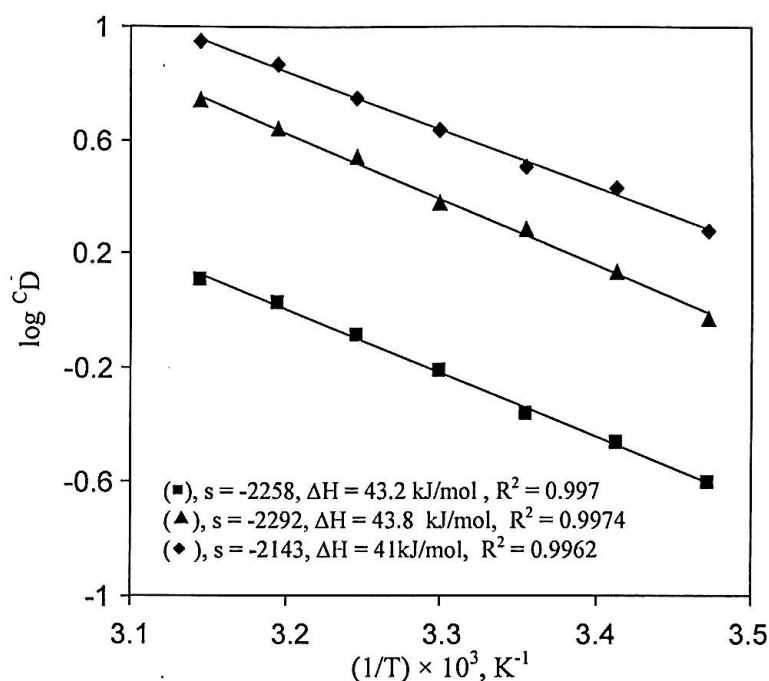


Fig. 10. Effect of temperature on the extraction of Mn(II) by Cyanex 272 (*cf.* Table X).

[Mn(II)]_(ini) = 0.40 kg/m³, [Ac⁻] = 0.25 kmol/m³, [SO₄²⁻] = 0.008 kmol/m³, Equilibration time = 5 min, O/A = 1, (◆) [H₂A₂]_(o,ini) = 0.025 kmol/m³ = [H₂A₂]_(o,eq) chosen, pH_(ini) = 4.25, constant pH_(eq) chosen = 4.20, (▲) [H₂A₂]_(o,ini) = 0.10 kmol/m³ = [H₂A₂]_(o,eq) chosen, pH_(ini) = 3.8, constant pH_(eq) chosen = 3.78, (■) [H₂A₂]_(o,ini) = 0.025 kmol/m³ = [H₂A₂]_(o,eq) chosen, pH_(ini) = 3.8, constant pH_(eq) chosen = 3.80.

The Vant Hoff (log ^cD vs. (1/T), K⁻¹) plots are shown Fig. 10. In all cases, it is found that the extraction ratio is increased with increasing temperature and the straight line relationship holds. From the slopes of the plots, the values of the heat of extraction reaction (ΔH) have been calculated (slope = -ΔH/2.303 R) to be 43.2, 43.8 and 41.0 kJ/mol for (constant pH_(eq) chosen /constant [H₂A₂]_(o,eq) in kmol/m³ chosen) values of 3.8/0.025, 3.78/0.10 and 4.2 / 0.025, respectively. It is therefore concluded that extraction of Mn(II) by Cyanex 272 is extensively increased with an increase in temperature with ΔH value of ~ 42 kJ/mol. In other words, the extraction system under consideration is endothermic in nature.

vi) Effect of added acetate ion concentration on the extraction ratio of Mn(II)

Two sets of aqueous solutions; one at pH 3.7 and other at 4.25 containing $\sim 0.407 \pm 0.08 \text{ kg/m}^3$ Mn(II) and 0.008 kmol/m^3 SO_4^{2-} and variable amounts of acetate ions ($0.10 - 2.00 \text{ kmol/m}^3$) have been prepared. The set of solutions at pH 3.7 have been equilibrated with either 0.025 or 0.10 kmol/m^3 Cyanex 272 solution at $O/A = 1$ ($A = 25 \text{ cm}^3$); whilst the other set with 0.025 kmol/m^3 Cyanex 272 solution. The experimental data are gathered in Table XI. The $\log {}^C D$ values have been calculated by Eq. (18). The $\log {}^C D$ vs. $\log ([\text{Ac}^-], \text{kmol/m}^3)$ plots at three different sets of experimental parameters is depicted in Fig. 11.

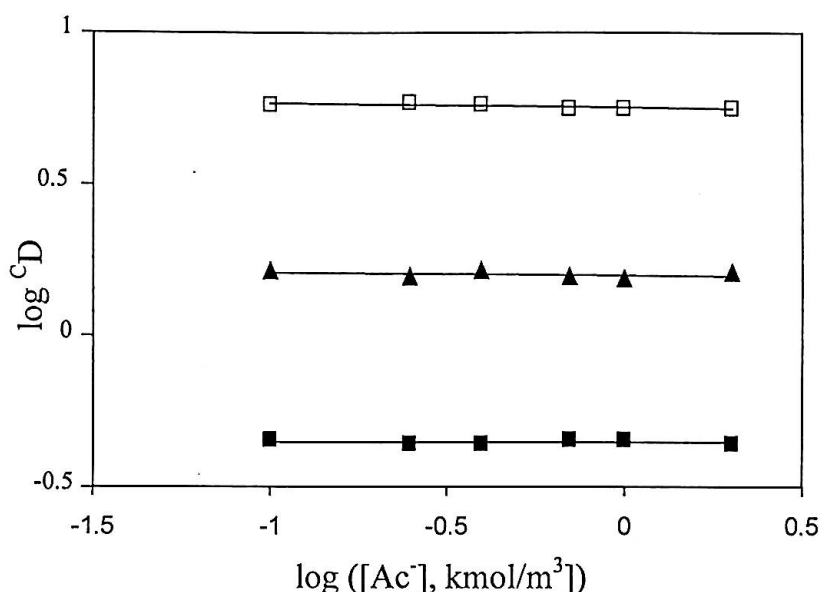


Fig. 11. Effect of added acetate ion concentration on the extraction equilibria of Mn(II)-Cyanex 272 system (cf. Table XI). $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, $O/A = 1$, (■), $[\text{H}_2\text{A}_2]_{(0,\text{ini})} = 0.025 \text{ kmol/m}^3 = [\text{H}_2\text{A}_2]_{(0,\text{eq})}$ chosen, $\text{pH}_{(\text{ini})} = 3.7$, constant $\text{pH}_{(\text{eq})}$ chosen = 3.69, (▲), $[\text{H}_2\text{A}_2]_{(0,\text{ini})} = 0.10 \text{ kmol/m}^3 = [\text{H}_2\text{A}_2]_{(0,\text{eq})}$ chosen, $\text{pH}_{(\text{ini})} = 3.7$, constant $\text{pH}_{(\text{eq})}$ chosen = 3.70, (□), $[\text{H}_2\text{A}_2]_{(0,\text{ini})} = 0.025 \text{ kmol/m}^3 = [\text{H}_2\text{A}_2]_{(0,\text{eq})}$ chosen, $\text{pH}_{(\text{ini})} = 4.25$, constant $\text{pH}_{(\text{eq})}$ chosen = 4.22.

In all cases, it is found that the extraction ratio of Mn(II) is not at all varied with increasing acetate ion concentration in the aqueous phase, provided equilibrium pH is maintained constant. The equilibrium pH values in the table indicate that 0.10 kmol/m^3 acetate buffer is as effective as 2 kmol/m^3 acetate buffer. The independence of extraction ratio of Mn(II) on acetate ion concentration indicates that Mn(II)- Ac^- complex existing in the aqueous phase does not influence the extent of extraction which is only possible whence Mn(II)- Ac^- is too much labile. If Mn(II)- Ac^- complex is labile, on a decrease in the free Mn(II) species (which is in equilibrium with Mn(II)- Ac^- complex) in the aqueous phase due to extraction, MnAc^+ complex is dissociated quickly to accomplish free Mn(II) in the aqueous phase for further extraction. In short, Mn(II) is the extractable species but not the MnAc^+ species.

vii) Effect of co-existing sulphate ion on the extraction ratio of Mn(II)

Two sets of aqueous solutions one at pH 3.82 and other at 4.3 containing 0.402 ± 0.01 kg/m³ Mn(II), 0.25 kmol/m³ Ac⁻ and variable amounts (0.008 - 2.00 kmol/m³) SO₄⁼ have been prepared and each solution has been equilibrated with 0.025 kmol/m³ Cyanex 272 solutions at 303 K and O/A of 1 in order to calculate the values of extraction ratios. The $\log {}^C D$ values have been calculated as usual. Results are shown in Table XII. The $\log {}^C D$ vs. $\log ([SO_4^{=}], \text{ kmol/m}^3)$ plots is displayed in Fig. 12.

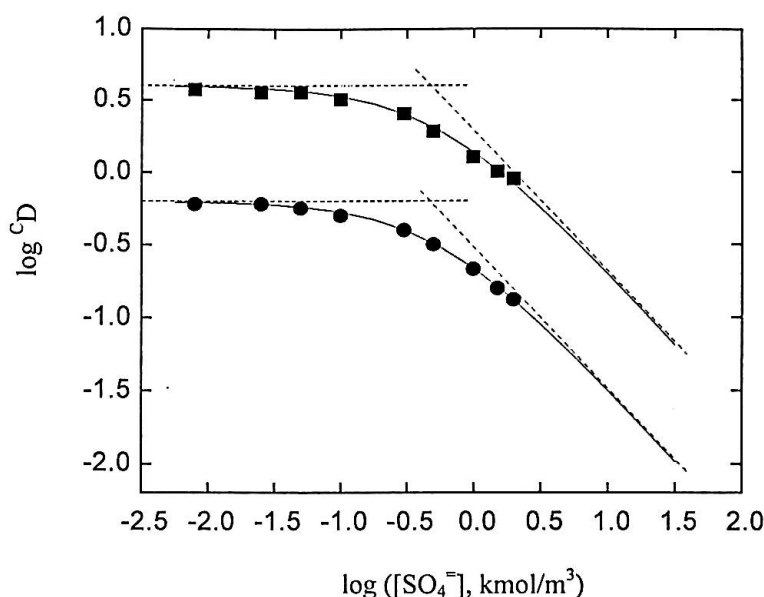


Fig. 12. Effect of co-existing sulfate ion in the aqueous phase on extraction ratio of Mn(II)

which is being extracted by Cyanex 272 (*cf.* Table XII). $[Mn(II)]_{(ini)} = (0.402 \pm 0.01)$ kg/m³, $[Ac^-] = 0.25$ kmol/m³, Temperature = (303 ± 0.50) K, Equilibration time = 5 min, (■); $[H_2A_2]_{(o,ini)} = 0.025$ kmol/m³ = $[H_2A_2]_{(o,eq)}$ chosen, $pH_{(ini)} = 4.30$, constant $pH_{(eq)}$ chosen = 4.22. The points are experimental and the solid curve is theoretical representing: $\log {}^C D = \log D_{[H_2A_2]_{(o,eq)}=0.025 \text{ kmol/m}^3}^{\text{const } pH_{(eq)}=4.22} = \log K_{ex} + 2 pH_{(eq)} + \log [H_2A_2]_{(o,eq)} - \log \{1 + K_{SO_4^{=}}^{Eq} [SO_4^{=}] \}$, where $K_{SO_4^{=}}^{Eq}$ is a proportionality constant and its value has been evaluated to be 1.90 by the Curve-Fitting method as follows: The horizontal dashed line is the asymptote at lower sulfate concentration region: $\log {}^C D = \log K_{ex} + 2 pH_{(eq)} + \log [H_2A_2]_{(o,eq)} = 0.60$ and the inclined dashed line is the asymptote at higher sulfate concentration region: $\log {}^C D = 0.60 - K_{SO_4^{=}}^{Eq} - \log [SO_4^{2-}]$. At the point of intersection of the two asymptotes, $-\log K_{SO_4^{=}}^{Eq} - \log [SO_4^{2-}]$ is equal to zero, giving, $+\log K_{SO_4^{=}}^{Eq} = -\log [SO_4^{2-}] = 0.28$; so that $\log K_{SO_4^{=}}^{Eq} = 1.90$. (●), $[H_2A_2]_{(o,ini)} = 0.025$ kmol/m³ = $[H_2A_2]_{(o,eq)}$ chosen, $pH_{(ini)} = 3.82$, constant $pH_{(eq)}$ chosen = 3.80. The points are experimental and the solid curve is theoretical representing: $\log {}^C D = \log D_{[H_2A_2]_{(o,eq)}=0.025 \text{ kmol/m}^3}^{\text{const } pH_{(eq)}=3.8} = -0.2 - \log \{1 + 1.9 [SO_4^{=}] \}$. The treatment is as above.

In either of the cases, experimental points fall on a curve rather than on a straight line. In lower concentration region of $\text{SO}_4^{=}$, the extraction ratio is seldom changed, whilst in the higher concentration region the extraction ratio is considerably decreased with increasing sulphate ion concentration. The experimental points in each case fall on a curve represented by:

$$\log {}^C D = \log K_{\text{ex}} + 2 \text{pH}_{(\text{eq})} \text{ (chosen as constant)} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} \text{ (chosen as constant)} \\ - \log (1 + 1.9 [\text{SO}_4^{=}]) \quad (22)$$

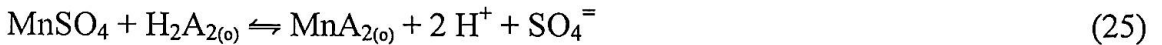
Equation (22) can be split into two equations:

$$\text{As } [\text{SO}_4^{=}] \rightarrow 0; \text{ then } \log {}^C D = \log K_{\text{ex}} + 2\text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} \quad (23)$$

which is in keeping with the Eq. (17) and consequently, Eq. (21) represents the extraction equilibrium reaction; and as $[\text{SO}_4^{=}] \rightarrow \infty$, then

$$\log {}^C D = \log K_{\text{ex}} - \log 1.9 + 2 \text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log [\text{SO}_4^{=}] \quad (24)$$

Eq. (24) is the representative of the following equilibrium reaction for the formation of extractable species:



As discussed in the aqueous chemistry of Mn(II) section, at pH over 3, HSO_4^- seldom exists and $\sim 25\%$ Mn(II) exists as MnSO_4 complex. MnSO_4 complex is probably not so labile like MnAc^+ complex. Here parallel reactions represented by Eqs. (21) and (25) occur to produce extractable MnA_2 complex. Sulphate ion does not take part in the formation of extractable complex.

viii) Loading of Cyanex 272 solutions with Mn(II)

An aliquot of 100 cm^3 0.05 kmol/m^3 Cyanex 272 solution in kerosene has been repeatedly equilibrated with 100 cm^3 portions of fresh aqueous solutions containing 1.05 kg/m^3 Mn(II), 0.019 kmol/m^3 $\text{SO}_4^{=}$ and 0.25 kmol/m^3 Ac^- at pH 6.0. A similar study has been done with 0.025 kmol/m^3 Cyanex 272 solution. The results are given in Table XIII. The last column of the table represents the cumulative Mn(II) concentration in the organic phase. The cumulative Mn(II) concentration in the organic phase (in kg/m^3) has been plotted against the phase contact number for both 0.025 and 0.05 kmol/m^3 Cyanex 272 systems (Fig. 13).

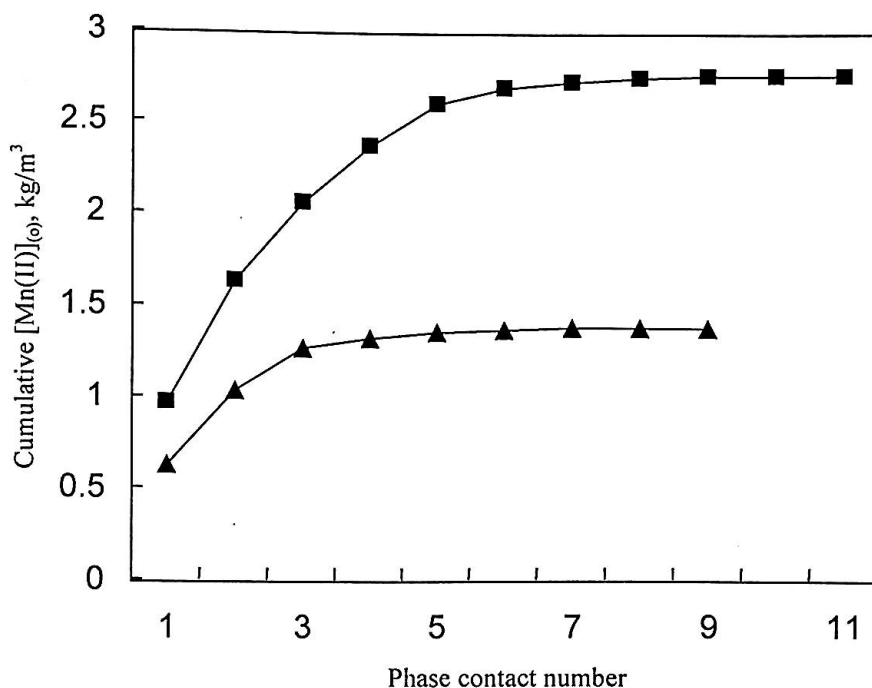


Fig. 13. Loading of Cyanex 272 with Mn(II) (*cf.* Table XIII). $[\text{Mn(II)}]_{(\text{ini})} = 1.05 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.019 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.00$, Stage equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A (Phase ratio) = 1, ($\blacktriangle$); $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, ($\blacksquare$); $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.05 \text{ kmol/m}^3$.

It is observed that loading of the organic phase with Mn(II) is ended up at the 6th and 5th contacts for 0.025 and 0.05 kmol/m^3 Cyanex 272 systems, respectively. The maximum loadings of 1.378 and 2.76 kg/m^3 Mn(II) are obtained for 0.025 and 0.05 kmol/m^3 Cyanex 272 systems respectively. Simple calculation shows that 1 L portion of 0.025 kmol/m^3 Cyanex 272 solution can extract $0.02508 \approx 0.025 \text{ mol}$ Mn(II), whilst 1 L portion of 0.050 kmol/m^3 Cyanex 272 solution can extract $0.0502 \approx 0.05 \text{ mol}$ Mn(II). Therefore, in saturated condition of Mn(II) in the organic phase, the mole ratio of Mn(II) to Cyanex 272 is 1, supporting the reaction represented by Eq. (21) as the extraction equilibrium reaction. In other words, the mechanism of extraction of Mn(II) is not changed with the extent of loading.

The loading capacity (defined as the maximum amount (g) of a metal ion being extracted by 100 g extractant) is a very useful parameter in selecting an extractant for a metal ion extraction system, at least when to be used in an industry. Simple calculations show that the loading capacity of Cyanex 272 (dissolved in kerosene) with Mn(II) is $\sim 9.52 \text{ g Mn(II)/100 g Cyanex 272}$.

ix) Effect of diluent on extraction ratio of Mn(II)

Although by definition the term diluent as used in solvent extraction chemistry is inert; in actual practices it is observed that the nature of diluent may tremendously affect the metal-ion distribution in a solvent extraction process. Some scientists try to correlate this behavior with the dipole moment of the diluent and others with the effective extractant concentration difference at the interface due to different degree of adsorption of extractant molecules at the interface.

In this work, the extraction ratios have been measured when the same aqueous phase has been extracted by 0.10 kmol/m³ Cyanex 272 dissolved in different diluents keeping all other parametric conditions identical. The results are represented in Table XIV. It is observed that the extraction ratio increases in the following order with the variation of diluent: n-heptanol ($D = 0.154$) < chloroform ($D = 0.35$) < n-hexanol ($D = 0.364$) < 1,2-dichloroethane ($D = 0.50$) < n-hexane ($D = 0.67$) < benzene ($D = 0.73$) < carbon tetrachloride ($D = 0.784$) < cyclohexane ($D = 0.875$) < kerosene ($D = 1.31$) < n-heptane ($D = 1.885$). The study help draw the conclusion that kerosene is a very good diluent just next to n-heptane for the extraction of Mn(II) by Cyanex 272.

The effective cross-sectional areas of BTMPPA (Cyanex 272) at the 0.5 kmol/m³ H₂SO₄ / BTMPPA in various diluent interface have been measured by Biswas and Singha [115]. The reported values of the cross-sectional area (A , Å²) of BTMPPA have been plotted (log-log) versus D (Y-axis) values in Fig. 14.

It is found that very good fit correlation exists between n-heptane, kerosene, benzene, chloroform and n-heptanol. In these cases, the extraction ratio decreases with the increase in cross-sectional area of BTMPP. A comparatively weak fit correlation exists also between cyclohexane, carbon tetrachloride, toluene, benzene and n-hexanol. For the first set of five diluents, the variation of $\log D$ with $\log (A, \text{Å}^2)$ is very sharp compared to the second set of five diluents. All point fit correlation is not obtained probably due to the change in the interface composition.

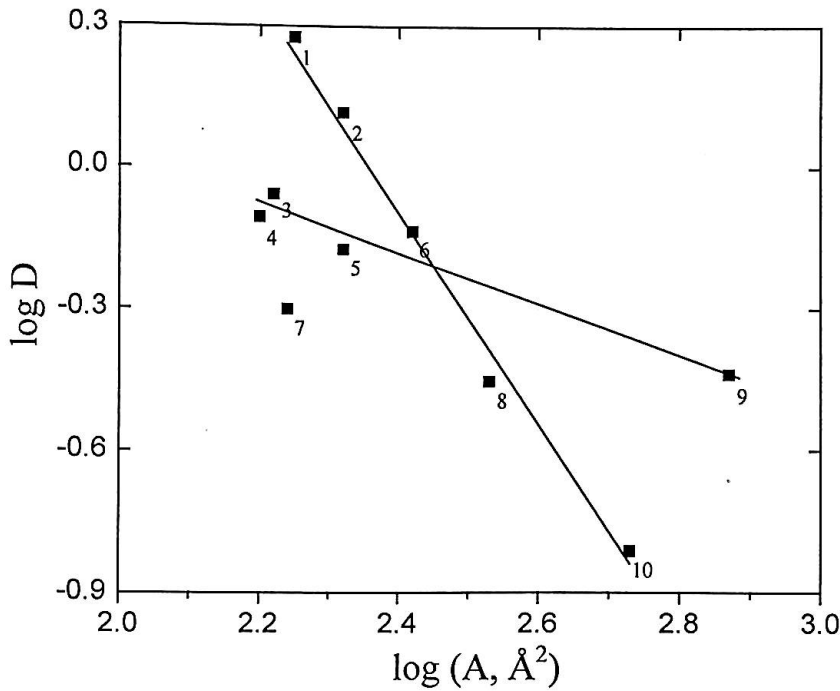


Fig. 14. Plot for showing correlation between distribution ratio of Mn(II) with cross sectional area of Cyanex 272 molecules (in different diluents) adsorbed at the aqueous / organic interface (*cf.* Table XIV). $[\text{Mn(II)}]_{(\text{ini})} = 0.45 \text{ kg/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.50$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, $\text{O/A} = 1$. (1) n-heptane; (2) kerosene; (3) cyclohexane; (4) carbon tetrachloride; (5) toluene; (6) benzene; (7) 1, 2-dichloroethane; (8) chloroform; (9) n-hexanol; (10) n-heptanol.

x) Evaluation of extraction equilibrium constant (K_{ex}) for Mn(II) extraction by Cyanex 272 at 303 K

From the intercepts of the lines in Figs. 8, 9, 11 and 12, the values of K_{ex} have been evaluated based on Eq. (22). The calculated values are shown in Table A. The average log K_{ex} value at 303 K is calculated to be -6.1696 with standard deviation of 0.0633.

Table A. Evaluation of the extraction equilibrium constant (K_{ex}) for the extraction of Mn(II) by Cyanex 272 at (303 ± 0.50) K

Fig. No.	Type of plot $\log C_D$ vs.	pH _(eq)	[H ₂ A ₂] _(o, eq) , kmol/m ³	[SO ₄ ²⁻] ₃ , kmol/m ³	[Ac ⁻] ₃ , kmol/m ³	Intercept (I)	log K_{ex}	Average log K_{ex}	Standard deviation
8	pH _(eq)	Variable	0.025 0.100	0.008 0.008	0.25 0.25	-7.77 -7.22	-6.1615 -6.2135		
9	$\log ([H_2A_2]_{(o, eq)}$ kmol/m ³)	3.74 4.13 4.35	Variable	0.008 0.008 0.008	0.25 0.25 0.25	1.45 2.06 2.51	-6.0235 -6.1935 -6.1835		
11	$\log ([Ac^-]_3$ kmol/m ³)	3.69 4.22 3.70	0.025 0.025 0.100	0.008 0.008 0.008	Variable	-0.35 0.76 0.20	-6.1215 -6.0715 -6.1935	-6.1696	0.0633
12	$\log ([SO_4^{2-}]_3$ kmol/m ³)	4.22	0.025	Variable	0.25	0.60(lcr) 0.33(hcr)	-6.2380 -6.2293 -6.1980 -6.2193		
		3.80	0.025			-0.20(lcr) -0.50(hcr)			

* hcr = higher concentration region and lcr = lower concentration region

The $\log K_{\text{ex}}$ value has been estimated also by the graphical method. Eq. (22) indicates that the plot of $\log {}^{\text{C}}\text{D}$ vs. $[2 \text{ pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 1.9 [\text{SO}_4^{=})]]$ should be a straight line with slope equaling to unity and intercept equaling to $\log K_{\text{ex}}$. All equilibrium data at 303 K, presented so far have been considered for this treatment and the calculated X-axis parameters are shown against the Y-axis parameter ($\log {}^{\text{C}}\text{D}$) in the Table XV. The corresponding plot is depicted in Fig. 15.

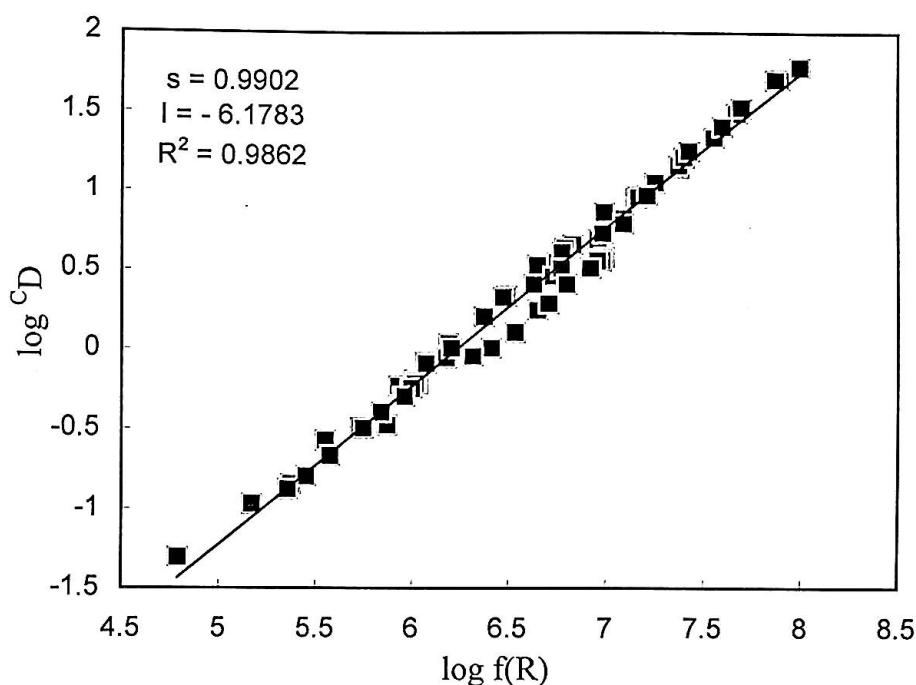


Fig. 15. Plot of $\log {}^{\text{C}}\text{D}$ vs. $\log f(R)$ for the estimation of extraction equilibrium constant (K_{ex}) of Mn(II) by Cyanex 272 at (303 ± 0.5) K, where, $\log f(R) = [2 \text{ pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 1.9 [\text{SO}_4^{=})]]$ (cf. Table XV).

A straight line is indeed obtained with the Least Squares slope of 0.9902 (should be 1.0) and correlation coefficient of 0.9862. The line has the intercept of -6.1783, which refers to the $\log K_{\text{ex}}$ value. So the value of $\log K_{\text{ex}}$ obtained by two methods matches well with each other.

xi) Stripping of Mn(II) loaded organic phase by mineral acids

The maximum Mn(II) loaded organic phase having theoretically no free extractant has been subjected for stripping study with 0.001, 0.01 and 0.10 kmol/m^3 H_2SO_4 , HNO_3 and HCl solutions at a temperature of 303 K and at O/A of 1. The stripping results are given in Table B (within the main body of results and discussion section). It is found that 0.1 kmol/m^3 H_2SO_4 , HCl or HNO_3 can strip Mn(II) quantitatively. With decrease in the

concentration of stripping acid, percentage of Mn(II)-stripped is decreased appreciably. The results are given for the organic phase Mn(II) concentration of 0.20 kg/m^3 . If the organic phase Mn(II) concentration is very high, then either more concentrated acid solution or stage-wise stripping may be needed.

Table B. Stripping of Mn(II) loaded organic phase using different acid solutions.

$\text{Mn(II)}_{(o,ini)} = 0.20 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.00364 \text{ kmol/m}^3$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1.

Stripping agent	Acid concentration, kmol/m^3	$[\text{Mn(II)}]_{(aq)}$, kg/m^3	% of Mn(II) stripped
H_2SO_4	0.100	0.2000	100.00
	0.010	0.1890	94.50
	0.001	0.1080	54.00
HNO_3	0.100	0.2000	100.00
	0.010	0.1740	87.00
	0.001	0.0800	40.00
HCl	0.100	0.2000	100.00
	0.010	0.1740	87.00
	0.001	0.0732	37.00

2. Studies on extraction equilibrium of the $\text{Ni(II)-SO}_4^{2-}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272 - kerosene-octanol system

Some preliminary experiments were carried out to examine the pH range at which Ni(II) could be extracted. During these experiments, it was observed that stable emulsions were formed in the $\text{Ni(II)-SO}_4^{2-}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene system at the extractable pH range of ~ 6 to 7. The stable emulsion formation hindered the extraction study. In solvent extraction studies, the formation of emulsion or the third phase formation is often overcome by adding 2-5% (v/v) higher alcohol (modifier) during constituting the organic phase. So in this section of study, the organic phase consists of Cyanex 272, kerosene and octan-1-ol. 3% (v/v) octan-1-ol addition in the organic phase is able to eliminate the emulsion formation. The title system has been investigated as follows:

i) Effect of phase contact time on extraction of Ni(II)

An aqueous solution containing 1.00 kg/m^3 Ni(II), 0.034 kmol/m^3 SO_4^{2-} and 0.25 kmol/m^3 acetate at pH 7 has been prepared and 25 cm^3 portion of this solution has been contacted vigorously with 25 cm^3 portion of 0.025 kmol/m^3 Cyanex 272 solution in kerosene containing 3% (v/v) octan-1-ol for different time intervals (15 s to 2.5 min). After agitation for a definite time, the concentration of Ni(II) left in the aqueous phase are determined. The results are given in Table XVI. The last column of the table shows the values of the logarithm of concentration ratio $([\text{Ni(II)}]_{(o)}/[\text{Ni(II)}])$. The variations of the aqueous phase Ni(II) concentration as well as the variation of $\log ([\text{Ni(II)}]_{(o)} / [\text{Ni(II)}])$ with extraction time are shown in Fig. 16.

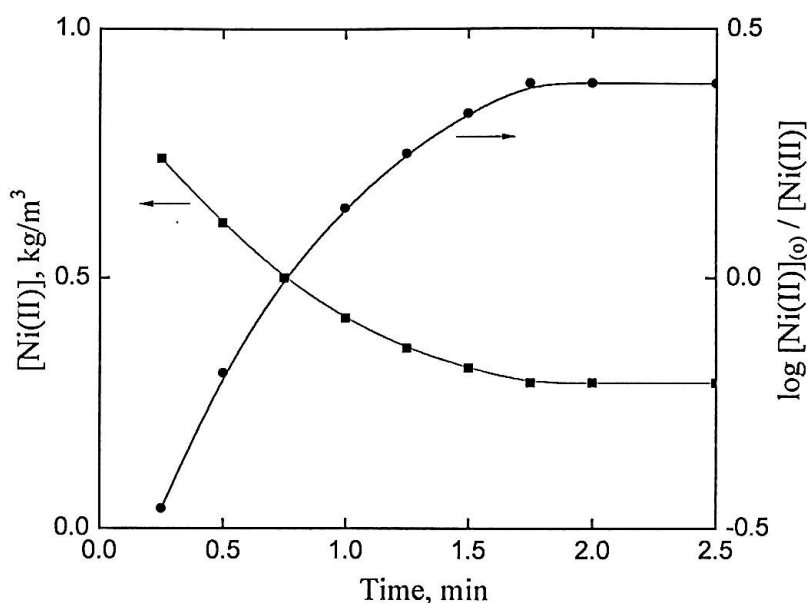


Fig. 16. Determination of equilibrium time in the extraction of Ni(II) by Cyanex 272 in kerosene (*cf.* Table XVI). $[\text{Ni(II)}]_{(ini)} = 1.00 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.034 \text{ kmol/m}^3$, $\text{pH}_{(ini)} = 7.00$, de-emulsifier = 3% (v/v) octan-1-ol, Temperature = (303 ± 0.50) , O/A (Phase ratio) = 1.

It is found that both curves level off at phase contact time of 1.75 min. It is therefore concluded that the equilibration time is only 1.75 min for the extraction of Ni(II) by Cyanex 272. In subsequent experiments, equilibration time of 2 min has been allowed to ensure equilibration at different experimental parameters.

ii) Effect of Ni(II) concentration on the extraction ratio of Ni(II)

At the parametric conditions mentioned in Table XVII, the extraction ratios have been estimated experimentally at various initial Ni(II) concentrations in the aqueous phase. As expected, the equilibrium pH values (3rd column of Table XVII) are changed by different extents from the initial pH values. The corrected D values in logarithmic form ($\log {}^cD$) at constant equilibrium pH of 6.95 and equilibrium extractant concentration of 0.025 kmol/m^3 have been calculated by the following Eq. (26):

$$\log {}^cD_{6.95/0.025} = \log D + x (6.95 - \text{pH}_{(\text{eq})}) + y [\log 0.025 - \log (0.025 - y [\text{Ni(II)}]_{(\text{o,eq})})] \quad (26)$$

where, all concentration terms are in kmol/m^3 , $x = \text{pH dependence}$ (taken as 2 which will be obtained later) and $y = \text{extractant dependence}$ (taken as 1 as will be obtained in the following section). The 8th column of Table XVII shows the $\log {}^cD$ values, whilst, the 9th column shows the $\log ([\text{Ni(II)}]_{(\text{eq})}, \text{kmol/m}^3)$ values. The experimental data have been plotted in two ways:

- firstly, as $\log D$ vs. $\log ([\text{Ni(II)}]_{(\text{ini})}, \text{kmol/m}^3)$ plot, and
- secondly, as $\log {}^cD_{6.95/0.025}$ vs. $\log ([\text{Ni(II)}]_{(\text{eq})}, \text{kmol/m}^3)$ plot.

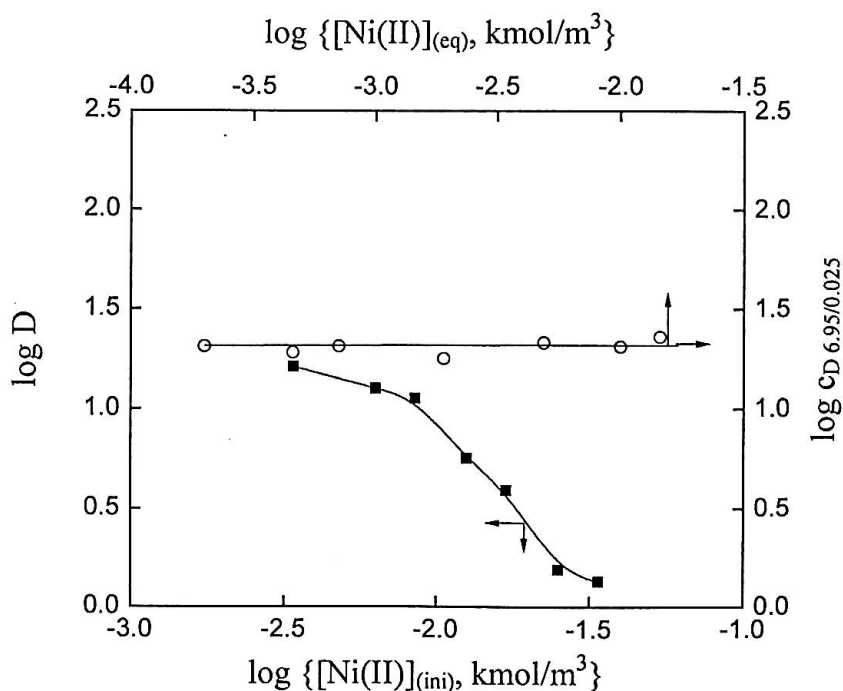


Fig. 17. Effect of Ni(II) concentration on the extraction ratio of Ni(II) by Cyanex 272 (cf. Table XVII). $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3 = \text{constant}$ $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen, $[\text{SO}_4^{2-}] = 0.034 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 7.40$, constant $\text{pH}_{(\text{eq})}$ chosen = 6.95, de-emulsifier = 3% (v/v) octan-1-ol, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1, Equilibration time = 2 min.

In the first case, the value of $\log D$ is apparently decreased with increasing the initial Ni(II) concentration in the aqueous phase which is contrary to the general principle of solvent extraction technique (*cf.* Eq. 17). On the other hand, the value of $\log {}^C D_{6.95/0.025}$ remains unchanged with increasing equilibrium Ni(II) concentration. It is therefore concluded that Ni(II) behaves ideally in the investigated system, as well, the aqueous or organic Ni(II) speciation is not changed with the variation of Ni(II) concentration in the system provided the equilibrium pH and extractant concentration remain unchanged.

iii) Effect of extractant concentration on the extraction ratio of Ni(II)

To find out the effect of extractant concentration on the extraction ratio of Ni(II), experiments have conducted to estimate extraction ratios at various extractant concentrations keeping all other parameters at constant values. The variations of extraction ratio with the variation of extractant concentration at initial pH values of 5.98, 6.30 and 7.08 are shown in Table XVIII. Although for a particular set of data, initial pH is kept constant, the 3rd column of the table shows the equilibrium pH values, which are varied considerably. So the corrected $\log D$ values at a chosen constant equilibrium pH values has been calculated by the relation: $\log {}^C D_{\text{const. pH}} = \log D + x (\text{constant equilibrium pH chosen} - \text{experimental equilibrium pH})$; where, x represents the pH-dependence (found to be 2 in the following section). Moreover, $\log [H_2A_2]_{(o,eq)}$ values have been calculated by using the relation: $\log [H_2A_2]_{(o,eq)} = \log [H_2A_2]_{(o,ini)} - y [Ni(II)]$; where, y represents the extractant dependence and all concentration terms are in kmol/m^3 . The calculated $\log {}^C D_{\text{const. pH}}$ and $\log [H_2A_2]_{(o,eq)}$, kmol/m^3 values are shown in the 8th and 9th columns, respectively.

Fig. 18 represents the $\log D$ vs. $\log([H_2A_2]_{(o,ini)}, \text{kmol/m}^3)$ and the $\log {}^C D_{\text{const. pH}}$ vs. $\log([H_2A_2]_{(o,eq)}, \text{kmol/m}^3)$ plots. The first type plot does not represent the typical plot as should be used in solvent extraction equilibrium studies. However, the slope of the plots at least at the lower concentration regions of Cyanex 272 is one. At the higher concentration region, it remains constant for the system of initial pH 7 but is considerably decreased for pH_(ini) of 6.30 and 5.90 systems. The second type of plots do not yield straight lines, but curves are obtained with limiting slopes of + 1 and + 3 at the lower and higher concentration regions of equilibrium extractant concentrations, respectively. The intercepts of the asymptotic lines are given in the figure.

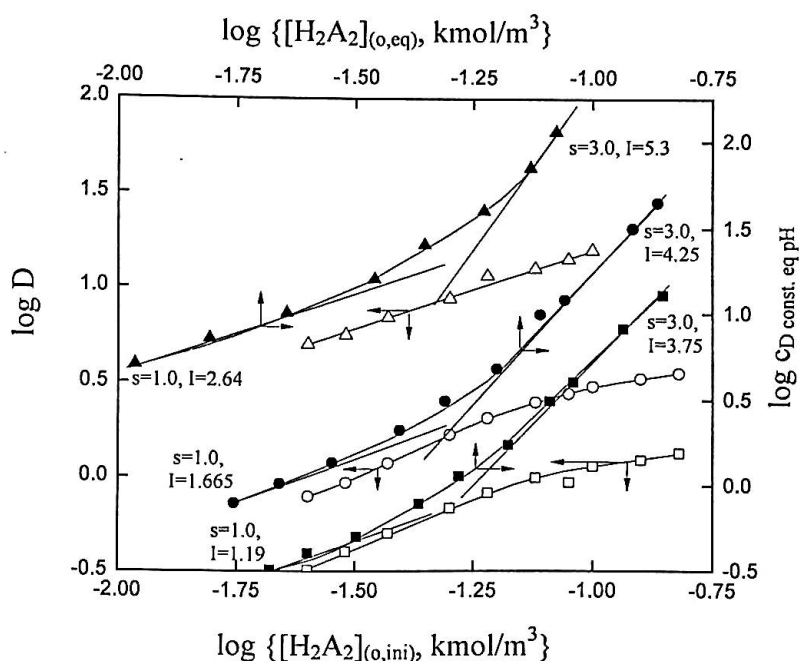


Fig. 18. Effect of extractant concentration on the extraction ratio of Ni(II) being extracted by Cyanex 272 (*cf.* Table XVIII). $[\text{Ni(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.017 \text{ kmol/m}^3$, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, Temperature = $(303 \pm 0.50) \text{ K}$, $\text{O/A} = 1$; (Δ), $\text{pH}_{(\text{ini})} = 7.08$; ($\blacktriangle$), $\text{pH}_{(\text{eq})}$ chosen constant = 6.55; ($\circ$), $\text{pH}_{(\text{ini})} = 6.30$; ($\bullet$), $\text{pH}_{(\text{eq})}$ chosen constant = 6.10; ($\square$), $\text{pH}_{(\text{ini})} = 5.90$; ($\blacksquare$), $\text{pH}_{(\text{eq})}$ chosen constant = 5.90.

It is concluded from this result that 1 mole of Cyanex 272 is added up with 1 g ion of Ni(II) to form the extractable species (NiA_2) where there is scarcity of extractant in system; and with the availability of the surplus extractant in the system, solvation of NiA_2 takes place to form extractable species like $\text{NiA}_2 \cdot \text{H}_2\text{A}_2$ and $\text{NiA}_2 \cdot 2\text{H}_2\text{A}_2$. For the first species to form, the extractant dependence should be 2 and for the formation of the second species, it should be 3.

iv) Effect of equilibrium pH on extraction ratio of Ni(II)

The experimental data on the variation of equilibrium pH on extraction ratio at three different initial extractant concentrations of 0.025, 0.05 and 0.10 kmol/m^3 are presented in Table XIX, where other experimental parametric conditions have also been cited. As the equilibrium extractant concentrations differ from its initial concentration due to various extents of extractions at various pH values, the $\log {}^cD$ values at a chosen constant equilibrium extractant concentration have been calculated by the formula given at the bottom of the Table XIX. Figure 19 shows the $\log D$ vs. $\text{pH}_{(\text{eq})}$ and $\log {}^cD$ vs. $\text{pH}_{(\text{eq})}$ plots.

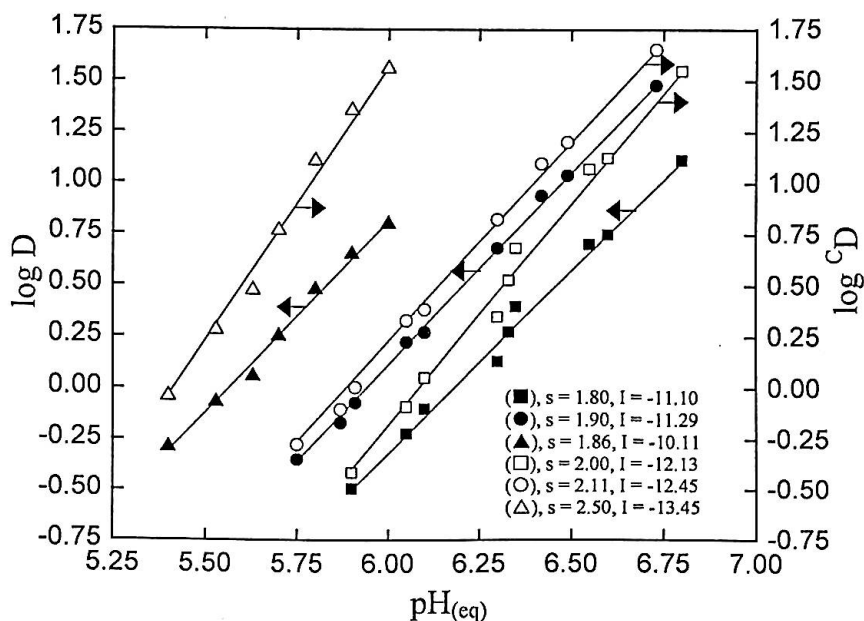


Fig. 19. Effect of equilibrium pH on the extraction of Ni(II) by Cyanex 272 in kerosene (*cf.* Table XIX). $[\text{Ni(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.017 \text{ kmol/m}^3$, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1; (■), $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$; (□), constant $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.025 kmol/m^3 ; (●), $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.050 \text{ kmol/m}^3$; (○), constant $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.050 kmol/m^3 ; (▲), $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.100 \text{ kmol/m}^3$; (△), constant $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.100 kmol/m^3 .

In both cases, straight lines are obtained for all three constant Cyanex 272 concentration systems. The slopes and intercepts are cited in the figure. It is found that the $\log D$ vs. $\text{pH}_{(\text{eq})}$ plot yields straight lines having slope within 1.8 to 1.9; whereas, the more acceptable type of plot: $\log C_D$ vs. $\text{pH}_{(\text{eq})}$ yields straight lines with slopes of 2.00, 2.11 and 2.50 for constant $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen systems of 0.025, 0.050 and 0.10 kmol/m^3 Cyanex 272 systems, respectively. The slope of the line at 0.10 kmol/m^3 system (2.5) is little higher than expected value of 2 during the extraction of a divalent metal ion by an acidic extractant. It is possibly due to errors encountered during data correction period for the non-constancy of the extractant dependency. It is, however, concluded that the pH-dependency in Ni(II) extraction by Cyanex 272 is 2; i.e. 2 g ions of H^+ eliminate from extractant during reaction with 1 g ion of Ni(II).

v) Effect of co-existing sulphate ion of the aqueous phase on extraction ratio of Ni(II)

The effect of co-existing sulphate ion concentration on the extraction ratio of Ni(II) has been examined at constant $\text{pH}_{(\text{eq})}$ (chosen) of 6.08 ($\text{pH}_{(\text{ini})} = 6.75 \pm 0.50$) and constant $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ (chosen) of 0.025 kmol/m^3 ; while the sulphate ion concentration is varied between 0.017 and 1.50 kmol/m^3 . The experimental data are given in Table XX, where, other experimental conditions are cited. The experimental $\log D$ values have been converted to the logarithms of corrected D values at constant equilibrium pH of 6.05 and constant equilibrium free extractant concentration of 0.025 kmol/m^3 i.e. $\log {}^cD$ using a formula given at the bottom of the Table XX. The $\log D$ vs. $\log [\text{SO}_4^{=}]$ plot is given in Fig. 20.

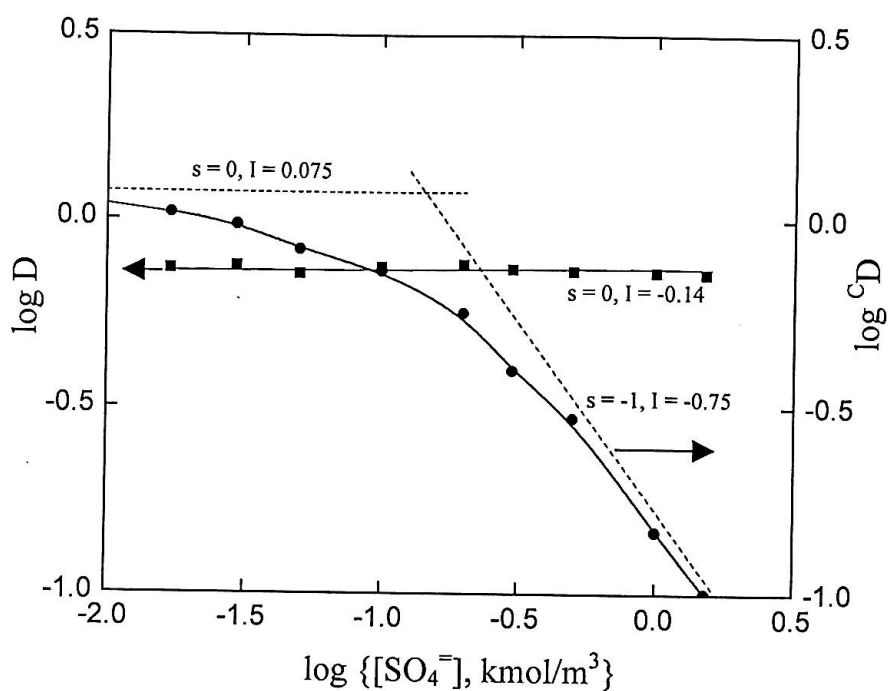


Fig. 20. Effect of co-existing sulfate ion concentration on the extraction of Ni(II) by Cyanex 272 (*cf.* Table XX). $[\text{Ni(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 6.75 \pm 0.05$; constant $\text{pH}_{(\text{eq})}$ chosen = 6.08, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3 = \text{constant } [\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, Temperature = $(303 \pm 0.50) \text{ K}$, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, $\text{O/A} = 1$, For $\log {}^cD$ vs. $\log [\text{SO}_4^{=}]$ plot, the points are experimental, whilst the curve is theoretical represented by: $\log {}^cD = 0.075 - \log (1 + K_{\text{SO}_4}^{\text{Eq}} [\text{SO}_4^{=}])$; where $K_{\text{SO}_4}^{\text{Eq}}$ is a proportionality constant whose value has been evaluated to be $6.92 \text{ m}^3/\text{kmol}$ by the Curve-Fitting method.

A straight line is obtained with slope and intercepts equaling to 0.1 and -0.14 respectively. This result apparently informs about the independency of sulphate ion concentration on the extraction ratio of Ni(II). However, the $\log D$ values which have been

put in this plot are at different $\text{pH}_{(\text{eq})}$ values (4th column of Table XX). So the $\log {}^{\text{C}}\text{D}$ vs. $\log [\text{SO}_4^{2-}]$ plot has been drawn and included in the same Fig. (Fig. 20). This plot is not a straight line. A curve is obtained showing a little and a huge effect at the lower and higher concentration regions of sulphate ion respectively. In this Figure, the curve is theoretical representing: $\log {}^{\text{C}}\text{D} = 0.075 - \log (1 + 6.92 [\text{SO}_4^{2-}])$.

vi) Effect of added acetate ion on the extraction ratio of Ni(II)

The $\log D$ and $\log {}^{\text{C}}\text{D}$ values at $\text{pH}_{(\text{ini})} = 6.65 \pm 0.05$, constant $\text{pH}_{(\text{eq})}$ chosen = 6.05 and $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = \text{constant}$ $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.025 kmol/m^3 but at various acetate ion concentrations (ranging from 0.10 to 2.00 kmol/m^3) are provided in Table XXI.

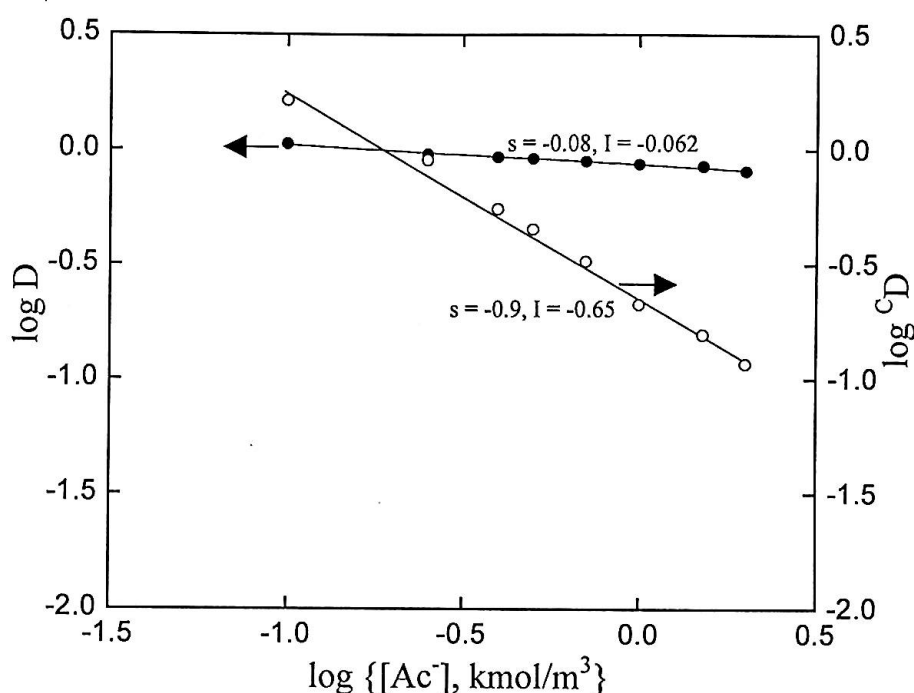


Fig. 21. Effect of acetate ion concentration on the extraction of Ni(II) by Cyanex 272 (*cf.* Table XXI). $[\text{Ni(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 6.65 \pm 0.05$, constant $\text{pH}_{(\text{eq})}$ chosen = 6.05, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3 = \text{constant}$ $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen, $[\text{SO}_4^{2-}] = 0.017 \text{ kmol/m}^3$, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, Temperature = $(303 \pm 0.50) \text{ K}$, $\text{O/A} = 1$.

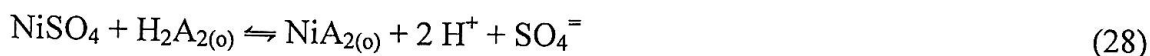
The $\log D$ vs. $\log [\text{Ac}^-]$ plot in Fig. 21 is a straight line with almost zero slope (-0.08); whereas, the $\log {}^{\text{C}}\text{D}$ vs. $\log [\text{Ac}^-]$ plot in the same figure is also a straight line but with a slope of ~ -1 (-0.9) and intercept of -0.65. It is therefore concluded that the extraction ratio by Ni(II) in the investigated system is inversely proportional to acetate ion concentration.

vii) Mechanism of extraction

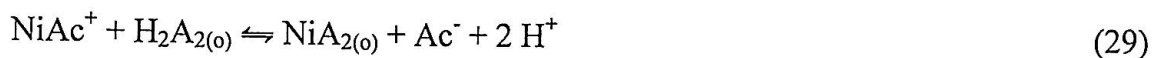
Almost similar solubility constants of NiHSO_4^+ and NiSO_4 with these of MnHSO_4^+ and MnSO_4 , respectively, like in the case of Mn(II) solution the aqueous solution of Ni^{2+} at pH above 4 contains some NiSO_4 but not NiHSO_4^+ . Moreover, NiAc^+ species also exists in the aqueous solutions (*cf.* Aqueous Chemistry of Mn(II) , Ni(II) and Zn(II) Section). Considering pH and extractant dependences of 2 and 1 (at lower concentration region of extractant), the extraction equilibrium reaction should as follows:



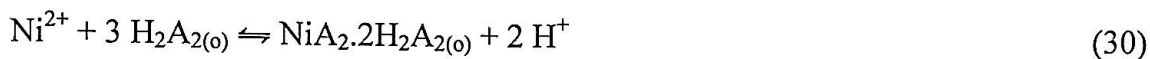
At higher sulphate ion concentration region, the equilibrium reaction would be as:



and at higher acetate ion concentration region, the equilibrium reaction would be as:



But at higher concentration regions of extractant, the disolvated species will be formed as:



viii) Effect of temperature on extraction ratio of Ni(II)

The temperature varied extraction data are given in Table XXII. It is observed that the extraction is increased with rise in temperature. At the mentioned experimental parameters in Table XXII, the $\log D$ vs. $(1/T)$, K^{-1} and the $\log {}^cD$ vs. $(1/T)$, K^{-1} plots are given in Fig. 22. In both cases, straight lines are obtained with negative slopes. From the slope (-2857) of the second type of plot, the enthalpy change (ΔH) in extraction reaction has been evaluated to be 54.66 kJ/mol. The higher ΔH for Ni(II) than that for Mn(II) (42 kJ/mol) indicate that Ni(II) extraction is more sensitive to temperature than Mn(II) extraction.

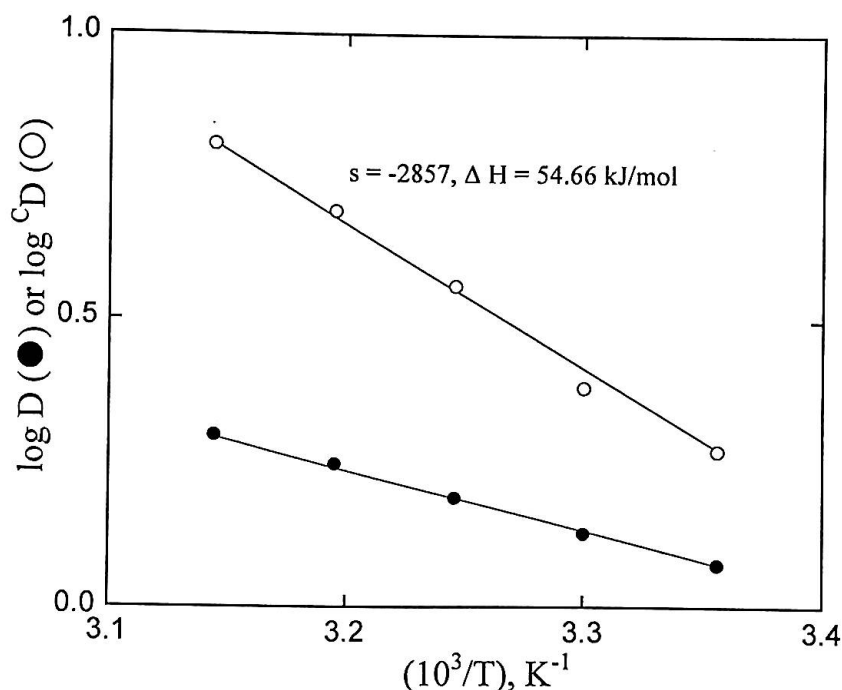


Fig. 22. Effect of temperature on the extraction of Ni(II) by Cyanex 272 (*cf.* Table XXII). $[\text{Ni(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.017 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.60$, $\text{pH}_{(\text{eq})}$ chosen = 6.34; $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3 = \text{constant}$ $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, O/A = 1.

ix) Loading of Cyanex 272 solution with Ni(II)

The loadings of 0.025 and 0.05 kmol/m³ Cyanex 272 solutions with Ni(II) has been performed accordingly and the experimental results together with the experimental conditions are presented in Table XXIII. The plots of cumulative Ni(II) concentration in the organic phase versus phase contact number are depicted in Fig. 23. It is found that the organic phase is saturated with Ni(II) after 7th and 8th contacts for 0.025 and 0.05 kmol/m³ Cyanex 272 systems, respectively. At saturation level, the Ni(II)-concentrations in 0.025 and 0.05 kmol/m³ Cyanex 272 solutions are 3.033 and 6.1714 kg/m³, respectively. A simple calculation shows that 0.025 kmol/m³ Cyanex 272 solution contains as much as 0.05167 kmol/m³ Ni(II) and 0.05 kmol/m³ Cyanex 272 solution contains as much as 0.1051 kmol/m³ Ni(II). These results indicate the presence of Ni₂A₂ or NiA⁻ type complex, which can be only possible when acetate ion takes part in the formation of extractable species as follows:



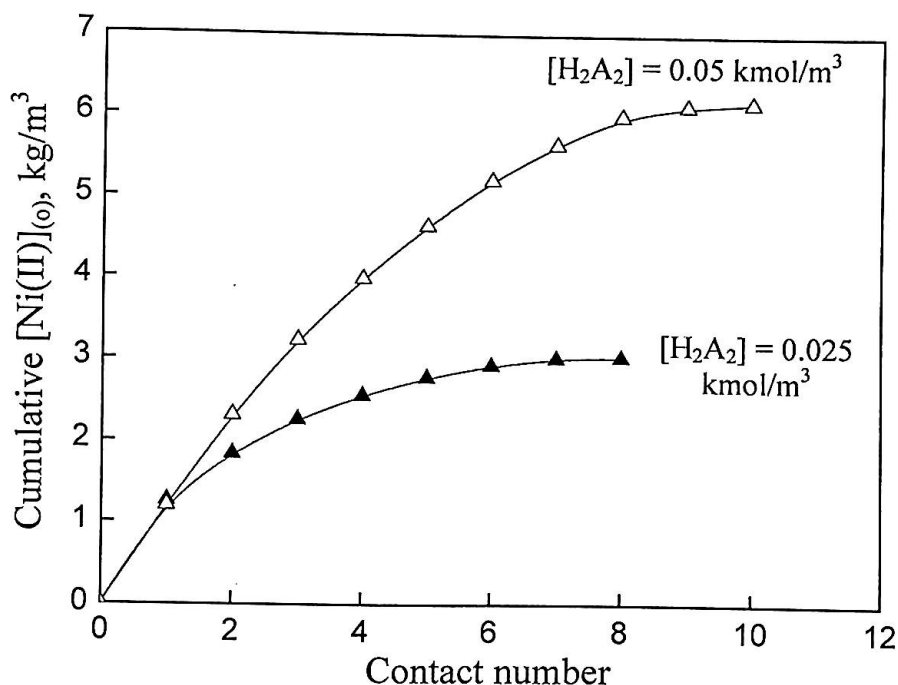


Fig. 23. Loading of Cyanex 272 with Ni(II) (cf. Table XXIII). $[\text{Ni(II)}]_{(\text{ini})} = 1.95 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 6.85$, de-emulsifier = 3%(v/v) octan-1-ol, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, equilibration time in each stage = 2 min, temperature = $(303 \pm 0.50) \text{ K}$, phase ratio = 1:1, organic phase recycled.

x) Evaluation of extraction equilibrium constant (K_{ex}) for Ni(II) extraction by Cyanex 272

Considering the following equations being valid for Ni(II) extraction by Cyanex 272 based on related foregoing results and discussion

$$\log {}^cD = \log K_{\text{ex}} + 2 \text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 6.92 [\text{SO}_4^{2-}]) - \log [\text{Ac}^-] \quad (32a)$$

valid at $[\text{H}_2\text{A}_2]_{(\text{o,eq})} \geq 0.05 \text{ kmol/m}^3$; and

$$\log {}^cD = \log K_{\text{ex}} + 2.5 \text{pH}_{(\text{eq})} + 3 \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 6.92 [\text{SO}_4^{2-}]) - \log [\text{Ac}^-] \quad (32b)$$

valid at $[\text{H}_2\text{A}_2]_{(\text{o,eq})} \leq 0.10 \text{ kmol/m}^3$, the values of K_{ex} have been estimated from the intercept of plots given in Figs. 18-21 and tabulated (Table C). The average $\log K_{\text{ex}}$ value is about -11.163 with standard deviation of 0.208 for systems having $[\text{H}_2\text{A}_2]_{(\text{o,eq})} \leq 0.05 \text{ kmol/m}^3$. This value is -11.56 with standard deviation of 0.04 for systems $[\text{H}_2\text{A}_2]_{(\text{o,eq})} \geq 0.10 \text{ kmol/m}^3$.

Table C. Evaluation of the value of extraction equilibrium constant (K_{ex}) at 303 K for the extraction of Ni(II) by Cyanex 272

Fig. No.	$\log^c D$ vs.	$[H_2A_2]_{(o,eq)}$, kmol/m ³	$pH_{(eq)}$	$[Ac^-]_3$, kmol/m ³	$[SO_4^{2-}]_3$, kmol/m ³	Intercept, I	$\log K_{ex}$	Average $\log K_{ex}$	Standard deviation	Remarks
i) $[H_2A_2]_{(o)} \leq 0.05 \text{ kmol/m}^3$, where extractant dependence is 1;										
18	$\log$ $([H_2A_2]_{(o,eq)},$ kmol/m ³)	Variable	5.90	0.250	0.017	1.190	-11.164			
			6.10			1.665	-11.089			
			6.55			2.640	-11.014			
19	$pH_{(eq)}$	0.050 0.025	Variable	0.250	0.017	-12.450 -12.130	-11.703 -11.082	-11.163 (-11.086)	0.208 (0.041)	Extractant dependence = 1 pH dependence = 2
21	$\log ([Ac^-],$ kmol/m ³)	0.025	6.05	Variable	0.017	-0.650	-11.100			
20	$\log ([SO_4^{2-}],$ kmol/m ³)	0.025	6.08	0.250	Variable	0.075(lcr) 0.750(hcr)	-11.085 -11.070			
ii) $[H_2A_2]_{(o)} \geq 0.10 \text{ kmol/m}^3$, where extractant dependence is 3;										
18	$\log$ $([H_2A_2]_{(o,eq)},$ kmol/m ³)	Variable	5.90	0.250	0.017	3.750	-11.554			
			6.10			4.250	-11.554			
			6.55			5.300	-11.629	-11.560	0.045	Extractant dependence = 3 pH dependence = 2.5
19	$pH_{(eq)}$	0.10	Variable	0.250	0.017	-13.95	-11.503			

Values in parenthesis are on exclusion of abnormal value of -11.703, which might be due to error in intercept measurement, and choosing extractant dependence as 1.

The value of $\log K_{\text{ex}}$ has also been evaluated graphically. The values of $(\log [\text{H}_2\text{A}_2]_{(\text{o},\text{eq})} + 2 \text{pH}_{(\text{eq})} - \log [\text{Ac}^-] - \log (1 + 6.92 [\text{SO}_4^{2-}]))$ at different parameters have been calculated and tabulated in Table XXIV together with corresponding $\log {}^{\text{C}}\text{D}$ values. The $\log {}^{\text{C}}\text{D}$ vs. $(\log [\text{H}_2\text{A}_2]_{(\text{o},\text{eq})} + 2 \text{pH}_{(\text{eq})} - \log [\text{Ac}^-] - \log (1 + 6.92 [\text{SO}_4^{2-}]))$ plot is given in Fig. 24.

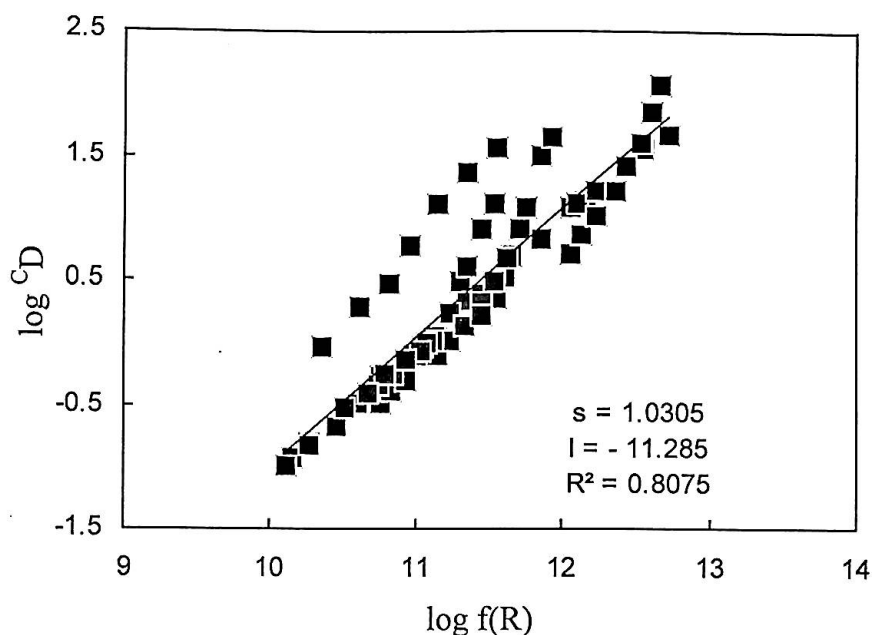


Fig. 24. Plot for the estimation of extraction equilibrium constant (K_{ex}) of Ni(II) being extracted by Cyanex 272 at 303 K (cf. Table XXIV). where, $(\log f(R) = \log [\text{H}_2\text{A}_2]_{(\text{o},\text{eq})} + 2 \text{pH}_{(\text{eq})} - \log [\text{Ac}^-] - \log (1 + 6.92 [\text{SO}_4^{2-}]))$.

It is found that the points are considerably scattered due to the change in extractant dependency on its concentration variation. The Least Squares slope of 1.0305 with intercept of -11.285 and correlation coefficient of only 0.8075 is obtained. The intercept (-11.285) apparently indicates the $\log K_{\text{ex}}$ value that is between the values obtained at lower and higher concentration regions of extractant.

3. Studies on extraction equilibrium of the $\text{Zn(II)}\text{-SO}_4^{2-}$ (H^+ , Na^+) - Cyanex 272-kerosene system

Some preliminary experiments showed that Zn(II) extraction in the title system could be done in the equilibrium pH region of 1 - 3.50. So this system has been investigated without buffering the aqueous phase. The title system has been investigated as narrated below:

i) Effect of phase contact time on extraction of Zn(II)

The related experimental data are given in Table XXV, which also includes the experimental parametric conditions. The variation of aqueous phase Zn(II) concentration together with the variation of $\log \{[Zn(II)]_{(o)} / [Zn(II)]\}$ with time are depicted in Fig. 25.

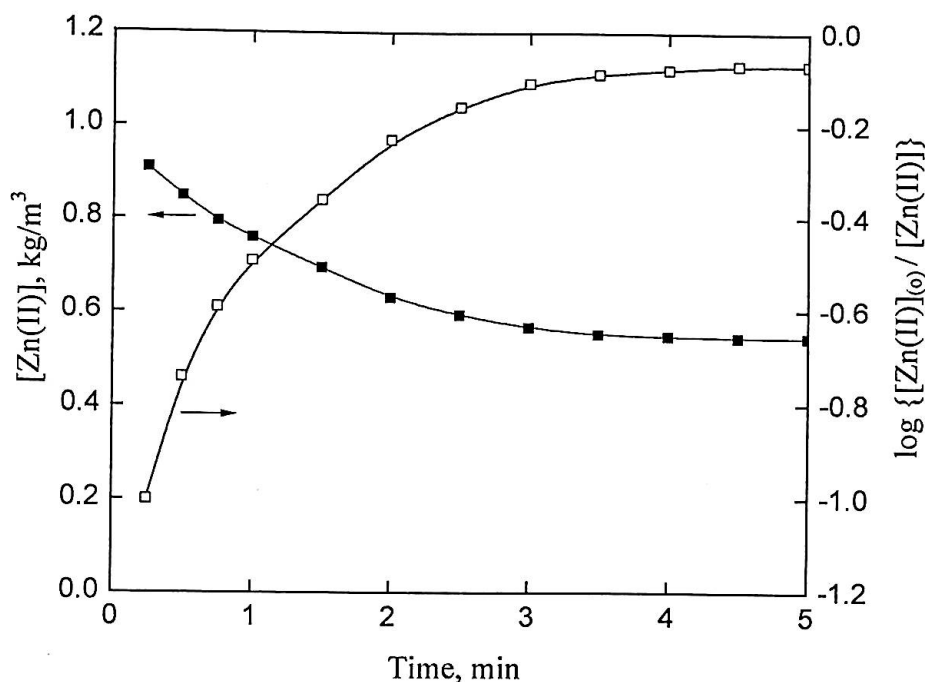


Fig. 25. Determination of equilibration time in the case of Zn(II) extraction by Cyanex 272 (cf. Table XXV). $[Zn(II)]_{(ini)} = 1.00 \text{ kg/m}^3$, $[H_2A_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.0153 \text{ kmol/m}^3$, $pH_{(ini)} = 6.00$, Temperature = $(303 \pm 0.50) \text{ K}$, O/A (Phase ratio) = 1.

Both curves level off after 3.5 min. It is therefore concluded that a phase contact time of 3.5 min is sufficient to attain equilibrium in the title system. However, in subsequent experiments, equilibration time of 5 min has been allowed to ensure equilibration at various experimental parameters.

ii) Effect of Zn(II) concentration on its extraction ratio

The variations of $\log D$ and $\log {}^cD$ ($= \log D + 2(2.50 - pH_{(eq)}) + (\log 0.025 - \log (0.025 - [Zn(II)]_{(o,eq)})$) with variations of the logarithmic aqueous Zn(II) concentration (0.20 - 3 kg/m^3) are given in Table XXVI together with the citation of experimental conditions. The $\log D$ versus $\log ([Zn(II)]_{(ini)}, \text{kmol/m}^3)$ as well the $\log {}^cD$ vs. $\log [Zn(II)]_{(eq)}$ plots are shown in Fig. 26.

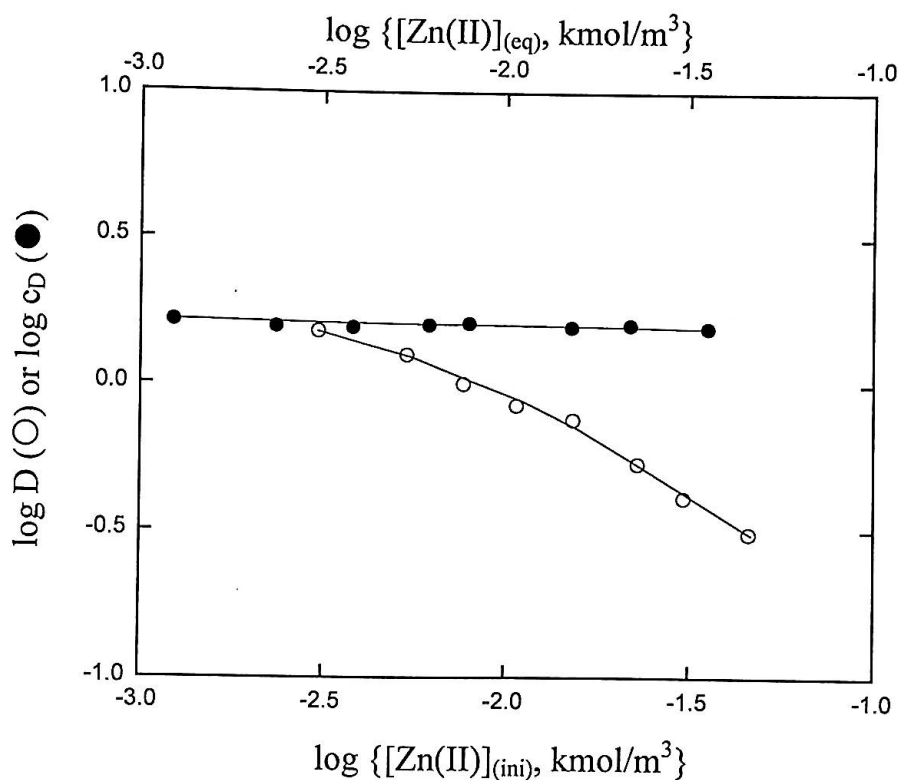


Fig. 26. Effect of Zn(II) concentration on extraction ratio in its extraction of by Cyanex 272 (*cf.* Table XXVI). $[\text{SO}_4^{2-}] = 0.046 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o},\text{ini})} = 0.025 \text{ kmol/m}^3 = \text{constant}$ $[\text{H}_2\text{A}_2]_{(\text{o},\text{eq})}$ chosen, $\text{pH}_{(\text{ini})} = 6.00$, constant $\text{pH}_{(\text{eq})}$ chosen = 2.5, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A (Phase ratio) = 1.

It is found that the $\log D$ values decrease; whilst the $\log c_D$ value remain unchanged with increasing Zn(II) concentration. It is therefore concluded that the extraction ratio is independent of Zn(II) concentration as expected from Eq. (17) provided the equilibrium pH and extractant concentration remain constant. This result also helps draw the conclusion that like in the cases of Mn(II) and Ni(II) extractions by Cyanex 272, the speciation of Zn(II) in either of the phases remain unaltered with variation of initial Zn(II) concentration in the aqueous phase.

iii) Effect of extractant concentration on extraction ratio of Zn(II)

The experimental data together with the experimental conditions are given in Table XXVII. The $\log c_D$ and $\log [\text{H}_2\text{A}_2]_{(\text{o},\text{eq})}$ values have been calculated accordingly considering pH dependence of 2 and extractant dependences as noted in the parentheses of the 8th column of the table. The $\log D$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o},\text{ini})}$ plots and the $\log c_D$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o},\text{eq})}$ plots are given in Figs. 27A and 27B respectively.

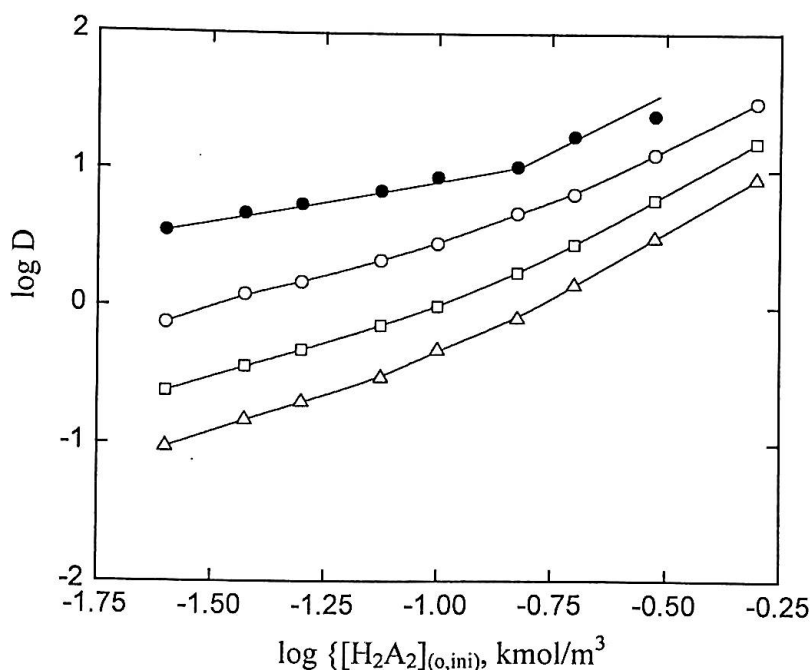


Fig. 27A. Effect of extractant concentration on the extraction of Zn(II) by Cyanex 272 (cf. Table XXVII). $[\text{Zn(II)}] = 1.00 \text{ kg/m}^3$, temperature = $(303 \pm 1) \text{ K}$, $[\text{SO}_4^{2-}] = 0.0153 \text{ kmol/m}^3$, Equilibration time = 5 min., phase ratio = 1:1, ($\bullet$), at variable pH when constant $\text{pH}_{(\text{eq})}$ chosen as = 2.70; ($\circ$), at variable pH when constant $\text{pH}_{(\text{eq})}$ chosen as = 2.40; ($\diamond$), at variable pH when constant $\text{pH}_{(\text{eq})}$ chosen as = 2.05; ($\triangle$), at variable pH when constant $\text{pH}_{(\text{eq})}$ chosen as = 1.85.

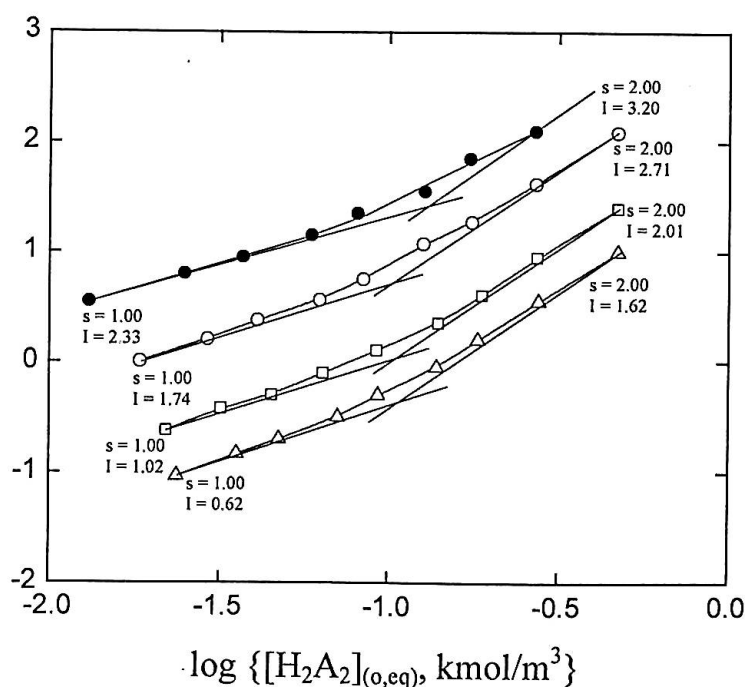


Fig. 27B. Effect of extractant concentration on the extraction of Zn(II) by Cyanex 272 (cf. Table XXVII). $[\text{Zn(II)}] = 1.00 \text{ kg/m}^3$, Temperature = $(303 \pm 1) \text{ K}$, $[\text{SO}_4^{2-}] = 0.0153 \text{ kmol/m}^3$, Equilibration time = 5 min., phase ratio = 1:1, ($\bullet$), constant $\text{pH}_{(\text{eq})}$ chosen = 2.70; ($\circ$), constant $\text{pH}_{(\text{eq})}$ chosen = 2.40; ($\diamond$), constant $\text{pH}_{(\text{eq})}$ chosen = 2.05; ($\triangle$), constant $\text{pH}_{(\text{eq})}$ chosen = 1.85.

In the second case, i.e. in Fig. 27B, the slopes of the curves (instead of getting straight lines) vary within 1 to 2 with increasing extractant concentration. In all four different constant $\text{pH}_{(\text{eq})}$ chosen, the intercepts of the asymptotic lines in the lower and higher concentration regions are cited in the body of the figure. It is concluded that in the limited concentration region of extractant, 1 g ion of Zn(II) combines with 1 mole of Cyanex 272 to form the extractable species like ZnA_2 ; but in the system containing surplus of extractant, 1 g ion of Zn(II) combines with 2 moles of Cyanex 272 to form $[\text{ZnA}_2 \cdot \text{H}_2\text{A}_2]$ or $[\text{Zn}(\text{HA}_2)_2]$ complex which is being extracted into the organic phase.

iv) Effect of equilibrium pH on extraction ratio of Zn(II)

Table XXVIII represents the values of $\log D$ at various equilibrium pH for Cyanex 272 concentrations of 0.025, 0.05, 0.10 and 0.30 kmol/m^3 systems. The other experimental parameters are also cited in the table. The $\log D$ values at constant $[\text{H}_2\text{A}_2]_{(\text{o},\text{eq})}$ values i.e. $\log {}^cD$ values have calculated accordingly and tabulated in the same table. The $\log D$ vs. $\text{pH}_{(\text{eq})}$ plots for four different Cyanex 272 concentration systems are displayed in Fig. 28A.

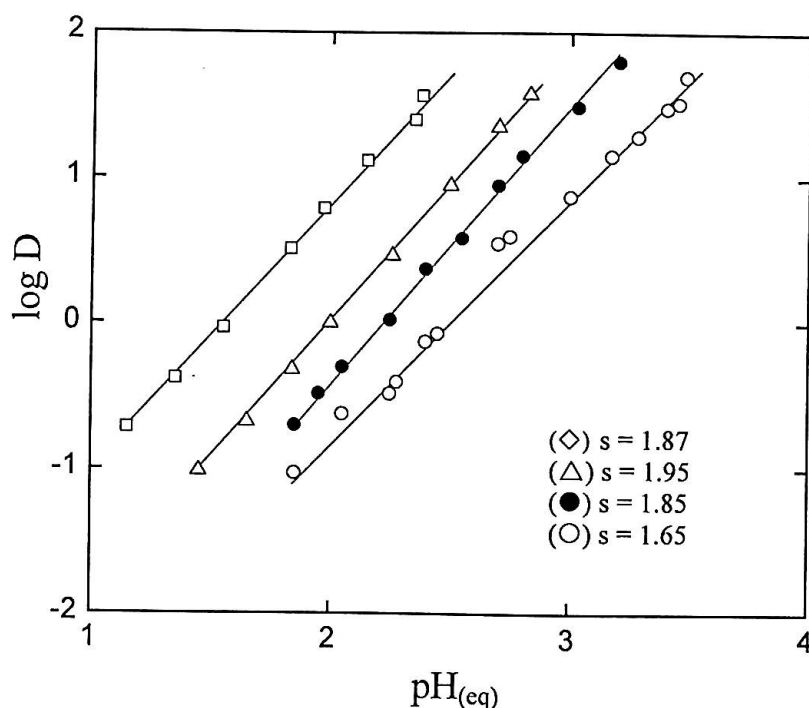


Fig. 28A. Effect of aqueous equilibrium pH on the extraction of Zn(II) by Cyanex 272 (cf. Table XXVIII). $[\text{Zn}(\text{II})] = 1.00 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 4.0153 \text{ kmol/m}^3$, Equilibration time = 5 min, temperature = $(303 \pm 0.50) \text{ K}$, $\text{O/A} = 1$; (○), $[\text{H}_2\text{A}_2]_{(\text{o},\text{ini})} = 0.025 \text{ kmol/m}^3$; (●), $[\text{H}_2\text{A}_2]_{(\text{o},\text{ini})} = 0.05 \text{ kmol/m}^3$; (△), $[\text{H}_2\text{A}_2]_{(\text{o},\text{ini})} = 0.10 \text{ kmol/m}^3$; (◇), $[\text{H}_2\text{A}_2]_{(\text{o},\text{ini})} = 0.30 \text{ kmol/m}^3$.

The straight lines are obtained with slopes ranging between 1.65 and 1.95. It is guessed from this result that the pH dependence of 2 might be obtained if $\log {}^cD$ vs. $pH_{(eq)}$ plots are drawn. Such plots are shown in Fig. 28B.

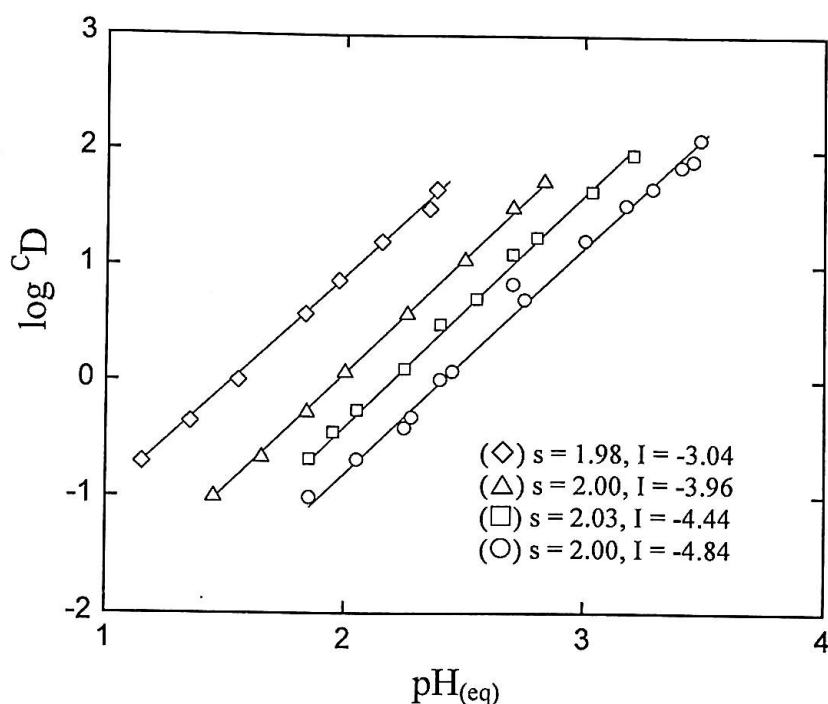


Fig. 28 B. Effect of aqueous equilibrium pH on the extraction of Zn(II) by Cyanex 272 (cf. Table XXVIII). Experimental parameters are as in Fig. 28A (O), $[H_2A_2]_{(o,ini)}$ = constant $[H_2A_2]_{(o,eq)}$ (chosen) = 0.025 kmol/m³; (Δ), $[H_2A_2]_{(o,ini)}$ = constant $[H_2A_2]_{(o,eq)}$ (chosen) = 0.05 kmol/m³; ($\triangle$), $[H_2A_2]_{(o,ini)}$ = constant $[H_2A_2]_{(o,eq)}$ (chosen) = 0.10 kmol/m³; ($\diamond$), $[H_2A_2]_{(o,ini)}$ = constant $[H_2A_2]_{(o,eq)}$ (chosen) = 0.30 kmol/m³.

As expected, straight lines are again obtained with slopes 2 ± 0.03 . The intercept of the lines are quoted on the body of the figure. It is concluded from this experimentation that 2 g ions H^+ will be liberated per 1 g ion of Zn(II) being complexed with Cyanex 272.

v) Effect of co-existing sulphate ion concentration on extraction ratio of Zn(II)

Related experimental data together with the experimental parameters are given in Table XXIX. Fig. 29 represents the $\log {}^cD$ vs. $\log [SO_4^{2-}]$ plot. A curve is obtained instead of a straight line. The curve represents:

$$\log {}^cD = 0.68 - \log (1 + 2 [SO_4^{2-}])$$

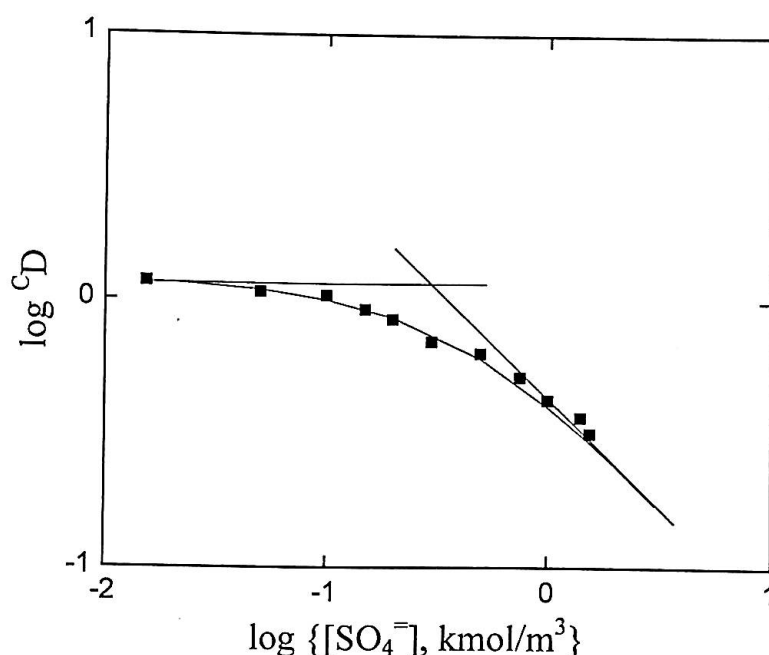


Fig. 29. The $\log C_D$ vs. $\log \{[SO_4^{2-}], \text{kmol/m}^3\}$ plot at constant equilibrium pH of 2.45 and extractant concentration of 0.025 kmol/m^3 (cf. Table XXIX). $[Zn(II)]_{(ini)} = 1.00 \text{ kg/m}^3$, temp. = $(303 \pm 0.50) \text{ K}$, equilibration time = 5 min, O/A = 1. The points are experimental whereas the curve is theoretical representing: $\log C_D = \log K_{ex} [H^+]^2_{(aq)} [H_2A_2]_{(aq)} - \log (1 + K_{SO_4}^{Eq} [SO_4^{2-}])$; where, $K_{SO_4}^{Eq}$ is a proportionality constant and its value has been calculated by the Curve- Fitting method. As $[SO_4^{2-}] \rightarrow 0$, then $\log C_D = \log K_{ex} [H^+]^2_{(aq)} [H_2A_2]_{(aq)} = 0.068$ (represented by the horizontal asymptote); whilst, when $[SO_4^{2-}] \rightarrow \infty$, then $\log C_D = 0.068 - \log K_{SO_4}^{Eq} - \log [SO_4^{2-}]$ (represented by the inclined asymptote). At the point of intersection of two asymptotes, $-\log K_{SO_4}^{Eq} - \log [SO_4^{2-}]$ equals to zero, giving $K_{SO_4}^{Eq} = \text{antilog of } -\log [SO_4^{2-}] = \text{antilog of } 0.3 = 2 \text{ m}^3/\text{kmol}$.

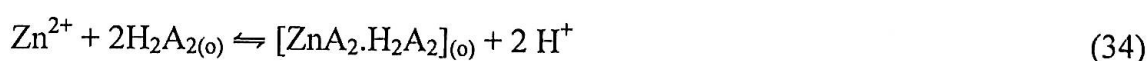
This result indicates that $[ZnSO_4]$ take part in the extraction reaction particularly when the sulphate concentration is very high in the medium, but sulphated species is not extracted into the organic phase.

vi) Mechanism of Zn(II) extraction by Cyanex 272

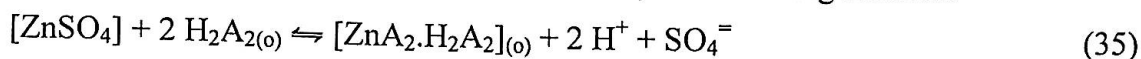
In lower sulphate and extractant concentration regions in the system, the pH, extractant and sulphate dependences of 2, 1 and zero, respectively suggest the following extraction equilibrium reaction:



In lower sulphate but higher extractant concentration region, the extraction equilibrium reaction is:

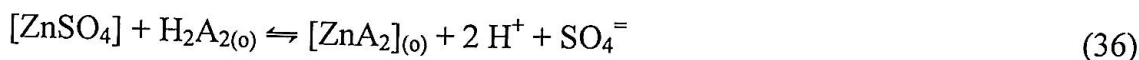


In higher sulphate and extractant concentration, the following reaction:



take place during extraction.

On the other hand, in higher sulphate but lower extractant concentration region, the equilibrium reaction will be represented by Eq. (36) given below:



In Eqs. (35) and (36), H^+ and SO_4^{2-} ions are liberated which may combine to form considerable amounts of HSO_4^- in the investigated pH regions.

Moreover, $\text{Zn(II)}\text{-HSO}_4^-$ complex existing in the investigated pH region may also take part in extraction reactions.

vii) Effect of temperature on extraction of Zn(II)

The effect of temperature on the extraction ratio of Zn(II) being extracted by Cyanex 272 has been determined at three different experimental parameters. The related data are shown in Table XXX. The log D values obtained at stated initial pH and extractant concentration have been used to calculate $\log {}^cD$ values at stated constant equilibrium pH and extractant concentration as usual. The $\log {}^cD$ values are given in the 8th column of the Table. The $\log {}^cD$ vs. $(1/T)$, K^{-1} plots are given in Fig. 30.

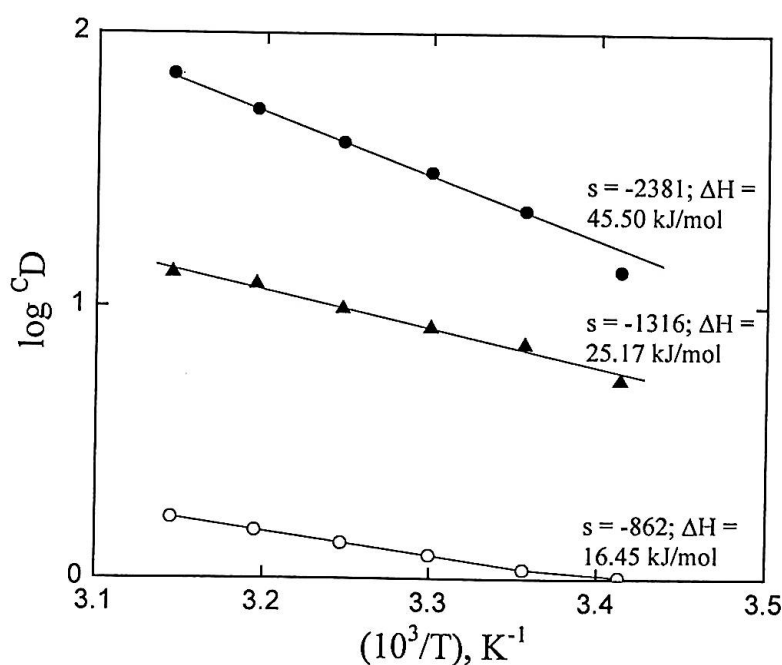


Fig. 30. Effect of temperature on the extraction ratio of Zn(II) being extracted by Cyanex 272 (cf. Table XXX). $[\text{SO}_4^{2-}] = 0.0153 \text{ kmol/m}^3$, $[\text{Zn(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, Equilibration time = 5 min, O/A = 1; (○), $\text{pH}_{(\text{ini})} = 6.0$, constant $\text{pH}_{(\text{eq})}$ chosen = 2.45, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = \text{constant}$ $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.025 kmol/m^3 ; (▲), $\text{pH}_{(\text{ini})} = 7.0$, constant $\text{pH}_{(\text{eq})}$ chosen = 2.45, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = \text{constant}$ $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.10 kmol/m^3 ; (●), $\text{pH}_{(\text{ini})} = 6.0$, constant $\text{pH}_{(\text{eq})}$ chosen = 2.35, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = \text{constant}$ $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.30 kmol/m^3 .

In all cases, straight lines are obtained, but the slopes of the lines differ. The highest sloped line is obtained for $\text{pH}_{(\text{eq})} = 2.35$ and $[\text{H}_2\text{A}_2]_{(\text{o,eq})} = 0.30 \text{ kmol/m}^3$. The value of the slope is -2381, giving ΔH value of 45.50 kJ/mol. Similarly ΔH values of 25.17 kJ/mol and 16.45 kJ/mol are obtained for 0.10 and 0.025 kmol/m³ $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ values, respectively. The ΔH value apparently depends on the $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ value; as this value increases, ΔH value is increased. In other words, ΔH value of ~ 16 kJ/mol is for the reaction forming ZnA_2 species; whereas, ~ 46 kJ/mol is for the reaction forming $[\text{ZnA}_2 \cdot \text{H}_2\text{A}_2]$ species. However, both reactions are endothermic i.e. the extent of extraction is enhanced by the rise of temperature.

viii) Loading Cyanex 272 solution by Zn(II)

The data on loading of 0.025 kmol/m³ and 0.100 kmol/m³ Cyanex 272 solutions with Zn(II) from an aqueous solution containing 0.9502 kg/m³ Zn(II) at pH 5.00 are given in Table XXXI. The cumulative Zn(II) concentrations in the organic phase have been plotted against the phase contact number for both systems in Fig. 31.

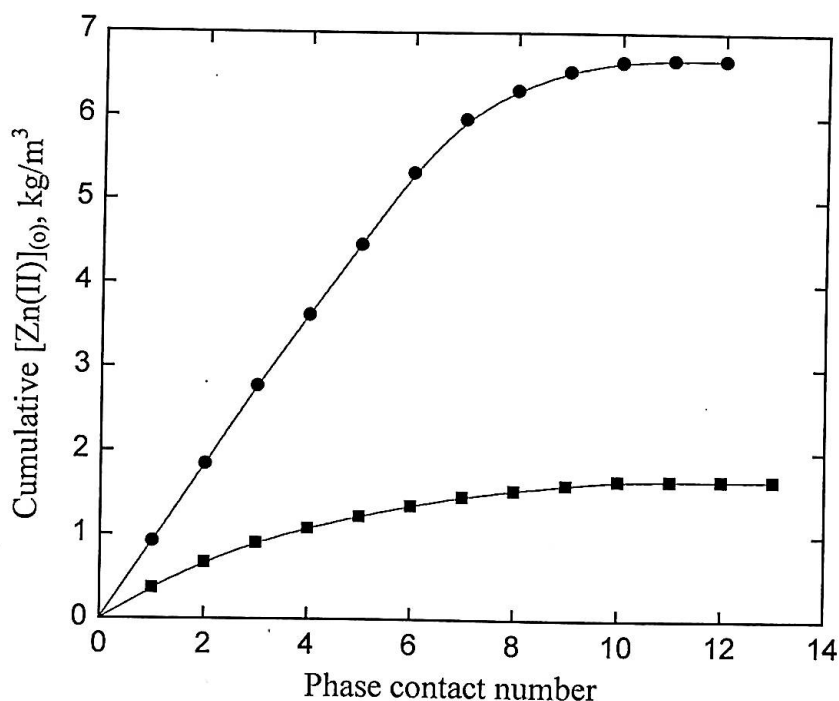


Fig. 31. Loading effect of Cyanex 272 with Zn(II) (*cf.* Table XXXI). $[\text{Zn(II)}]_{(\text{ini})} = 0.9502 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.015 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 5.00$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1 (O = 100 cm³), (●), $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, (■), $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$; organic phase recycled.

It is seen from the figure that the saturation of 0.025 kmol/m^3 Cyanex 272 solution with Zn(II) occurs at the 10th contact; whereas, it is at the 11th contact for the 0.10 kmol/m^3 Cyanex 272 system. At saturation, 0.025 kmol/m^3 Cyanex 272 solution can load 1.6655 kg/m^3 Zn(II); whereas, 0.10 kmol/m^3 Cyanex 272 solution can load 6.6856 kg/m^3 Zn(II). The amounts of 1.6655 kg/m^3 and 6.6856 kg/m^3 Zn(II) are equivalent to 0.0255 kmol/m^3 and 0.1022 kmol/m^3 Zn(II), respectively. So the existing species at saturation is no doubt ZnA_2 . The maximum loading capacity is estimated to be about $11.50 \text{ g Zn(II)/100 g Cyanex 272}$.

ix) Evaluation of extraction equilibrium constant (K_{ex}) for Zn(II) extraction by Cyanex 272

From the intercepts of the straight lines or of the asymptotic lines of the curves in Figs. 26, 27B, 28B and 29, the values of the extraction equilibrium constant (K_{ex}) for Zn(II) extraction by Cyanex 272 at 303 K have been elucidated. The evaluated K_{ex} values are given in Table D placed at the main body of the text.

The basic equations for calculating K_{ex} values are given at the bottom of this table. The K_{ex} values have been evaluated at lower and higher concentration regions of extractant i.e. for the formation of $[\text{ZnA}_2]$ and $[\text{ZnA}_2 \cdot \text{H}_2\text{A}_2]$ complexes, respectively. The $\log K_{\text{ex}}$ value given at the 9th row differs considerably from other values evaluated and the reason for this deviation is the high concentration of extractant. So this value has been excluded to calculate the average $\log K_{\text{ex}}$ value. The average $\log K_{\text{ex}}$ value evaluated at low concentration region of extractant is -3.111 with standard deviation of 0.091 . The value at high concentration region of extractant is -2.078 with standard deviation of 0.065 . The $\log K_{\text{ex}}$ value has also been estimated by the graphical method. The plot of $\log {}^cD$ vs. $[(1 - 2) \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} + 2 \text{pH}_{(\text{eq})} - \log (1 + 2 \text{SO}_4^{2-})]$ should be a straight line with a slope of unity and intercept equaling to $\log K_{\text{ex}}$ (Fig. 32). The related data are given in Table XXXII.

Table D. Evaluation of extraction equilibrium constant (K_{ex}) in the case of extraction of Zn(II) by Cyanex 272 at 303 K.

Fig. No.	$\log {}^CD$ vs. $\log..$	$[H_2A_2]_{(o,eq)}$, $kmol/m^3$	$pH_{(eq)}$	$[SO_4^{2-}]$, $kmol/m^3$	Intercept, I	$[H_2A_2]$ dependence (y)	pH -dependence (x)	$\log K_{ex}$	Average $\log K_{ex}$	Standard deviation
<i>i) At low concentration region of extractant</i>										
26	$[Zn(II)]_{(eq)}$	0.025	2.50	0.046	0.20	1.00	2.00	-3.160		
27B	$[H_2A_2]_{(o,eq)}$	Variable	1.85	0.0153	0.62	1.00	2.00	-3.067		
			2.05	0.0153	1.02	1.00	2.00	-3.036		
			2.40	0.0153	1.74	1.00	2.00	-3.047		
			2.70	0.0153	2.33	1.00	2.00	-3.057		
28B	$[H^+]^{-1}_{(eq)}$	0.025	Variable	0.0153	-4.84	1.00	2.00	-3.225	-3.111	0.091
		0.050		0.0153	-4.44	1.00	2.00	-3.126		
		0.100		0.0153	-3.96	1.00	2.00	-2.947		
		(0.300)		0.0153	-3.04	1.00	2.00	(-2.504)		
29	$[SO_4^{2-}]$	0.025	2.45	Variable	0.068 (lcr) -0.230 (hcr)	1.00	2.00	-3.220		
<i>ii) At high concentration region of extractant</i>										
27B	$[H_2A_2]_{(o,eq)}$	Variable	1.85	0.0153	1.62	2.00	2.00	-2.067		
			2.05	0.0153	2.01	2.00	2.00	-2.077		
			2.40	0.0153	2.71	2.00	2.00	-2.077	-2.078	0.065
			2.70	0.0153	3.20	2.00	2.00	-2.187		
28B	$pH_{(eq)}$	0.30	Variable	0.0153	-3.04	2.00	2.00	-1.981		

Basic equation for calculating K_{ex} :

$$\log {}^CD = \log K_{ex} + y \log [H_2A_2]_{(o,eq)} + x pH_{(eq)} - \log \{1 + 2 [SO_4^{2-}]\}, \text{ where } y = 1 \text{ at lcr of extractant and } 2 \text{ at hcr of extractant, whilst } x = 2 \text{ always.}$$

* hcr = highest concentration region and lcr = lowest concentration region.

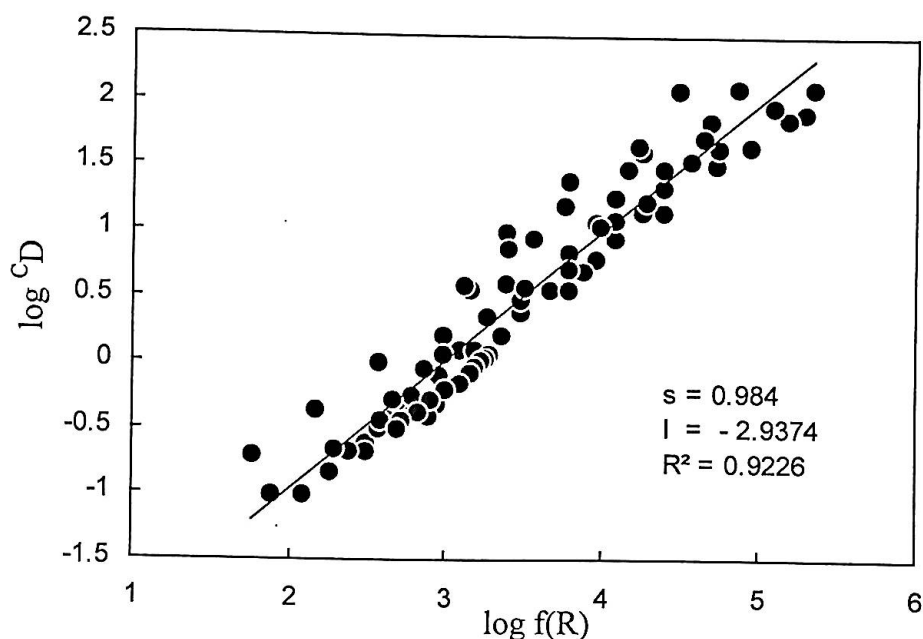


Fig. 32. Plot for the estimation of extraction equilibrium constant (K_{ex}) of Zn(II) being extracted by Cyanex 272 at 303 K; where, $\log f(R) = ((1 - 2) \log [H_2A_2]_{(o,eq)} + 2 \text{pH}_{(eq)} - \log (1 + 2 [SO_4^{=}]))$ (cf. Table XXXII).

A straight line is indeed obtained with slope of 0.984 (should be 1.00) and intercept of -2.9374. However, the correlation coefficient is rather small (0.9226 instead of 1); which is attributed to the variation of extractant dependence. The intercept gives $\log K_{ex}$ value of -2.9374, which is between the values obtained from the calculation method.

x) Stripping of Zn(II) from ZnA_2 complex by mineral acid solutions:

It is found that 100% stripping of Zn(II) from the ZnA_2 complex existing in the organic phase having almost no free extractant is possible by 0.10 kmol/m³ sulphuric, hydrochloric and nitric acid solutions.

4. Studies on the rate of forward extraction of Mn(II) by Cyanex 272

The rates of forward extractions of Mn(II) by Cyanex 272 solutions have been measured by the single (falling) drop method. By experimentations, the Mn(II)-transfer fluxes (amount Mn(II) transferred from a drop / (drop fall time $\times$ surface area of a drop)) have been measured at different experimental parameters. At a constant temperature, the manganese(II)-transfer flux in the forward extraction can be represented by the following equation:

$$F_f (\text{kmol/m}^2\text{s}) = k_f \cdot [Mn(II)]^a_{(ini)} [H^+]^b [H_2A_2]^c_{(o)} [SO_4^{=}]^d [Ac^-]^e \quad (37)$$

In logarithmic form, Eq. (37) can be expressed as:

$$\log (F_f, \text{ kmol/m}^2\text{s}) = \log k_f + a \log [\text{Mn(II)}]_{(\text{ini})} + b \log [\text{H}^+] + c \log [\text{H}_2\text{A}_2]_{(\text{o})} + d \log [\text{SO}_4^{=}] + e \log [\text{Ac}^-] \quad (38)$$

Equation (38) states that if on keeping other parameters constant, the $\log F_f$ values are measured at different $[\text{Mn(II)}]_{(\text{ini})}$, then the plot of $\log F_f$ vs. $\log [\text{Mn(II)}]_{(\text{ini})}$ will give a straight line with slope equaling to 'a' - the reaction order with respect to Mn(II) concentration and intercept equaling to $\log k_f + b \log [\text{H}^+] + c \log [\text{H}_2\text{A}_2]_{(\text{o})} + d \log [\text{SO}_4^{=}] + e \log [\text{Ac}^-]$; from which the value of $\log k_f$ can be evaluated after determining the values of 'b', 'c', 'd' and 'e'. The values of 'b', 'c', 'd' and 'e' can be determined as the slopes of the $\log F_f$ vs. $\log [\text{H}^+]$, $\log F_f$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o})}$, $\log F_f$ vs. $\log [\text{SO}_4^{=}]$ and $\log F_f$ vs. $\log [\text{Ac}^-]$ plots, respectively. The intercepts of the lines or the asymptotic lines of the curves obtained can be used for other sets of $\log k_f$ values.

The rate of forward extraction of Mn(II) by Cyanex 272 has been thoroughly investigated as narrated in the following sections:

i) Determination of time needed for drop formation and coalescence

In order to determine the time needed for drop formation and coalescence the amount of Mn(II)-transferred at different drop fall time (drop fall time has been varied by varying the column height). The experimental data are given in Table XXXIII. The amount of Mn(II)-transferred from a drop during falling through the organic continuum versus drop fall time plot is shown in Fig. 33.

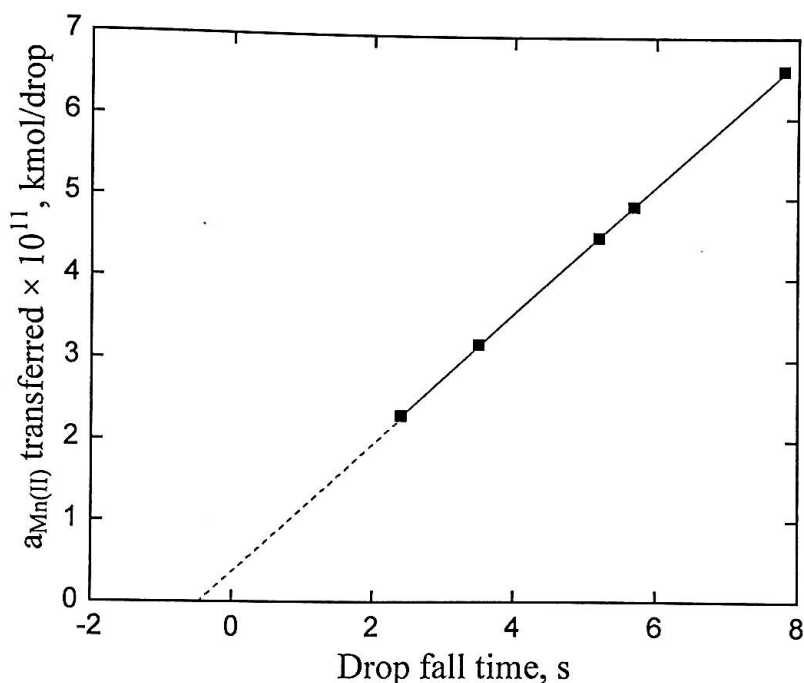


Fig. 33. Effect of time needed for drop formation and coalescence in a single drop experiment in Mn(II) extraction by Cyanex 272 (*cf.* Table XXXIII). $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, $[\text{Mn(II)}]_{(\text{ini})} = 0.4371 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.80$, Temperature = 303 K, Number of collected drops = 100.

The experimental parameters are noted both in Table and legend of figure. It is found that with the increase in drop fall time, amount of Mn(II)-transferred from a drop is increased linearly; however, the relating straight line does not pass through the origin. The line intersects the fall time axis at -0.50 s. This time (0.50 s) is attributed to time for drop formation and coalescence. In calculating fluxes, the time for drop formation and coalescence ($\Delta t = 0.50 \text{ s}$) must be added to the drop fall time; otherwise errors in flux calculation will appear; which is demonstrated as follows:

In Table XXXIV; the Mn(II) transfer flux has been calculated in two different ways for different column heights used: F'_f has been calculated by neglecting the Δt value ($F'_f = a_{\text{Mn(II)}} \text{ transferred} / (A \cdot t)$); whereas, F_f has been calculated by taking into account the Δt value ($F_f = a_{\text{Mn(II)}} \text{ transferred} / A \cdot (t + \Delta t)$). The F'_f , F_f , $\log F'_f$ and $\log F_f$ values at different column heights are given in the 6th, 7th, 8th and 9th columns of the Table XXXIV. The $\log F'_f$ vs. column height and $\log F_f$ vs. column height plots are presented in Fig. 34.

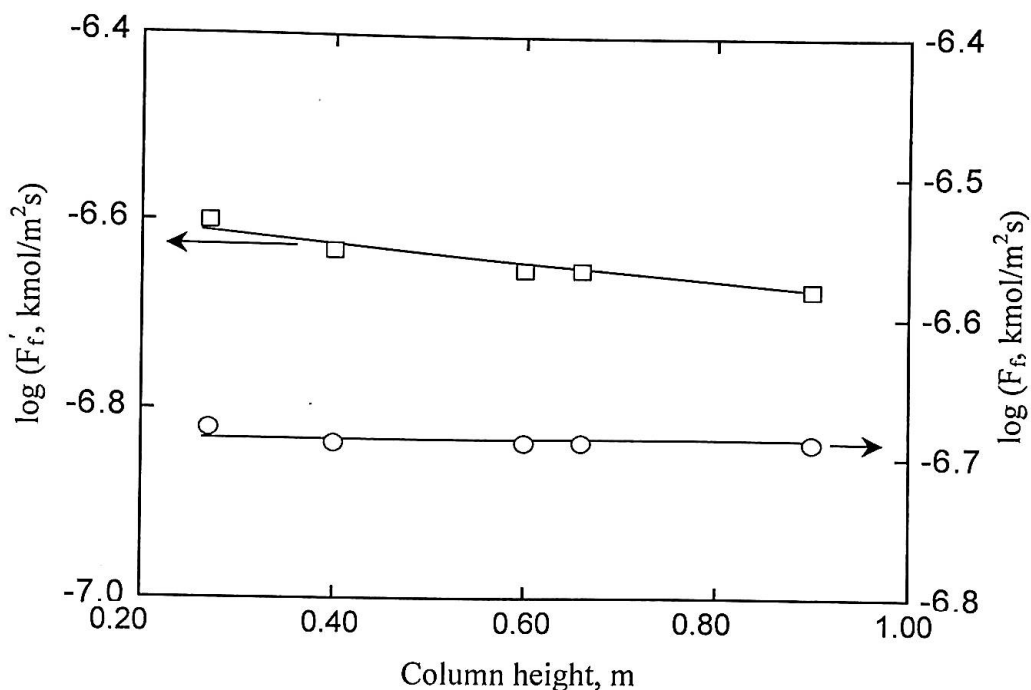


Fig. 34. Effect of column height on rate of Mn(II) transfer in a single drop experiment in Mn(II) extraction by Cyanex 272 (*cf.* Table XXXIV). $[H_2A_2]_{(0,ini)} = 0.025 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.008 \text{ kmol/m}^3$, $[Mn(II)]_{(ini)} = 0.437 \text{ kg/m}^3$, $[Ac^-] = 0.25 \text{ kmol/m}^3$, $pH_{(ini)} = 4.80$, Temperature = 303 K, $\Delta t = 0.50 \text{ s}$, Number of collected drops = 100

It is seen that the value of $\log F'_f$ decreases, whilst $\log F_f$ remains unchanged with increasing column height. Moreover, for every column height used, $\log F_f$ is smaller than $\log F'_f$ value. It is concluded from this result that the calculated flux of Mn(II)-transfer will be independent of column height if Δt is added to the drop fall time; and the column of any height can be used for flux measurement if F_f in lieu of F'_f is measured.

ii) Effect of initial Mn(II) concentration of the aqueous phase on the flux of Mn(II) transfer in its forward extraction by Cyanex 272

On varying Mn(II) concentration between 0.316 and 1.949 kg/m^3 , the single drop experiments have been conducted keeping all other conditions identical. The related experimental data are given in Table XXXV. Two sets of experimentation have been conducted with constituting the organic continuum with 0.025 and 0.20 kmol/m^3 Cyanex 272 solution in kerosene. The $\log (F_f, \text{kmol/m}^2\text{s})$ vs. $\log ([Mn(II)]_{(ini)}, \text{kmol/m}^3)$ plots are shown in Fig. 35.

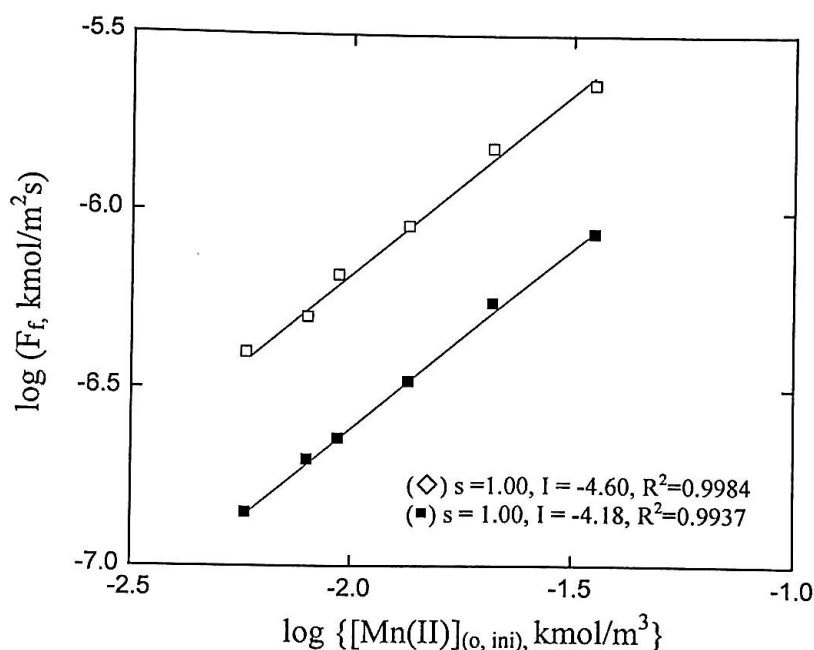


Fig. 35. Effect of initial Mn(II) concentration in the aqueous phase on the flux of Mn(II) transfer in its forward extraction by Cyanex 272 (*cf.* Table XXXV). $[Ac^-] = 0.25 \text{ kmol/m}^3$, (■), $[H_2A_2]_{(o, ini)} = 0.025 \text{ kmol/m}^3$, (◇), $[H_2A_2]_{(o, ini)} = 0.20 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.04 \text{ kmol/m}^3$, $pH_{(ini)} = 4.70$, Column height = 0.60 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$.

For both cases, good fit straight lines are obtained. The Least Squares slopes, intercepts and correlation coefficients for the systems are quoted in body of the figure. The unity slope indicates that the rate of forward extraction of Mn(II) by Cyanex 272 solution is directly proportional to initial Mn(II) concentration in the aqueous phase. In other words, the reaction order with respect to Mn(II) concentration (i.e. 'a' in Eq. (38)) is unity.

iii) Effect of initial extractant concentration of the organic phase on the flux of Mn(II) transfer

On varying the initial Cyanex 272 concentration between 0.025 and 0.30 kmol/m^3 , the fluxes of Mn(II) transfer have been measured for initial aqueous pH values of 4.80 and 4.00. Experimental results at 303 K are given in Table XXXVI. Figure 36 shows the $\log (F_f, \text{kmol/m}^2 \text{ s})$ vs. $\log ([H_2A_2]_{(o, ini), \text{kmol/m}^3})$ plots for initial aqueous pH values of 4.8 and 4.00. In both cases, straight lines are obtained.

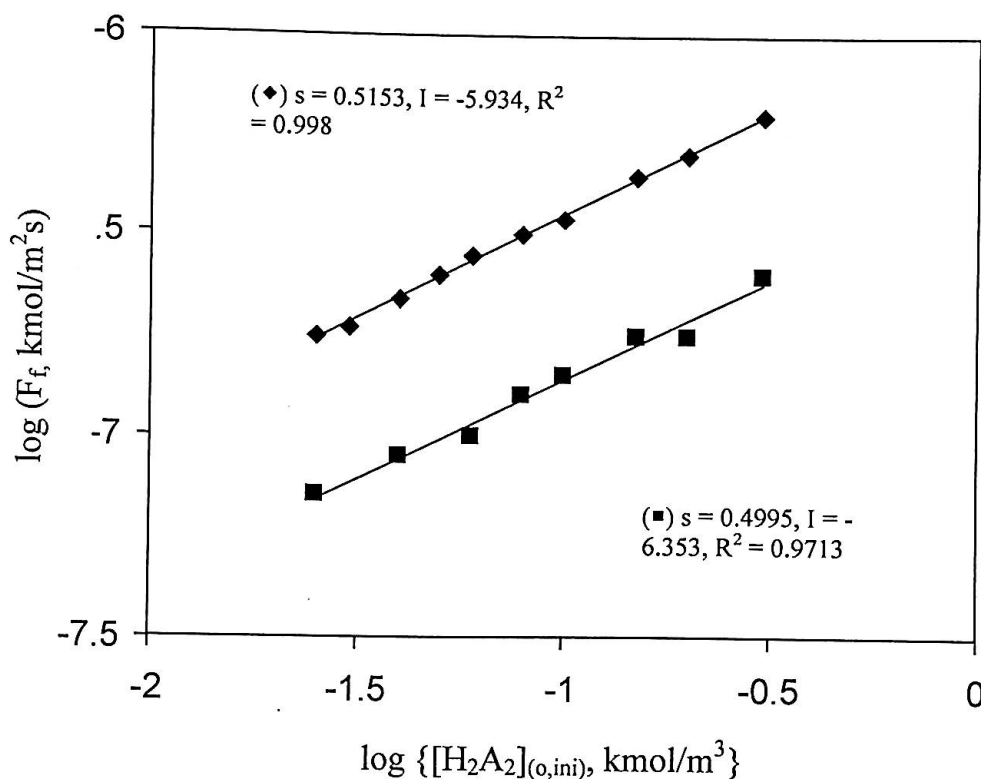


Fig. 36. Effect of initial extractant concentration of the organic phase on the flux of Mn(II) transfer in its forward extraction by Cyanex 272 (*cf.* Table XXXVI). $[Mn(II)]_{(ini)} = 0.437 \text{ kg/m}^3$, $[Ac^-] = 0.25 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.60 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$ ($\blacksquare$) $pH_{(ini)} = 4.00$, ($\blacklozenge$) $pH_{(ini)} = 4.80$.

The Least Squares slopes of the lines are 0.4995 and 0.5153 for pH 4.0 and 4.8 systems, respectively. Intercepts and correlation coefficients are given on the body of the figure. The slope of ~ 0.50 points out that the reaction order with respect to extractant concentration (i.e. 'c' in Eq. (38)) is a one-half. In other words, the rate of forward extraction Mn(II) in the $Mn(II)-SO_4^{2-}-Ac^-(Na^+, H^+) - \text{Cyanex 272-kerosene}$ system is directly proportional to the square root of the initial extractant concentration.

iv) Effect of initial aqueous pH on the flux of Mn(II) transfer

Fluxes of Mn(II) transfer have been determined on changing the initial aqueous pH between 3.74 and 5.48 for constant extractant concentrations of 0.025 and 0.10 kmol/m^3 . The experimental data are shown in Table XXXVII. An observation on the first and last columns of this table indicates that the $\log F$ value increases with increasing initial pH of the aqueous phase. In order to find out the degree of this dependency, the $\log(F_f, \text{kmol/m}^2 \text{s})$ vs. $pH_{(ini)}$ plots have been drawn and shown in Fig. 37.

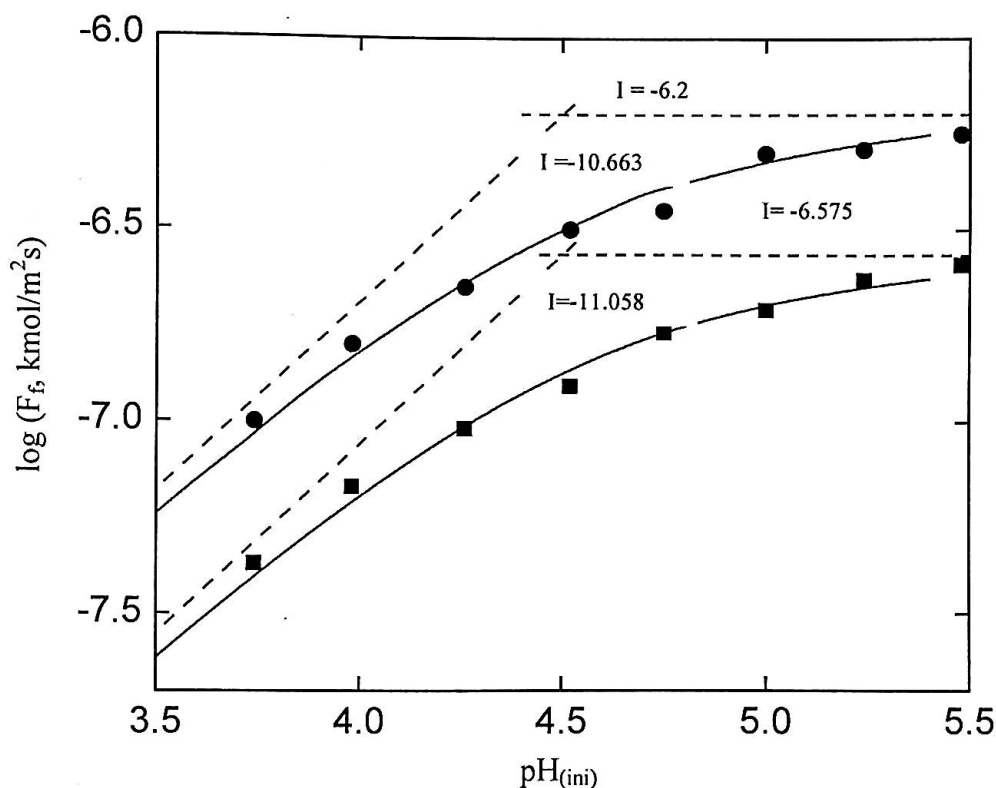


Fig. 37. Effect of initial pH of the aqueous phase on the flux of Mn(II) transfer in the forward extraction of Mn(II) by Cyanex 272 (*cf.* Table XXXVII). $[\text{Mn(II)}]_{(\text{ini})} = 0.437 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.60 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$; ($\blacksquare$), $[\text{H}_2\text{A}_2] = 0.025 \text{ kmol/m}^3$. Points are experimental and the solid curve is theoretical representing: $\log F_f = \log k_f [\text{Mn(II)}] [\text{H}_2\text{A}_2]_{(\text{o})}^{0.5} - \log(1 + K_H^f [\text{H}^+])$, where K_H^f is a proportionality constant and its value has been calculated by the Curve-Fitting method. The horizontal dashed line is an asymptote at low H^+ concentration region represented by eq. : $\log F_f = \log k_f [\text{Mn(II)}] [\text{H}_2\text{A}_2]_{(\text{o})}^{0.5} = -6.575$; whereas the inclined dashed line is the asymptote at high $[\text{H}^+]$ concentration region represented by eq. : $\log F_f = -6.575 - \log K_H^+ - \log [\text{H}^+]$. At the point of intersection of two asymptotes, $-\log K_H^+ + \text{pH} = 0$; giving $K_H^+ = 10^{\text{pH}} = 10^{4.5} = 31623 \text{ m}^3/\text{kmol}$. ($\bullet$), $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, Points are experimental and the solid curve is theoretical representing; $\log F_f = -6.2 - \log\{1 + K_H^f [\text{H}^+]\}$, where, K_H^f is a proportionality constant and its value has been evaluated to be $10^{4.5} = 31623 \text{ m}^3/\text{kmol}$ as described above.

For both extractant concentration systems used, the experimental points do not fall on a straight line, rather can be set on a curve represented by: $\log(F_f, \text{kmol/m}^2 \text{ s}) = -6.575$ (for $0.025 \text{ kmol/m}^3 \text{ H}_2\text{A}_2$ system) or, -6.20 (for $0.10 \text{ kmol/m}^3 \text{ H}_2\text{A}_2$ system) $-\log(1 + 10^{4.5} [\text{H}^+])$. Therefore, the flux of Mn(II) transfer in its forward extraction is inversely proportional to the term $(1 + 10^{4.5} [\text{H}^+])$ i.e. at higher concentration of H^+ (i.e. at low pH region), the rate is inversely proportional to $[\text{H}^+]$; whereas, at lower concentration region of H^+ (i.e. at high pH region), the rate is independent of H^+ concentration. This result points out that the extraction mechanism at lower pH region will differ from that at the higher pH region.

v) Effect of coexisting sulphate ion concentration on the flux of Mn(II) transfer

As it is seen during the extraction equilibrium study that the extraction is considerably decreased with increasing sulphate ion concentration of the aqueous phase, it is expected that the rate of Mn(II) extraction will also depend on the sulphate ion concentration that will exist in the aqueous phase. In order to examine this effect, experiments have been carried out to calculate the fluxes of Mn(II) transfer at various sulphate ion concentrations keeping all other conditions unchanged. The experimental results are given in Table XXXVIII. The $\log (F_f, \text{kmol/m}^2\text{s})$ vs. $\log ([\text{SO}_4^{=}], \text{kmol/m}^3)$ plot is shown in Fig. 38 for the system comprising of parameters mentioned in both respected table and figure caption.

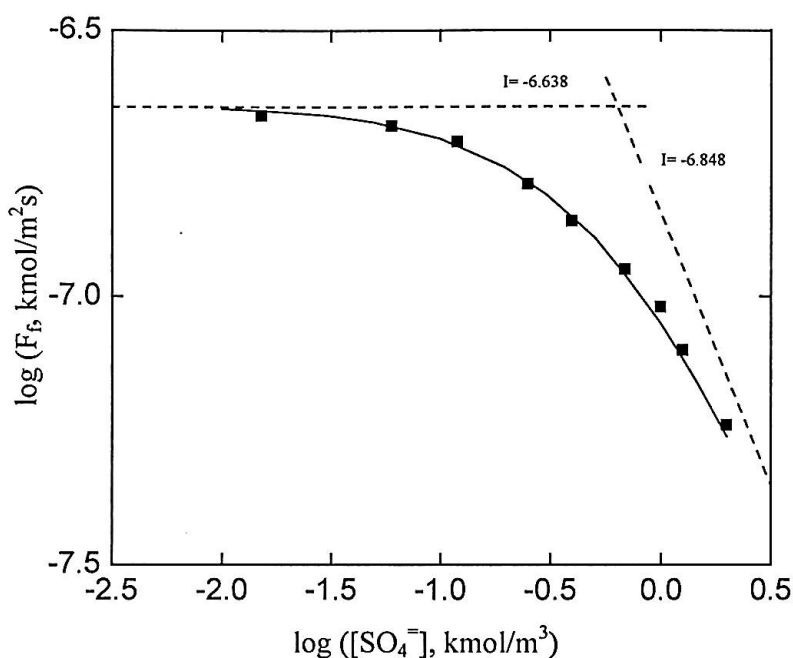


Fig. 38. Effect of sulfate ion concentration in the aqueous phase on the flux of Mn(II) transfer in its forward extraction by Cyanex 272 (*cf.* Table XXXVIII). $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.05 \text{ kmol/m}^3$, $[\text{Mn(II)}]_{(ini)} = (0.452 \pm 0.005) \text{ kg/m}^3$, $\text{pH}_{(ini)} = 4.80$, Column height = 0.60 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$. Points are experimental and the solid curve is theoretical representing; $\log F_f = \log k_f [\text{Mn(II)}] [\text{H}_2\text{A}_2]_{(o)}^{0.5} (1 + 31623 [\text{H}^+])^{-1} - \log (1 + K_{\text{SO}_4}^f [\text{SO}_4^{=}]$); where $K_{\text{SO}_4}^f$ is a proportionality constant and its value has been calculated by the Curve-Fitting method. The horizontal dashed line is an asymptote at low $\text{SO}_4^{=}$ concentration region represented by eq. : $\log F_f = \log k_f [\text{Mn(II)}] [\text{H}_2\text{A}_2]_{(o)}^{0.5} (1 + 31623 [\text{H}^+])^{-1} = -6.64$; whereas the inclined dashed line is the asymptote at high $\text{SO}_4^{=}$ concentration region represented by eq : $\log F_f = -6.64 - \log K_{\text{SO}_4}^f - \log [\text{SO}_4^{=}]$. At the point of intersection of two asymptotes, $-\log K_{\text{SO}_4}^f - \log [\text{SO}_4^{=}] = 0$; giving $K_{\text{SO}_4}^f = 1.58 \text{ m}^3/\text{kmol}$.

It is found that the flux of Mn(II) transfer is decreased with increasing sulphate ion concentration prevailing in the aqueous phase; but the log-log plot is not a straight line. Rather the experimental points can be put on a curve represented by: $\log (F_f, \text{ kmol/m}^2 \text{ s}) = -6.64 - \log (1 + 1.58 [\text{SO}_4^{2-}])$ for the system comprising of $(0.452 \pm 0.005) \text{ kg/m}^3$ Mn(II), 0.25 kg/m^3 Ac^- , $\text{pH}_{(\text{ini})}$ of 4.80 and 0.05 kmol/m^3 extractant system. Therefore, the rate of forward extraction of Mn(II) is inversely proportional to the term $(1 + 1.58 [\text{SO}_4^{2-}])$ which implies that the rate is independent of sulphate ion concentration in its lower concentration region, whilst it is inversely proportional to sulphate ion concentration in its higher concentration region. Intercepts of the asymptotic lines are shown in the figure.

vi) Effect of added acetate ion concentration on the flux of Mn(II) transfer

Effect of acetate ion concentration on the flux of Mn(II) transfer has been investigated by measuring the flux values at various acetate ion concentrations ranging from 0.125 kmol/m^3 to 2.00 kmol/m^3 keeping other parameters constant. Data gathered from these experimentations are given in Table XXXIX. The $\log (F_f, \text{ kmol/m}^2 \text{ s})$ vs. $\log \{[\text{Ac}^-], \text{ kmol/m}^3\}$ plot is displayed in Fig. 39.

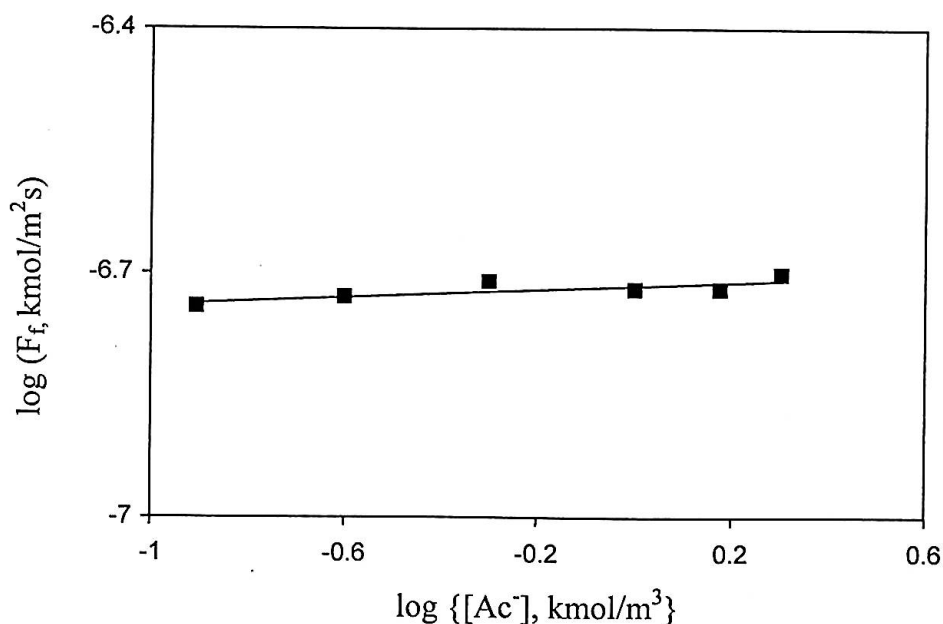


Fig. 39. Effect of acetate ion concentration in the aqueous phase on the flux of Mn(II) transfer in its forward extraction by Cyanex 272 (*cf.* Table XXXIX). $[\text{Mn(II)}]_{(\text{ini})} = (0.436 \pm 0.016) \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.80$, Column height = 0.60 m , Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$, Temperature = 303 K .

The experimental points fall on a horizontal straight line indicating the independence of acetate ion concentration on the rate of Mn(II) transfer. The data at still lower acetate concentration have been excluded for obtaining abnormal low values of Mn(II)-transfer flux. However, this behavior might be due to the loss of buffer action at lower concentration region of acetate ion allowing the interfacial pH to be decreased considerably and corresponding lower flux values are obtained. Therefore, it is concluded that as long as buffer action of acetate system prevails, the rate of Mn(II) transfer is independent of acetate ion concentration.

vii) Effect of temperature on the flux of Mn(II) transfer

All above experiments stated above were performed at 303 K. But according to the Arrhenius theory, the rate of a process involving chemical reaction is increased by increasing temperature. So, it is certain that the Mn(II)-transfer flux in the investigated system will be increased by increasing temperature, but in order to measure the degree of enhancement of reaction rate with temperature rise (or to estimate the activation energy, E_a), this study has been made. Three sets of experiments have been carried out; (a) at $\text{pH}_{(\text{ini})} = 5.50$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$; (b) at $\text{pH}_{(\text{ini})} = 4.80$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$; and (c) at $\text{pH}_{(\text{ini})} = 3.75$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$. Results are presented in Table XL and the corresponding Arrhenius plots are shown in Fig. 40.

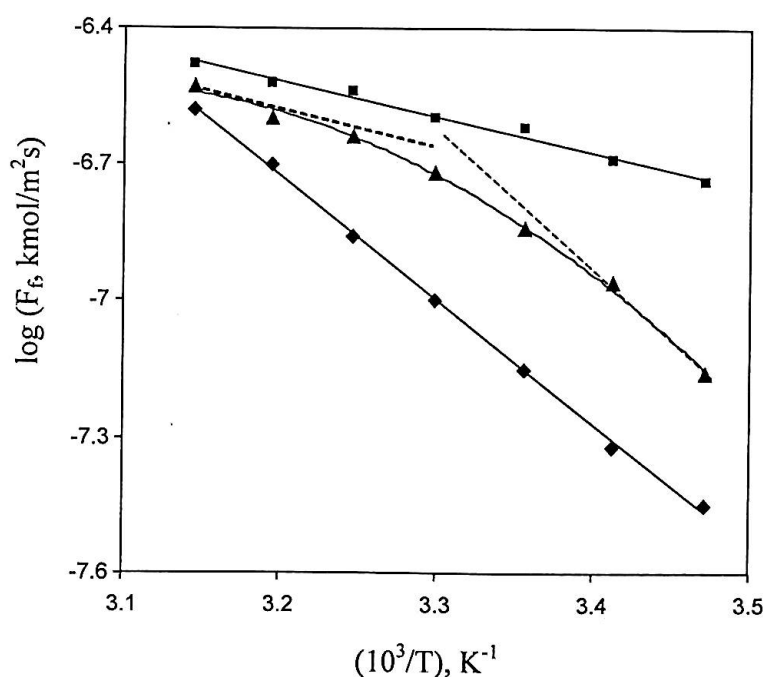


Fig. 40. Effect of temperature on the flux of Mn(II) transfer in its forward extraction by Cyanex 272 (*cf.* Table XL). $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{Mn(II)}]_{(\text{ini})} = 0.437 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.60 m, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$, (■), $\text{pH}_{(\text{ini})} = 5.50$, $[\text{H}_2\text{A}_2] = 0.025 \text{ kmol/m}^3$, $s = -776$, $E_a = 14.85 \text{ kJ/mol}$; (▲), $\text{pH}_{(\text{ini})} = 4.80$, $[\text{H}_2\text{A}_2] = 0.025 \text{ kmol/m}^3$, $s_{(\text{t.r})} = -3061$, $E_a = 59.10 \text{ kJ/mol}$, $s_{(\text{h.t.r})} = -875$, $E_a = 16.70 \text{ kJ/mol}$; (◆), $\text{pH}_{(\text{ini})} = 3.75$, $[\text{H}_2\text{A}_2] = 0.10 \text{ kmol/m}^3$, $s = -2700$, $E_a = 51.60 \text{ kJ/mol}$.

For the (a) and (c) systems, straight lines are obtained whose slopes give the activation energy (E_a) of 14.85 kJ/mol and 51.60 kJ/mol, respectively. It is apparent that the activation energy is decreased considerably on increasing pH of the aqueous phase. On the other hand, for the (b) system, experimental points fall on a curve having lower asymptotic (-ve) slope in the higher temperature region (htr) and higher asymptotic (-ve) slope in the lower temperature region (ltr). These limiting slopes give E_a values of 59.10 kJ/mol and 16.70 kJ/mol at lower and higher temperature regions, respectively.

The temperature dependence flux data of Mn(II) extraction have also been treated by the Activated Complex Theory of reaction rate. According to this theory, the plot $\log \left(\frac{F_r h}{kT} \right)$ vs. $(1/T)$, K^{-1} plots would be a straight line with slope equaling to $\Delta H^\ddagger / 2.303R$ whilst the intercept would be equal to $\log f(R) + (\Delta S^\ddagger / 2.303 R)$. The necessary calculated data are collected in Table XLI and the $\log \left(\frac{F_r h}{kT} \right)$ vs. $(1/T)$, K^{-1} plots are shown in Fig. 41.

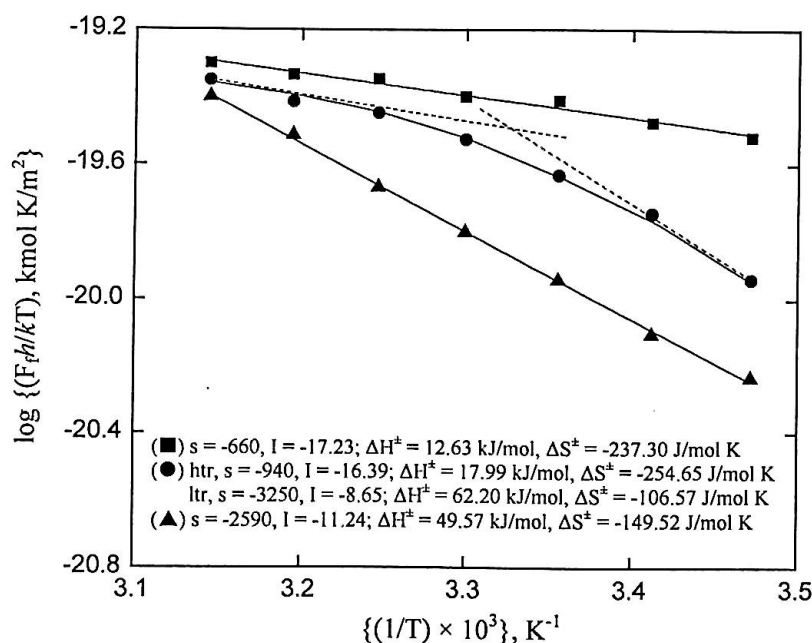


Fig. 41. The $\log (F_r h / kT)$ vs. $(1/T)$ plots of the forward extraction of Mn(II) by Cyanex 272 (cf. Table XLI). $[Ac^-] = 0.25 \text{ kmol/m}^3$, $[Mn(II)]_{(ini)} = 0.437 \text{ kg/m}^3$, $[SO_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.60 m, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$, (■), $pH_{(ini)} = 5.50$, $[H_2A_2] = 0.025 \text{ kmol/m}^3$, $\log f(R) = -2.9486$; (●), $pH_{(ini)} = 4.80$, $[H_2A_2] = 0.025 \text{ kmol/m}^3$, $\log f(R) = -3.0837$; (▲), $pH_{(ini)} = 3.75$, $[H_2A_2] = 0.10 \text{ kmol/m}^3$, $\log f(R) = -3.4273$; $h = 6.6252 \times 10^{-37} \text{ kJ s}$, $k = 1.38 \times 10^{-26} \text{ kJ/deg}$.

For the (a) and (c) systems mentioned in the above paragraph, the plots are straight line with slopes and intercepts noted in the body of the figure. The $\Delta H^\pm$ and $\Delta S^\pm$ values are determined as 12.63 kJ/mol and -237.30 J/mol K and 49.57 kJ/mol and -149.52 J/mol K for (a) and (c) systems, respectively. In calculating $\Delta S^\pm$ value from the intercept values, $\log f(R)$ i.e. logarithm of the function of reactants should be needed; which the relation has calculated:

$$\log f(R) = \log [\text{Mn(II)}] + 0.5 \log [\text{H}_2\text{A}_2]_{(o)} - \log (1 + 10^{4.5} [\text{H}^+]) - \log (1 + 1.58 [\text{SO}_4^{2-}])$$

For the (b) system, the plot is not a straight line, but a curve is obtained with lower slope at higher temperature region (htr) and higher slope at lower temperature region (ltr). The slopes and intercepts give $\Delta H^\pm$ and $\Delta S^\pm$ values of 17.99 kJ/mol and -254.65 J/mol K; and 62.20 kJ/mol and -149.52 J/mol K at htr and ltr respectively.

viii) Elucidation of the value of forward extraction rate constant (k_f) in Mn(II)-Cyanex 272 system

The intercepts of the straight lines or asymptotic lines of plots in Figs. 35 - 39 have been used to calculate $\log k_f$ values based on the following flux equation derived (*Vide.* Eq. 38):

$$\log F_f = \log k_f + \log [\text{Mn(II)}] + 0.5 \log [\text{H}_2\text{A}_2] - \log (1 + 10^{4.5} [\text{H}^+]) - \log (1 + 1.58 [\text{SO}_4^{2-}])$$

The calculated $\log k_f$ values are given in the text as Table E.

The average $\log k_f$ value -3.635 is obtained with standard deviation of 0.0565.

The $\log k_f$ value has also been calculated graphically. The above equation shows that the plot of $\log F_f$ vs. $\log f(R)$; where $f(R)$ represents $[\text{Mn(II)}] [\text{H}_2\text{A}_2]^{0.5} (1 + 10^{4.5} [\text{H}^+])^{-1} (1 + 1.58 [\text{SO}_4^{2-}])^{-1}$ would be a straight line with unity slope and intercept equaling to $\log k_f$. For this propose, all experimental parameters given in Fig. 35 - 39 have been considered for calculating $\log f(R)$ values. The set of calculated $\log f(R)$ values with experimentally determined $\log F_f$ values are given in Table XLII and the $\log F_f$ vs. $\log f(R)$ is shown in Fig. 42.

Table E. Evaluation of the forward extraction rate constant (k_f) for the extraction of Mn(II) by Cyanex 272 at 303 K

Fig. No.	Plot type log F_f vs.	$[\text{Mn(II)}]_{(\text{ini})}$, kmol/m^3	$\text{pH}_{(\text{ini})}$	$[\text{H}_2\text{A}_2]_{(\text{o,ini})}$, kmol/m^3	$[\text{SO}_4^{2-}]$, kmol/m^3	$[\text{Ac}^-]$, kmol/m^3	Intercept (I)	log k_f	Average log k_f	Standard deviation
35	log $[\text{Mn(II)}]_{(\text{ini})}$	Variable	4.70	0.025	0.04	0.25	-4.600	-3.5300		
		Variable	4.70	0.200	0.04	0.25	-4.165	-3.5760		
36	log $[\text{H}_2\text{A}_2]_{(\text{o,ini})}$	0.00795	4.80	Variable	0.01	0.25	-5.934	-3.6512		
		0.00795	4.00	Variable	0.01	0.25	-6.350	-3.6213		
37	$\text{pH}_{(\text{ini})}$	0.00795	Variable	0.100	0.01	0.25	-6.200(lcr)	-3.5936		
			e				-	-3.5936		
		0.00795		0.025	0.01	0.25	10.700(hcr)	-3.6676	-3.635	0.0565
			Variable				-6.575(lcr)	-3.6726		
38	log $[\text{SO}_4^{2-}]$						-			
		0.00801	4.80	0.050	Variable	0.25	11.080(hcr)	-3.7118		
39	log $[\text{Ac}^-]$						-6.635(lcr)	-3.7261		
		0.00796	4.80	0.025	0.01	Variable	-6.848(hcr)	-3.6412		

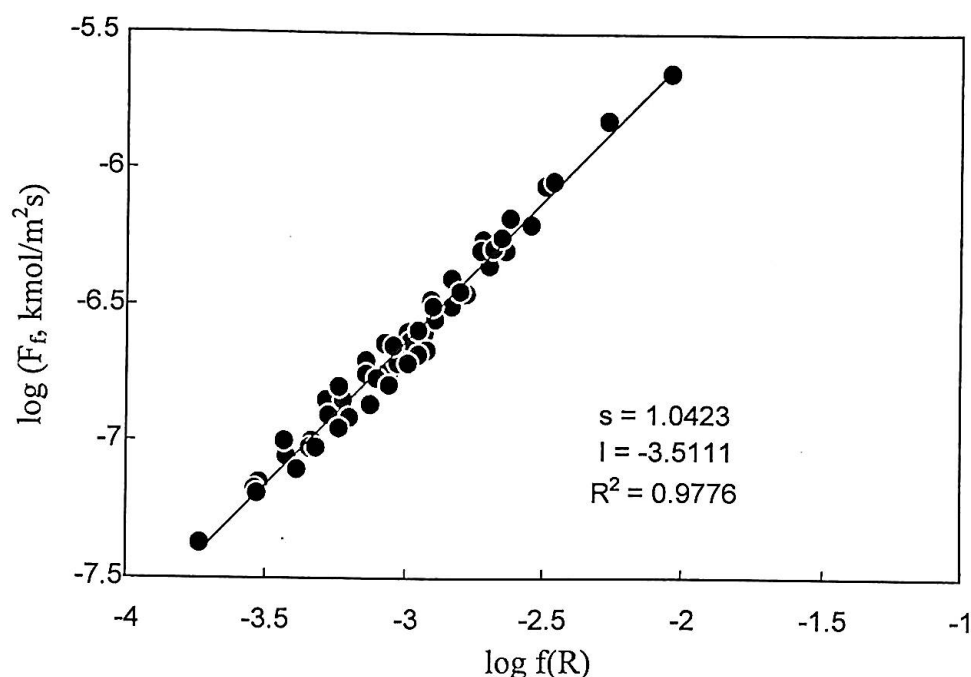
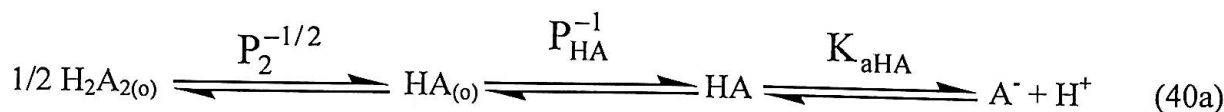
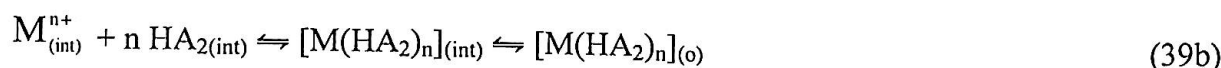
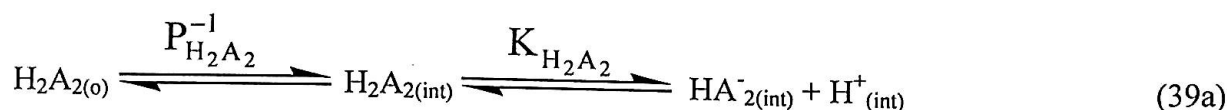


Fig. 42. Plot of $\log F_f$ vs. $\log f(R)$ for the estimation of forward extraction rate constant (k_f) of Mn(II) by Cyanex 272 at 303 K (cf. Table XLII). where, $\log f(R) = [\log [\text{Mn(II)}] + 0.5 \log [\text{H}_2\text{A}_2] - \log (1 + 31623 [\text{H}^+]) - \log (1 + 1.58 [\text{SO}_4^{=})]$.

A straight line is obtained with slope, intercepts and correlation coefficient of 1.0423, -3.5111 and 0.9776, respectively. Intercept value gives $\log k_f$ value of -3.5111, which is comparable to, obtained above (-3.635).

viii) Mechanism of Mn(II) extraction

The extractant, Cyanex 272 (H_2A_2) is dimeric in organic non-polar solvents like kerosene [96]. The dimerization constant (K_2), distribution coefficient (K_d) (or partition coefficient, P) and acid ionization constant (K_a) of purified Cyanex 272 have been estimated to be 190, 53 and 5.52×10^{-4} respectively. The dimeric extractant can extract metal ion in two possible different paths: One (the dimeric model) involves the ionization of the dimeric species at the interface and subsequently, the extraction involving the reaction of HA_2^- with the metal ion within the aqueous side (the diffusion layer) of the interface; and the other (monomeric model) involves the partitioning of the monomer (HA) in the aqueous phase and on subsequent ionization, A^- reacts with the metal ion in the bulk aqueous phase to form the extractable species (in the bulk aqueous phase not at the interface). Two paths may be depicted as follows:



From Eq. (39a), one can get the following relation for dimeric model [34]:

$$[\text{H}_2\text{A}_2]_{(\text{o})} = P_{\text{H}_2\text{A}_2} [\text{H}_2\text{A}_2]_{(\text{int})} = P_{\text{H}_2\text{A}_2} K_{\text{aH}_2\text{A}_2}^{-1} [\text{HA}_2^-]_{(\text{int})} [\text{H}^+] \quad (41)$$

where, $P_{\text{H}_2\text{A}_2}$ is the partition coefficient of dimeric extractant between the organic phase and the interface, $K_{\text{aH}_2\text{A}_2}$ is the first ionization constant of dimeric extractant at the interface, K_2 is the dimerization constant of the extractant in the organic phase, P_{HA} is the partition coefficient of monomeric extractant between the organic and aqueous phases and K_{aHA} is the ionization constant of the monomeric extractant in the aqueous phase.

On the other hand, for monomeric model, the following relationship can be obtained from Eq. (40a) [34]:

$$[\text{H}_2\text{A}_2]_{(\text{o})} = (K_2)^{1/2} [\text{HA}]_{(\text{o})}^2 = (K_2)^{1/2} P_{\text{HA}} [\text{HA}]^2 = K_2 P_{\text{HA}}^2 K_{\text{aHA}}^{-2} [\text{A}^-]^2 [\text{H}^+]^2 \quad (42)$$

The flux equation for Mn(II) transfer in its forward extraction may be expressed as:

$$F_f = 10^{-3.635} [\text{Mn}^{2+}] [\text{H}_2\text{A}_2]_{(\text{o})}^{1/2} (1 + 31623 [\text{H}^+])^{-1} (1 + 1.58 [\text{SO}_4^{=}])^{-1} \quad (43)$$

Equation (43) can be split into four different flux equations depending on reaction conditions:

a) At high concentrations of H^+ and $\text{SO}_4^{=}$:

$$F_f = (10^{-3.635/31623 \times 1.58}) [\text{Mn}^{2+}] [\text{H}_2\text{A}_2]_{(\text{o})}^{1/2} [\text{H}^+]^{-1} [\text{SO}_4^{=}]^{-1} \quad (44)$$

- b) At high concentration of H^+ but low concentration of $SO_4^{=}$:

$$F_f = (10^{-3.635/31623}) [Mn^{2+}] [H_2A_2]_{(o)}^{1/2} [H^+]^{-1} \quad (45)$$

- c) At low concentration of H^+ but high concentration of $SO_4^{=}$:

$$F_f = (10^{-3.635/1.58}) [Mn^{2+}] [H_2A_2]_{(o)}^{1/2} [SO_4^{=}]^{-1} \quad (46)$$

- d) At low concentration of H^+ and $SO_4^{=}$:

$$F_f = (10^{-3.635}) [Mn^{2+}] [H_2A_2]_{(o)}^{1/2} \quad (47)$$

Since these flux equations contains the square root term of extractant concentration, the monomeric model will be applicable to explain the rate/flux data. With the help of Eq. (42), Equations (44 - 47) can be modified, respectively to

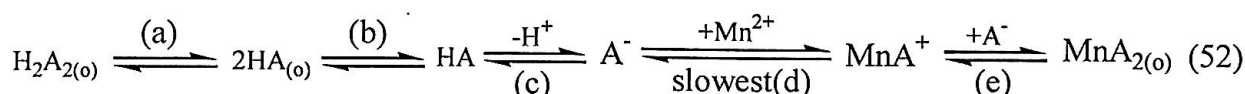
$$F_f = 10^{-8.334} K \frac{1}{2} P_{HA} K_{aHA}^{-1} [Mn^{2+}] [A^-] [SO_4^{=}]^{-1} \quad (48)$$

$$F_f = 10^{-8.135} K \frac{1}{2} P_{HA} K_{aHA}^{-1} [Mn^{2+}] [A^-] \quad (49)$$

$$F_f = 10^{-3.834} K \frac{1}{2} P_{HA} K_{aHA}^{-1} [Mn^{2+}] [A^-] [H^+] [SO_4^{=}]^{-1} \quad (50)$$

$$\text{and, } F_f = 10^{-3.635} K \frac{1}{2} P_{HA} K_{aHA}^{-1} [Mn^{2+}] [A^-] [H^+] \quad (51)$$

Equation (49) indicates that at high concentration region of H^+ (lower pH region) together with low concentration region of $SO_4^{=}$, the rate determining (slowest) reaction step is the chemical reaction between Mn^{2+} and monomerized anion of the extractant (A^-) in the bulk aqueous phase to form the complex $[MnA^+]$. Thus among the following steps:



The d-step is the rate controlling.

If it is considered that at a high concentration region of $SO_4^{=}$, $Mn(II)$ exists mainly as $MnSO_4$, then with the help of the stability constant equation ($\beta_{MnSO_4} = [MnSO_4] / [Mn^{2+}] [SO_4^{=}]$), one can modify Eqs. (48) and (50), respectively as:

$$F_f = 10^{-8.334} K \frac{1}{2} P_{HA} K_{aHA}^{-1} \beta_{MnSO_4} [Mn^{2+}] [A^-] \quad (53)$$

$$F_r = 10^{-3.834} \beta_{\text{MnSO}_4} K_2^{1/2} P_{\text{HA}} K_{\text{aHA}} [\text{Mn}^{2+}] [\text{A}^-] [\text{H}^+] \quad (54)$$

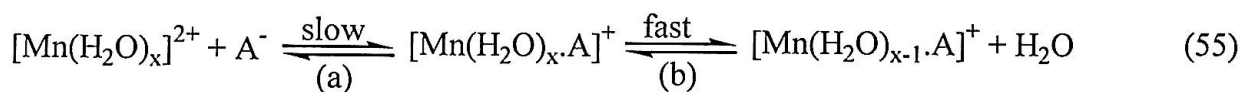
Equation (53), valid at high concentrations of H^+ and SO_4^{2-} , indicates that the combination of Mn^{2+} , remaining in equilibrium with MnSO_4 in the aqueous phase, with an anion of monomeric extractant (A^-) to form MnA^+ in the bulk aqueous phase is rate determining. Therefore, at high concentration region of H^+ irrespective of sulphate ion concentration, the slow step is the 'd'th step in Eq. (52). At high sulphate ion concentration medium, Mn(II) is supposed to exist mostly in MnSO_4 form and as the reaction order with respect to manganese(II) species has been determined by considering the total Mn(II) concentration in the aqueous phase, the $[\text{Mn}^{2+}]$ terms in Eqs. (44), (46), (48) and (50) represent virtually the $[\text{MnSO}_4]$ terms. On such a consideration, Eqs. (48) and (50) take the forms given, respectively, in Eqs. (53) and (54).

Eqs. (51) and (54) are of the same type in terms of the reactant concentration factors (both contain the terms: $[\text{Mn}^{2+}] [\text{A}^-] [\text{H}^+]$) and contain three concentration terms. Since termolecular reactions are highly improbable and the stability constant of Mn(OH)^+ indicates the presence of almost no such species in the medium, no elementary chemical reaction can be suggested as rate determining at low concentration region of H^+ (i.e. high pH region). It is therefore suggested that at high pH region, the extraction process is diffusion controlled. Diffusion of Mn^{2+} and HA species to the reaction site (probably at the aqueous side of the interface) is rate controlling. In such cases, the terms $K_{\text{aHA}}^{-1} [\text{A}^-] [\text{H}^+]$ in Eqs. (51) and (54) should be put equal to $[\text{HA}]$.

For a chemical control reaction, the activation energy is usually of higher magnitude (> 48 kJ/mol); whereas for a diffusion or mass-transfer controlling step, the activation energy is very low of the order of less than < 20 kJ/mol [467]. At high pH (5.5), the calculated activation energy is 14.85 kJ/mol; whereas at low pH (3.75), it is 51.60 kJ/mol. These values indicates that at high pH (i.e. low acidity), the forward extraction, Mn(II) by Cyanex 272 should be a diffusion or mass-transfer controlled process. Therefore, rate equations at high pH (or low acidities) are for diffusion controlled processes as they contain three concentration terms. On the other hand, high value of E_a at low pH region is an indicative to that the chemical reaction step represented by Eq. (52d) is the rate controlling. For the system at moderate pH (4.8), the E_a value at htr is 16.70 kJ/mol, whereas at ltr is 59.1 kJ/mol; which is indicative to the fact that the extraction process is diffusion controlled

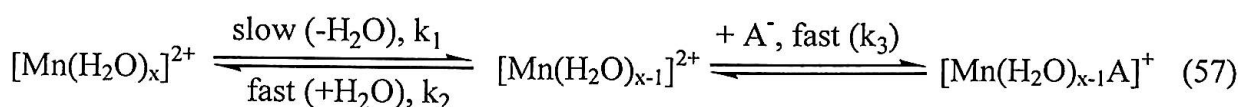
at htr; whereas, it is chemically controlled at ltr. At around 303 K, the E_a value will be within 25 - 40 kJ/mol, so around this temperature region, the extraction process will be an intermediate controlled i.e. both the rate of mass-transfer by diffusion and the rate by chemical reaction will be almost equal. A chemically controlled reaction at low temperature region may be shifted to the diffusion controlled at high temperature region. The cause of this shiftment is that with the increase of temperature, the chemical reaction rate is increased exponentially (i.e. if temperature in K is doubled, the rate constant and consequently, the rate of reaction is increased by a factor of about 10^2 (i.e., 100 times); whereas, the diffusional rate is increased arithmetically (i.e., if temperature in K is doubled, the rate constant and consequently, the rate of diffusion is increased by a factor of 2; since the temperature dependence of a diffusion controlled rate is governed by the Stokes-Einstein equation ($\delta \propto T$); whereas, the temperature dependence of a chemically controlled rate is governed by the Arrhenius equation [467].

The chemically controlled rate-determining step ($Mn^{++} + A^- \rightarrow MnA^+$ given in the d-th step of Eq. (52)) may occur either by S_N1 or S_N2 mechanism [468]. For S_N2 mechanism, the bimolecular reaction step may be shown as:



$$\text{with the rate expression : } F_f = k_f [[Mn(H_2O)_x]^{2+}] [A^-] \quad (56)$$

which is identical to Eqs. (49) and (53). Consequently in an S_N2 mechanism, the attachment of an additional ligand to the restricted co-ordination sphere of Mn^{2+} acts as the rate determining step. The other is the S_N1 mechanism as a unimolecular process as follows:



The steady state approximation results the rate expression for the S_N1 mechanism as:

$$F_f = k_1 k_3 [Mn(H_2O)_x]^{2+} [A^-] / (k_2 + k_3 [A^-]) \quad (58)$$

and if $k_2 \gg k_3 [A^-]$, then the Eq. (58) takes form of Eq. (56) whereby $(k_1 k_3 / k_2)$ will represent k_f .

Thus, it is possible to explain the same rate data by both S_N1 and S_N2 mechanisms,; and as a result, it is difficult to decide whether the reaction proceeds via Eq. (55) or (57). But this difficulty may effectively be overcome by the use of the thermodynamic data of the activated state, especially the change of the entropy of activation for the system.

The solution effect dominates the entropy of activation where charged ions are involved. If the solvent molecules are tightly attached around Mn^{2+} ions, their entropy is lost i.e. the value of $\Delta S^\ddagger$ becomes negative. On the other hand, if the solvent molecules dissociate from the metal ions, their entropy is increased; and as a result, $\Delta S^\ddagger$ becomes positive. Thus for the S_N2 mechanism, where the ligand (A^-) co-ordinates to the metal ion, $[Mn(H_2O)_x]^{2+}$ to form the higher co-ordinated activated complex, $[Mn(H_2O)_x.A]^\ddagger$, the value of the $\Delta S^\ddagger$ would be expected to be more negative than the ground state and for the S_N1 mechanism, where the formation of lower co-ordinated activated complexes, $[Mn(H_2O)_{x-1}]^{2+}$ take place, the value of $\Delta S^\ddagger$ should be positive.

In the case of the forward extraction of Mn(II), the values of $\Delta S^\ddagger$ calculated at three experimental parameters are highly negative; and so the rate controlling chemical reaction step represented by Eq. (52d) occurs via S_N2 mechanism.

5. Studies on the kinetics of forward extraction of Ni(II) in the Ni(II)- $SO_4^{=}$ -Ac⁻ (Na^+ , H^+) - Cyanex 272-kerosene system

The kinetics of forward extraction of Ni(II) in the above titled system have been investigated thoroughly as narrated in the following sections:

i) Determination of time needed for drop formation and coalescence

The time needed for drop formation and coalescence during the forward extraction rate measurement by single drop falling technique of Ni(II) in the title system has been determined. For this purpose, using columns of different height, the amounts of mass-transferred (Ni(II)-transferred) from a drop have been measured for a particular set of experimental parameters. Together with the experimental conditions, the related experimental data on mass-transfer are given in Table XLIII. The $a_{Ni(II)}$ transferred from a drop versus drop fall time (t , varied by using columns of different height) plot is given in Fig. 43.

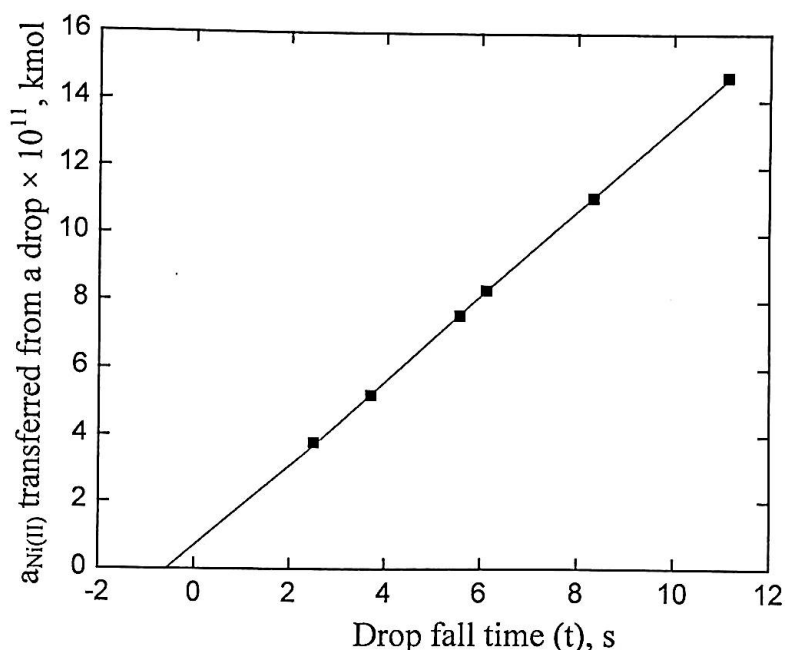


Fig. 43. Determination of time needed for drop formation and coalescence in a single drop experiment in the case of extraction of Ni(II) by Cyanex 272 (*cf.* Table XLIII). $[H_2A_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$, $[Ni(II)]_{(ini)} = 1.3405 \text{ kg/m}^3$, $[Ac^-] = 0.25 \text{ kmol/m}^3$, $pH_{(ini)} = 6.70$, $[SO_4^{2-}] = 0.023 \text{ kmol/m}^3$, Temperature = 303 K, Number of drops collected = 100.

It is found that a straight line is obtained which does not pass through origin, rather cuts the time axis at -0.5 s ($\Delta t = 0.5 \text{ s}$). This time is attributed to the time for drop formation and coalescence. In flux calculations, Δt term must be added to the drop fall time; otherwise, errors in flux calculation will appear as demonstrated below:

In Table XLIV, the Ni(II)-transfer flux has been calculated in two ways for each column height used: F'_f has been calculated by neglecting the Δt value ($F'_f = a_{Ni(II)}$ transferred / $A \cdot t$) and F_f has been calculated by taking into account the Δt value ($F_f = a_{Ni(II)}$ transferred / $A(t + \Delta t)$). The F'_f , $\log F'_f$, F_f and $\log F_f$ values at different column heights are presented in the 5th, 6th, 7th and 8th columns of the table. The $\log F'_f$ and the $\log F_f$ vs. column height plots are displayed in Fig. 44.

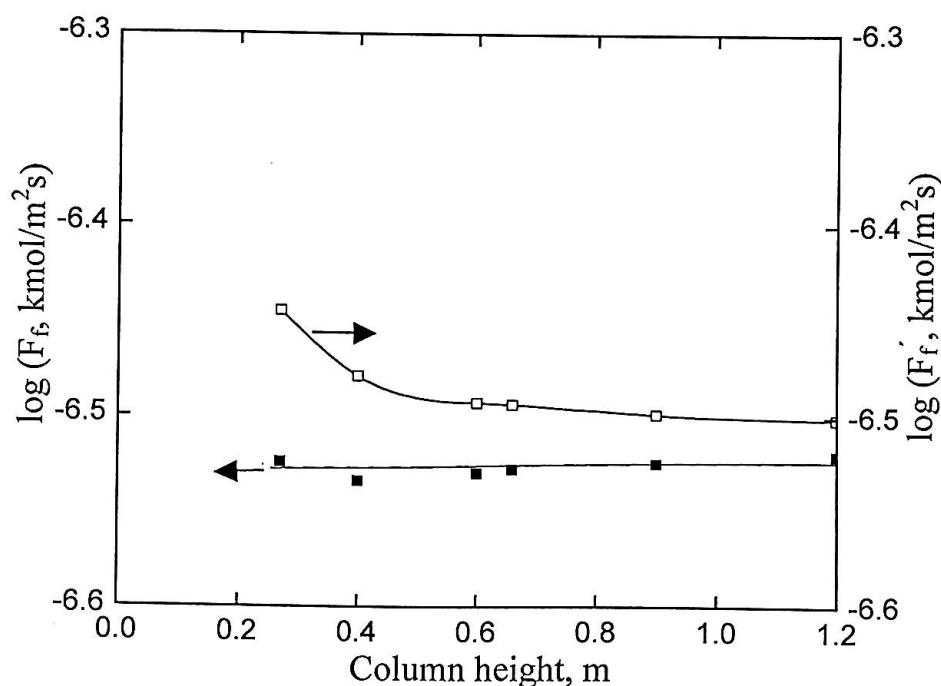


Fig. 44. Effect of column height on rate of Ni(II) extraction by Cyanex 272 using single drop devices (*cf.* Table XLIV). $[\text{H}_2\text{A}_2]_{(0,\text{ini})} = 0.025 \text{ kmol/m}^3$, $[\text{Ni(II)}]_{(\text{ini})} = 1.3405 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.023 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.70$, Temperature = 303 K, $\Delta t = 0.50 \text{ s}$, Number of collected drops = 100.

It is seen that $\log F'_f$ is decreased, whilst $\log F_f$ remains unchanged with increasing column height. On addition, $\log F_f$ is smaller than $\log F'_f$. It is concluded that the calculated flux will be independent of column height if Δt term is added to the drop fall time (t) and the column of any height can be used for flux measurement if F_f in lieu of F'_f being calculated.

ii) Effect of initial Ni(II) concentration of the aqueous phase on the flux of Ni(II) transfer in its forward extraction by Cyanex 272

The related experimental data together with respective experimental parameters are collected in Table XLV. The $\log (F_f, \text{kmol/m}^2 \text{ s})$ vs. $\log ([\text{Ni(II)}], \text{kmol/m}^3)$ for three sets of parameters are displayed in Fig. 45.

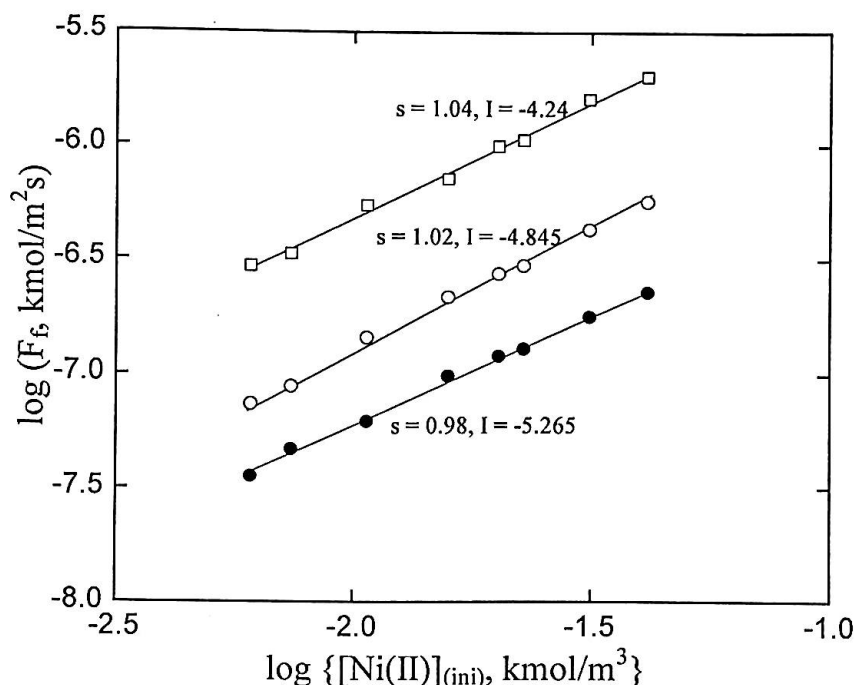


Fig. 45. Dependence of initial Ni(II) concentration on the flux of Ni(II) transfer in the system: $Ni(II)-SO_4^{2-}-Ac^-H^+$ - Cyanex 272-kerosene during aqueous drop fall in a single drop column (*cf.* Table XLV). $[Ac^-] = 0.25 \text{ kmol/m}^3$, $\Delta t = 0.50 \text{ s}$, Temperature = 303 K, Number of collected drops = 100, Column height = 0.66 m; (○), $pH_{(ini)} = 6.70$, $[H_2A_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$; (●), $pH_{(ini)} = 6.00$, $[H_2A_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$; (□), $pH_{(ini)} = 6.70$, $[H_2A_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3$.

In all three cases, straight lines are obtained with slope of (1.01 ± 0.03) and the intercepts as typed on the body of figure. The unity slope indicates that the rate of forward extraction of Ni(II) by Cyanex 272 solution is directly proportional to the initial Ni(II) concentration. In other words, the reaction order with respect to Ni(II) concentration is unity.

iii) Effect of initial aqueous pH on the flux of Ni(II) transfer

The related experimental data are collected in Table XLVI, showing also the experimental conditions. The $\log F_f$ vs. $pH_{(ini)}$ plots for extractant concentrations of 0.025, 0.10 and 0.30 kmol/m^3 are shown in Fig. 46.

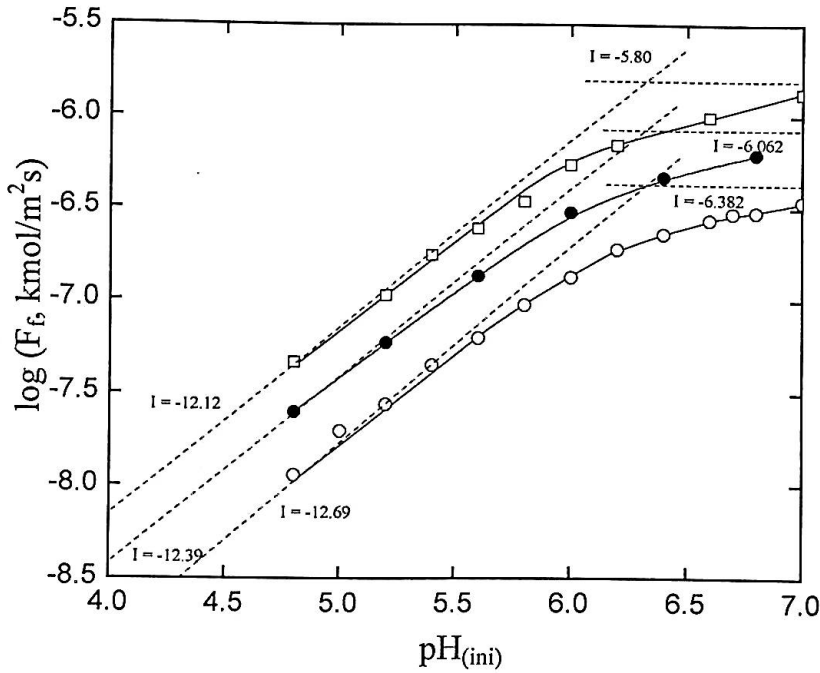


Fig. 46. Effect of aqueous pH on Ni(II) transfer flux in the system: Ni(II)-SO₄²⁻-Ac⁻-H⁺ - Cyanex 272-kerosene (cf. Table XLVI). [Ni(II)]_(ini) = 1.3405 kg/m³, [SO₄²⁻] = 0.05 kmol/m³, [Ac⁻] = 0.25 kmol/m³, Temperature = 303 K, Δt = 0.50 s, Number of collected drops = 100, (○); H₂A₂]_(o,ini) = 0.025 kmol/m³, (●), H₂A₂]_(o,ini) = 0.10 kmol/m³, (□), H₂A₂]_(o,ini) = 0.30 kmol/m³.

The experimental points for a particular system do not fall on a straight line. Points fall on a curve having higher slope in the lower pH region and lower slope in the higher pH region. The experimental points for a particular set of parameters fall on curve represented by:

$$\begin{aligned} \log F_f &= \log [k_f [\text{Ni}^{2+}] [\text{H}_2\text{A}_2]^c [\text{SO}_4^{2-}]^d [\text{Ac}^-]^e] - \log (1 + K_H^f [\text{H}^+]) \\ &= -6.382 \text{ (for } \bigcirc) / -6.062 \text{ (for } \bullet) / -5.80 \text{ (for } \square) - \log (1 + K_H^f [\text{H}^+]) \end{aligned} \quad (59)$$

Equation (59) has two asymptotes as presented below:

$$\text{As } [\text{H}^+] \rightarrow 0; \log F_f = -6.382 \text{ (for } \bigcirc), \text{ or } -6.062 \text{ (for } \bullet), \text{ or } -5.80 \text{ (for } \square) \quad (60)$$

$$\text{and As } [\text{H}^+] \rightarrow \infty; \log F_f = -6.382 \text{ (for } \bigcirc) / -6.062 \text{ (for } \bullet) / -5.80 \text{ (for } \square) - \log K_H^f + \text{pH} \quad (61)$$

At the points of intersection of two asymptotes, $-\log K_H^f + \text{pH} = 0$; giving $K_H^f = 10^{\text{pH}}$. Here in all three cases, at the point of intersection, the pH value is 6.32; so the value of K_H^f is $10^{6.32} \text{ m}^3/\text{kmol}$. Intercepts of the asymptotic lines are given in the figure. It is concluded from this figure that the rate of Ni(II) extraction is independent of H⁺ or pH in lower [H⁺] (or higher pH) region, whereas inversely proportional to the [H⁺] in higher [H⁺]

(or lower pH) region. In other words, the reaction order with respect to $[H^+]$ in the forward extraction of Ni(II) by Cyanex 272 is -1 and 0 at the higher and lower $[H^+]$ regions (or at lower and higher pH regions), respectively.

iv) Effect of initial extractant concentration on the flux of Ni(II) transfer

Keeping all other parameters constant, flux variations at various extractant concentrations have measured at constant $pH_{(ini)}$ values of 6.70, 6.10 and 5.20. The data are given Table XLVII and in Fig. 47 as $\log F_f$ vs. $\log [H_2A_2]_{(o,ini)}$ plots.

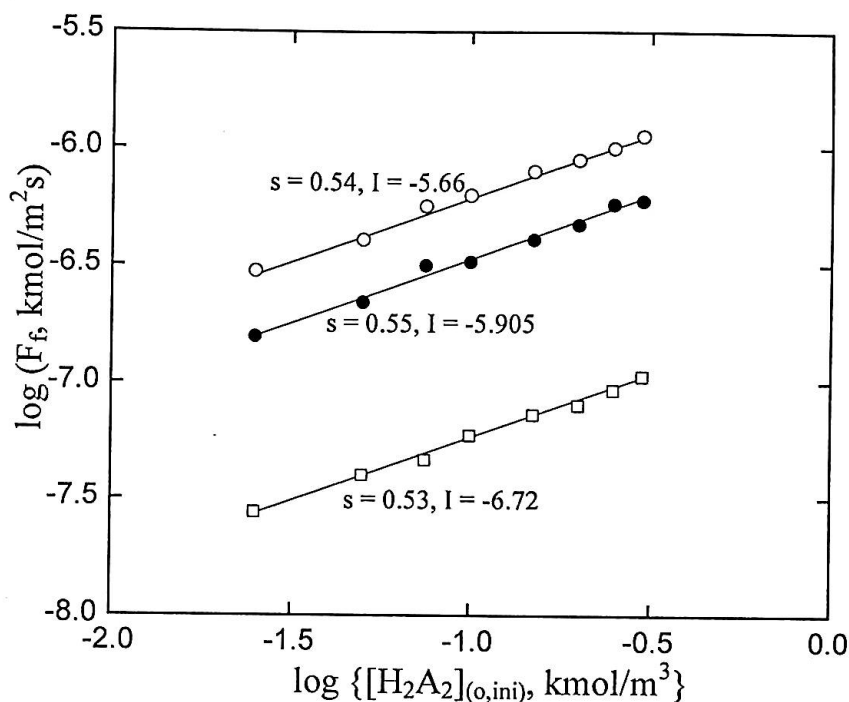


Fig. 47. Effect of extractant concentration on Ni(II) transfer flux in the system: Ni(II)- SO_4^{2-} - Ac^- - H^+ - Cyanex 272-kerosene (cf. Table XLVII). $[Ni(II)]_{(ini)} = 1.3405 \text{ kg/m}^3$, $[Ac^-] = 0.25 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.05 \text{ kmol/m}^3$, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$; (O), $pH_{(ini)} = 6.70$, Column height = 0.66 m, (●), $pH_{(ini)} = 6.10$, Column height = 0.90 m, (□), $pH_{(ini)} = 5.20$, Column height = 1.20 m.

For each constant pH system, the experimental points fall on a straight line. The slopes of the lines are 0.54, 0.55 and 0.53; whereas, intercepts are -5.66, -5.905 and -6.72, for pH systems of 6.70, 6.10 and 5.20, respectively. The slopes of the lines indicate that like in the case of Mn(II) extraction by Cyanex 272, the rate of forward extraction of Ni(II) by Cyanex 272 is directly proportional to the square root of the extractant concentration.

v) Effect of coexisting sulphate ion concentration on the flux of Ni(II) transfer

The experimentally determined $\log F_f$ values at different sulphate ion concentrations at two different sets of (constant pH and extractant concentration) of (6.70 and 0.025 kmol/m³) and (6.40 and 3.30 kmol/m³) are presented in Table XLVIII. The nature and extent of variation of $\log F_f$ value with the variation of $[\text{SO}_4^{=}]$ can be noticed from the Fig. 48, where $\log F_f$ vs. $\log [\text{SO}_4^{=}]$ plots are displayed.

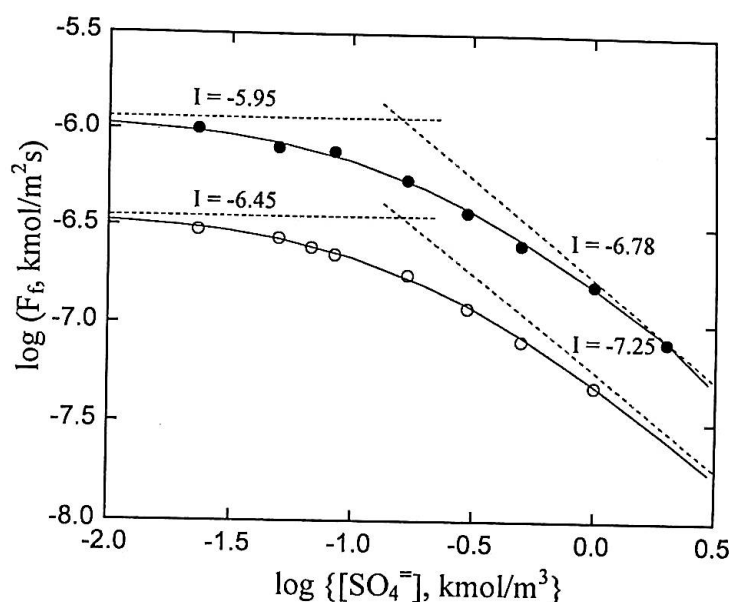


Fig. 48. Effect of sulfate ion concentration on flux of Ni(II) transfer in the case of Ni(II) extraction by Cyanex 272 (*cf.* Table XLVIII). $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, Temperature = 303 K, Temp. = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$; (O), $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$ and (●); $\text{pH}_{(\text{ini})} = 6.40$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$. The points are experimental and the solid curves are theoretical representing: $\log F_f = -6.45$ (O) or -5.95 (●) $-\log \{1 + K_{\text{SO}_4}^f [\text{SO}_4^{=}]$, where $K_{\text{SO}_4}^f$ is a proportionality constant and whose value in both cases is estimated to be $6.30 \text{ m}^3/\text{kmol}$ by the Curve- Fitting method.

For both cases, the experimental points for a particular set of parameters do not fall on a straight line; rather fall on a curve having lower and higher limiting negative slopes at the lower and higher concentration regions of $\text{SO}_4^{=}$, respectively. The experimental points for a particular set of parameters fall on a curve (theoretical) represented by:

$$\log F_f = -6.4 \text{ or, } -5.95 - \log (1 + K_{\text{SO}_4}^f [\text{SO}_4^{=}]) \quad (62)$$

for ($\text{pH}_{(\text{ini})} = 6.4$ and $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$) and ($\text{pH}_{(\text{ini})} = 6.7$ and $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$) systems, respectively. In each case, the proportionality constant, $K_{\text{so}_4}^{\text{f}}$ has been estimated to be $6.3 \text{ m}^3/\text{kmol}$ by the Curve-Fitting method. The rate of Ni(II) transfer is therefore inversely proportional to the term $(1 + 6.4 [\text{SO}_4])$. The intercepts of the asymptotic lines are shown in the respective figure.

vi) Effect of acetate ion concentration on the flux of Ni(II) transfer

The effect has been measured at a single set of experimental parameters involving $\text{pH}_{(\text{ini})} = 6.60$ and $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$. The measured flux values at various acetate on concentrations are given in Table II. The $\log (F_{\text{f}}, \text{kmol/m}^2 \text{ s})$ vs. $\log [\text{Ac}^-], \text{kmol/m}^3$ plot is shown in Fig. 49. Like in the case of $[\text{SO}_4^-]$ dependence, the experimental points fall on a curve represented by:

$$\log F_{\text{f}} = -6.50 - \log (1 + 0.55 [\text{Ac}^-]) \quad (63)$$

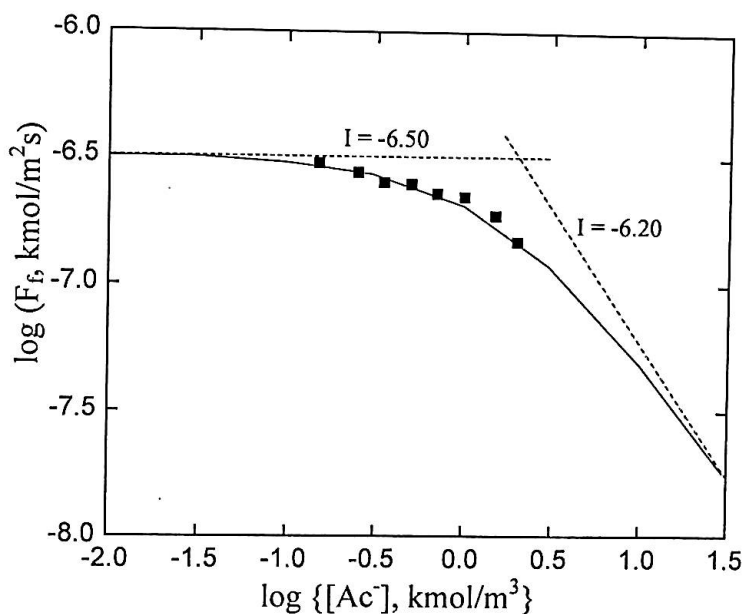


Fig. 49. Effect of acetate ion concentration on the flux of Ni(II) transfer in the case of Ni(II) extraction by Cyanex 272 (*cf.* Table II). $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, Temperature = 303 K, $[\text{SO}_4^{2-}] = 0.023 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.6$, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$, Height of column = 0.66 m. The points are experimental and the solid curve is theoretical representing: $\log F_{\text{f}} = -6.5 - \log \{1 + K_{\text{Ac}}^{\text{f}} [\text{Ac}^-]\}$, where K_{Ac}^{f} is a proportionality constant and its value has been estimated as $0.55 \text{ m}^3/\text{kmol}$ by the Curve-Fitting method.

The intercepts of the asymptotic lines are quoted in this figure. The rate of Ni(II) transfer is therefore inversely proportional to the term $(1 + 0.55 [\text{Ac}^-])$.

viii) Effect of temperature on the flux of Ni(II) transfer

Defining the systems ($\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.05 \text{ kmol/m}^3$ and $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$), ($\text{pH}_{(\text{ini})} = 5.20$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$; $[\text{SO}_4^{2-}] = 0.05 \text{ kmol/m}^3$ and $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$), ($\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 1.00 \text{ kmol/m}^3$ and $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$) and ($\text{pH}_{(\text{ini})} = 6.60$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.023 \text{ kmol/m}^3$ and $[\text{Ac}^-] = 2.00 \text{ kmol/m}^3$) as system-1, system-2, system-3 and system-4, respectively; this part will be discussed. The temperature dependence data for the systems mentioned are given in Table L. The $\log F_f$ vs. $1/T$ (Arrhenius) plots are given in Fig. 50.

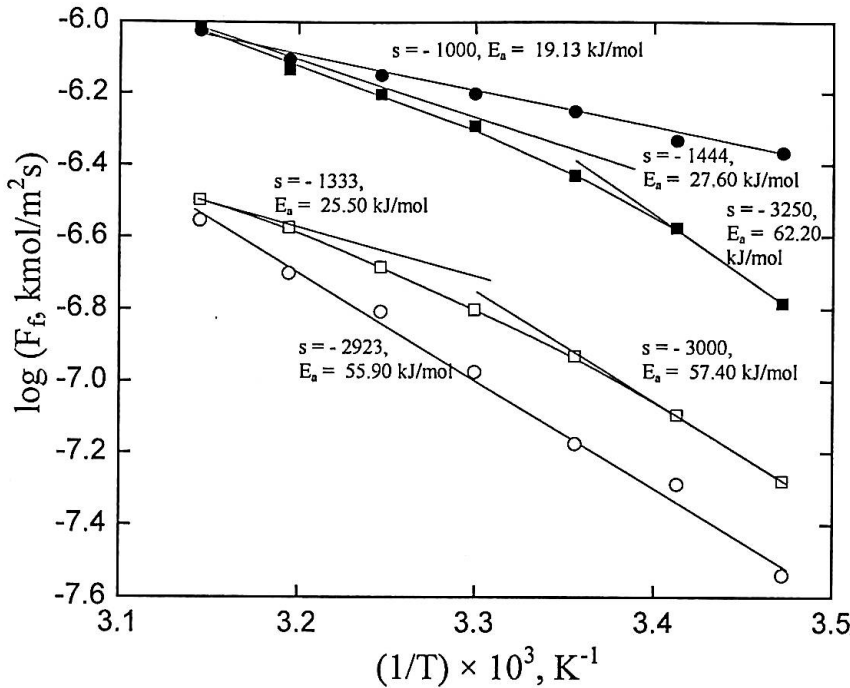


Fig. 50. Effect of temperature on the flux of Ni(II) transfer during Ni(II) extraction by Cyanex 272 in kerosene (*cf.* Table L). $[\text{Ni(II)}]_{(\text{ini})} = 1.3405 \text{ kg/m}^3$, $\Delta t = 0.50 \text{ s}$, Number of collected drops = 100, (●); $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.05 \text{ kmol/m}^3$, (○); $\text{pH}_{(\text{ini})} = 5.20$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.05 \text{ kmol/m}^3$, (□); $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 1.00 \text{ kmol/m}^3$, (■); $\text{pH}_{(\text{ini})} = 6.60$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$, $[\text{Ac}^-] = 2.00 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.023 \text{ kmol/m}^3$.

For systems-1 and 2, straight lines are obtained and the slopes of these lines give E_a values of 19.13 and 55.90 kJ/mol, respectively. On the other hand, for systems-3 and 4, curves are obtained. From the limiting slopes of the curves, E_a values of 25.50 kJ/mol and 57.40 kJ/mol are obtained at htr and ltr, respectively for system-3; whereas, 27.60 kJ/mol and 62.2 kJ/mol are obtained at htr and ltr respectively, for system-4.

The temperature dependence rate data have also been treated by the Activated Complex Theory to estimate the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values. The related data are given in Table LI and the $\log \left(\frac{F_r h}{kT} \right)$ vs. $(1/T)$ plots for the above stated four systems are shown in Fig. 51.

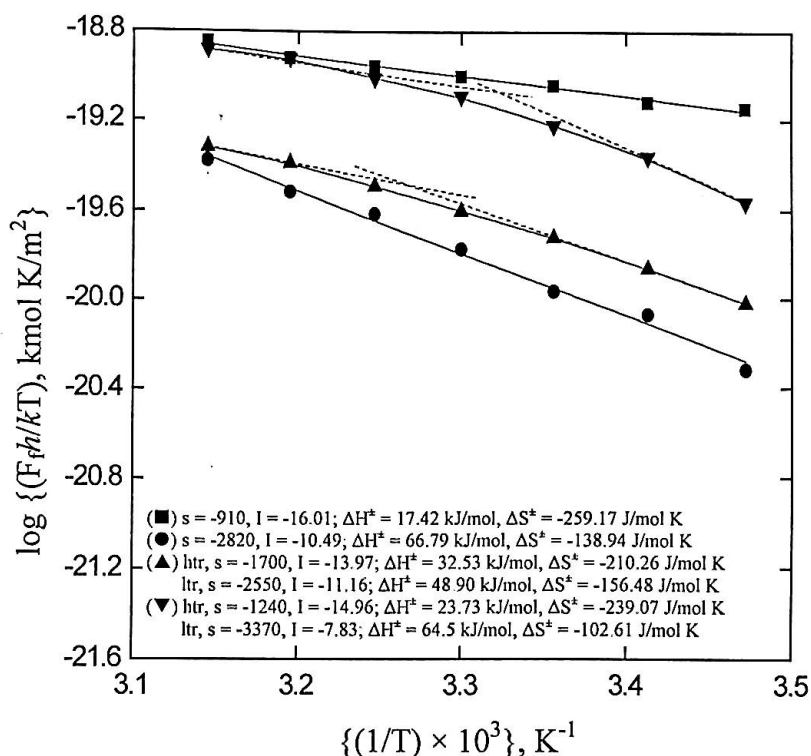


Fig.51 The $\log (F_r h / kT)$ vs. $(1/T)$ plots of the forward extraction of Ni(II) by Cyanex 272 (*cf.*

Table LI). $[\text{Ni(II)}]_{(\text{ini})} = 1.3405 \text{ kg/m}^3$, $\Delta t = 0.50 \text{ s}$, Number of collected drops =100, (■), $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.05 \text{ kmol/m}^3$, $\log f(R) = -2.4679$; (●), $\text{pH}_{(\text{ini})} = 5.20$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.05 \text{ kmol/m}^3$, $\log f(R) = -3.2299$; (▲), $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 1.00 \text{ kmol/m}^3$, $\log f(R) = -2.9834$; (▼), $\text{pH}_{(\text{ini})} = 6.60$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$, $[\text{Ac}^-] = 2.00 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.023 \text{ kmol/m}^3$, $\log f(R) = -2.4682$; $h = 6.6252 \times 10^{-37} \text{ kJ s}$, $k = 1.38 \times 10^{-26} \text{ kJ/deg}$

Like in the Arrhenius plots, systems-1 and 2 yield straight lines with slopes of -910 and -2820 and intercepts of -16.01 and -10.49, respectively. The slope values give $\Delta H^\ddagger$ values of 17.42 kJ/mol and 66.79 kJ/mol, respectively for system-1 and 2, respectively. The intercept values give $\Delta S^\ddagger$ values of -259.17 J/mol K and -138.94 J/mol K, respectively for system 1 and 2 respectively, on calculating respective $\log f(R)$ values of -2.4679 and -3.2299.

For the system-3, the slope, intercept, $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\log f(R)$ values are -1700, -13.97, 32.53 kJ/mol, -210.26 J/mol K and -2.9834, respectively at htr; whereas are -2550,

-11.16, 48.90 kJ/mol, -156.48 J/mol K and -2.9832, respectively at ltr. On the other hand, for the system 4, respective above values are -1240, -14.96, 23.73 kJ/mol, -239.07 J/mol K and -2.4682 at htr; whereas are -3370, -7.83, 64.5 kJ/mol, -102.61 J/mol K and -2.4682 at ltr.

viii) Elucidation of the value of forward extraction rate constant (k_f) in Ni(II) Cyanex 272 system

From the intercepts of the straight lines or the asymptotic lines in Figs. 45 - 49, the values of $\log k_f$ have been evaluated and given in Table F (within the text). The calculated $\log k_f$ value at 303 K is -3.742, with standard deviation of 0.04. The value of $\log k_f$ has also been obtained graphically. The working formula given at the bottom of Table F indicates that the plot of $\log F_f$ versus $\log f(R)$; where $\log f(R) = [\log [\text{Ni}^{2+}] + 0.5 \log [\text{H}_2\text{A}_2] - \log (1 + 10^{6.32} [\text{H}^+]) - \log (1 + 6.3 [\text{SO}_4^{=}) - \log (1 + 0.55 [\text{Ac}^-])]$ should be a straight line with unity slope and intercept value equaling to the value of $\log k_f$. The experimental $\log F_f$ values obtained at various experimental parameters (those used in Figs. 45 - 49) have been used for this purpose. The calculated values of $\log f(R)$ with $\log F_f$ values are given in Table LII and the corresponding plot is given in Fig. 52. A good fit Least Square straight line (correlation coefficient = 0.9957) is obtained with slope equaling to 1.0288 (should be 1) and intercept equaling to -3.6781. This value is very comparative to that obtained above (-3.742). In subsequent discuss, k_f value of $10^{-3.7} \text{ m}^{5/2}/\text{kmol}^{1/2} \text{ s}$ will be considered as an average value.

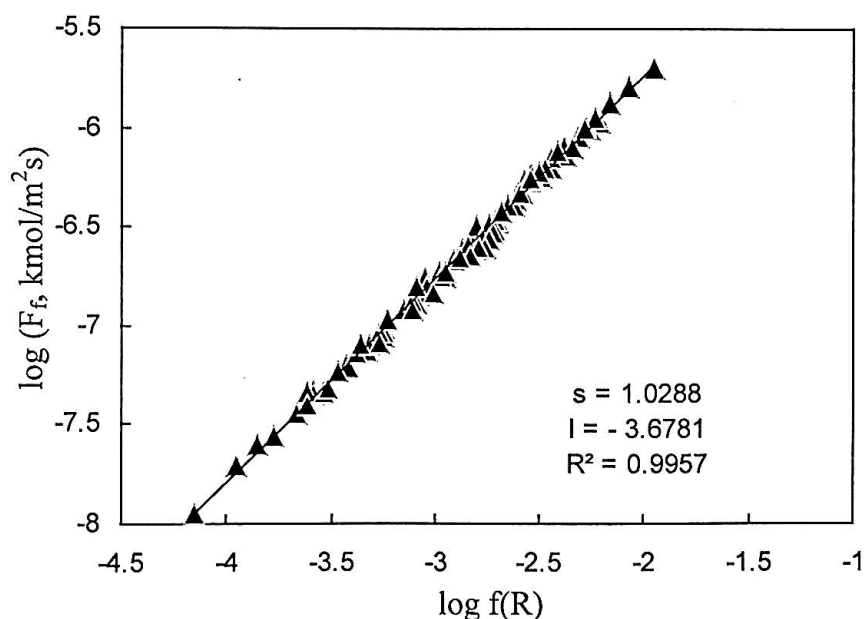


Fig. 52. Plot of $\log F_f$ vs. $\log f(R)$ for the estimation of forward extraction rate constant (k_f) of Ni(II) by Cyanex 272 at $(303 \pm 0.5) \text{ K}$ (cf. Table LII). where, $\log f(R) = [\log [\text{Ni(II)}]_{(o,ini)} + 0.5 \log [\text{H}_2\text{A}_2] - \log (1 + 10^{6.32} [\text{H}^+]) - \log (1 + 6.3 [\text{SO}_4^{=}) - \log (1 + 0.55 [\text{Ac}^-])]$.

Table F. Evaluation of rate constant (k_f) in the forward extraction of Ni(II) by Cyanex 272 at 303 K

Fig. No.	log F_f vs.	[Ni(II)], kmol/m ³	pH _(ini)	[H ₂ A ₂] _(o,ini) , kmol/m ³	[SO ₄ ²⁻], kmol/m ³	[Ac ⁻], kmol/m ³	Intercept (I)	log k_f	Average log k_f	Standard deviation
45	log [Ni(II)], kmol/m ³	-	6.7	0.025	0.042	0.25	-4.845	-3.735		
		-	6.0	0.025	0.042	0.25	-5.265	-3.816		
		-	6.7	0.300	0.042	0.25	-4.240	-3.670		
46	pH _(ini)	0.02283	-	0.025	0.050	0.25	-12.690(lcr)	-3.753		
			-	0.100	0.050	0.25	-6.382(hcr)	-3.765		
			-	0.100	0.050	0.25	-12.390(lcr)	-3.754		
			-	0.300	0.050	0.25	-6.062(hcr)	-3.746		
			-	0.300	0.050	0.25	-12.120(lcr)	-3.723		
47	log [H ₂ A ₂], kmol/m ³	0.02283	6.7	-	0.050	0.25	-5.660	-3.694	-3.742	0.04
		0.02283	6.1	-	0.050	0.25	-5.905	-3.664		
		0.02283	5.2	-	0.050	0.25	-6.720	-3.752		
48	log [SO ₄ ²⁻], kmol/m ³	0.02283	6.7	0.025	-	0.25	-6.450(lcr)	-3.801		
		0.02283	6.4	0.300	-	0.25	-7.250(hcr)	-3.802		
		0.02283	6.4	0.300	-	0.25	-5.950(lcr)	-3.723		
49	log ([Ac ⁻] _i , kmol/m ³)	0.02283	6.6	0.025	0.023	-	-6.780(hcr)	-3.754		
		0.02283	6.6	0.025	0.023	-	-6.500(lcr)	-3.760		

Working formula: $\log F_f = \log k_f + \log [\text{Ni(II)}] + 0.5 \log [\text{H}_2\text{A}_2] - \log (1 + 10^{6.32} [\text{H}^+]) - \log (1 + 6.3 [\text{SO}_4^{2-}]) - \log (1 + 0.55 [\text{Ac}^-])$

x) Mechanism of forward extraction of Ni(II) by Cyanex 272

Based on the results obtained in the above studies on the rate of forward extraction of Ni(II) by Cyanex 272, the rate or flux equation for this process can be expressed as:

$$F_f = 10^{-3.7} [\text{Ni(II)}] [\text{H}_2\text{A}_2]^{1/2}_{(o)} (1 + 10^{6.32} [\text{H}^+]^{-1}) (1 + 6.3 [\text{SO}_4^{=}]^{-1}) (1 + 0.55 [\text{Ac}^-]^{-1}) \quad (63)$$

Equation (63) is a too much complicated flux (rate) equation. It can be changed to a number of simplified flux equations depending on the concentration regions of H^+ , $\text{SO}_4^{=}$ and Ac^- . These equations are

(i) At low concentrations of H^+ , $\text{SO}_4^{=}$ and Ac^-

$$F_f = 10^{-3.7} [\text{Ni(II)}] [\text{H}_2\text{A}_2]^{1/2}_{(o)} \quad (64)$$

(ii) At high concentration of H^+ but low concentrations of $\text{SO}_4^{=}$ and Ac^-

$$F_f = 10^{-10.02} [\text{Ni(II)}] [\text{H}_2\text{A}_2]^{1/2}_{(o)} [\text{H}^+]^{-1} \quad (65)$$

(iii) At high concentration of H^+ and $\text{SO}_4^{=}$ but low concentrations of Ac^-

$$F_f = 10^{-10.82} [\text{Ni(II)}] [\text{H}_2\text{A}_2]^{1/2}_{(o)} [\text{H}^+]^{-1} [\text{SO}_4^{=}]^{-1} \quad (66)$$

(iv) At high concentration of H^+ , $\text{SO}_4^{=}$ and Ac^-

$$F_f = 10^{-10.56} [\text{Ni(II)}] [\text{H}_2\text{A}_2]^{1/2}_{(o)} [\text{H}^+]^{-1} [\text{SO}_4^{=}]^{-1} [\text{Ac}^-]^{-1} \quad (67)$$

(v) At low concentration of H^+ and $\text{SO}_4^{=}$ but high concentration of Ac^-

$$F_f = 10^{-3.44} [\text{Ni(II)}] [\text{H}_2\text{A}_2]^{1/2}_{(o)} [\text{Ac}^-]^{-1} \quad (68)$$

(vi) At low concentration of H^+ and Ac^- but high concentration of $\text{SO}_4^{=}$

$$F_f = 10^{-4.5} [\text{Ni(II)}] [\text{H}_2\text{A}_2]^{1/2}_{(o)} [\text{SO}_4^{=}]^{-1} \quad (69)$$

(vii) At low concentration of H^+ but high concentration of $\text{SO}_4^{=}$ and Ac^-

$$F_f = 10^{-4.24} [\text{Ni(II)}] [\text{H}_2\text{A}_2]^{1/2}_{(o)} [\text{SO}_4^{=}]^{-1} [\text{Ac}^-]^{-1} \quad (70)$$

(viii) At low concentration of $\text{SO}_4^{=}$ but high concentration of H^+ and Ac^-

$$F_f = 10^{-9.76} [\text{Ni(II)}] [\text{H}_2\text{A}_2]^{1/2}_{(o)} [\text{H}^+]^{-1} [\text{Ac}^-]^{-1} \quad (71)$$

Therefore, the system should be discussed under eight different experimental conditions. The rate Eq. (64) can be modified to Eq. (72) on considering the monomeric model of the extractant (*cf.* Eq. 42):

$$F_f = 10^{-3.7} K_2^{1/2} P_{HA} K_{aHA}^{-1} [Ni(II)] [A^-] [H^+] \quad (72)$$

The flux Eq. (72) contains three concentration terms and so does not represent a rate equation for an elementary reaction step, as a termolecular reaction step is very rare. As the stability constant of $Ni(OH)^+$ is $10^{4.1}$, a simple calculation shows that its concentration at around pH 7 is almost zero. So the involvement of $NiOH^+$ species in rate determining step is ruled out. Rather it is concluded that Eq. (64) is a representative flux equation for a diffusion controlled reaction; where the diffusion of $Ni(II)$ from the aqueous phase and monomeric extractant from the organic phase to the aqueous film of the interface is the rate controlling. This conclusion is supported by the low activation energy (19.13 kJ/mol) obtained at low concentration regions of H^+ (pH 6.7), $SO_4^{=}$ (0.05 kmol/m^3) and Ac^- (0.25 kmol/m^3).

The flux Eq. (65) valid at high concentration of H^+ but at low concentrations of Ac^- and $SO_4^{=}$ can be transformed into the following form with the help of Eq. (42):

$$F_f = 10^{-10.02} K_2^{1/2} P_{HA} K_{aHA}^{-1} [Ni(II)] [A^-] \quad (73)$$

The above flux equation gives the rate determining chemical reaction step as $Ni^{2+} + A^- \rightarrow [NiA]^+$ in the bulk aqueous phase. In this experimental parametric condition, the $Ni(II)$ extraction by Cyanex 272 is therefore chemically controlled and this statement is supported by the high activation energy (55.90 kJ/mol) obtained at the investigated high concentration region of H^+ (pH = 5.2). Moreover, highly negative $\Delta S^\ddagger$ value indicates that the rate determining chemical reaction step ($Ni^{2+} + A^- \rightarrow [NiA]^+$) occurs through S_N2 mechanism.

At very high concentration levels of sulphate and hydrogen ions but at low concentration level of Ac^- , most $Ni(II)$ species in the aqueous phase will be $[NiSO_4]$. In such a condition $[Ni(II)]$ term in Eq. (66) will virtually represent the $[NiSO_4]$ term; and on considering the stability constant of $[NiSO_4]$ species is $\beta_{NiSO_4} = \left(\frac{[NiSO_4]}{[Ni(II)][SO_4^{=}]}\right)$ the flux equation (66) can be modified to

$$F_f = 10^{-10.87} \beta_{NiSO_4} [Ni(II)] [H_2A_2]^{1/2}_{(o)} [H^+]^{-1} \quad (74a)$$

$$\text{or, } F_f = 10^{-10.87} \beta_{\text{NiSO}_4} K_2^{1/2} P_{\text{HA}} K_{\text{aHA}}^{-1} [\text{Ni(II)}] [\text{A}^-] \quad (74b)$$

Equation (74b) is similar to Eq. (73) and so similar mechanism is applicable.

At very high concentration levels of Ac^- and H^+ but at low concentration level of $\text{SO}_4^{=}$, the flux equation (71) can be transformed to the following form:

$$F_f = 10^{-9.76} \beta_{\text{NiAc}^+} K_2^{1/2} P_{\text{HA}} K_{\text{aHA}}^{-1} [\text{Ni(II)}] [\text{A}^-] \quad (75)$$

Equation (75) is similar to Eqs. (73) and (74b) and so similar mechanism is again applicable.

It is realized that whether the extraction process would be diffusion or chemical controlling that will be governed solely by H^+ concentration range (at low pH, chemical controlling and at high pH diffusion controlling). At high sulphate concentration, flux of Ni(II) -transfer is decreased owing to the decrease in the $[\text{Ni(II)}]$ concentration for its complexation with $\text{SO}_4^{=}$.

In certain cases, the activation energy in the high temperature region is lower than that in the lower temperature region. In those cases, the processes are either diffusion or intermediate controlled at high temperature region and chemically controlled at low temperature region. The reason for this has been discussed earlier (in the forward extraction of Mn(II) section).

6. Studies on the kinetics of forward extraction of Zn(II) in the $\text{Zn(II)} - \text{SO}_4^{=}$ (Na^+ , H^+) - Cyanex 272-kerosene system

The kinetics of the title system have been thoroughly investigated using single drop (falling) technique as described in the following sections:

i) Determination of time needed for drop formation and coalescence

The drop formation and coalescence time has been determined for the investigated system by using columns of different heights by estimating the amount of Zn(II) -transferred from a drop for a particular set of experimental parameters. The related data together with the experimental conditions used are given in Table LIII. The amount of Zn(II) ($a_{\text{Zn(II)}}$) transferred from a drop versus drop fall time (t which is varied by using columns of different height) plot is given in Fig. 53.

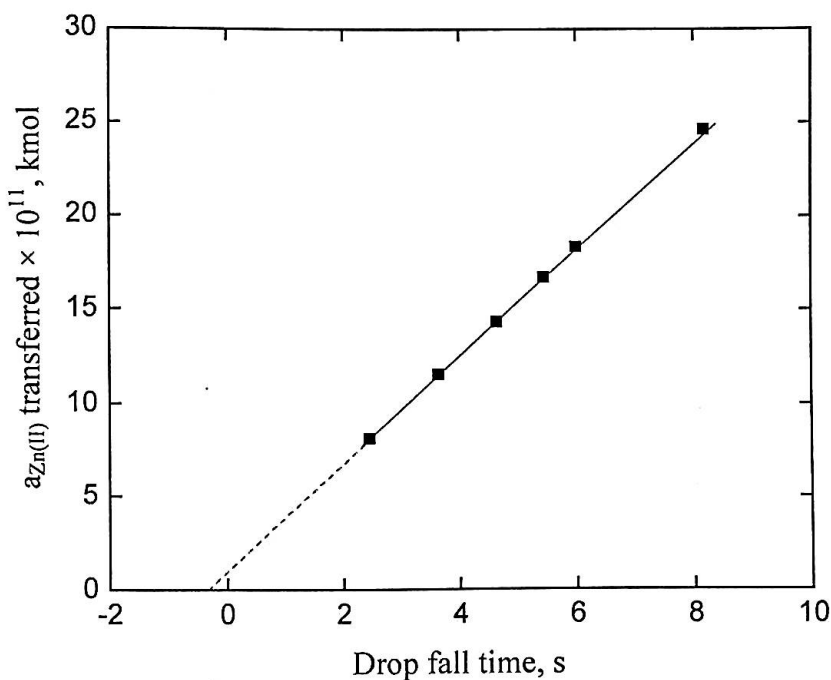


Fig. 53. Determination of time needed for drop formation and coalescence in a single drop experiment in the case of extraction of Zn(II) by Cyanex 272 (*cf.* Table LIII). $[Zn(II)]_{(ini)} = 1.15 \text{ kg/m}^3$, $[SO_4^{2-}] = 0.0176 \text{ kmol/m}^3$, $[H_2A_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$, $pH_{(ini)} = (6.00 \pm 0.01)$, Temperature = 303 K, Number of collected drops = 100.

The plot is a straight line and not passing through the origin. It cuts the time axis at -0.4 s ($\Delta t = 0.4 \text{ s}$). This time is attributed to the drop formation and coalescence time. The Δt term must be added to the drop fall time ($t + \Delta t$) to be used in calculating flux values; otherwise; errors in flux values will appear as demonstrated below:

In Table LIV, the Zn(II)-transfer flux has been calculated in two ways for each column height used: F'_f has been calculated by neglecting the Δt value ($F'_f = a_{Zn(II)} \text{ transferred} / \Delta t$) and F_f has been calculated by taking into account of Δt value ($F_f = a_{Zn(II)} \text{ transferred} / A(t + \Delta t)$). The values of F'_f , $\log F'_f$, F_f and $\log F_f$ are given in the 5, 6, 7 and 8th columns of the table, respectively. The $\log F'_f$ and $\log F_f$ vs. column height plots are displayed in Fig. 54.

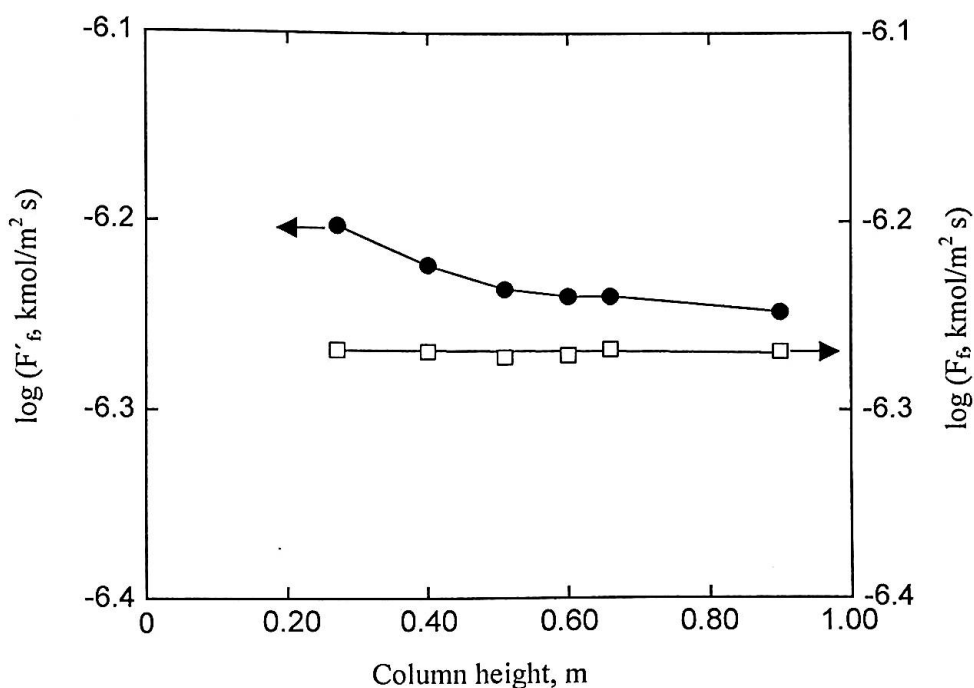


Fig. 54. Effect of column height on the flux of Zn(II) transfer in a Single Drop experiment in the case of extraction of Zn(II) by Cyanex 272 (*cf.* Table LIV). $[\text{Zn(II)}]_{(\text{ini})} = 1.15 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.0176 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = (6.00 \pm 0.01)$, Temperature = 303 K, $\Delta t = 0.40 \text{ s}$, Number of collected drops = 100.

It is observed that the value of $\log F'_f$ is decreased with increasing column height. On the other hand, $\log F_f$ remains unchanged with increasing column height. The $\log F_f$ value is found smaller than the $\log F'_f$ value for a particular column height and the difference between these two values diminishes with increasing column height. It is concluded that the calculated flux will be independent of column height if Δt term is added to the drop fall time (t); and the column of any height can be used for flux measurement if F_f instead of F'_f being calculated.

ii) Effect of initial Zn(II) concentration of the aqueous phase on the flux of Zn(II) transfer in its forward extraction by Cyanex 272

Together with the respective experimental parameters, the related experimental data are given in Table LV. Figure 55 displays the $\log F_f$ vs. $\log [\text{Zn(II)}]_{(\text{ini})}$ plots for five different sets of experimental parameters.

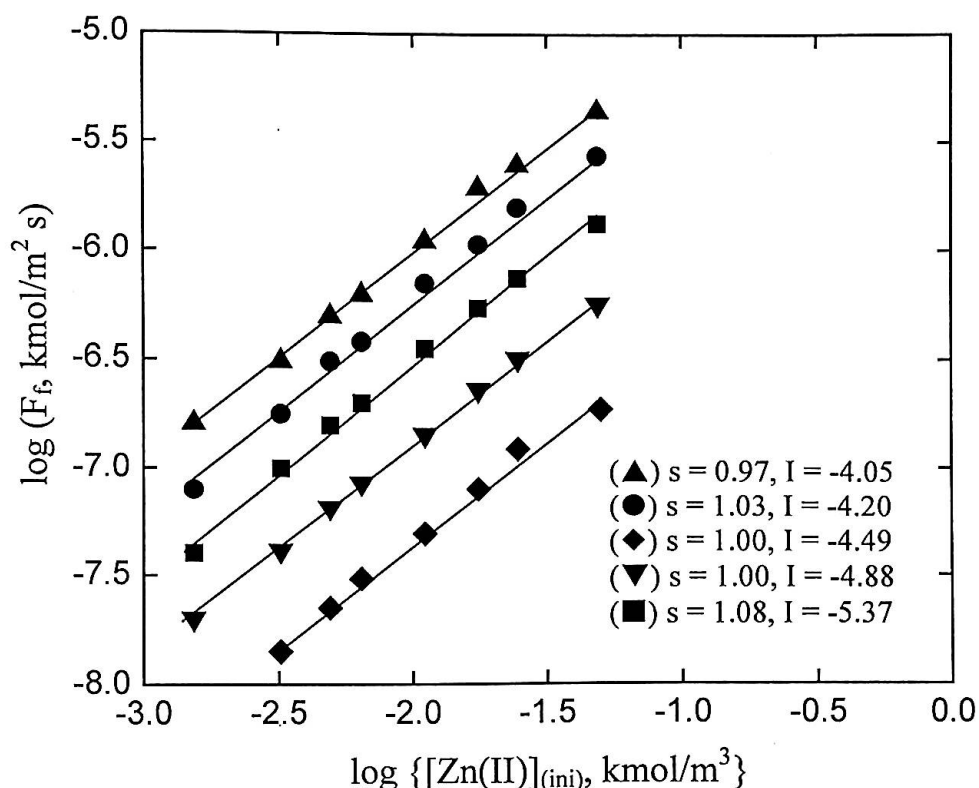


Fig. 55. Effect of the initial Zn(II) concentration in the aqueous phase on the flux of Zn(II) transfer during forward extraction of Zn(II) by Cyanex 272 in kerosene (*cf.* Table LV). $[\text{SO}_4^-] = 0.05 \text{ kmol/m}^3$, Temperature = 303 K, $\Delta t = 0.40 \text{ s}$, Number of collected drops = 100, (▲); $\text{pH}_{(\text{ini})} = (6.00 \pm 0.02)$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$, Column height = 0.40 m, (●); $\text{pH}_{(\text{ini})} = (6.00 \pm 0.02)$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, Column height = 0.60 m, (◆); $\text{pH}_{(\text{ini})} = (6.00 \pm 0.02)$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, Column height = 0.66 m, (▼); $\text{pH}_{(\text{ini})} = (5.00 \pm 0.02)$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, Column height = 0.66 m, (■); $\text{pH}_{(\text{ini})} = (4.00 \pm 0.02)$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, Column height = 0.90 m.

In all cases, straight lines are obtained. The slopes and intercepts of the lines are given in the body of the figure. Almost unity slope (0.97 - 1.08) indicates that the rate of forward extraction of Zn(II) by Cyanex 272 solution is directly proportional to the initial Zn(II) concentration; i.e. the reaction order with respect to Zn(II) concentration is unity.

iii) Effect of initial extractant concentration of the organic phase on the flux of Zn(II) transfer

The experimental data on the variation of flux with variations of extractant concentration on keeping all other parametric conditions identical (three sets) are given in Table LVI and the $\log F_f$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o,ini})}$ plots are given in Fig. 56.

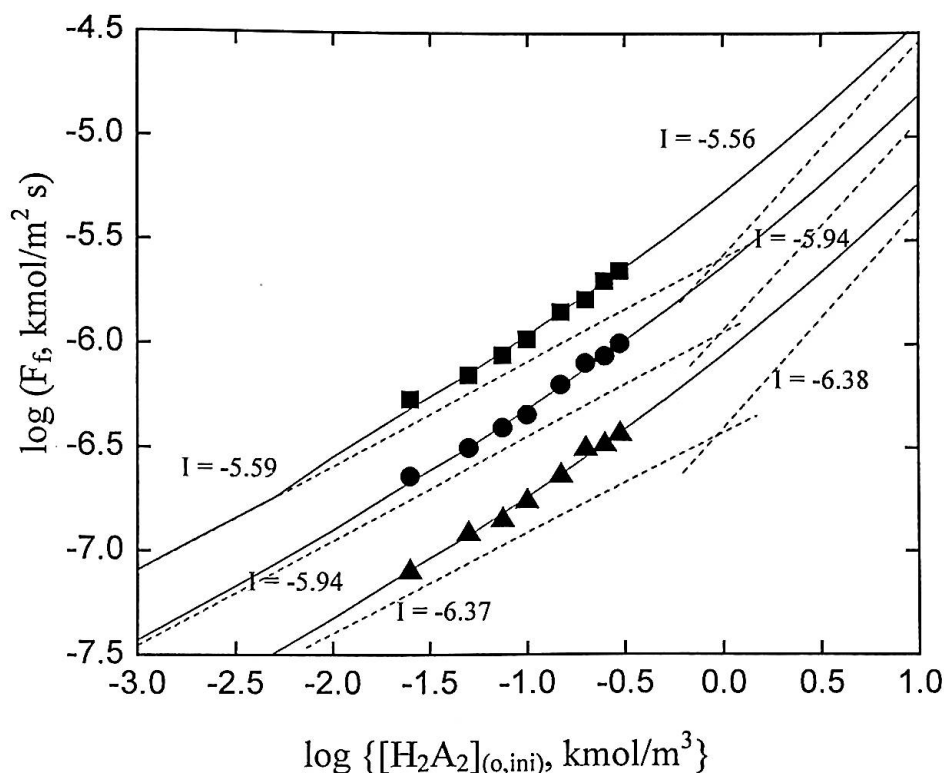


Fig. 56. Effect of extractant concentration on the flux of Zn(II) transfer in the forward extraction of Zn(II) by Cyanex 272 (*cf.* Table LVI). $[\text{Zn(II)}]_{\text{(ini)}} = 1.15 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.0176 \text{ kmol/m}^3$, Temp. = 303 K, $\Delta t = 0.40 \text{ s}$, Number of collected drops = 100, (■), $\text{pH}_{\text{(ini)}} = (6.00 \pm 0.02)$, Column height = 0.30 - 0.66 m, (●), $\text{pH}_{\text{(ini)}} = (5.00 \pm 0.02)$; Column height = 0.66 m (▲), $\text{pH}_{\text{(ini)}} = (4.00 \pm 0.01)$; Column height = 0.90 m. The points are experimental whilst the solid curves are theoretical representing; $\log F_f = -5.59 (\blacksquare) / -5.945 (\bullet) / -6.37 (\blacktriangle) + 0.50 \log [\text{H}_2\text{A}_2]_{\text{(o,ini)}} + \log (1 + K_{\text{H}_2\text{A}_2}^f [\text{H}_2\text{A}_2]_{\text{(o,ini)}}^{0.5})$, where $K_{\text{H}_2\text{A}_2}^f$ is a proportionality constant whose value can be evaluated by the Curve – Fitting method. The less inclined dashed lines (represented by $\log F_f = -5.59 (\blacksquare) / -5.945 (\bullet) / -6.37 (\blacktriangle) + 0.50 \log [\text{H}_2\text{A}_2]_{\text{(o,ini)}}$) are the asymptote at low concentration region of H_2A_2 , whereas the more inclined dashed lines (represented by $\log F_f = -5.59 (\blacksquare) / -5.945 (\bullet) / -6.37 (\blacktriangle) + 0.50 \log [\text{H}_2\text{A}_2]_{\text{(o,ini)}} + \log K_{\text{H}_2\text{A}_2}^f [\text{H}_2\text{A}_2]_{\text{(o,ini)}}^{0.5}$) are the asymptotes at high concentration region of H_2A_2 ; so that at the point of intersection of these two asymptotes; $\log K_{\text{H}_2\text{A}_2}^f + 0.5 \log [\text{H}_2\text{A}_2]_{\text{(o,ini)}} = 0$, giving $K_{\text{H}_2\text{A}_2}^f = \text{anti-logarithm of } -0.5 \log [\text{H}_2\text{A}_2]_{\text{(o,ini)}} = 1.07 \text{ m}^{3/2}/\text{kmol}^{1/2}$ in all three cases.

For each constant pH system, the experimental points do not fall on a straight line but can be put on a curve represented by:

$$\log F_f = -5.59 / -5.945 / -6.37 + (\log [\text{H}_2\text{A}_2]_{\text{(o,ini)}}^{1/2} + 1.07 [\text{H}_2\text{A}_2]_{\text{(o,ini)}}) \quad (76)$$

for $\text{pH}_{\text{(ini)}}$ values of 6.00/ 5.00/ 4.00, respectively. Equation (76) can be split into the following two forms:

at low concentration region of $[\text{H}_2\text{A}_2]_{\text{(o,)}}$; $[\text{H}_2\text{A}_2]_{\text{(o,ini)}}^{1/2} \gg 1.07 [\text{H}_2\text{A}_2]_{\text{(o,ini)}}$; so that

$$\log F_f = -5.59/-5.945/-6.37 + 0.5 \log [H_2A_2]_{(o,ini)} \quad (77)$$

at high concentration region of $[H_2A_2]_{(o)}; [H_2A_2]_{(o,ini)}^{1/2} \ll 1.07 [H_2A_2]_{(o,ini)}$; so that

$$\log F_f = -5.59/-5.945/-6.37 + \log 1.07 + \log [H_2A_2]_{(o,ini)} \quad (78)$$

Equation (77) indicates that the rate of forward extraction of Zn(II) is directly proportional to the square root of extractant concentration in its lower concentration region; whereas, it is directly proportional to the extractant concentration in its higher concentration region. Intercepts of the asymptotic lines are embodied in figure.

iv) Effect of the aqueous pH on the flux of Zn(II) transfer

Table LVII contains the related flux measurement data at specified various experimental parameters. Figure 57 shows the $\log F_f$ vs. $pH_{(ini)}$ plots at constant extractant concentrations of 0.025, 0.10 and 0.30 kmol/m³ keeping all other parameters unchanged. For a particular set of experimental parameters, the experimental points do not fall on a straight line. At low pH region, the points fall however on a portion of a straight line.

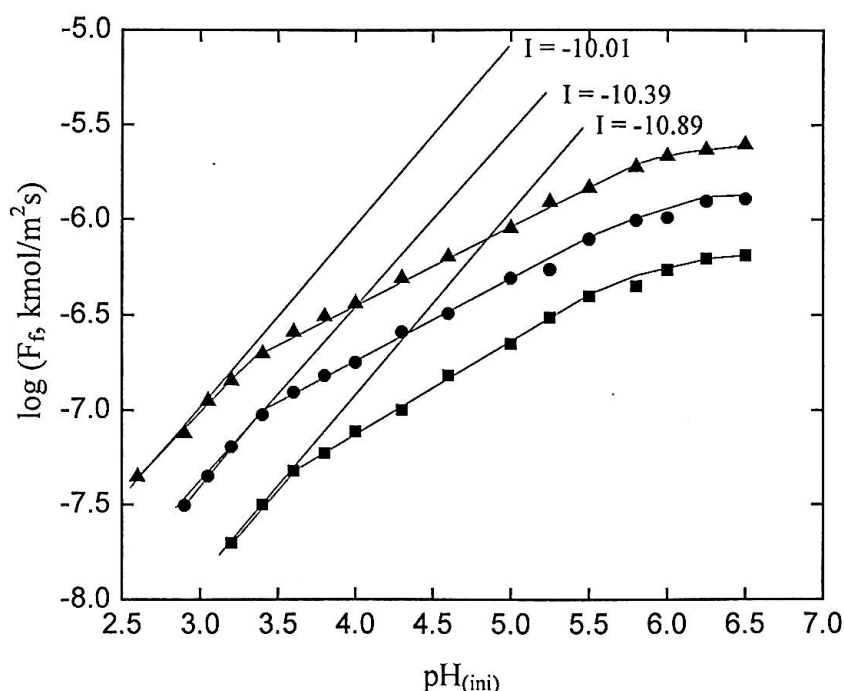


Fig. 57. Effect of aqueous initial pH on the flux of Zn(II) transfer in the forward extraction of Zn(II) by Cyanex 272 in kerosene (*cf.* Table LVII). $[Zn(II)]_{(ini)} = 1.15$ kg/m³, $[SO_4^{2-}] = 0.0176$ kmol/m³, Number of collected drops = 100, Temperature = 303 K; $\Delta t = 0.40$ s, Column height = variable; (■), $[H_2A_2]_{(o,ini)} = 0.025$ kmol/m³; (●), $[H_2A_2]_{(o,ini)} = 0.10$ kmol/m³; (▲), $[H_2A_2]_{(o,ini)} = 0.30$ kmol/m³.

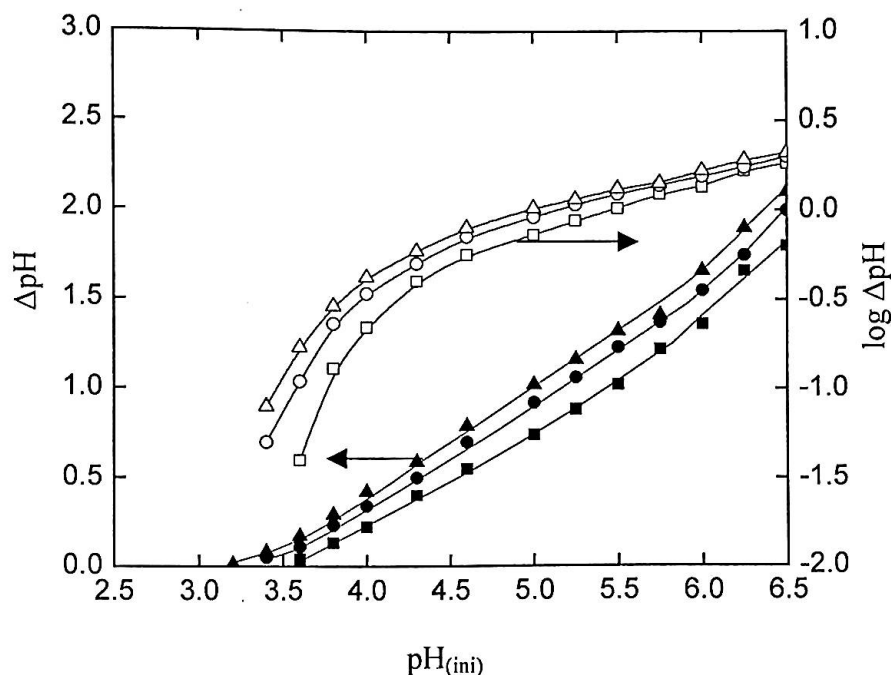


Fig. 58. Variation of ΔpH ($\text{pH}_{(\text{ini})} - \text{pH}_{(\text{int})}$) in the aqueous side of the interface with the variation of $\text{pH}_{(\text{ini})}$ at various extractant concentrations (*cf.* Table LVIII). Open symbols: $\log \Delta\text{pH}$ vs. $\text{pH}_{(\text{ini})}$; closed symbols: ΔpH vs. $\text{pH}_{(\text{ini})}$; Squares: $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$; Circles: $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$; Triangles: $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$

It is mentionable here that as the aqueous phases is not buffered, the aqueous high pH system on contact with the organic phase results in the decrease in interfacial pH due to instantaneous adsorption and ionization of the extractant at the interface. So it is expected that the $\log F_f$ vs. $\text{pH}_{(\text{int})}$ plot should describe the actual situation. Consequently, a ΔpH term ($= \text{pH}_{(\text{ini})} - \text{pH}_{(\text{int})}$) should be introduced which would transfer the experimental flux data on a definite straight line of unity slope. On such consideration, it may be concluded that the rate of forward extraction of Zn(II) from a non-buffered system is directly proportional to the interfacial pH or inversely proportional to the interfacial H^+ concentration.

The empirical ΔpH term for each extractant concentration system at various initial pH values are given in Table LXIII. The ΔpH and $\log \Delta\text{pH}$ versus $\text{pH}_{(\text{ini})}$ plots are shown in Fig. 58. From these type of plots, the values of ΔpH can be derived at any $\text{pH}_{(\text{ini})}$ values. It is also noticed that the ΔpH is not only dependent on the initial pH but also on the extractant concentration in the organic phase that forms the interface.

v) Effect of coexisting sulphate ion concentration on the flux of Zn(II) transfer

The effect has been measured at a single parametric condition. The flux values at different sulphate concentrations are given in Table LIX. The $\log F_f$ vs. $\log [\text{SO}_4^{=}]$ plot is displayed in Fig. 59. A straight line is not obtained; rather the experimental points can be put on curve represented by:

$$\log F_f = -6.26 - \log (1 + 0.708 [\text{SO}_4^{=}]) \quad (79)$$

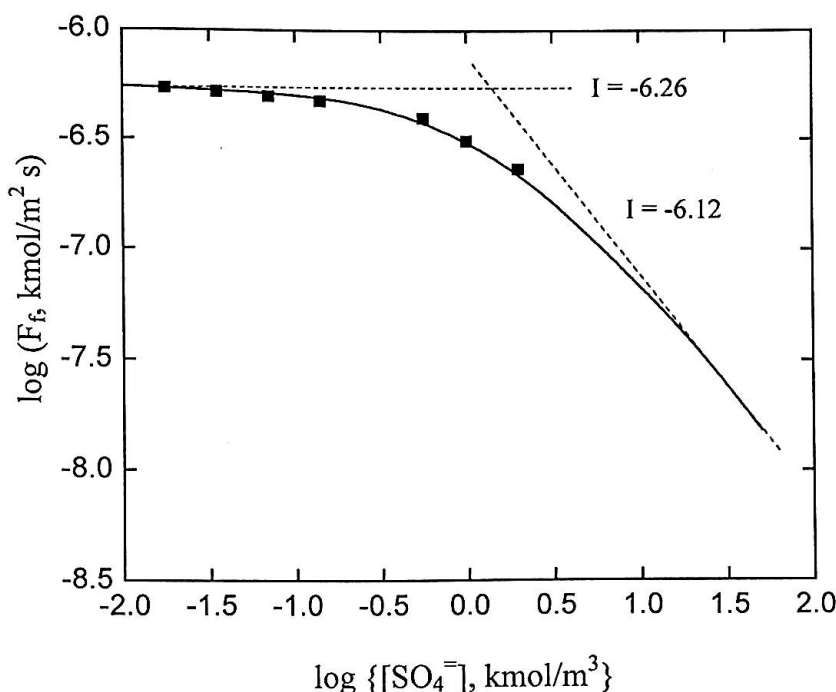


Fig. 59. Effect of $[\text{SO}_4^{2-}]$ on the flux of Zn(II) transfer in the forward extraction of Zn(II) by Cyanex 272 (*cf.* Table LIX). $[\text{Zn(II)}]_{(\text{ini})} = (1.15 \pm 0.08) \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = (6.00 \pm 0.01)$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.40 \text{ s}$, Column height = 0.66 m. Points are experimental and the solid curve is theoretical representing: $\log F_f = -6.26 - \log \{1 + K_{\text{SO}_4}^f [\text{SO}_4^{2-}]\}$, where $K_{\text{SO}_4}^f$ is a proportionality constant. Dashed lines are asymptotes at lower and higher SO_4^{2-} concentration regions. The value of $K_{\text{SO}_4}^f$ has been calculated to be $0.708 \text{ m}^3/\text{kmol}$ by the Curve-Fitting method.

The rate of Zn(II) transfer is therefore inversely proportional to the term $(1 + 0.708 [\text{SO}_4^{2-}])$. In other words, the rate is independent of SO_4^{2-} concentration in its lower concentration region and inversely proportional to the SO_4^{2-} concentration in its higher concentration region. The intercepts of the asymptotic lines are embodied in the figure.

vi) Effect of temperature on the flux of Zn(II) transfer

The effect of temperature on the flux of Zn(II) transfer has been investigated at three sets of experimental conditions; viz. (i) $\text{pH}_{(\text{ini})} = 6$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.0176 \text{ kmol/m}^3$; (ii) $\text{pH}_{(\text{ini})} = 4$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.0176 \text{ kmol/m}^3$ and (iii) $\text{pH}_{(\text{ini})} = 6$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 2 \text{ kmol/m}^3$. The related data are given in Table LX. The Arrhenius plots ($\log F_f$ vs. $1/T$) are shown in Fig. 60.

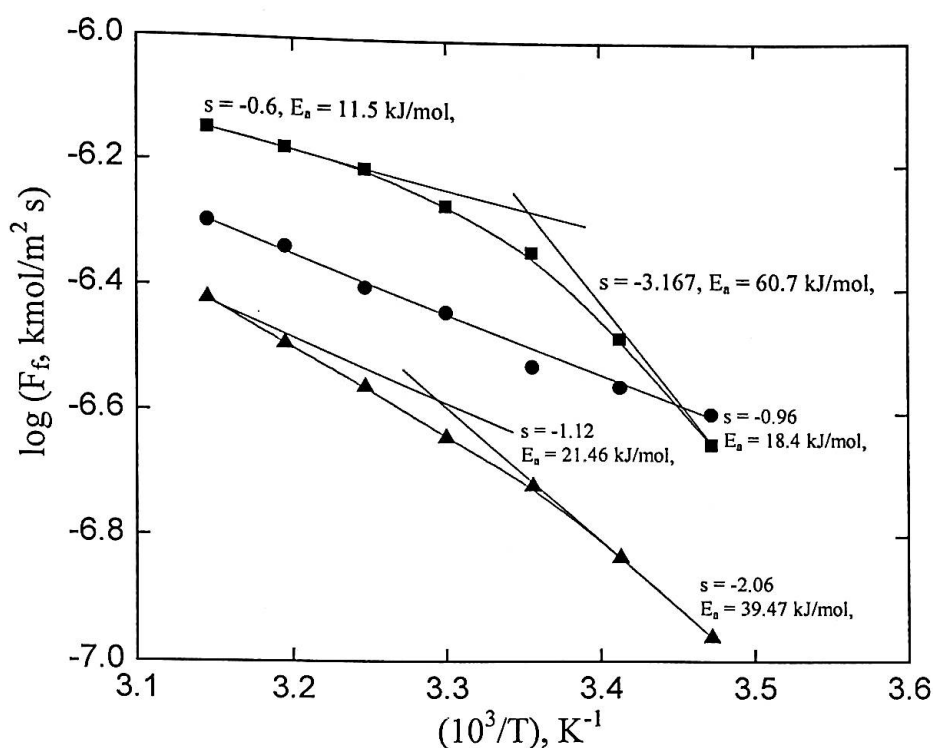


Fig. 60. Effect of temperature on the flux of Zn(II) transfer in the forward extraction of Zn(II) by Cyanex 272 in kerosene (*cf.* Table LX). $[Zn(II)]_{(ini)} = 1.15 \text{ kg/m}^3$, Number of collected drops = 100, $\Delta t = 0.40 \text{ s}$; (■), $pH_{(ini)} = 6.00$, $[H_2A_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.0176 \text{ kmol/m}^3$, Column height = 0.60 m; (●), $pH_{(ini)} = 4.00$, $[H_2A_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.0176 \text{ kmol/m}^3$, Column height = 0.90 m; (▲), $pH_{(ini)} = 6.00$, $[H_2A_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$, $[SO_4^{2-}] = 2.00 \text{ kmol/m}^3$, Column height = 0.66 m.

For system (ii), the plot is a straight line and its slope gives the activation energy of 18.4 kJ/mol. On the other hand, the plots for systems (i) and (iii) are curves with lower negative asymptotic slopes at higher temperature region and vice versa. The slopes of the asymptotic lines give activation energies of 11.50 kJ/mol and 21.46 kJ/mol, respectively, for systems (i) and (iii) at higher temperature region. These respective values are 60.70 and 39.47 kJ/mol at lower temperature region.

In order to estimate the values of the enthalpy of activation ($\Delta H^\ddagger$) and the entropy of activation ($\Delta S^\ddagger$), the temperature dependence flux data have also been treated by the Activated Complex Theory. The data are given in Table LXI and the $\log \left(\frac{F_f h}{kT} \right)$ vs. $1/T$ plots for the systems stated in preceding paragraph are given Fig. 61.

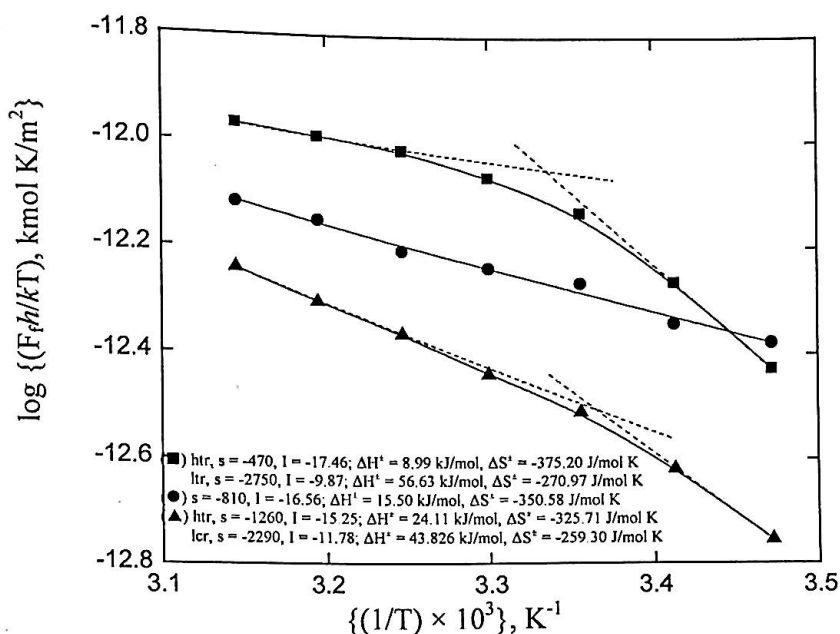


Fig. 61. The $\log (Fh/kT)$ vs. $(1/T)$ plots in the forward extraction of Zn(II) by Cyanex 272 (cf. Table LXI). $[Zn(II)]_{(ini)} = 1.15$ kg/m³, Number of collected drops = 100, $\Delta t = 0.40$ s; (■), $pH_{(ini)} = 6.00$, $[H_2A_2]_{(o,ini)} = 0.025$ kmol/m³, $[SO_4^{2-}] = 0.0176$ kmol/m³, Column height = 0.60 m, $\log f(R) = 2.147$; (●), $pH_{(ini)} = 4.00$, $[H_2A_2]_{(o,ini)} = 0.30$ kmol/m³, $[SO_4^{2-}] = 0.0176$ kmol/m³, Column height = 0.90 m; $\log f(R) = 1.759$; (▲), $pH_{(ini)} = 6.00$, $[H_2A_2]_{(o,ini)} = 0.025$ kmol/m³, $[SO_4^{2-}] = 2.00$ kmol/m³, Column height = 0.66 m, $\log f(R) = 1.769$; $h = 6.6252 \times 10^{-37}$ kJ s, $k = 1.38 \times 10^{-26}$ kJ/deg.

Like in the Arrhenius plots, the system (ii) yields a straight line with slope and intercept equaling to -810 and -16.56 respectively; yielding respective $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values of 15.50 kJ/mol and -350.58 J/mol K. The systems-(i) and (iii) yield curves with slopes and intercepts of the asymptotic lines at higher temperature region (htr) of -470 and -17.46; and -1260 and -15.25 respectively. These values at lower temperature region (ltr) are -2750 and -9.87; and -2290 and -11.78 for systems (i) and (iii) respectively. The estimated $\Delta H^\ddagger$ values at htr are 8.99 and 24.11 kJ/mol for systems (i) and (iii), respectively; whereas the respective values at ltr are 56.30 and 43.83 kJ/mol. On the other hand, the estimated $\Delta S^\ddagger$ values at htr are -375.20 and -325.71 J/mol K for systems (i) and (ii) respectively; whereas the respective values at ltr are -229.97 and -259.30 J/mol K. In the estimation of $\Delta S^\ddagger$ values, the logarithmic value of the function reactant ($f(R)$) for each system is needed and the calculated $\log f(R)$ values are given in the figure caption.

vii) Elucidation of the value of forward extraction rate constant (k_f) in Zn(II) - Cyanex 272 system

From the intercepts of the straight lines or the asymptotic lines in Figs. 55 - 57 and 59, the values of $\log k_f$ have been calculated and shown in Table G. The calculation is based on the empirical formula derived for flux calculation as illustrated at the bottom of the Table G. The average $\log k_f$ value obtained for Zn(II) extraction by Cyanex 272 is found to be -8.372 with standard deviation of 0.093 at the lcr of the extractant. This value is -8.442 with standard deviation of 0.045 at the hcr of the extractant.

Table G. Evaluation of rate constant (k_f) in the forward extraction of Zn(II) by Cyanex 272 at 303 K at lower and higher concentration regions of extractant.

Fig. No.	[Zn(II)], kmol/m ³	pH _(ini)	ΔpH	[H ₂ A ₂] _(o,ini) , kmol/m ³	[SO ₄ ²⁻] _i , kmol/m ³	Intercept, I	*log k _f	Average log k _f	Standard deviation
i) At lower concentration region of extractant									
55	Variable	6.00	1.36	0.025	0.05	-4.49	-8.382		
		6.00	1.55	0.100		-4.20	-8.262		
		6.00	1.66	0.300		-4.05	-8.314		
		5.00	0.74	0.025		-4.88	-8.392		
		4.00	0.22	0.025		-5.37	-8.402		
56	0.0176	6.00	1.3	Variable	0.0176	-5.59(lcr) ^f	-8.530	-8.372	0.093
		5.00	0.7			-5.94(lcr)	-8.470		
		4.00	0.2			-6.37(lcr)	-8.410		
57	0.0176	Variable	Variable	0.025	0.0176	-10.89	-8.397		
				0.100		-10.39	-8.257		
				0.300		-10.01	-8.190		
59	0.0176	6.00	1.36	0.025	Variable	-6.26(lcr)	-8.413		
						-6.12(hcr)	-8.423		
ii) At higher concentration region of extractant									
56	0.0176	6.00	1.3	Variable	0.0176	-5.56(hcr)	-8.481	-8.442	0.045
		5.00	0.7			-5.94(hcr)	-8.452		
		4.00	0.2			-6.38(hcr)	-8.392		

*log $F_f = \log k_f + \log [Zn(II)] + (pH_{(ini)} - \Delta pH = pH_{(ini)}) + \log (\sqrt{[H_2A_2]} + 1.07 [H_2A_2]) - \log (1 + 0.708 [SO_4^{2-}])$
 F_{hcr} = higher concentration region and lcr = lower concentration region.

The value of $\log k_f$ has also been obtained graphically. The working formula given at the bottom of Table G predicts that the plot of $\log F_f$ versus $\log f(R)$; where, $\log f(R) = \log [\text{Zn(II)}] + (\text{pH}_{(\text{ini})} - \Delta\text{pH}) + \log (\sqrt{[\text{H}_2\text{A}_2]_{(\text{o})}} + 1.07 [\text{H}_2\text{A}_2]_{(\text{o})}) - \log (1 + 0.708 [\text{SO}_4^{=}])$ should be a straight line with unity slope and the intercept value equaling to the value of $\log k_f$. The experimental $\log F_f$ values obtained at various experimental parameters those used in Figs. 55-57 and 59 have been used to fulfill this purpose.

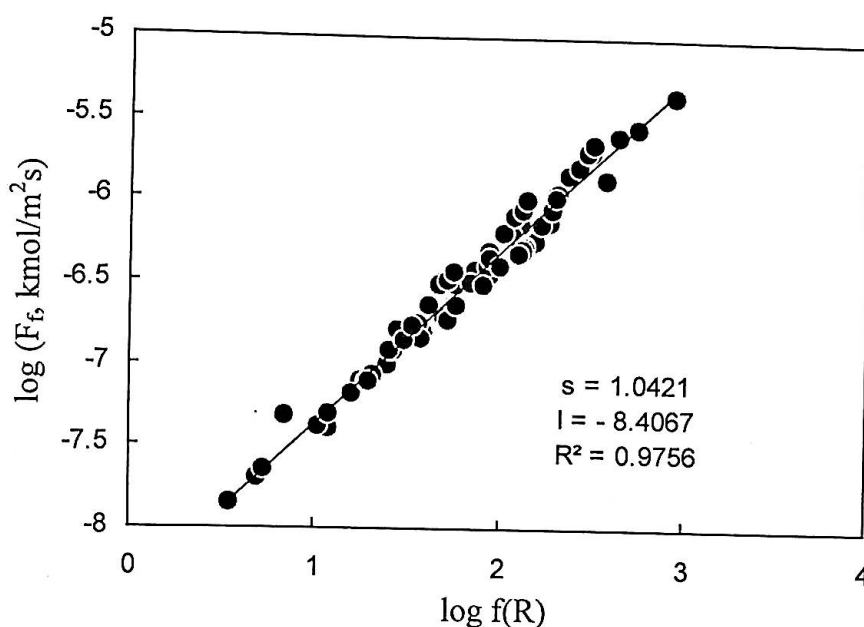


Fig. 62: Plot of $\log F_f$ vs. $\log f(R)$ for the estimation of rate constant (k_f) in the forward extraction of Zn(II) by Cyanex 272 at 303 K; where $\log f(R) = [\log [\text{Zn(II)}] + \log ([\text{H}_2\text{A}_2]^{0.5} + 1.07 [\text{H}_2\text{A}_2]) + (\text{pH}_{(\text{ini})} - \Delta\text{pH}) - \log (1 + 0.708 [\text{SO}_4^{=}])]$ (cf. Table LXII).

The calculated values of $\log f(R)$ are shown in Fig. 62. A considerable good fit Least Squares straight line (correlation coefficient, $R^2 = 0.9756$) with slope equaling to 1.0421 and intercept equaling to -8.4067 ($= \log k_f$) is obtained. This value is comparative to the average value of $\log k_f$ obtained above. In subsequent discussion, k_f value of $10^{-8.4} \text{ kmol}^{1/2} / \text{m}^{1/2} \text{ s}$ will be considered at both lcr and hcr of extractant.

viii) Mechanism of forward extraction of Zn(II) by Cyanex 272

Based on the results obtained from the above investigations on the rate of forward extraction of Zn(II) in the system $\text{Zn(II)}\text{-SO}_4^{=}\text{(H}^+, \text{Na}^+) \text{ - Cyanex 272-kerosene}$, the empirical rate or flux equation for this process can be expressed as:

$$F_f = 10^{-8.4} [\text{Zn(II)}] [\text{H}^+]^{-1}_{(\text{int})} ([\text{H}_2\text{A}_2]^{1/2}_{(\text{o})} + 1.07 [\text{H}_2\text{A}_2]_{(\text{o})}) (1 + 0.708 [\text{SO}_4^{=}])^{-1} \quad (80)$$

Equation (80) in the form presented is a complicated one for giving extraction mechanism. However, it can be simplified to the following forms based on different experimental conditions, which can be analyzed to give extraction mechanisms:

(i) At low concentrations of H_2A_2 and $\text{SO}_4^{=}$

$$F_f = 10^{-8.4} [\text{Zn(II)}] [\text{H}^+]^{-1}_{(\text{int})} ([\text{H}_2\text{A}_2]^{1/2}_{(\text{o})}) \quad (81)$$

(ii) At low concentrations of H_2A_2 but high concentrations of $\text{SO}_4^{=}$

$$F_f = 10^{-8.55} [\text{Zn(II)}] [\text{H}^+]^{-1}_{(\text{int})} ([\text{H}_2\text{A}_2]^{1/2}_{(\text{o})} [\text{SO}_4^{=}]^{-1}) \quad (82)$$

(iii) At high concentrations of H_2A_2 but low concentrations of $\text{SO}_4^{=}$

$$F_f = 10^{-8.37} [\text{Zn(II)}] [\text{H}^+]^{-1}_{(\text{int})} ([\text{H}_2\text{A}_2]_{(\text{o})}) \quad (83)$$

(iv) At high concentrations of H_2A_2 and $\text{SO}_4^{=}$

$$F_f = 10^{-8.52} [\text{Zn(II)}] [\text{H}^+]^{-1}_{(\text{int})} [\text{H}_2\text{A}_2]_{(\text{o})} [\text{SO}_4^{=}]^{-1} \quad (84)$$

The flux equation represented by Eq. (81) can be modified to the following equation on considering the monomeric model of the extractant (*vide* Eq. 42):

$$F_f = 10^{-8.4} K_2^{1/2} P_{\text{HA}} K_{\text{aHA}}^{-1} [\text{Zn(II)}] [\text{A}^-]_{(\text{int})} \quad (85)$$

The rate equation (85) suggests that the monomeric extractant existing in equilibrium with dimeric extractant in the organic phase is partitioned to the aqueous film (side) of the interface and ionizes to form the monomeric anion (A^-). The complexation of this monomeric anion with Zn(II) ion is the slowest process. So the slowest process in the investigated system at low concentration of H_2A_2 and $\text{SO}_4^{=}$ is the following chemical reaction:



The activation energy measured at low concentration of H_2A_2 (0.025 kmol/m^3) and $\text{SO}_4^{=}$ (0.0176 kmol/m^3) is 60.7 kJ/mol at 1 ltr which supports the chemical reaction represented by Eq. (86) is rate controlling. But the value of E_a is decreased with increasing temperature and becomes only $\sim 11.5 \text{ kJ/mol}$ at $\sim 318 \text{ K}$. With the temperature rise, the chemical reaction rate is so much increased that it exceeds the diffusion rate (as diffusion rate is usually not so much temperature dependent). At high temperature, the diffusion of reacting species or / and the reaction product to or / and from the reaction site is rate controlling. At around 303 K , at which most experiments have been carried out, the process is intermediate controlled i.e. both the chemical reaction represented by Eq. (86) and diffusions are rate controlling at the 1 ltr of H_2A_2 and $\text{SO}_4^{=}$.

Equation (82) is valid at high sulphate concentration. At high sulphate concentration, most of Zn(II) in the aqueous phase will exist as $[ZnSO_4]$ complex. So, Eq. (82) actually stands for the following equation:

$$F_f = 10^{-8.55} [ZnSO_4] [H^+]^{-1}_{(int)} [H_2A_2]^{1/2}_{(o)} [SO_4^{=}]^{-1} \quad (87)$$

Defining β_{ZnSO_4} as $[ZnSO_4] / [Zn(II)][SO_4^{=}]$ and applying the monomeric model of extractant, Eq. (87) can be transformed into the following form:

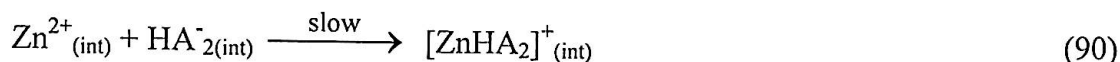
$$F_f = 10^{-8.55} \beta_{ZnSO_4} K_2^{1/2} P_{HA} K_{aHA}^{-1} [Zn(II)] [A^-]_{(int)} \quad (88)$$

Equation (88) and (85) are of the same form and so the similar mechanism is applicable as discussed above. However, the activation energy (21.46 - 39.47 kJ/mol) indicates that within the temperature range investigated, the process is always intermediate controlled i.e. both the chemical reaction represented by Eq. (86) and the diffusion of reacting species to the reaction site or of product species from the reaction site are slow.

At high concentration of H_2A_2 , the dimeric model will be applicable (*vide* Eq. 41) and the rate Eq. (83) can be modified to:

$$F_f = 10^{-8.37} P_{H_2A_2} K_{aHA}^{-1} [Zn(II)] [HA_2^-]_{(int)} \quad (89)$$

Equation (89) indicates that at high concentration region of H_2A_2 and low concentration region of $SO_4^{=}$, the following interfacial reaction is rate controlling:



But the activation energy of 18.40 kJ/mol obtained at hcr of H_2A_2 (0.3 kmol/m³) does not support the chemical reaction represented by Eq. (90) is rate controlling, rather supports that the diffusion of Zn^{2+} and HA_2^- to the interface to react as presented in Eq. (90) is rate controlling.

Finally, Eq. (84) virtually represents

$$F_f = 10^{-8.52} [ZnSO_4] [H^+]^{-1}_{(int)} [H_2A_2]_{(o)} [SO_4^{=}] \quad (91)$$

at high concentrations region of sulphate. This equation can be transformed to

$$F_f = 10^{-8.52} \beta_{ZnSO_4} P_{H_2A_2} K_{aHA}^{-1} [Zn(II)] [HA_2^-]_{(int)} \quad (92)$$

The rate equation (92) indicates that the chemical reaction step represented by Eq. (90) is rate controlling. But the activation energy at high concentrations of H_2A_2 and $SO_4^{=}$ has not estimated to support this statement.

The highly negative $\Delta S^\ddagger$ values indicate that the chemical reaction step represented by Eq. (90) proceeds through the S_N2 mechanism.

7. Studies on the kinetics of backward extraction/stripping of Mn(II) in the $\text{MnA}_2\text{-H}_2\text{A}_2\text{-kerosene} - (\text{H}^+, \text{Na}^+) \text{SO}_4^{2-}\text{-Ac}^-$ system

The kinetics of the title system have been investigated thoroughly using the falling single drop technique as described in the following sections:

i) Determination of time needed for the drop formation and coalescence

The time needed for the drop formation and coalescence has been determined to be 0.50 s. This time (Δt) has been added to the drop fall time (t) during calculation of flux value ($= a_{\text{Mn(II)}} \text{ transferred} / A (t + \Delta t)$).

ii) Effect of Mn(II) concentration in the organic phase on the stripping rate of MnA_2 complex by sulphate-acetato buffer solution

On varying the MnA_2 complex concentration within 0.00182 and 0.02730 kmol/m^3 , the falling single drop experiments have been conducted keeping all other parameters constant. The experimental data together with the experimental parameters are given Table LXIII. The $\log F_b$ vs. $\log [\text{Mn(II)}]_{(\text{o}, \text{ini})}$ plot is shown in Fig. 63.

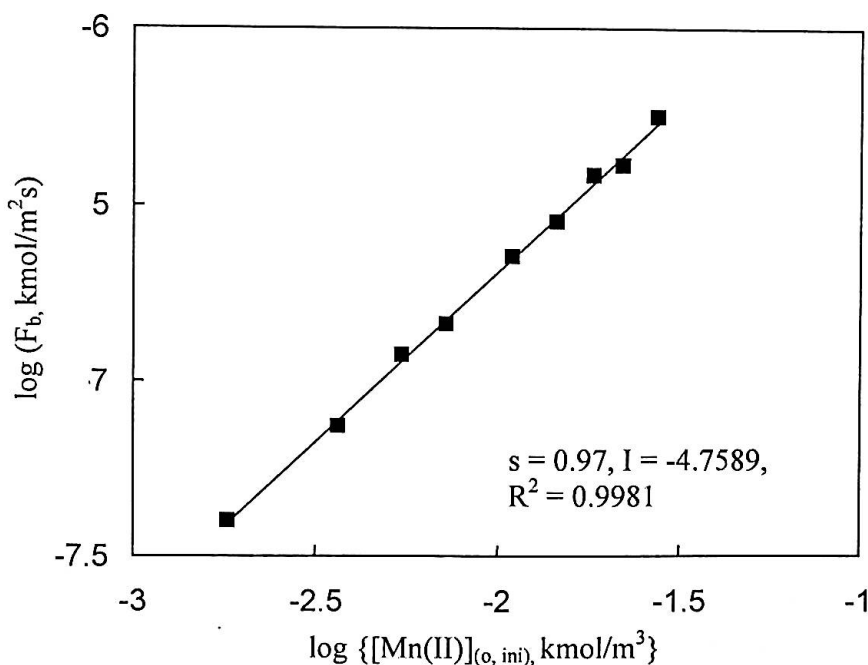


Fig. 63. Effect of Mn(II) concentration in the organic phase on stripping rate of Mn(II)-Cyanex 272 complex by sulfate-acetato buffer solution (*cf.* Table LXIII). $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o}, \text{ini})} = 0.11 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 2.70$, Column height = 0.66 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$.

The plot is a very good fit straight line ($R^2 = 0.9981$) with the Least Squares slope of 0.97 and intercept of -4.7589. Almost unity slope indicates that the rate of stripping of Mn(II) in the $\text{MnA}_2\text{-H}_2\text{A}_2\text{-kerosene} - (\text{Na}^+, \text{H}^+) \text{SO}_4^{2-}\text{-Ac}^-$ system is directly proportional to the Mn(II) Cyanex 272 complex concentration. In other words, the reaction order with respect to Mn(II)-Cyanex 272 complex concentration is unity.

iii) Effect of initial pH on the stripping rate of Mn(II)-A₂ complex by sulphate-acetate buffer solution

The variation of stripping flux (F_b) at various $\text{pH}_{(\text{ini})}$ values of the aqueous phase for two constant free extractant concentration systems are given in Table LXIV. The table also contains the parametric conditions used in experimentation. The $\log F_b$ versus $\text{pH}_{(\text{ini})}$ plots at 0.025 kmol/m^3 and 0.125 kmol/m^3 free Cyanex 272 systems are displayed in Fig. 64.

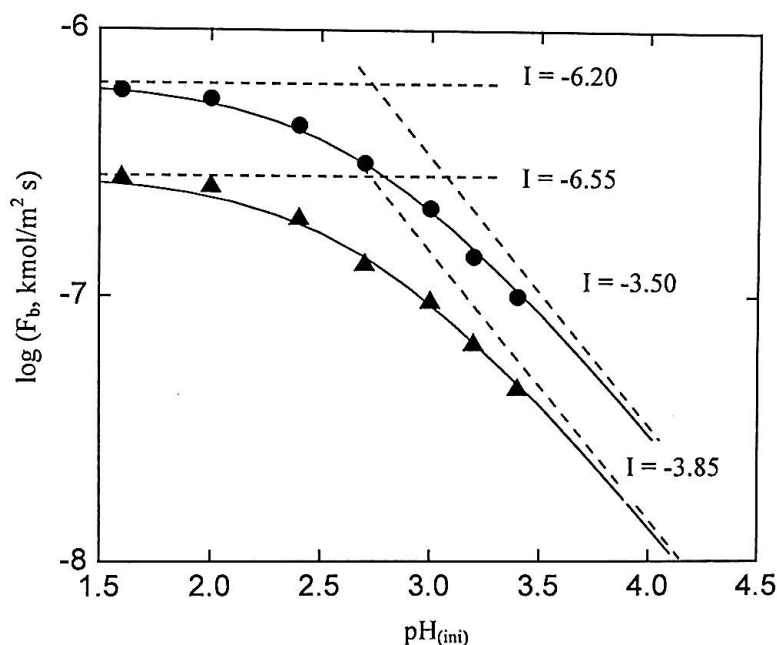


Fig. 64. Effect of initial pH on the stripping rate of Mn(II) (cf. Table LXIV). $[\text{Mn(II)}]_{(\text{o,ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.66 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$, (●), $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$; points are experimental and the solid curve is theoretical representing: $\log (F_b, \text{kmol/m}^2\text{s}) = \log k_b \cdot [\text{Mn(II)}]_{(\text{o,ini})} [\text{H}_2\text{A}_2]_{(\text{o,ini})}^{-0.5} - \log (1 + K_H^b [\text{H}^+]^{-1})$. The value of K_H^b is evaluated to be as $0.002 \text{ m}^3/\text{kmol}$. (▲), $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.125 \text{ kmol/m}^3$, points are experimental and the solid curve is theoretical representing: $\log (F_b, \text{kmol/m}^2\text{s}) = \log k_b \cdot [\text{Mn(II)}]_{(\text{o,ini})} [\text{H}_2\text{A}_2]_{(\text{o,ini})}^{-0.5} - \log (1 + K_H^b [\text{H}^+]^{-1})$ with K_H^b value of 0.002 kmol/m^3 as determined by the Curve-Fitting method.

It is found that the stripping flux is increased with decreasing $\text{pH}_{(\text{ini})}$ (i.e. increasing H^+ concentration). However, the variation in the figure is not linear. A curve is obtained with negative higher slope (-1) at higher pH region and with almost zero slope at lower pH region. The experimental points for a particular set of experimental parameters can be put on a curve represented by

$$\log F_b = -6.20 / -6.55 - \log (1 + 0.002 [\text{H}^+]^{-1}) \quad (93)$$

for 0.025 or 0.125 kmol/m^3 Cyanex 272 systems, respectively. The rate of stripping of Mn(II) from Mn(II)-Cyanex 272 complex by sulphate-acetato solution is inversely proportional to the term $(1 + 0.002 [\text{H}^+]^{-1})$. This term on splitting indicates that rate is independent of H^+ concentration in its higher concentration region, whereas, it is directly proportional to the H^+ concentration in its lower concentration region. The intercepts of the asymptotic lines are embodied in the figure.

iv) Effect of free extractant concentration of the organic phase on the stripping rate of Mn(II)-Cyanex 272 complex by sulphate-acetato solution

Table LXV contains the related experimental data. The $\log F_b$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o},\text{ini})}$ plots are shown in Fig. 65 at constant initial pH values of 2.00 and 3.00. In both cases, straight lines are obtained with slopes of -0.489 and -0.522 for pH 2.00 and 3.00 systems, respectively. Intercepts and correlation coefficients are embodied in the figure.

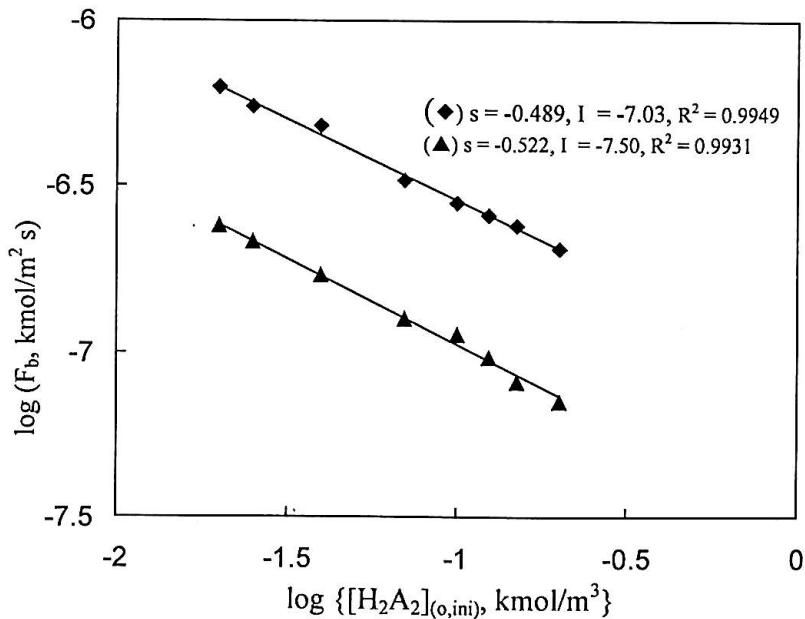


Fig. 65. Effect of free extractant concentration in the organic phase on the stripping rate of Mn(II)-Cyanex 272 complex by sulfate-acetato buffer solution (cf. Table IXV). $[\text{Mn(II)}]_{(\text{o},\text{ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.66 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$; (♦), $\text{pH}_{(\text{ini})} = 2.00$; (▲), $\text{pH}_{(\text{ini})} = 3.00$.

This result indicates that the rate of stripping of Mn(II) from MnA₂ complex is inversely proportional to the square root of free extractant concentration i.e. the reaction order with respect to free extractant concentration is -1/2.

v) Effect of sulphate ion concentration in the aqueous phase on stripping rate of Mn(II) from Mn(II)-A₂ complex by sulphate-acetato solution

Figure 66 displays the $\log F_b$ vs. $\log [\text{SO}_4^{2-}]$ plot at the specified single set of experimental parameters. The related experimental data are collected in Table LXVI. The experimental points do not yield a straight line, though the flux (F_b) is found to be increased by increasing the sulphate ion concentration. Rather the experimental points in the figure fall on a curve represented by:

$$\log F_b = \log k_b [\text{Mn(II)}]_{(o,ini)} [\text{H}_2\text{A}_2]_{(o,ini)}^{-0.5} (1 + 0.002 [\text{H}^+]^{-1})^{-1} + \log (1 + 5.129 [\text{SO}_4^{2-}]) \quad (94)$$

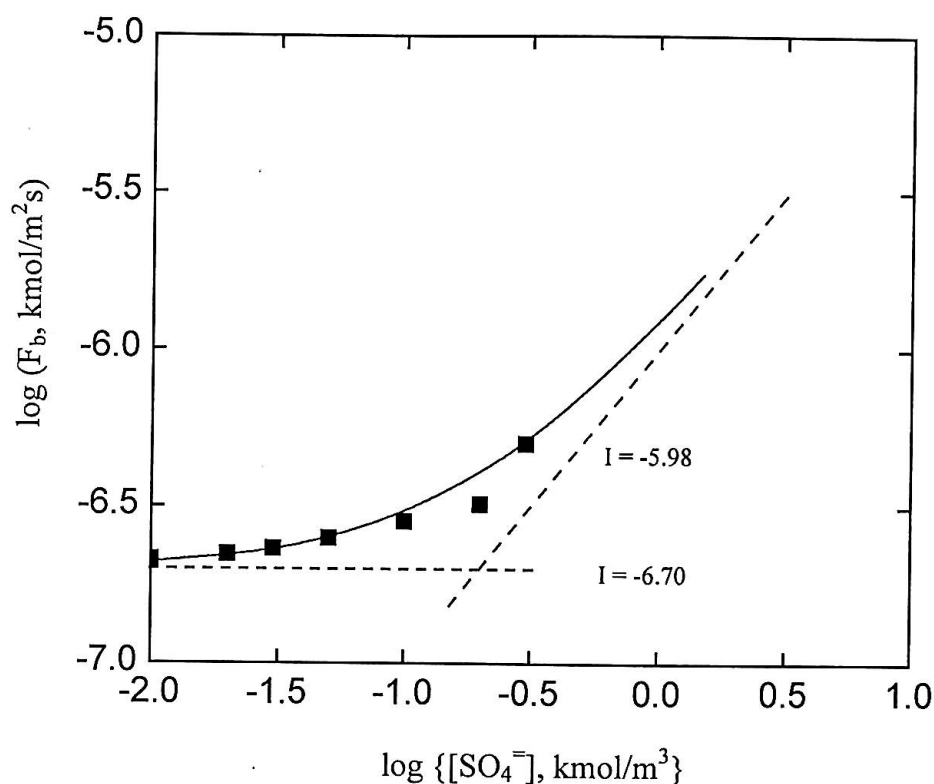


Fig. 66. Effect of sulfate ion concentration in the aqueous phase on stripping rate of Mn(II)- Cyanex 272 complex by sulfate-acetato buffer solution. (cf. Table LXVI) $[\text{Mn(II)}]_{(o,ini)} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $\text{pH}_{(ini)} = 3.00$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$, Column height = 0.66 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$. Points are experimental. The solid curve is theoretical representing: $\log F_b (\text{kmol/m}^2\text{s}) = \log k_b [\text{Mn(II)}] [\text{H}_2\text{A}_2]_{(o)}^{-0.5} (1 + 0.002 [\text{H}^+]^{-1})^{-1} + \log \{1 + K_{\text{SO}_4^2}^b [\text{SO}_4^{2-}]\}$, $K_{\text{SO}_4^2}^b$ is proportionality constant and its value has been calculated by the Curve Fitting method. The horizontal dashed line is an asymptote at low SO_4^{2-} concentration region represented by eq.: $\log F_b = \log k_b [\text{Mn(II)}] [\text{H}_2\text{A}_2]_{(o)}^{-0.5} (1 + 0.002 [\text{H}^+]^{-1}) = -6.70$ and the inclined dashed line is the asymptote at high SO_4^{2-} concentration region representing: $\log F_b = -6.70 + \log K_{\text{SO}_4^2}^b + \log [\text{SO}_4^{2-}]$. At the point of intersection of two asymptotes, $-\log K_{\text{SO}_4^2}^b + \log [\text{SO}_4^{2-}] = 0$; giving $K_{\text{SO}_4^2}^b = 5.129 \text{ m}^3/\text{kmol}$.

It is concluded from this result that the rate of stripping is directly proportional to the term $(1 + 5.125 [\text{SO}_4^{=}])$ i.e. it is independent on sulphate ion concentration in its lower concentration region; whereas, directly proportional to the sulphate ion concentration in its higher concentration region. The intercepts of the asymptotic lines of the curve are embodied in the figure.

vi) Effect of temperature on the stripping rate of Mn(II) from MnA_2 complex by sulphate-acetato solution

The temperature dependences of stripping rate have been measured for systems: (i) $\text{pH} = 3.50$, $[\text{H}_2\text{A}_2]_{(o)} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{=}] = 1.00 \text{ kmol/m}^3$; (ii) $\text{pH} = 1.50$, $[\text{H}_2\text{A}_2]_{(o)} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{=}] = 0.05 \text{ kmol/m}^3$; (iii) $\text{pH} = 2.70$, $[\text{H}_2\text{A}_2]_{(o)} = 0.055 \text{ kmol/m}^3$, $[\text{SO}_4^{=}] = 0.01 \text{ kmol/m}^3$; (iv) $\text{pH} = 3.50$, $[\text{H}_2\text{A}_2]_{(o)} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{=}] = 0.05 \text{ kmol/m}^3$ and (v) $\text{pH} = 1.50$, $[\text{H}_2\text{A}_2]_{(o)} = 0.20 \text{ kmol/m}^3$, $[\text{SO}_4^{=}] = 1.00 \text{ kmol/m}^3$. The experimental data are given in Table LXVII.

The Arrhenius plots ($\log F_b$ vs. $1/T$) for all systems, are displayed in Fig. 67. For systems (i) and (ii), straight lines are obtained. The slopes of the lines give the values of energy of activation as 59.7 and 18 kJ/mol for system (i) and (ii), respectively. For systems (iii) - (v), curves are obtained with less flux variation in the higher temperature region (htr) and high flux variation in the lower temperature region (ltr). From the slopes of the asymptotic or limiting lines of the curves, the values of E_a have been calculated. The calculated E_a values are 18.70, 15.00 and 23.00 kJ/mol for systems (iii), (iv) and (v), respectively at the htr. At ltr, the respective E_a values are 59.70, 67.00 and 58.60 kJ/mol.

The temperature dependence data have also been treated by the Activated Complex Theory. The necessary data for this treatment are shown in Table LXVIII. The $\log (F_b h/kT)$ vs. $(1/T)$ plots for previously mentioned five systems are depicted in Fig. 68.

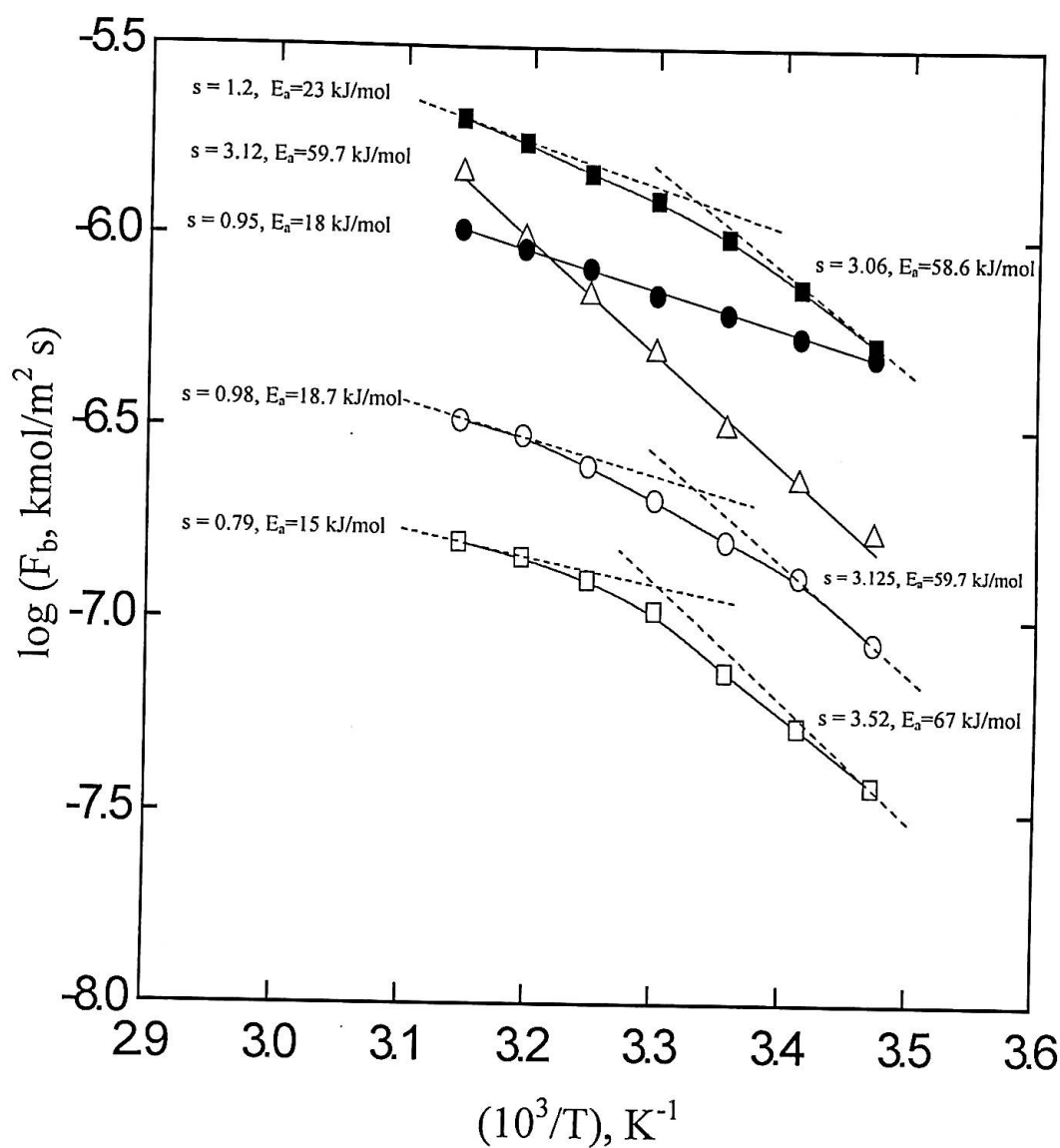


Fig. 67. Effect of temperature on the stripping rate of Mn(II)-Cyanex 272 complex by sulfate-acetate solution (cf. Table LXVII). $[\text{Mn(II)}]_{(\text{o, ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, Number of collected drops = 100, Column height = 0.66 m, $\Delta t = 0.5 \text{ s}$. (Δ), $\text{pH}_{(\text{ini})} = 3.50$, $[\text{H}_2\text{A}_2] = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 1.00 \text{ kmol/m}^3$; ($\bullet$), $\text{pH}_{(\text{ini})} = 1.50$, $[\text{H}_2\text{A}_2]_{(\text{o, ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.05 \text{ kmol/m}^3$; ($\circ$), $\text{pH}_{(\text{ini})} = 2.70$, $[\text{H}_2\text{A}_2]_{(\text{o, ini})} = 0.055 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$; ($\square$), $\text{pH}_{(\text{ini})} = 3.50$, $[\text{H}_2\text{A}_2]_{(\text{o, ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.05 \text{ kmol/m}^3$; ($\blacksquare$), $\text{pH}_{(\text{ini})} = 1.50$, $[\text{H}_2\text{A}_2]_{(\text{o, ini})} = 0.20 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 1.00 \text{ kmol/m}^3$.

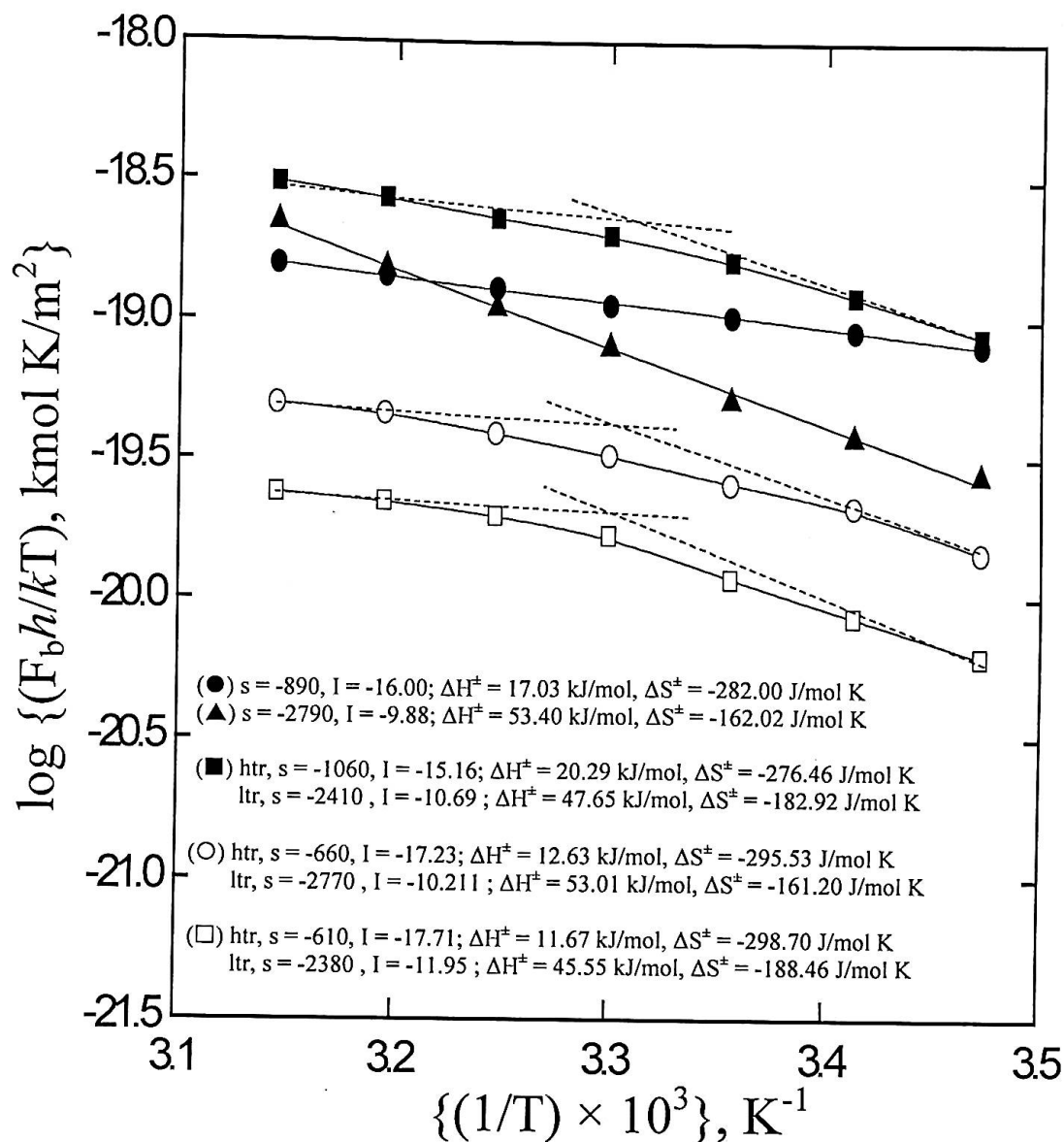


Fig. 68. The $\log (F_b h / kT)$ vs. $1/T$ plots in the backward extraction of Mn(II) in the Mn(II)-Cyanex 272 complex-kerosene - $(Na^+, H^+) SO_4^{2-} Ac^-$ system (cf. Table LXVIII). $[Mn(II)]_{(o,ini)} = 0.40$ kg/m³, $[Ac^-] = 0.25$ kmol/m³, Number of collected drops = 100, Height of column = 0.66 m, $\Delta t = 0.5$ s, (▲), $pH_{(ini)} = 3.50$, $[H_2A_2] = 0.025$ kmol/m³, $[SO_4^{2-}] = 1.00$ kmol/m³, $\log f(R) = -1.414$; (●), $pH_{(ini)} = 1.50$, $[H_2A_2]_{(o,ini)} = 0.025$ kmol/m³, $[SO_4^{2-}] = 0.05$ kmol/m³, $\log f(R) = -1.264$; (○), $pH_{(ini)} = 2.70$, $[H_2A_2]_{(o,ini)} = 0.055$ kmol/m³, $[SO_4^{2-}] = 0.01$ kmol/m³, $\log f(R) = -1.788$; (□), $pH_{(ini)} = 3.50$, $[H_2A_2]_{(o,ini)} = 0.025$ kmol/m³, $[SO_4^{2-}] = 0.05$ kmol/m³, $\log f(R) = -2.102$; (■), $pH_{(ini)} = 1.50$, $[H_2A_2]_{(o,ini)} = 0.20$ kmol/m³, $[SO_4^{2-}] = 1.00$ kmol/m³, $\log f(R) = -1.028$; $h = 6.6252 \times 10^{-37}$ kJ s, $k = 1.38 \times 10^{-26}$ kJ/deg.

For systems (i) and (ii), here again straight lines are obtained. The slopes of these lines give $\Delta H^\pm$ values of 17.03 kJ/mol and 53.40 kJ/mol for systems (i) and (ii), respectively. On calculating $\log f(R)$ values as -1.414 and -1.26 for systems (i) and (ii), respectively, the intercept of the plots give respective $\Delta S^\pm$ values of -282 and -162 J/mol K.

From the slopes and intercepts of the asymptotic lines of the curves for systems (iii), (iv) and (v), the values of $\Delta H^\pm$ and $\Delta S^\pm$ at htr and ltr have been calculated and embodied in the figure together with the $\log f(R)$ values. It is noticed that $\Delta S^\pm$ value is negative in all cases.

vii) Evaluation of the value of rate constant (k_b) in stripping of Mn(II) from MnA_2 complex by sulphate-acetato solution

From the intercepts of the straight lines or the asymptotic lines in Figs. 63 - 66, the (k_b) values at 303 K have been evaluated based on the following general equation:

$$\begin{aligned} \log F_b = & \log k_b + \log [MnA_2]_{(o)} - 0.5 \log [H_2A_2]_{(o)} - \log (1 + 0.002 [H^+]^{-1}) \\ & + \log (1 + 5.129 [SO_4^{=}]) \end{aligned} \quad (95)$$

and given in the Table H. The average value of $\log k_b$ estimated is -4.8873 with standard deviation of 0.037.

On the basis of Eq. (95), the $\log k_f$ value has also been estimated as the intercept of the $\log F_b$ vs. $\log f(R)$ plot; where $\log f(R)$ represents $\log [MnA_2]_{(o)} - 0.5 \log [H_2A_2]_{(o)} - \log (1 + 0.002 [H^+]^{-1}) + \log 1 + 5.129 [SO_4^{=}]$. For this purpose all, experimental data at 303 K used in Fig. 63 - 66 or Tables LXIII - LXVI have been used to calculate $\log f(R)$ values. Such calculated values together with the experimentally determined $\log F_b$ values are collected in Table LXIX. The $\log F_b$ vs. $\log f(R)$ plot at 303 K is given in Fig. 69. A good fit Least Squares straight line ($R^2 = 0.9915$) is obtained with slope equaling to 1.0057 (should be 1.00) and intercept equaling to -4.8708. The last value corresponds to the value of $\log k_b$ at 303 K which is very close to the value obtained above (-4.8873). The unit of k_b is found to be $\text{kmol}^{1/2} / \text{m}^{1/2} \text{ s}$.

Table H. Evaluation of the rate constant (k_b) in backward extraction/stripping of Mn(II) in the Mn(II)-Cyanex 272 complex- H_2A_2 -kerosene - $(Na^+, H^+) SO_4^{2-}$ -Ac⁻ system at 303 K

Fig. No	[Mn(II)] _(ini) , kmol/m ³	pH _(ini)	[H ₂ A ₂] _(o,ini) , kmol/m ³	[SO ₄ ²⁻] _i , kmol/m ³	Intercept (I)	log (k_b)	Average log (k_b)	Standard deviation
63	Variable	2.70	0.11	0.01	-4.69	-4.9692		
64	0.007281	Variable	0.025	0.01	-6.20(hcr)	-4.8849		
					-3.50(lcr)	-4.8839		
		Variable	0.125	0.01	-6.55(hcr)	-4.8854	-4.8873	0.037
					-3.85(lcr)	-4.8844		
65	0.007281	2.00	Variable	0.01	-7.018	-4.8227		
		3.00	Variable	0.01	-7.486	-4.8928		
66	0.007281	3.00	0.025	Variable	-6.70(lcr)	-4.8861		

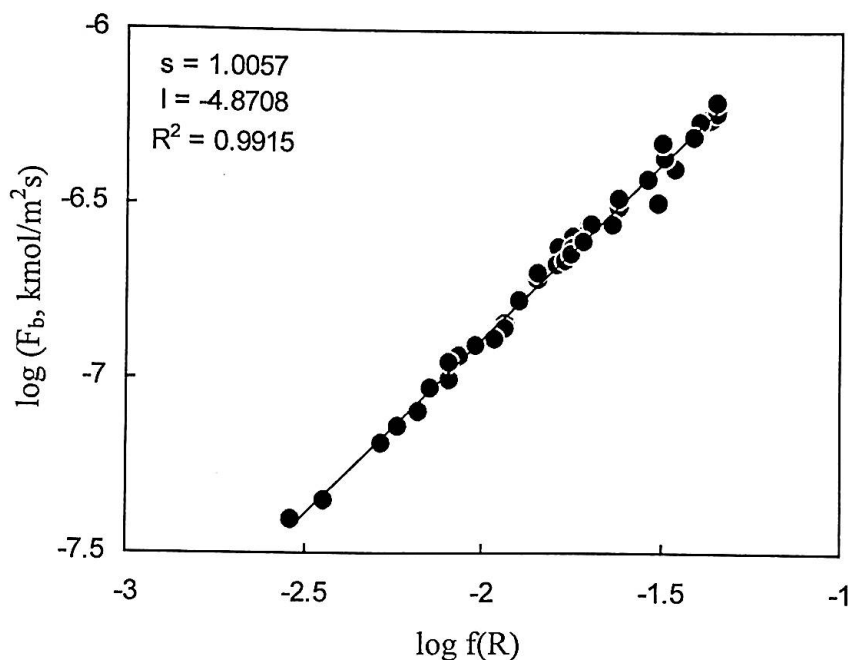


Fig. 69. Plot of $\log F_b$ vs. $\log f(R)$ for the estimation of rate constant (k_b) in backward extraction of Mn(II) from Mn(II)-Cyanex 272 complex by sulfate-acetato solution at 303 K, where, $\log f(R) = [\log [\text{Mn(II)}]_{(o,ini)} - \log (1 + 0.002 [\text{H}^+]^{-1}) - 0.5 \log [\text{H}_2\text{A}_2]_{(o)} + \log (1 + 5.129 [\text{SO}_4^-])]$ (cf. Table LXIX).

viii) Mechanism of stripping of Mn(II) from $[\text{MnA}_2]$ complex by sulphate-acetato solution

As the rate of forward extraction of Mn(II) has been found to be independent of acetate ion concentration, its effect on stripping rate has not been investigated. From the foregoing results, the rate or flux of Mn(II) transfer during stripping of $[\text{MnA}_2]$ complex by acidic sulphate-acetato solution in 0.25 kmol/m^3 acetate medium at 303 K can be expressed as follows:

$$F_b = 10^{-4.88} [\text{MnA}_2]_{(o)} [\text{H}_2\text{A}_2]_{(o)}^{-1/2} (1 + 0.002 [\text{H}^+]^{-1})^{-1} (1 + 5.129 [\text{SO}_4^-]) \quad (96)$$

The extraction equilibrium study together with loading of Mn(II) into the Cyanex 272 solution and the rate of forward extraction of Mn(II) by Cyanex 272 studies point out that the existing Mn(II)-species in the organic phase is the $[\text{MnA}_2]$ complex in which two monomeric anion of the extractant (A^-) are coordinated to Mn^{2+} to satisfy its four coordination positions. A Mn(II) is generally 6-coordinated, the remaining two coordination positions in $[\text{MnA}_2]$ complex are obviously satisfied by two water molecules. Equation (96) valid at 303 K, can be split into the following four simplified equations depending on four different parametric conditions:

(i) At low concentrations of H^+ and $SO_4^{=}$

$$\begin{aligned} F_b &= 10^{-4.88} [MnA_2]_{(o)} [H_2A_2]_{(o)}^{-1/2} (0.002 [H^+]^{-1})^{-1} \\ &= 10^{-2.18} [MnA_2]_{(o)} [H_2A_2]_{(o)}^{-1/2} [H^+] \end{aligned} \quad (97)$$

(ii) At low concentration of H^+ and high concentration of $SO_4^{=}$

$$F_b = 10^{-1.47} [MnA_2]_{(o)} [H_2A_2]_{(o)}^{-1/2} [H^+] [SO_4^{=}] \quad (98)$$

(iii) At high concentrations of H^+ and $SO_4^{=}$

$$F_b = 10^{-4.17} [MnA_2]_{(o)} [H_2A_2]_{(o)}^{-1/2} [SO_4^{=}] \quad (99)$$

(iv) At high concentration of H^+ and low concentration of $SO_4^{=}$

$$F_b = 10^{-4.88} [MnA_2]_{(o)} [H_2A_2]_{(o)}^{-1/2} \quad (100)$$

since a) at high concentration of H^+ : $(1 + 0.002 [H^+]^{-1})^{-1} \approx 1$

b) at low concentration of H^+ : $(1 + 0.002 [H^+]^{-1})^{-1} \approx [H^+] / 0.002$

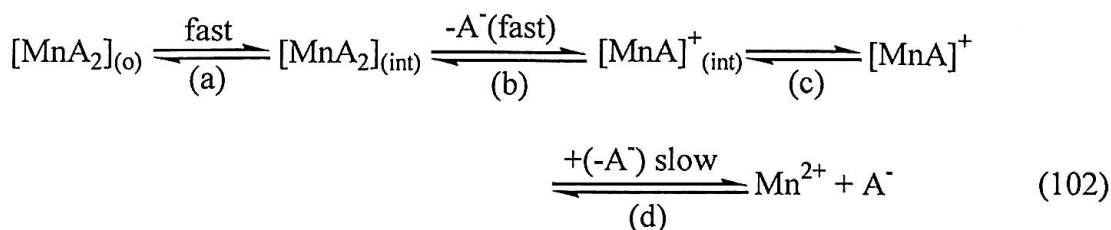
c) at high concentration of $SO_4^{=}$: $(1 + 5.129 [SO_4^{=}]) \approx 5.129 [SO_4^{=}]$

and d) at low concentration of $SO_4^{=}$: $(1 + 5.129 [SO_4^{=}]) \approx 1$

The monomeric model of Cyanex 272 (H_2A_2) as illustrated in Eq. (42) can modify Eq. (97) into the following form:

$$F_b = 10^{-2.18} K_2^{1/2} P_{HA}^{-1} K_{aHA} [MnA_2]_{(o)} [A^-]^{-1} \quad (101)$$

The flux equation (101) involves two concentration terms but one of which is an organic species and the other is an aqueous species. It is therefore concluded that on dissociation of A^- from $[MnA_2]$ at the organic side of the interface, $[MnA]^+$ is formed first which then diffused to the bulk aqueous phase. In the aqueous phase, the dissociation of second A^- from $[MnA]^+$ takes place which is identified as the rate controlling chemical reaction step. Thus among the following steps:

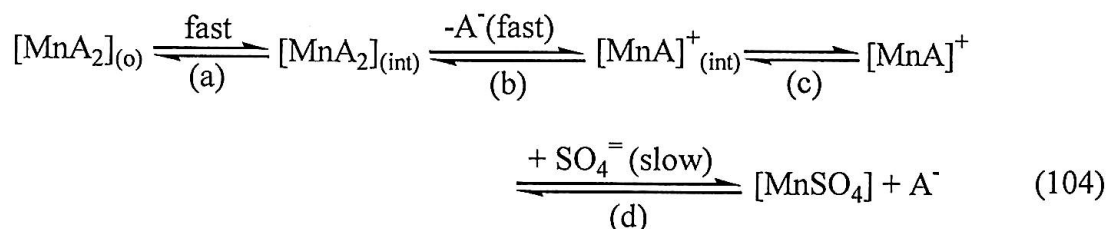


the reaction step represented by Eq. (102d) is the rate determining step. At lcr of H^+ and $SO_4^{=}$ (system-(iv) in temperature dependence section), the activation energy of 67 kJ/mol at ltr (~ 288 K) varied to 18.7 kJ/mol at htr (~ 318 K) is obtained. Therefore the chemical reaction step represented by Eq. (102d) is rate controlling below 293 K and as temperature increases, the rate constant for the reaction step represented by Eq. (102d) is so much increased that this chemical reaction rate surpasses the diffusion rate; and the result is that over 313 K the process becomes solely diffusion controlling. At 303 K where most of the experiments have been carried out, the process is intermediate controlling i.e. both the reaction step (102d) as well as the diffusion of various reactant species to the reaction site or of the product from the reaction site are rate controlling. The highly negative $\Delta S^\pm$ value at the considered parametric condition indicates that the chemical reaction represented by Eq. (102d) occurs via S_N2 mechanism.

Equation (98) valid at low concentration of H^+ and high concentration of $SO_4^{=}$, can be changed to the following form by the use of the monomeric model of the extractant:

$$F_b = 10^{-1.47} K_2^{1/2} P^{-1}_{HA} K_{aHA} [MnA_2]_{(o)} [A^-]^{-1} [SO_4^{=}] \quad (103)$$

Rate equation (103) suggests that among the following steps:



the reaction step represented by Eq. (104d) is rate controlling. This statement is supported by the high activation energy (59.7 kJ/mol) obtained at pH 3.5 and $[SO_4^{=}]$ of 1.00 kmol/m³ (system-(i) of temperature dependence section). The negative $\Delta S^\pm$ again suggests that the rate determining chemical reaction step occurs via S_N2 mechanism.

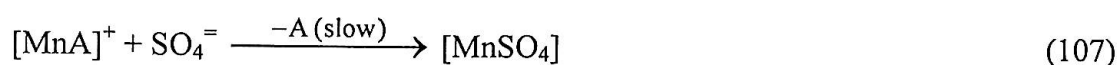
Equation (99) derived for system at high concentrations of H^+ and $SO_4^{=}$ can be changed by the help of Eq. (42) to the following form:

$$F_b = 10^{-4.17} K_2^{1/2} P^{-1}_{HA} K_{aHA} [MnA_2]_{(o)} [A^-]^{-1} [H^+]^{-1} [SO_4^{=}] \quad (105)$$

At high concentration region of H^+ , most $SO_4^{=}$ virtually exists as HSO_4^- in the aqueous phase. Therefore, the $[SO_4^{=}]$ term in Eq. (105) can be replaced by $[HSO_4^-]$. There, Eq. (105) can be modified as follows:

$$\begin{aligned} F_b &= 10^{-4.17} K_2^{1/2} P_{HA}^{-1} K_{aHA} [MnA_2]_{(o)} [A^-]^{-1} [H^+]^{-1} [HSO_4^-] \\ &= 10^{-4.17} \beta_{HSO_4^-} K_2^{1/2} P_{HA}^{-1} K_{aHA} [MnA_2]_{(o)} [A^-]^{-1} [SO_4^{=}] \end{aligned} \quad (106)$$

where, $\beta_{HSO_4^-} = [HSO_4^-] / [H^+] [SO_4^{=}]$. Equation (106) suggests the following reaction step as rate determining:



However, the activation energy measured at high H^+ and $SO_4^{=}$ concentration region (system (v) in the temperature dependence section) varies from 58.6 kJ/mol to 23 kJ/mol when temperature is varied from 15°C to 45°C. The high activation energy at least at the ltr supports that the reaction step represented by Eq. (107) is rate controlling. However, with rise of temperature, the chemical reaction rate is so much increased that it becomes almost equal to diffusion rate. Therefore, at higher temperature region (20 - 45°C), the process is intermediate controlling. The reaction step represented by Eq. (107) occurs via S_N2 mechanism as $\Delta S^\ddagger$ value is negative.

The rate equation (100) valid at high concentration region of H^+ and low concentration region of $SO_4^{=}$ can be modified to

$$F_b = 10^{-4.88} K_2^{1/2} P_{HA}^{-1} K_{aHA} [MnA_2]_{(o)} [A^-]^{-1} [H^+]^{-1} \quad (108)$$

Equation (108) involves three concentration terms and so at the specified parametric condition, diffusion is rate controlling which is supported by the low activation energy (18 kJ/mol) measured at the specified parametric condition.

8. Studies on the kinetics of backward extraction / stripping of Ni(II) in the Ni(II)-Cyanex 272 complex-H₂A₂-kerosene - (H⁺, Na⁺) SO₄⁼-Ac⁻ system

On considering the drop formation and coalescence time of 0.5 s in the study, the variation of flux of Ni(II) transfer in the title system with the variation of various experimental parameters have been extensively investigated as described in the following subsections.

i) Effect of Ni(II) concentration in the organic phase on the (stripping) rate of Ni(II) transfer in the Ni(II)-Cyanex 272 complex-H₂A₂-kerosene - (Na⁺, H⁺) SO₄⁼ - Ac⁻ system

The flux of Ni(II) transfer during stripping of the above system has been determined at various Ni(II)-Cyanex 272 complex concentration in the organic phase keeping all other variables at constant values. The related experimental data together with statements on the constant parametric conditions are given in Table LXX and the log F_b vs. log [Ni(II)]_(o,ini) plot at a single set of parametric conditions is given in Fig. 70.

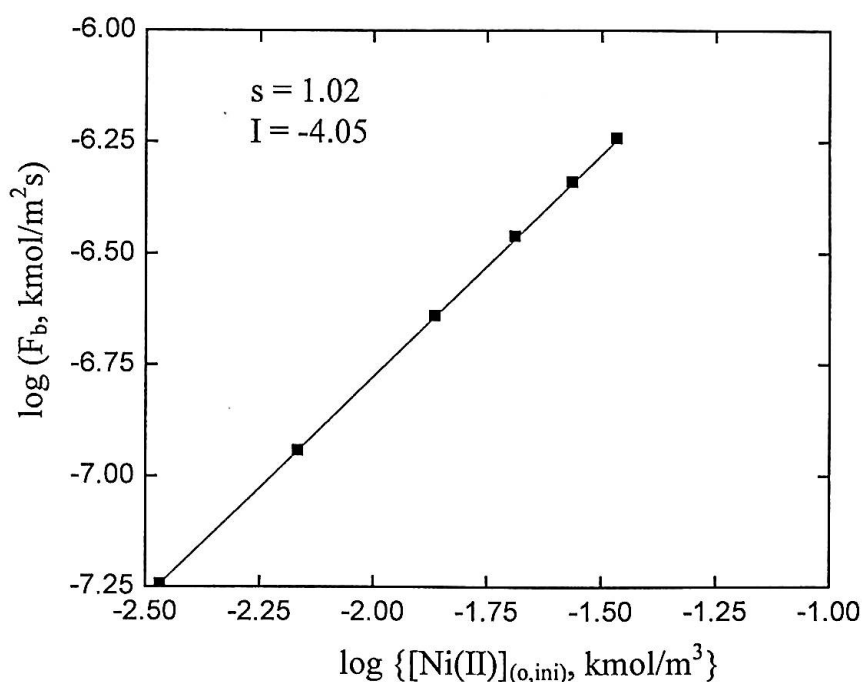


Fig. 70. Dependence of organic phase Ni(II) concentration on the flux of Ni(II) transfer during stripping by sulphuric acid - acetic acid mixture (*cf.* Table LXX). pH_(ini) = 5.0, [H₂A₂]_(o,ini) = 0.025 kmol/m³, [SO₄⁼] = 0.1 kmol/m³, [Ac⁻] = 0.25 kmol/m³, Δt = 0.5 s, Temp. = 303 K.

The plot is a straight line with slope equaling to 1.02 and intercept equaling to -4.05. The slope value indicates that the rate of stripping is directly proportional to initial Ni(II) - complex concentration in the organic phase, or the reaction order with respect to [Ni(II)-Cyanex 272 complex] is unity.

ii) Effect the aqueous acidity on the Ni(II) transfer flux in stripping of Ni(II) - Cyanex 272 complex by sulphate-acetato solution

The related aqueous pH dependence data of stripping flux at 0.025 kmol/m³ and 0.300 kmol/m³ free extractant concentrations keeping other parametric conditions constants are given in Table LXXI and the log F_b vs. pH_(ini) plots for the mentioned two systems are displayed in Fig. 71.

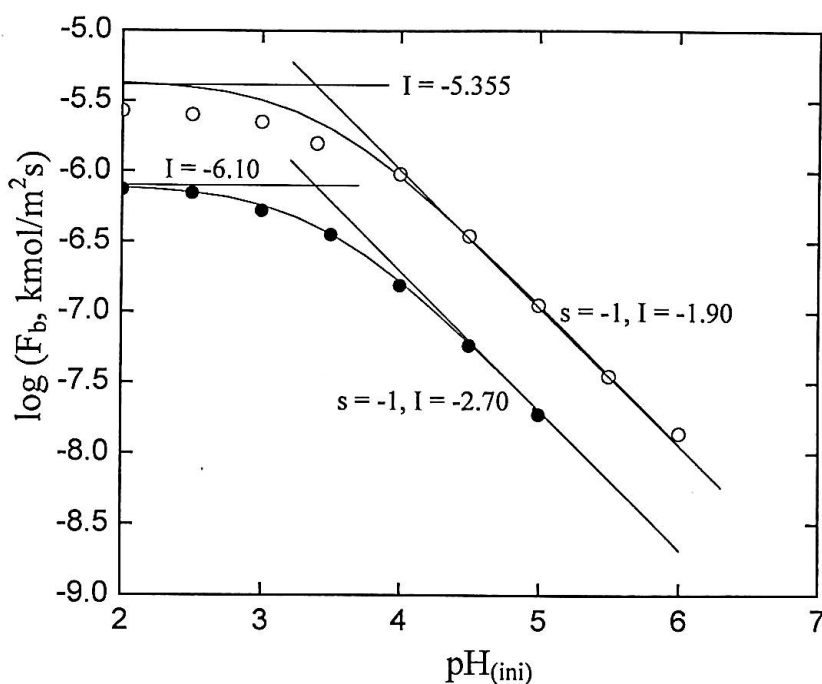


Fig. 71. Dependence of aqueous phase acidity on the Ni(II)-transfer flux in stripping of Ni(II)-Cyanex 272 complex by sulphate-acetato solution (*cf.* Table LXXI). [Ni(II)_(o,ini)] = 0.40 kg/m³, [SO₄²⁻] = 0.1 kmol/m³, [Ac⁻] = 0.25 kmol/m³, Δt = 0.5 s, Temp. = 303 K; (O), [H₂A₂]_(o,ini) = 0.025 kmol/m³; points are experimental, whilst the solid curve is theoretical represented by: log F_b = -5.355 - log (1+10^{-3.42} [H⁺]⁻¹); (●), [H₂A₂]_(o,ini) = 0.300 kmol/m³; points are experimental, whilst the solid curve is theoretical represented by: log F_b = -6.10 - log (1+10^{-3.42} [H⁺]⁻¹).

The experimental points for a particular condition do not yield a straight line as the flux variation with $\text{pH}_{(\text{ini})}$ variation levels off at low $\text{pH}_{(\text{ini})}$ regions. However, the experimental points can be put on a curve as represented below:

$$\log F_b = -5.355 / -6.10 - \log (1 + 10^{-3.42} [\text{H}^+]^{-1}) \quad (109)$$

for 0.025 / 0.30 kmol/m³ free Cyanex 272 concentration systems, respectively. These results indicate that the rate of Ni(II)-transfer in stripping is inversely proportional to the factor $(1 + 10^{-3.42} [\text{H}^+]^{-1})$ i.e.

- a) at lcr of $[\text{H}^+]$: $F_b \propto [\text{H}^+]$; and
- b) at hcr of $[\text{H}^+]$: F_b is independent of $[\text{H}^+]$.

The intercepts of the asymptotic lines of the curves have been embodied in the related figure.

iii) Effect of the organic phase free extractant concentration on the Ni(II) transfer flux in stripping of Ni(II)-Cyanex 272 complex by sulphate-acetate solution

The experimental data on the estimated flux values (F_b) at different free extractant concentrations in the organic phase for two sets of experimental parameters have been tabulated (Table LXXII). Figure 72 illustrates the $\log F_b$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o,ini})}$ plots for constant pH values of 4.0 and 4.5.

As above, the experimental points for a particular set of parametric conditions do not fall on a straight line, rather the points can be placed on a curve represented by:

$$\log F_b = -7.10 / -6.70 - 0.5 \log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log (1 + 2.5 [\text{H}_2\text{A}_2]_{(\text{o,ini})}^{0.5}) \quad (110)$$

for 4.50 and 4.00 $\text{pH}_{(\text{ini})}$ systems, respectively. The last two terms in Eq. (110) can be put as $-\log ([\text{H}_2\text{A}_2]_{(\text{o,ini})}^{0.5} + 2.5 [\text{H}_2\text{A}_2]_{(\text{o,ini})})$. From this relationship, it is concluded that the stripping rate is inversely proportional to the term: $([\text{H}_2\text{A}_2]_{(\text{o,ini})}^{0.5} + 2.5 [\text{H}_2\text{A}_2]_{(\text{o,ini})})$; i.e

- a) at high concentration region of extractant : $F_b \propto [\text{H}_2\text{A}_2]_{(\text{o,ini})}^{-1}$; and
- b) at low concentration region of extractant : $F_b \propto [\text{H}_2\text{A}_2]_{(\text{o,ini})}^{-0.5}$

The intercepts of the asymptotic lines of the plots have been embodied.

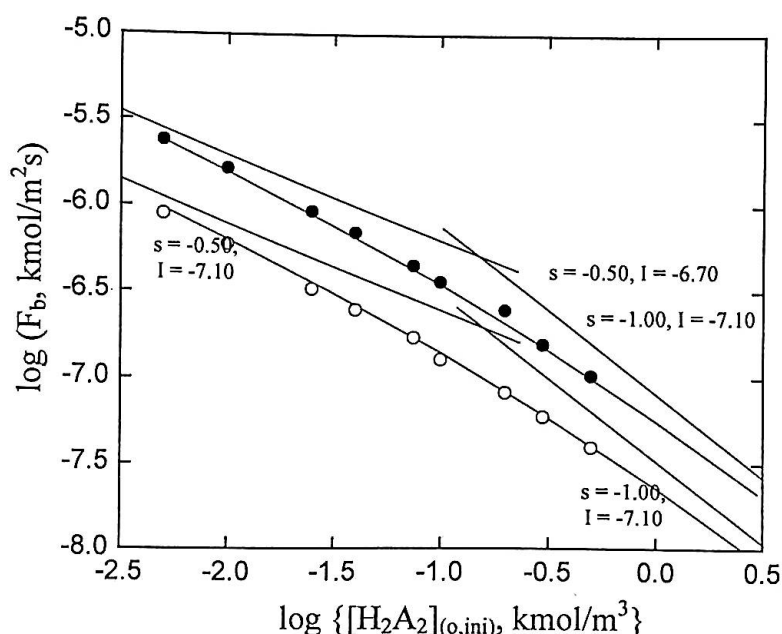


Fig. 72. Dependence of organic phase free-extractant concentration on the stripping flux of Ni(II) in the system: Ni(II)-complex- H_2A_2 -kerosene – $(\text{Na}^+, \text{H}^+) \text{SO}_4^{=}-\text{Ac}^-$ (cf. Table LXXII). $[\text{Ni(II)}]_{(\text{o,ini})} = 0.40 \text{ kg/m}^3$, $[\text{SO}_4^{=}] = 0.10 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.100 \text{ kmol/m}^3$, $\Delta t = 0.5 \text{ s}$, Temp. = 303 K, (O); $\text{pH}_{(\text{ini})} = 4.50$. Points are experimental, and the solid curve is theoretical represented by: $\log F_b = -7.10 - 0.5 \log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log (1 + 2.5 [\text{H}_2\text{A}_2]_{(\text{o,ini})}^{0.5})$; (●), $\text{pH}_{(\text{ini})} = 4.00$. Points are experimental, whilst the solid curve is theoretical represented by: $\log F_b = -6.7 - 0.5 \log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log (1 + 2.5 [\text{H}_2\text{A}_2]_{(\text{o,ini})}^{0.5})$.

iv) **Effect of sulphate ion concentration of the aqueous phase on the stripping flux Ni(II) in the Ni(II)-Cyanex 272 complex - H_2A_2 -kerosene- $(\text{Na}^+, \text{H}^+) \text{SO}_4^{=}-\text{Ac}^-$ system**

The related experimentally found out data at two sets of experimental parameters are given in Table LXXIII and Fig. 73.

Figure 73 represents the $\log F_b$ variation with logarithmic sulphate concentration at constant $\text{pH}_{(\text{ini})}$ values of 4.5 and 4. In both the cases, the experimental points can be set on a curve represented as follows:

$$\log F_b = -7.45 / -7.02 + \log (1 + 6 [\text{SO}_4^{=}]) \quad (111)$$

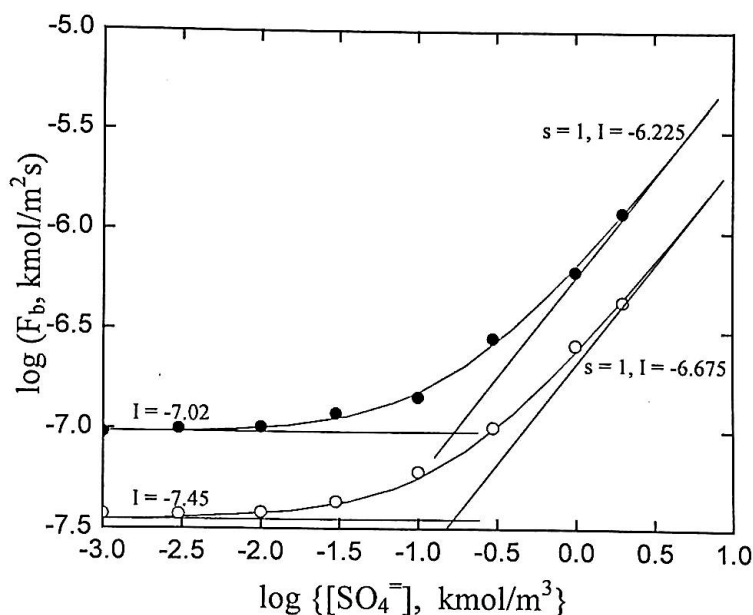


Fig.73. Dependence of sulphate ion concentration on the stripping flux of Ni(II) in the Ni(II)-Cyanex 272 complex- H_2A_2 - kerosene - $(\text{Na}^+, \text{H}^+) \text{SO}_4^{2-}\text{-Ac}^-$ solution (cf. Table LXXIII). $[\text{Ni(II)}]_{(0,\text{ini})} = 0.40 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 4.5$, $[\text{H}_2\text{A}_2]_{(0,\text{ini})} = 0.30 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $\Delta t = 0.5 \text{ s}$, Temp. = 303 K; (O), $\text{pH}_{(\text{ini})} = 4.50$. Points are experimental and the solid curve is theoretical represented by $\log F_b = -7.45 + \log (1 + 6 [\text{SO}_4^{2-}])$; (●), $\text{pH}_{(\text{ini})} = 4.00$. Points are experimental, whilst the solid curve is theoretical represented by: $\log F_b = -7.02 + \log (1 + 6 [\text{SO}_4^{2-}])$.

for initial pH systems of 4.5 and 4.0 respectively. It is concluded from this flux equation that the rate of Ni(II) stripping is directly proportional to the term $(1 + 6 [\text{SO}_4^{2-}])$. This relationship gives the following two statements:

- at lcr of SO_4^{2-} : F_b is independent of $[\text{SO}_4^{2-}]$; and
- at hcr of SO_4^{2-} : $F_b \propto [\text{SO}_4^{2-}]$.

The intercepts of the asymptotic lines are given in the body of the figure.

v) Effect of acetate ion concentration of the aqueous phase on the stripping flux of Ni(II) in the Ni(II)-Cyanex 272 complex- H_2A_2 -kerosene - $(\text{Na}^+, \text{H}^+) \text{SO}_4^{2-}\text{-Ac}^-$ system

Table LXXIV represents the flux variation data with the variation of acetate ion concentration in the aqueous phase. The $\log F_b$ vs. $\log [\text{Ac}^-]$ plot at $[\text{Ni(II)}]_{(0,\text{ini})} = 0.40 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 4.0$, $[\text{H}_2\text{A}_2]_{(0,\text{ini})} = 0.30 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.10 \text{ kmol/m}^3$ and Temp. = 303 K is given in Fig. 74. The experimental points yield a curve represented by:

$$\log F_b = -7.025 + \log (1 + 3.2 [\text{Ac}^-]) \quad (112)$$

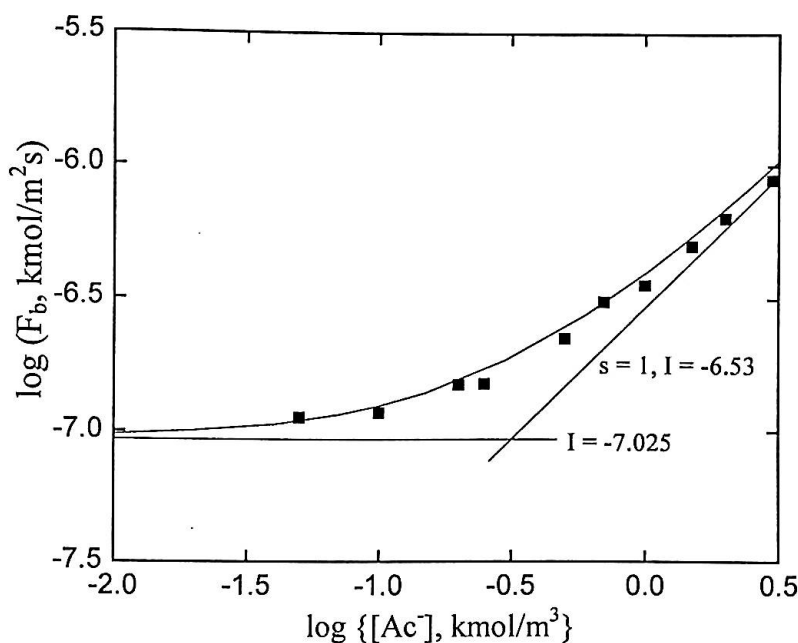


Fig. 74. Dependence of acetate ion concentration on the stripping flux of Ni(II) in the Ni(II)- H_2A_2 complex- H_2A_2 -kerosene - $(\text{Na}^+, \text{H}^+) \text{SO}_4^- \text{Ac}^-$ solution. (cf. Table LXXIV). $[\text{Ni(II)}]_{(o,ini)} = 0.40 \text{ kg/m}^3$, $\text{pH}_{(ini)} = 4.0$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.30, \text{ kmol/m}^3$, $[\text{SO}_4^-] = 0.10 \text{ kmol/m}^3$, $\Delta t = 0.5 \text{ s}$, Temp. = 303 K. Points are experimental, whilst the solid curve is theoretical represented by: $\log F_b = -7.025 + \log (1 + 3.2 [\text{Ac}^-])$.

Equation (112) represents that the stripping flux is directly proportional to the term $(1 + 3.2 [\text{Ac}^-])$ i.e. as $[\text{Ac}^-] \rightarrow 0$, F_b will be independent of $[\text{Ac}^-]$ concentration; whereas, as $[\text{Ac}^-] \rightarrow \infty$, F_b will be directly proportional to $[\text{Ac}^-]$. The intercept the asymptotic line at hcr is -6.53.

vi) Effect of temperature on the stripping flux of Ni(II) in the Ni(II)-Cyanex 272 complex- H_2A_2 -kerosene - $(\text{Na}^+, \text{H}^+) \text{SO}_4^- \text{Ac}^-$ system

The effect of temperature on the stripping flux of Ni(II) has been investigated at four sets of experimental parameters, viz. system (i); $\text{pH}_{(ini)} = 5$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.01 \text{ kmol/m}^3$, $[\text{SO}_4^-] = 0.01 \text{ kmol/m}^3$ and $[\text{Ac}^-] = 0.10 \text{ kmol/m}^3$; system (ii); $\text{pH}_{(ini)} = 2.50$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3$, $[\text{SO}_4^-] = 0.01 \text{ kmol/m}^3$ and $[\text{Ac}^-] = 0.10 \text{ kmol/m}^3$; system (iii); $\text{pH}_{(ini)} = 2.50$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3$, $[\text{SO}_4^-] = 1.00 \text{ kmol/m}^3$ and $[\text{Ac}^-] = 0.10 \text{ kmol/m}^3$ and system (iv); $\text{pH}_{(ini)} = 2.50$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3$, $[\text{SO}_4^-] = 1.00 \text{ kmol/m}^3$ and $[\text{Ac}^-] = 0.10 \text{ kmol/m}^3$. Related experimental data are collected in Table LXXV.

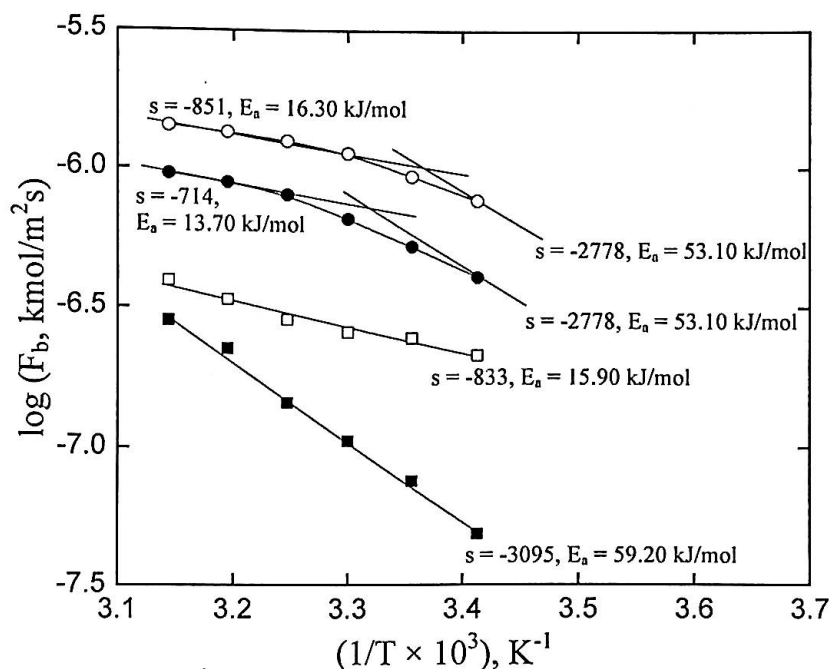


Fig. 75. Effect of temperature on the stripping flux of Ni(II) in the Ni(II)-H₂A₂ complex-H₂A₂-kerosene - (Na⁺,H⁺)SO₄⁼-Ac⁻ solution. (cf. Table LXXV).
 [Ni(II)]_(o,ini) = 0.40 kg/m³, Δt = 0.5 s; (■), pH_(ini) = 5.00, [H₂A₂]_(o,ini) = 0.01 kmol/m³, [SO₄⁼] = 0.01 kmol/m³, [Ac⁻] = 0.10 kmol/m³; (□), pH_(ini) = 2.50, [H₂A₂]_(o,ini) = 0.30 kmol/m³, [SO₄⁼] = 0.01 kmol/m³, [Ac⁻] = 0.10 kmol/m³; (●), pH_(ini) = 2.50, [H₂A₂]_(o,ini) = 0.30 kmol/m³, [SO₄⁼] = 0.01 kmol/m³, [Ac⁻] = 1.00 kmol/m³; (○), pH_(ini) = 2.50, [H₂A₂]_(o,ini) = 0.30 kmol/m³, [SO₄⁼] = 1.00 kmol/m³, [Ac⁻] = 0.10 kmol/m³.

The figure 75 shows the Arrhenius plots for the four systems described above. For the system (ii) i.e. system with high aqueous acidity together with high free extractant concentration, a straight line is obtained with slope equaling to -833; giving E_a = 15.90 kJ/mol. For systems (i) also, a straight line with slope -3095 is obtained and from this slope, E_a of 59.20 kJ/mol has been calculated.

On the other hand, for systems (iii) and (iv) straight lines are not obtained. With the temperature rise, the extent of flux variation is decreased. Actually curves are obtained for these two systems. From the slopes of the asymptotic or limiting lines of the curves, the activation energies have been calculated. In both cases, E_a of 53.1 kJ/mol is obtained at ltr; whereas this value is ~16 and 13 kJ/mol at htr for systems (iii) and (iv), respectively.

As in the other cases, the temperature dependence data have also been treated by the Activated Complex Theory. For this purpose, the $\log \left(\frac{F_b h}{kT} \right)$ values at different (1/T) values have been calculated. Moreover the values of log f(R) (to be used in calculating ΔS[±] values)

for each set of experimental parametric conditions have been calculated. The relevant data are collected in Table LXXVI. The $\log \left(\frac{F_b h}{kT} \right)$ vs. $(1/T)$ plots for the four systems under consideration are presented in Fig. 76.

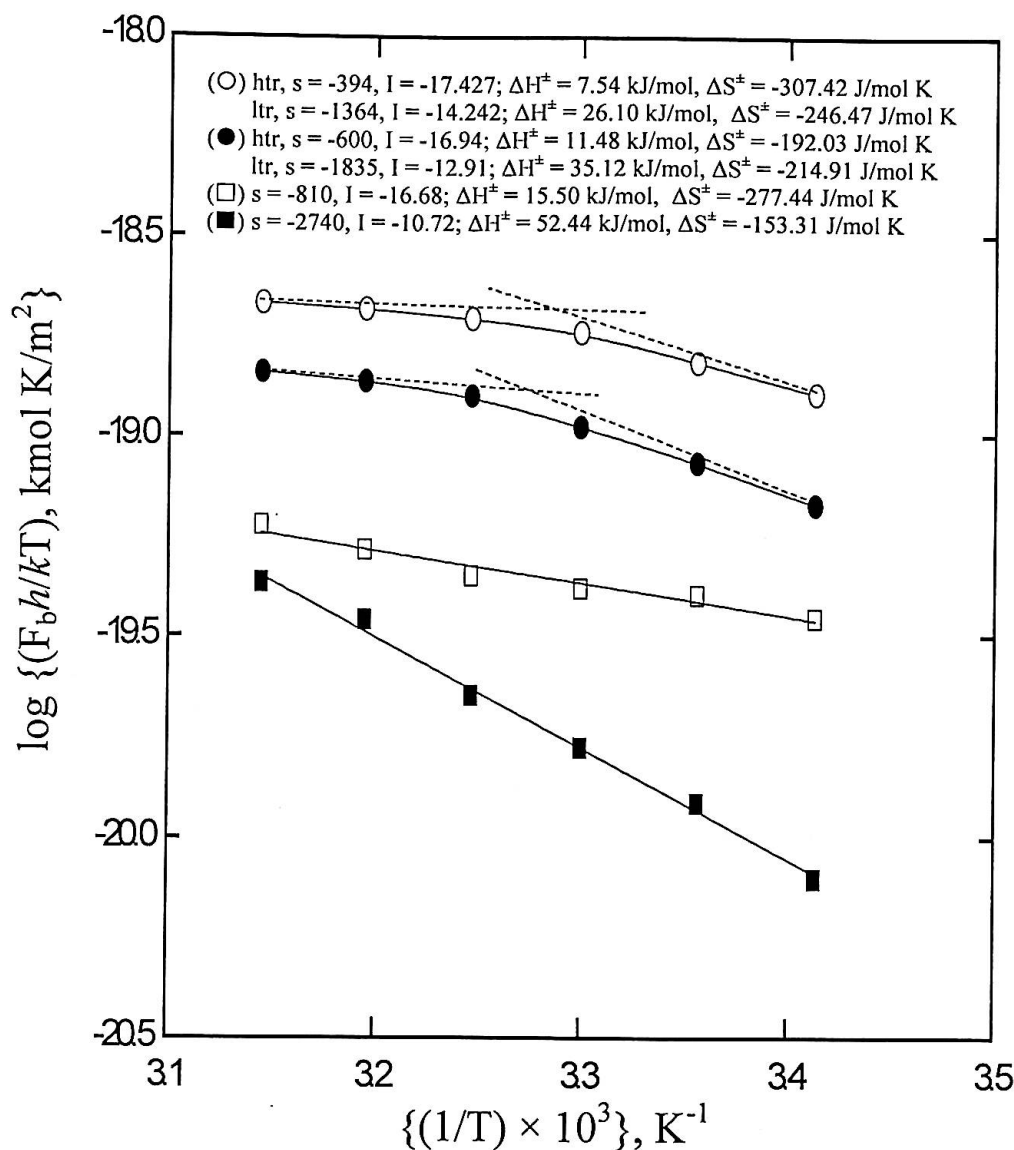


Fig. 76. The $\log \{(F_b h / kT)\}$ vs. $1/T$ plots in the backward extraction of Ni(II) in the Ni(II)- H_2A_2 complex-kerosene - $(Na^+, H^+) SO_4^{=}-Ac^-$ solution (cf. Table LXXVI). $[Ni(II)]_{(o,ini)} = 0.40$ kg/m³, $\Delta t = 0.5$ s; (■), $pH_{(ini)} = 5.00$, $[H_2A_2]_{(o,ini)} = 0.01$ kmol/m³, $[SO_4^{=}] = 0.01$ kmol/m³, $[Ac^-] = 0.10$ kmol/m³, $\log f(R) = -2.709$; (□), $pH_{(ini)} = 2.50$, $[H_2A_2]_{(o,ini)} = 0.30$ kmol/m³, $[SO_4^{=}] = 0.01$ kmol/m³, $[Ac^-] = 0.10$ kmol/m³, $\log f(R) = -2.183$; (●), $pH_{(ini)} = 2.50$, $[H_2A_2]_{(o,ini)} = 0.30$ kmol/m³, $[SO_4^{=}] = 0.01$ kmol/m³, $[Ac^-] = 1.00$ kmol/m³, $\log f(R) = -1.680$, (○), $pH_{(ini)} = 2.50$, $[H_2A_2]_{(o,ini)} = 0.30$ kmol/m³, $[SO_4^{=}] = 1.00$ kmol/m³, $[Ac^-] = 0.10$ kmol/m³, $\log f(R) = -1.363$. $h = 6.6252 \times 10^{-37}$ kJ s, $k = 1.38 \times 10^{-26}$ kJ/deg

From the slopes of the straight lines or the asymptotic lines at ltr and htr, the values of $\Delta H^\pm$ have been calculated. On the other hand, from the intercepts of the straight lines or the asymptotic lines at ltr and htr the values of $\Delta S^\pm$ have been calculated with the help of the $\log f(R)$ values calculated for each set of experimental parameters. Slopes, intercepts, $\Delta H^\pm$ and $\Delta S^\pm$ values are embodied in the figure; whereas $\log f(R)$ values are given in legends of figure.

vii) Evaluation of stripping rate constant (k_b) for Ni(II) stripping in the Ni(II)-Cyanex 272 complex- H_2A_2 - kerosene - (Na^+ , H^+) $SO_4^{=}$ - Ac^- system

From the intercepts of the straight lines or the asymptotic lines in Figs. 70 - 74, the values of $\log k_b$ at 303 K have been calculated on the basis of the following empirical relationship:

$$\begin{aligned} \log F_b = & \log k_b + \log [Ni^{2+}]_{(o,ini)} - \log (1 + 10^{-3.42} [H^+]^{-1}) - \log ([H_2A_2]^{0.5} + 2.5 [H_2A_2]_{(o)}) \\ & + \log (1 + 6 [SO_4^{=}]) + \log (1 + 3.2 [Ac^-]) \end{aligned} \quad (113)$$

The calculated $\log k_b$ values and the average $\log k_b$ with the standard deviation of estimated $\log k_b$ are given in Table I at 303 K. It is seen that the value of k_b at 303 K is $10^{-4.292}$ with standard deviation of $\log k_b$ being 0.004, The unit of k_b is found to be $kmol^{1/2} / m^{1/2} s$.

The value of $\log k_b$ has also been directly determined as the intercept of the $\log F_b$ vs. $\log f(R)$ plot (where, $\log f(R)$ represents the last five parts of Eq. (113). For all the conditions used for the experimental points in Figs. 70 - 74, the values of $\log f(R)$ have been calculated. The $\log f(R)$ values with the corresponding experimentally estimated $\log F_b$ values are given Table LXXVII. Figure 77 shows the $\log F_b$ vs. $\log f(R)$ plot at 303 K. The plot is indeed a good fit straight line ($R^2 = 0.975$) with slope 0.9544 (should be 1) and intercept of -4.4148. Therefore, the value of k_b estimated by this method is $10^{-4.4148} kmol^{1/2}/m^{1/2} s$. The average k_b value of $10^{-4.35} kmol^{1/2}/m^{1/2} s$ will be considered in the following section.

Table I. Evaluation of stripping rate constant (k_b) at 303 K in the Ni(II)-H₂A₂-complex-H₂A₂-kerosene/(Na⁺, H⁺) SO₄⁼ - Ac⁻ system

Fig. No.	Plot of log F _b vs.	[Ni] (o,ini) ₃ kmol/m ³	pH _(ini)	[H ₂ A ₂] _(o,ini) ₃ kmol/m ³	[SO ₄ ⁼] ₃ kmol/m ³	[Ac ⁻] ₃ kmol/m ³	Intercept (I)	*log k _b	Average log k _b	Standard deviation
70	log [Ni(II)] _(o,ini)	Variable	5.0	0.025	0.10	0.25	-4.750(hcr)	-4.274		
71	pH _(ini)	0.00682	Variable	0.025	0.10	0.25	-5.355(lcr) -1.900(lcr) -6.100(hcr) -2.700(lcr)	-4.303 -4.268 -4.279 -4.299		
72	log [H ₂ A ₂] _(o,ini)	0.00682	4.0 4.5	Variable		0.25	-6.700(lcr) -7.100(hcr) -7.100(lcr) -7.500(hcr)	-4.311 -4.313 -4.278 -1.280	-4.292	0.004
73	log [SO ₄ ⁼]	0.00682	4.0 4.5	0.30	Variable	0.25	-7.020(lcr) -6.225(hcr) -7.450(lcr) -6.615(hcr)	-4.314 -4.297 -4.311 -4.314		
74	log [Ac ⁻]	0.00682	4.0	0.30	0.10	Variable	-7.025(lcr) -6.530(hcr)	-4.263 -4.278		

* Basic equation for calculation: $\log F_b = \log k_b + \log [Ni(II)]_{(o,ini)} - \log [1 + 10^{3.42}[H^+]^{-1}] - \log (\sqrt{[H_2A_2]} + 2.5 [H_2A_2]) + \log (1+6[SO_4^{=}]) + \log (1+3.2 [Ac^-])$

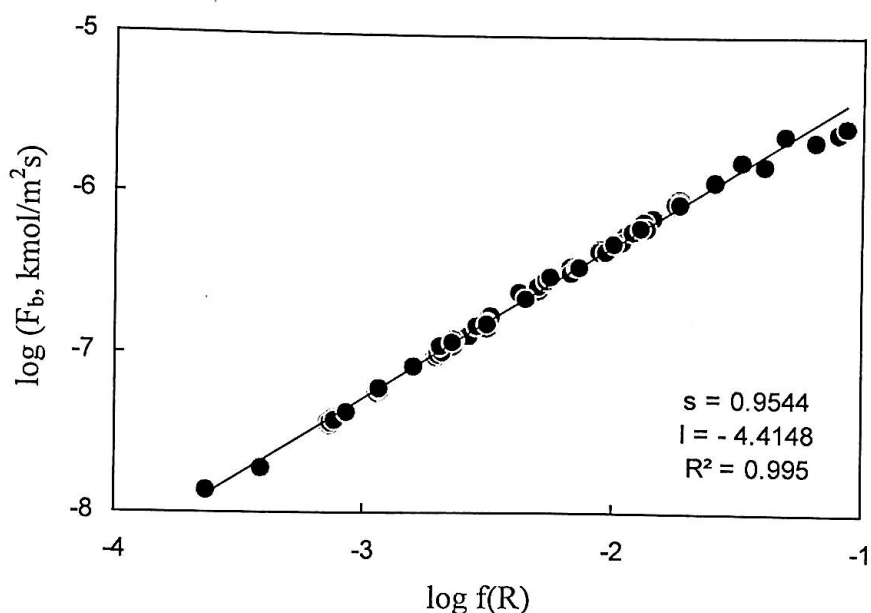


Fig. 77. Plot of $\log F_b$ vs. $\log f(R)$ for the estimation of the stripping rate constant (k_b) of Ni(II) in the Ni(II)-Cyanex 272 complex- H_2A_2 -kerosene - $(Na^+, H^+) SO_4^{2-}-Ac^-$ solution at 303 K, where, $\log f(R) = [\log [Ni(II)]_{(o,ini)} - \log (1 + 10^{-3.42} [H^+]^{-1}) - \log (\sqrt{[H_2A_2]_{(o)}} + 2.5 [H_2A_2]_{(o)}) + \log (1 + 6 [SO_4^{2-}]) + \log (1 + 3.2 [Ac^-])]$ (cf. Table LXXVII).

viii) Mechanism of stripping of Ni(II) from Ni(II)-Cyanex 272 complex by sulphate-acetato solution

From the above results, the following flux equation valid at 303K can be cited:

$$F_b = 10^{-4.35} [Ni(II)]_{(o,ini)} (1 + 10^{-3.42} [H^+]^{-1} ([H_2A_2]_{(o)}^{1/2} + 2.5 [H_2A_2]_{(o)}^{-1} (1 + 6 [SO_4^{2-}]) (1 + 3.2 [Ac^-]) \quad (114)$$

Equation (114) is a very complicated rate equation to use as whole to give the stripping mechanism. However, it can be reduced to the following form at lcr of SO_4^{2-} and Ac^- :

$$F_b = 10^{-4.35} [Ni(II)]_{(o,ini)} (1 + 10^{-3.42} [H^+]^{-1})^{-1} ([H_2A_2]_{(o)}^{1/2} + 2.5 [H_2A_2]_{(o)}^{-1})^{-1} \quad (115)$$

The above equation can be split into the following four forms:

(i) At low concentration regions of $[H^+]$ and $[H_2A_2]_{(o)}$:

$$F_b = 10^{-0.93} [Ni(II)]_{(o,ini)} [H^+] [H_2A_2]_{(o)}^{-1/2} \quad (116)$$

(ii) At lcr of H^+ and hcr of $[H_2A_2]_{(o)}$:

$$F_b = 10^{-1.33} [Ni(II)]_{(o,ini)} [H^+] [H_2A_2]_{(o,ini)}^{-1} \quad (117)$$

(iii) At hcr of H^+ and lcr of $[H_2A_2]_{(o)}$:

$$F_b = 10^{-4.35} [Ni(II)]_{(o,ini)} [H_2A_2]_{(o,ini)}^{-1/2} \quad (118)$$

(iv) At hcr of H^+ and $[H_2A_2]_{(o)}$:

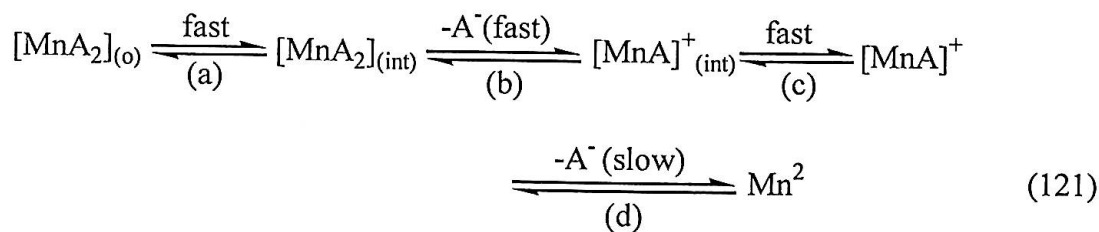
$$F_b = 10^{-4.75} [Ni(II)]_{(o,ini)} [H_2A_2]_{(o,ini)}^{-1} \quad (119)$$

The extraction equilibrium studies on the extraction of Ni(II) by Cyanex 272 have indicated that at lcr of extractant in the organic phase, $[NiA_2]$ exists in the organic phase; whereas, at hcr of extractant, the existing species is $[NiA_2 \cdot 2H_2A_2]$ or $[Ni(HA_2)_2 \cdot H_2A_2]$. Moreover, the loading of Cyanex 272 by Ni(II) has pointed out that at high loading, the existing species is 1 : 1 Ni^{2+}/A^- complex which may be $[NiAcA]$. In stripping studies, the organic phases have contained some free extractant and so the involvement of $[NiAcA]$ may be ruled out. It is considered in the following paragraphs of this section that the organic Ni(II)-species at lcr of the extractant is $[NiA_2]$ and that at hcr of the extractant is $[Ni(HA_2)_2 \cdot H_2A_2]$.

At lcr of H^+ and $SO_4^{=}$, the Eq. (116) can be modified by the monomeric model of Cyanex 272 to the following form:

$$F_b = 10^{-0.93} K_2^{1/2} P_{HA}^{-1} K_{aHA} [NiA_2]_{(o)} [A^-] \quad (120)$$

The rate equation (120d) contains two concentration terms; one in the organic phase and the other in the aqueous phase. Consequently, among the following diffusional and chemical reaction steps:



the reaction step represented by Eq. (121b) appears as the rate determining. The dissociation of first A^- from $[MnA_2]$ at the interface is considered to be a faster process. The diffusional processes involved in steps-121a and 121c are also faster than the step 121d. The activation energy measured at lcr of H^+ and H_2A_2 as well as of $SO_4^{=}$ and Ac^- (system (i) in the temperature dependence section) is 59.2 kJ/mol. This high activation energy supports that the chemical reaction step (d step in Eq. 121) stated above i.e. the dissociation of the second anion ligand (A^-) from the $[MnA]^+$ complex existing in the aqueous phase is the rate determining.

On the other hand, the rate Eq. (119) valid at hcr of H^+ and H_2A_2 can be modified to the following form with the help of the dimeric model of the extractant (*Vide.* eq. 41):

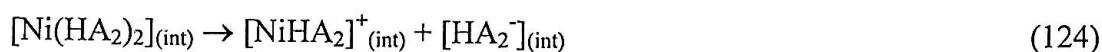
$$F_b = 10^{-4.75} K^{-1} a_{H_2A_2} P_{H_2A_2} [Ni(HA_2)_2.H_2A_2]_{(o)} [HA_2^-]^{-1}_{(int)} [H^+]^{-1}_{(int)} \quad (122)$$

The above rate equation involves three concentration terms; one in the organic phase and two at the interface. So no rate determining chemical reaction step can be assigned from this rate equation. Rather, it is concluded that the stripping at hcr of H^+ and H_2A_2 is controlled by diffusion of the reacting species to the reaction site or of the product species from the reaction site. This is supported by the activation energy of the system at hcr of H^+ and H_2A_2 (system (ii) in temperature dependence section) being only 15.90 kJ/mol.

The Eq. (117), the representative of the flux equation at lcr of H^+ and lcr of H_2A_2 , can be changed to Eq. (123) with the help of dimeric model of the extractant,

$$F_b = 10^{-1.33} K^{-1} a_{H_2A_2} P_{H_2A_2} [Ni(HA_2)_2.H_2A_2]_{(o)} [HA_2^-]^{-1}_{(int)} \quad (123)$$

This equation suggests the following reaction step as the rate determining:



On the other hand, at hcr H^+ and lcr of H_2A_2 , the rate Eq. (118) can be transformed to the following form:

$$F_b = 10^{-4.35} K_2^{1/2} P_{HA}^{-1} K_{aHA} [NiA_2]_{(o)} [A^-]^{-1} [H^+]^{-1} \quad (125)$$

Like Eq. (122), the Eq. (125) represents that the diffusion of the reacting species to the reaction site or of the product from the reaction site is rate determining.

The sulphate and acetate ions are found to enhance the rate probably by attacking the Ni(II)-complex to form the Ni(II) - SO_4^- or Ni(II) - Ac^- complex.

9. Studies on the kinetics of backward extraction or stripping of Zn(II) in the Zn(II)-Cyanex 272 complex- H_2A_2 -kerosene - SO_4^- (Na^+ , H^+) system

The title system has been investigated kinetically using the single drop (falling) technique as described below:

i) Dependence of the organic phase Zn(II) concentration on the flux of Zn(II) transfer during the stripping of Zn(II)-Cyanex 272 complex by sulphuric acid solution

The Zn(II) - transfer flux values at various $[\text{Zn(II)}]_{(o)}$ in the system: ($[\text{H}_2\text{A}_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$)- kerosene - ($\text{pH}_{(ini)} = 1.00$) - ($[\text{SO}_4^{=}] = 0.10 \text{ kmol/m}^3$) have been determined and given in Table LXXVIII. The $\log F_b$ vs. $\log [\text{Zn(II)}]_{(o,ini)}$ plot is shown in Fig. 78.

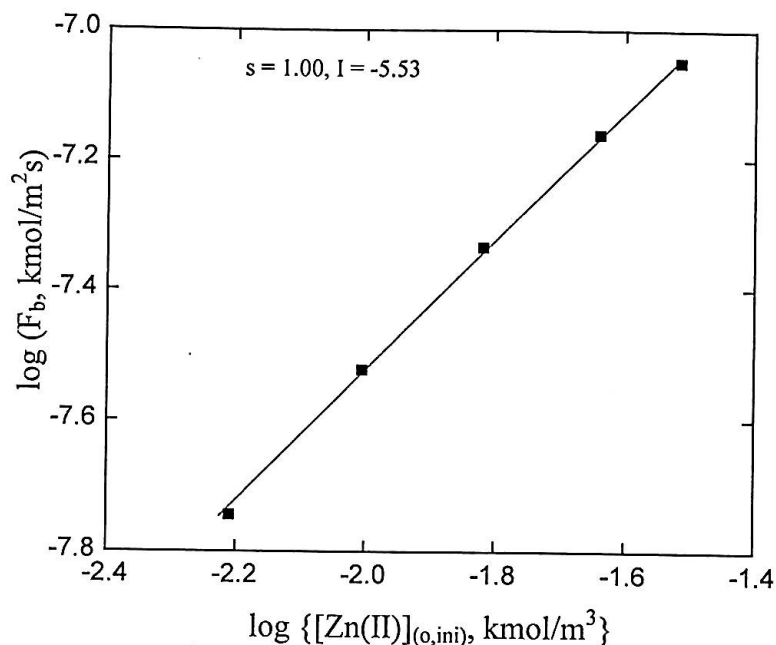


Fig. 78. Dependence of organic phase Zn(II) concentration on the flux of Zn(II) transfer during stripping of Zn-Cyanex 272 complex by sulphuric acid solution (*cf.* Table LXXVIII). $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.05 \text{ kmol/m}^3$, $[\text{SO}_4^{=}] = 0.10 \text{ kmol/m}^3$, $\text{pH}_{(ini)} = 1$, $\Delta t = 0.40 \text{ s}$, Temp. = 303 K, Column height = 0.90 m.

The plot is a straight line with unity slope and intercept of -5.53. It is concluded that the rate of backward extraction of Zn(II) in the title system is directly proportional to the initial Zn(II)-Cyanex 272 complex in the organic phase.

ii) Dependence of the aqueous pH on the flux of Zn(II) transfer during stripping of Zn(II) - Cyanex 272 complex by sulphuric acid solution

The related data on flux variation with aqueous pH for a particular set of experimental parameter are shown in Table LXXIX. The $\log F_b$ vs. $\text{pH}_{(ini)}$ plot is shown in Fig. 79.

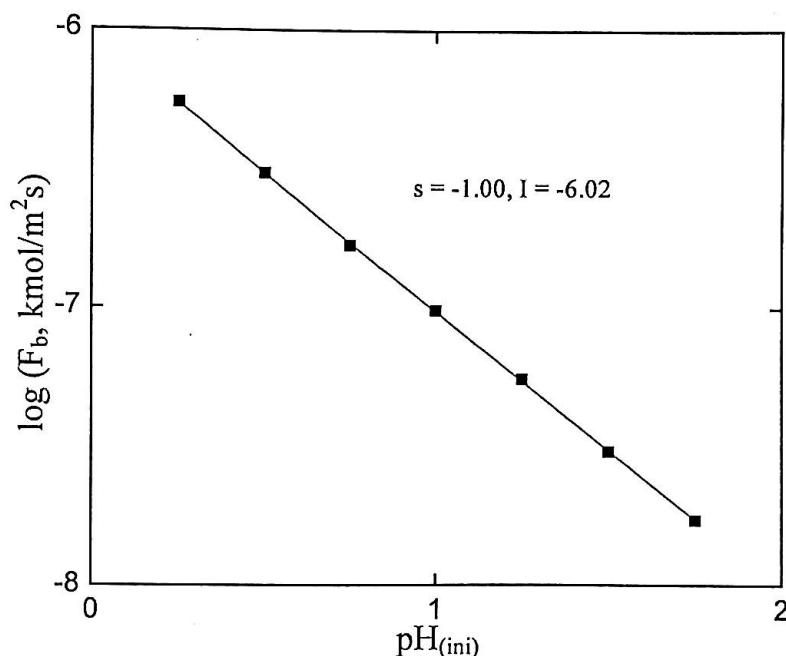


Fig. 79. Dependence of the aqueous pH on the flux of Zn(II) transfer during stripping of Zn-Cyanex 272 complex by sulphuric acid solution (*cf.* Table LXXIX). $[\text{Zn(II)}]_{(\text{o},\text{ini})} = \sim 1.00 \text{ kg/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o},\text{ini})} = 0.05 \text{ kmol/m}^3$, $[\text{SO}_4^{=}] = 1.00 \text{ kmol/m}^3$, $\Delta t = 0.4 \text{ s}$, Temp. = 303 K, Column height = 0.90 m.

The experimental points fall on a straight line of unity slope having intercept of -6.02. It is concluded from this result that the rate of Zn(II) stripping from Zn(II)-Cyanex 272 complex by sulphuric acid solution is directly proportional to H^+ concentration or inversely proportional to pH.

iii) Dependence of free extractant (H_2A_2) concentration in the organic phase on the flux of Zn(II) transfer during stripping of Zn(II)-Cyanex 272 complex by sulphuric acid solution

The relevant data are given in Table LXXX. The $\log F_b$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o},\text{ini})}$ plot of a system consisting of $[\text{Zn(II)}]_{(\text{o},\text{ini})} = \sim 1.0058 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 1.00$ and $[\text{SO}_4^{=}] = 0.10 \text{ kmol/m}^3$ at 303 K is given in Fig. 80.

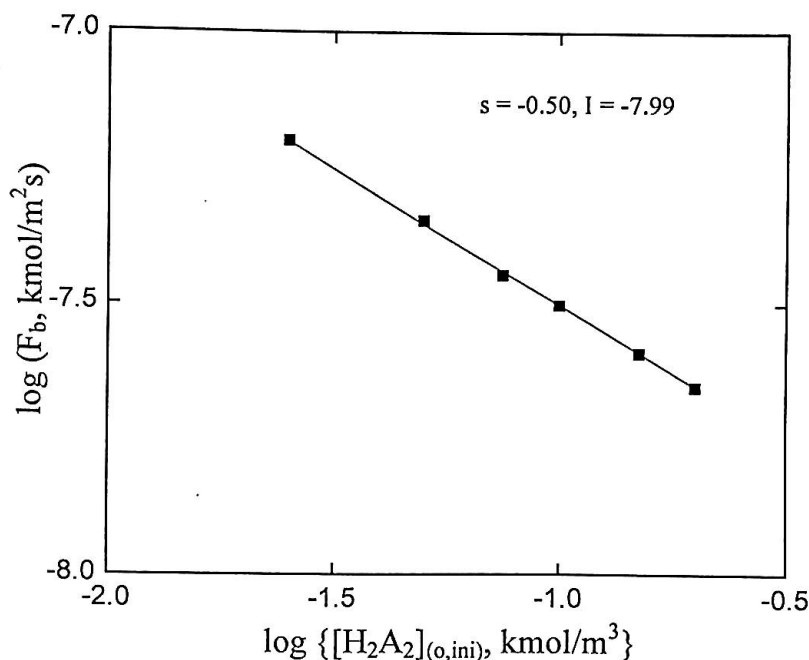


Fig. 80. Dependence of free extractant (H_2A_2) concentration in the organic phase on the flux of $Zn(II)$ transfer during stripping of Zn -Cyanex 272 complex by sulphuric acid solution (*cf.* Table LXXX). $[Zn(II)]_{(o,ini)} = \sim 1.0058 \text{ kg/m}^3$, $pH_{(ini)} = 1$, $[SO_4^{=}] = 0.1 \text{ kmol/m}^3$, $\Delta t = 0.4 \text{ s}$, Temp. = 303 K, Column height = 0.90 m.

A straight line is obtained with slope equating to -0.50 and intercept equaling to -7.90. The slope value indicates that the rate of stripping is inversely proportional to the square root of the extractant concentration in the organic phase.

iv) Dependence of sulphate ion concentration on the flux of $Zn(II)$ -transfer during stripping of $Zn(II)$ -Cyanex 272 complex by sulphuric acid solution

The data on the variation of flux (F_b) with the variation of sulphate concentration in the aqueous phase are presented in Table LXXXI. Figure 81 shows the $\log F_b$ vs. $\log [SO_4^{=}]$ plot. The experimental points do not yield a straight line; rather the experimental points can be put on a curve represented by:

$$\log F_b = -7.414 + \log (1 + 1.5 [SO_4^{=}]) \quad (126)$$

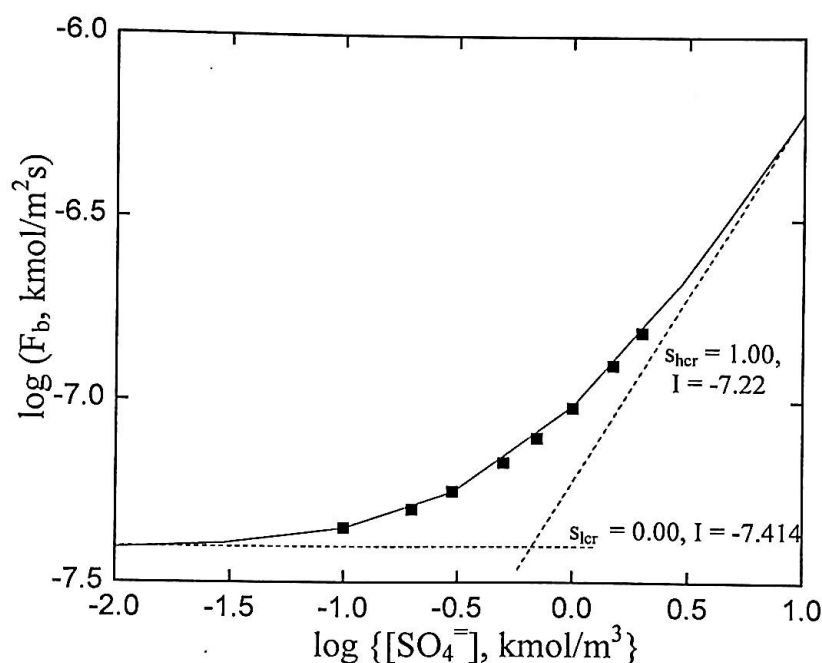


Fig. 81. Dependence of sulphate ion concentration of the aqueous phase on the flux of Zn(II) transfer during stripping of Zn-Cyanex 272 complex by sulphuric acid solution (*cf.* Table LXXXI). $[H_2A_2]_{(o,ini)} = 0.05 \text{ kmol/m}^3$, $[Zn(II)]_{(o,ini)} = \sim 1.00 \text{ kg/m}^3$, $pH_{(ini)} = 1.0$, $\Delta t = 0.4 \text{ s}$, Temp. = 303 K, Column height = 0.90 m.

Intercepts of the asymptotic lines are noted in the figure. It is concluded from this result that the stripping flux is independent of sulphate ion concentration in its lower concentration region; but at higher concentration region, the stripping flux is directly proportional to the sulphate ion concentration.

v) Effect of temperature on the flux of Zn(II) transfer during stripping of Zn(II) - Cyanex 272 complex by sulphuric acid solution

The stripping flux of Zn(II) transfer in the system ($[Zn(II)]_{(o,ini)} = 01 \text{ kg/m}^3$) - ($pH_{(ini)} = 0.5$) - ($[H_2A_2]_{(o,ini)} = 0.05 \text{ kmol/m}^3$) - ($[SO_4^{2-}] = 1 \text{ kmol/m}^3$) has been measured at different temperatures (288 - 318 K). The experimental data are shown in Table LXXXII. The Arrhenius plot is shown in Fig. 82. A straight line is not obtained. A curve is obtained with asymptotic slopes of -1300 and -2830 at htr and ltr, respectively; giving respective E_a values of 24.87 and 54.13 kJ/mol.

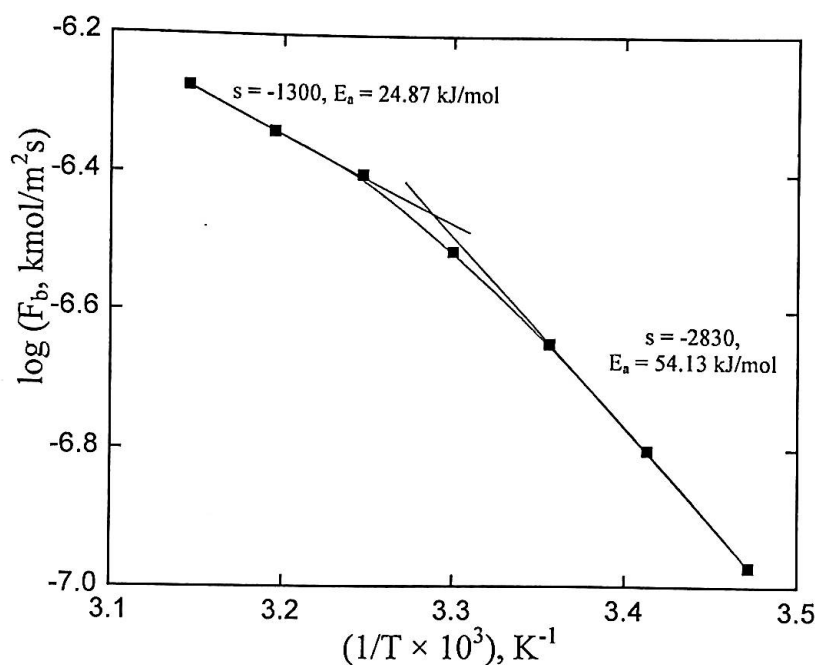


Fig. 82. Effect of temperature on the stripping flux of Zn(II) in $\text{ZnA}_2\text{-H}_2\text{A}_2\text{-kerosene} / \text{H}_2\text{SO}_4\text{-SO}_4^-$ system (cf. Table LXXXII). $[\text{Zn(II)}]_{(0,\text{ini})} = 1.00 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 0.5$, $[\text{H}_2\text{A}_2]_{(0,\text{ini})} = 0.05 \text{ kmol/m}^3$, $[\text{SO}_4^-] = 1 \text{ kmol/m}^3$, $\Delta t = 0.4 \text{ s}$, Column height = 0.90 m.

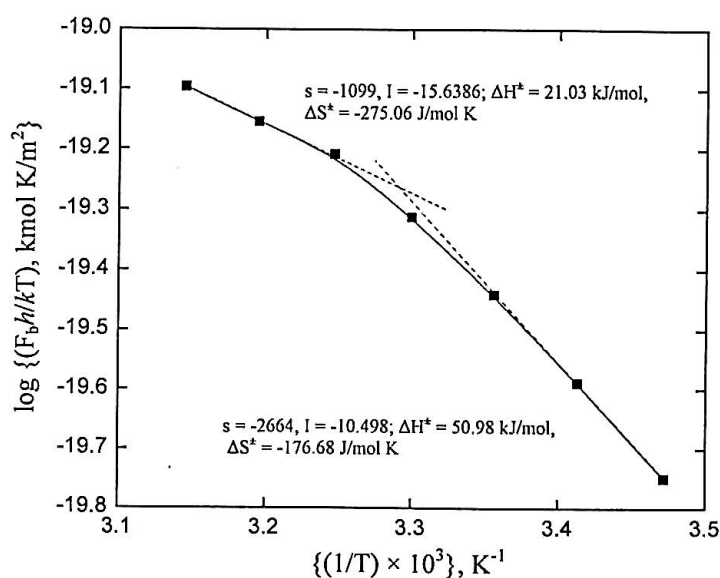


Fig. 83. The $\log \{(F_b h / kT)\}$ vs. $1/T$ plots in the backward extraction of Zn(II) in the $\text{Zn(II)-H}_2\text{A}_2$ complex- $\text{H}_2\text{A}_2\text{-kerosene} - (\text{Na}^+, \text{H}^+) \text{SO}_4^-$ system. $[\text{Zn(II)}]_{(0,\text{ini})} = 1.00 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 0.5$, $[\text{H}_2\text{A}_2]_{(0,\text{ini})} = 0.05 \text{ kmol/m}^3$, $[\text{SO}_4^-] = 1 \text{ kmol/m}^3$, $\Delta t = 0.4 \text{ s}$, Column height = 0.90 m, $\log f(R) = -1.266$, $h = 6.6252 \times 10^{-37} \text{ kJ s}$, $k = 1.38 \times 10^{-26} \text{ kJ/deg}$ (cf. Table LXXXIII).

The temperature dependence data have also been treated by the Activated Complex Theory. The $\log \left(\frac{F_b h}{kT} \right)$ vs. $(1/T)$ plot is shown in Fig. 83. The slope and intercept of the asymptotic line at htr give $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values of 21.03 kJ/mol and -275.06 J/mol K, respectively. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values at ltr are calculated to be ~51 kJ/mol and -176.8 J/mol K, respectively.

vi) Evaluation of stripping rate constant (k_b) for Zn(II) stripping from Zn(II) - Cyanex 272 complex by sulphuric acid solution

The values of $\log k_b$ at 303 K have been calculated from the intercepts of the straight lines in Figs. 78 - 80 and the asymptotic lines in Fig. 81 considering the following empirical rate equation:

$$\begin{aligned} \log F_b = & \log k_b + \log [\text{Zn(II)}]_{(o)} + \log [\text{H}^+] - 0.5 \log [\text{H}_2\text{A}_2]_{(o)} \\ & + \log (1 + 1.5 [\text{SO}_4^{=}]) \end{aligned} \quad (126)$$

The calculated $\log k_b$ values are presented in Table J. The average $\log k_b$ is -5.23 with standard deviation of 0.025. The $\log k_b$ value has also been estimated directly as the intercept of the $\log F_b$ vs. $[\log [\text{Zn(II)}]_{(o)} + \log [\text{H}^+] - 0.5 \log [\text{H}_2\text{A}_2]_{(o)} + \log (1 + 1.5 [\text{SO}_4^{=}])]$ plot. The calculated X-axis parameters and the corresponding experimentally determined Y-axis parameters are given in Table LXXXIV. The plot is given in Fig. 84. The plot is a good fit ($R^2 = 0.9997$) straight line with slope of 0.983 (should be unity) and intercept of -5.2495. So the estimated $\log k_b$ value obtained by this method is -5.2495, which is very close to the value obtained earlier (-5.23). So k_b value of $10^{-5.24} \text{ m}^{5/2}/\text{kmol}^{1/2} \text{ s}$ will be used in the following discussion.

Table J. Evaluation of stripping rate constant (k_b) in ZnA_2 - H_2A_2 -kerosene / H_2SO_4 - SO_4^- system at 303 K

Fig. No.	$[\text{Zn(II)}]_{(o,ini)}$, kmol/m^3	$\text{pH}_{(ini)}$	$[\text{H}_2\text{A}_2]_{(o,ini)}$, kmol/m^3	$[\text{SO}_4^-]$, kmol/m^3	Intercept, I	* $\log k_b$	Average $\log k_b$	Standard deviation
78	Variable	1.00	0.05	0.10	-5.530	-5.241		
79	0.0153	Variable	0.05	1.00	-6.020	-5.253		
80	0.0153	1.00	Variable	0.10	-7.990	-5.236	-5.23	0.025
81	0.0153	1.00	0.05	Variable	-7.412(lcr)	-5.187		
					-7.220(hcr)	-5.231		

* Value of $\log k_b$ is calculated based on the following relationship: $\log F_b = \log k_b + \log [\text{Zn(II)}]_{(o,ini)} - \text{pH} - 0.5 \log [\text{H}_2\text{A}_2] + \log (1+1.5 [\text{SO}_4^-])$
 * hcr = higher concentration region; lcr = lower concentration region.

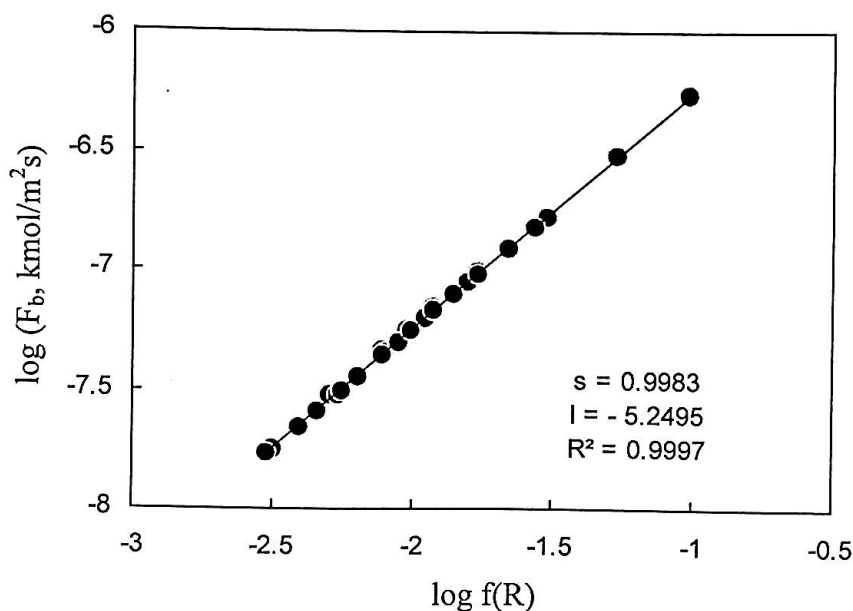


Fig. 84. Plot of $\log F_b$ vs. $\log f(R)$ for the estimation of backward extraction rate constant (k_b) of Zn(II) in ZnA_2 - H_2A_2 -kerosene - (Na^+, H^+) SO_4^- system at 303 K, where $\log f(R) = [\log [\text{Zn(II)}]_{(o,ini)} - \text{pH}_{(ini)} - 0.5 \log [\text{H}_2\text{A}_2] + \log (1 + 1.5 [\text{SO}_4^-])]$ (cf. Table LXXXIV).

vii) Mechanism of stripping of Zn(II) from Zn(II)-Cyanex 272 complex by sulphuric acid solution

Based on the kinetic measurements of the system at 303 K, the following empirical equation will represent the rate of stripping of Zn(II):

$$F_b = 10^{-5.24} [\text{Zn(II)}]_{(o,ini)} [\text{H}^+] [\text{H}_2\text{A}_2]_{(o,ini)}^{-0.5} (1 + 1.5 [\text{SO}_4^-]) \quad (127)$$

From the loading test, it has been identified that the extractable organic species in Zn(II) - Cyanex 272 system is $[\text{ZnA}_2]$. However, in presence of the surplus of free extractant, the solvated species $[\text{ZnA}_2 \cdot \text{H}_2\text{A}_2]$ may exist. So, the $[\text{Zn(II)}]_{(o)}$ term in Eq. (127) actually represents the concentration of $[\text{ZnA}_2 \cdot \text{H}_2\text{A}_2]_{(o)}$. Consequently, Eq. (127) can be split into the following two forms:

(i) At lcr of $[\text{SO}_4^-]$;

$$F_b = 10^{-5.24} [\text{ZnA}_2 \cdot \text{H}_2\text{A}_2]_{(o)} [\text{H}^+] [\text{H}_2\text{A}_2]_{(o)}^{-0.5} \quad (128)$$

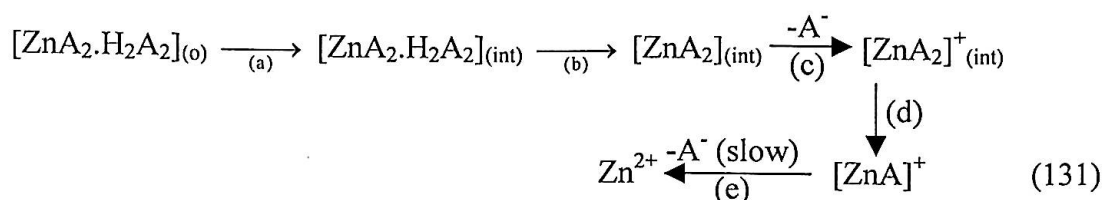
(ii) At hcr of $[\text{SO}_4^-]$;

$$F_b = 10^{-5.06} [\text{ZnA}_2 \cdot \text{H}_2\text{A}_2]_{(o)} [\text{H}^+] [\text{H}_2\text{A}_2]_{(o)}^{-0.5} [\text{SO}_4^-] \quad (129)$$

with the help of monomeric model of Cyanex 272, the rate / flux equation represented by Eq. (128) can be modified to Eq. (130):

$$F_b = 10^{-5.24} K_2^{1/2} P_{HA}^{-1} K_{aHA} [ZnA_2.H_2A_2]_{(o)} [A^-]^{-1} \quad (130)$$

Equation (130) follows that among the following steps:



The reaction step represented by Eq. (131e) is rate controlling i.e. the dissociation of the last anionic ligand in the aqueous phase is the solvent. As activation energy has not been measured at low lcr of $SO_4^{=}$, there is no way to support the above statement.

$$F_b = 10^{-5.06} K_2^{1/2} P_{HA}^{-1} K_{aHA} [ZnA_2.H_2A_2]_{(o)} [A^-]^{-1} [SO_4^{=}] \quad (132)$$

Equation (132) states that the slow rate-determining step may be:



Equation (133) as rate determining is supported by high activation energy (54 kJ/mol) obtained at ltr in 1 kmol/m³ $SO_4^{=}$ medium. However, the system might be intermediate controlling at 303 K as E_a decreases with increasing temperature.

10(a). Over-all discussion on the correlation of the respective equilibrium data with kinetic data

i) For Mn(II) extraction

The K_{ex} value for extraction of Mn(II) by Cyanex 272 has been estimated to be $10^{-6.17}$. The values of k_f and k_b have been evaluated as $10^{-3.60}$ and $10^{-4.88}$; so equilibrium constant derivable from rate study will be:

$$K_{ex (rate)} = (k_f/k_b) = (10^{-3.6} / 10^{-4.88}) = 10^{1.28}$$

Obviously, the equilibrium constant measured from equilibrium study does not at all match with the equilibrium constant derived from the rate study.

However, the situation can be reviewed otherwise. At hcr of H^+ , the value of k_f may be regarded as $10^{-8.334}$ (*vide*, Eq. (48)). On the other hand, Equation (97) indicates k_b value of $10^{-2.18}$; so that $K_{ex(rate)}$ appears as $10^{-6.15}$ which is very close to $10^{-6.17}$ that determined by the equilibrium study. This discrepancy might be attributed to the fact that in the common pH region where the forward and backward extraction rates have been determined the processes are chemically controlled; but at higher and lower pH regions of the forward and backward extractions, respectively, the processes are diffusion controlled.

ii) For Ni(II) extraction

The K_{ex} values derived for nickel(II) extraction by Cyanex 272 are $10^{-11.16}$ and $10^{-11.56}$ for systems having H_2A_2 concentration less than 0.05 kmol/m^3 and greater than 0.10 kmol/m^3 , respectively. The evaluated k_f and k_b values for this system are $10^{-3.7}$ and $10^{-4.35}$, respectively, so that the $K_{ex(rate)}$ will be $10^{-0.65}$; which is not at all near to the value obtained from the equilibrium study.

However, Eq. (65) (valid at hcr of H^+ and lc of SO_4^- and Ac^-) and Eq. (66) (valid at hc of H^+ and SO_4^- but lc of Ac^-) indicate that the values of k_f are $10^{-10.02}$ and $10^{-10.82}$, respectively. On the other hand, Eq. (116) (valid at lc of H^+ and H_2A_2) and Eq. (117) (valid at lc of H^+ but hc of H_2A_2) give the value of k_b as $10^{-0.93}$ and $10^{-1.33}$, respectively. So the minimum possible $K_{ex(rate)}$ will be $10^{-10.80} / 10^{-0.93} = 10^{-9.91}$, which is still more than 10 times greater than that obtained from the equilibrium study. The reason for this anomaly is not known, though one reason may be the loss of acetate buffer action in the whole range of pH used in the study resulting in decrease in interfacial pH.

iii) For Zn(II) extraction

In Zn(II) extraction by Cyanex 272, the values of K_{ex} obtained from the equilibrium study are $10^{-3.11}$ and $10^{-2.08}$ at lcr and hcr of extractant, respectively. The evaluated k_f value is $10^{-8.4}$, whereas k_b value is $10^{-5.24}$; giving $K_{ex(rate)} = 10^{-3.16}$, which is very close to that obtained from equilibrium study for lcr of extractant.

So the kinetic data obtained in the Mn(II) and Zn(II) systems matches well with the extraction equilibrium data ; and there exists some sort of discrepancy in the Ni(II) - extraction system.

10(b). Prediction on actual separation possibility of Mn(II), Ni(II) and Zn(II) by Cyanex 272

From equilibrium studies, the equations for $\log {}^C D$ (D at constant equilibrium parameters) have been derived as follows:

(i) For Mn(II)

$$\log {}^C D = -6.17 + 2\text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 1.9 [\text{SO}_4^{=}]) \quad (134)$$

(ii) For Ni(II)

At $[\text{H}_2\text{A}_2] < 0.05 \text{ kmol/m}^3$

$$\log {}^C D = -11.16 + 2 \text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 6.92 [\text{SO}_4^{=}]) - \log [\text{Ac}^-]$$

and at $[\text{H}_2\text{A}_2] > 0.10 \text{ kmol/m}^3$ (135)

$$\log {}^C D = -11.56 + 2\text{pH}_{(\text{eq})} + 3 \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 6.92 [\text{SO}_4^{=}]) - \log [\text{Ac}^-] \quad (136)$$

(iii) For Zn(II)

At lcr of extractant

$$\log {}^C D = -3.11 + 2\text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 2 [\text{SO}_4^{=}]) \quad (137)$$

at hcr of extractant

$$\log {}^C D = -2.08 + 2\text{pH}_{(\text{eq})} + 2 \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log (1 + 2 [\text{SO}_4^{=}]) \quad (138)$$

Defining $\beta_{\text{Zn/Mn}}$ as ${}^C D_{\text{Zn}} / {}^C D_{\text{Mn}}$; the value $\log \beta_{\text{Zn/Mn}}$ can be evaluated from the following relationships.

iv) At lcr of equilibrium extractant concentration of less than 0.05 kmol/m^3 ; one gets:

$$\begin{aligned} \log \beta_{\text{Zn/Mn}} &= \log {}^C D_{\text{Zn}} - \log {}^C D_{\text{Mn}} = 3.11 + 6.17 - \log (1 + 2 [\text{SO}_4^{=}]) \\ &\quad + \log (1 + 1.9 [\text{SO}_4^{=}]) \approx 3.06 \end{aligned} \quad (139)$$

with the help of Eqs. (134) and (137) and considering $\log (1 + 2 [\text{SO}_4^{=}])$

$$\approx \log (1 + 1.9 [\text{SO}_4^{=}])$$

(v) At hcr of equilibrium extraction concentration of greater than 0.1 kmol/m^3 ; one gets:

$$\begin{aligned}\log \beta_{\text{Zn/Mn}} &= \log {}^cD_{\text{Zn}} - \log {}^cD_{\text{Mn}} = -2.08 + 6.17 + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} \\ &= 4.09 + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})}\end{aligned}\quad (140)$$

with the help of Eqs. (134) and (138)

Again, on defining $\beta_{\text{Mn/Ni}}$ as ${}^cD_{\text{Mn}} / {}^cD_{\text{Ni}}$, the value of $\log \beta_{\text{Mn/Ni}}$ can be derived theoretically from the following relationships:

(vi) At lcr of equilibrium extractant concentration of less than 0.05 kmol/m^3 ; one gets from Eqs. (134) and (135)

$$\begin{aligned}\log \beta_{\text{Mn/Ni}} &= \log {}^cD_{\text{Mn}} - \log {}^cD_{\text{Ni}} = -6.17 + 11.16 - \log (1 + 1.9 [\text{SO}_4^=]) + \log \\ &(1 + 6.92 [\text{SO}_4^=]) + \log [\text{Ac}^-] \\ &= 4.99 + \log [(1 + 6.92 [\text{SO}_4^=]) / (1 + 1.9 [\text{SO}_4^=])] + \log [\text{Ac}^-]\end{aligned}\quad (141)$$

(vii) At hcr of equilibrium extractant concentration of greater than 0.10 kmol/m^3 ;

$$\begin{aligned}\log \beta_{\text{Mn/Ni}} &= \log {}^cD_{\text{Mn}} - \log {}^cD_{\text{Ni}} = -6.17 + 11.56 - 2 \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} + \log \\ &\left(\frac{1 + 6.92 [\text{SO}_4^=]}{1 + 1.9 [\text{SO}_4^=]} \right) + \log [\text{Ac}^-] \\ &= 5.39 - 2 \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} + \log \left(\frac{1 + 6.92 [\text{SO}_4^=]}{1 + 1.9 [\text{SO}_4^=]} \right) + \log [\text{Ac}^-]\end{aligned}\quad (142)$$

At last defining $\beta_{\text{Zn/Ni}}$ as ${}^cD_{\text{Zn}} / {}^cD_{\text{Ni}}$, the value of $\log \beta_{\text{Zn/Ni}}$ can be estimated theoretically from the following relationships:

(viii) At lcr of equilibrium extractant concentration of less than 0.05 kmol/m^3 , one gets from Eqs. (135) and (137)

$$\begin{aligned}\log \beta_{\text{Zn/Ni}} &= \log {}^cD_{\text{Zn}} - \log {}^cD_{\text{Ni}} = -3.11 + 11.16 - \log (1 + 2 [\text{SO}_4^=]) \\ &+ \log (1 + 6.92 [\text{SO}_4^=]) + \log [\text{Ac}^-] = 8.05 + \left(\frac{1 + 6.92 [\text{SO}_4^=]}{1 + 2 [\text{SO}_4^=]} \right) + \log [\text{Ac}^-]\end{aligned}\quad (143)$$

(ix) At hcr of equilibrium extractant concentration of greater than 0.1 kmol/m^3 , one gets from Eqs. (136) and (138):

$$\begin{aligned} \log \beta_{Zn/Ni} &= \log {}^C D_{Zn} - \log {}^C D_{Ni} = -2.08 + 11.56 - \log [H_2A_2]_{(o,eq)} + \log \left(\frac{1+6.92[SO_4^{=}]}{1+2[SO_4^{=}]} \right) \\ &+ \log [Ac^-] = 9.48 - [H_2A_2]_{(o,eq)} + \log \left(\frac{1+6.92[SO_4^{=}]}{1+2[SO_4^{=}]} \right) + \log [Ac^-] \end{aligned} \quad (144)$$

Now the relation between the % extraction and extraction ratio is as follows:

$$\% \text{ Extraction} = \left(\frac{D}{D+1} \right) \times 100 \quad (145)$$

So by determining the % extraction and the separation factor at a particular set of equilibrium parameter, the comment on the actually feasible separability can be predicted. This can be illustrated as follows:

At $pH_{(eq)} = 4$, $[H_2A_2]_{(o,eq)} = 0.025$, $[SO_4^{=}] = 0.1 \text{ kmol/m}^3$ and $[Ac^-] = 0.25 \text{ kmol/m}^3$, the calculated $\log {}^C D$ values of Mn(II), Ni(II) and Zn(II) using Eqs. (134), (135) and (137) are 0.15, -4.39 and 3.21, respectively. The values of the separation factors: $\beta_{Zn/Mn}$, $\beta_{Mn/Ni}$ and $\beta_{Zn/Ni}$ are calculated to be 1148, 34673 and 39810717, respectively. Moreover, at the experimental parameters stated, % extractions of Mn(II), Ni(II) and Zn(II) are 58.55, 0.0041 and 99.94%, respectively. Therefore, for the Zn/Ni system, separation factor of 39810717 together with Zn(II) and Ni(II) extraction percentages of 99.94% and 0.0041%, respectively direct that complete separation of Zn(II) from Ni(II) is possible in a single contact with 99.94% Zn(II) being extracted in the organic phase; whereas, 99.996% of Ni(II) left in the aqueous phase. At the same experimental condition, the separation factor of 1148 (${}^C D_{Zn} / {}^C D_{Mn}$; cf. Eq. 139) for Zn/Mn system together with respective Zn(II) and Mn(II) extraction percentages of 99.94% and 58.55% indicate that although the separation factor is quite high, the complete separation of Zn(II) from Mn(II) is not possible in a single stage operation. So for better separation of Zn(II) and Mn(II), an alternative experimental condition should be chosen where the value of separation factor will be very high and the extraction percentage of Mn(II) will be very low with high extraction percentage of Zn(II) (obviously less than 99.94%). This condition can be achieved by decreasing the equilibrium pH. For example, keeping all other parameters as stated previously but fixing $pH_{(eq)}$ value at 3.0; the $\beta_{Zn/Mn}$ will be unchanged as indicated by Eq. (139), but extraction percentages of Zn(II) and Mn(II) will be 94.2 and 1.56%, respectively.

Now, the situation regarding Mn(II) - Ni(II) separation will be examined. $\beta_{Mn/Ni}$ is 34737 (cf. Eq. 141). At $pH_{(eq)} = 5$; the % extractions of Mn(II) and Ni(II) are 99.3 and 0.406%, respectively. Therefore, single stage extraction can provide almost clear cut separation of Mn(II) from Ni(II).

SUMMARY

In the present work, $\text{Mn(II)-SO}_4^{2-}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene, $\text{Ni(II)-SO}_4^{2-}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-octanol-kerosene and $\text{Zn(II)-SO}_4^{2-}(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene extraction systems have been investigated thoroughly from both equilibrium and kinetic points of view. Results obtained from these investigations are summarized below:

A) Equilibrium study on $\text{Mn(II)-SO}_4^{2-}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene system

The title system has been investigated to find out the extent of extraction (expressed by extraction ratio, D) at various parametric conditions. The equilibration is determined to be 5 min. The $\log D$ values at constant equilibrium pH and extractant concentration are found to be independent of initial or equilibrium Mn(II) concentration in the aqueous phase following the general principle of solvent extraction chemistry. The $\log {}^C D$ (D at constant extractant concentration) vs. $\text{pH}_{(\text{eq})}$ and the $\log {}^C D$ (D at constant equilibrium pH) vs. $\log [\text{H}_2\text{A}_2]_{(\text{o})}$ plots are straight lines with slopes 2 and 1, respectively. These results indicate that 1 mole of extractant combines with 1 g ion of Mn(II) to form the extractable Mn(II) -species (MnA_2) with elimination of 2 g ion H^+ . Acetate ion used to buffer the solution has no effect on extraction ratio; but coexisting sulphate ion has an adverse effect on D . It is found that D is inversely proportional to the term $(1+1.9 [\text{SO}_4^{2-}])$. The temperature dependence of D data show that the process is endothermic with ΔH value of ~ 42 kJ/mol. The extraction equilibrium constant (K_{ex}) has been determined two ways and found to match well. The estimated K_{ex} value at 303 K is $10^{-6.17}$. The loading capacity is found to be maximum 9.52 g Mn(II) by 100 g extractant under consideration. The loading study also indicates that the extractable species at high loading is MnA_2 , which is not changed when extracted by surplus of extractant.

B) Equilibrium study on $\text{Ni(II)-SO}_4^{2-}\text{-Ac}^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-octanol-kerosene system

This system has included 3% (v/v) octanol in the organic phase to enhance phase separation by avoiding emulsion formation. Equilibration time in this system is 2 min. D values at constant equilibrium pH and extractant concentration is independent of Ni(II) concentration in the aqueous phase. The $\log {}^C D$ vs. $\text{pH}_{(\text{eq})}$ plots at constant equilibrium extractant concentrations are straight lines with the slope equaling to 2; whereas, the slopes of $\log {}^C D$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o,eq})}$ plots at some constant equilibrium pH values vary from 1 (at low concentration region, lcr) to 3 (at high concentration region, hcr). Hence, at lcr of

extractant the equilibrium reaction is: $\text{Ni}^{2+} + \text{H}_2\text{A}_{2(\text{o})} \rightleftharpoons [\text{NiA}_2]_{(\text{o})} + 2 \text{H}^+$; whereas, at hcr of extractant, it is: $\text{Ni}^{2+} + 3\text{H}_2\text{A}_{2(\text{o})} \rightleftharpoons [\text{Ni}(\text{HA}_2)_3]_{(\text{o})} + 2\text{H}^+$. Extraction ratio (D) is found to be inversely proportional to $(1+6.92 [\text{SO}_4^{2-}])$ and $[\text{Ac}^-]$. The extraction process is found to be endothermic with ΔH value of 54.66 kJ/mol. The extraction equilibrium constants (K_{ex}) are evaluated at 303 K to be $10^{-11.163}$ and $10^{-11.56}$ at lcr and hcr regions of extractant, respectively. The maximum loading capacity is calculated to be 21.28 g Ni(II) per 100 g extractant. At high loadings, the extracted species being suggested to be NiAcA as at maximum loading Ni(II): H_2A_2 mole ratio becomes 2:1.

C) Equilibrium study on $\text{Zn(II)-SO}_4^{2-}(\text{Na}^+, \text{H}^+)$ - Cyanex 272-kerosene system

The study has been carried out without buffering the aqueous phase as it is found to be extracted at relatively pH region. The equilibration time is 5 min. The $\log {}^cD$ vs. $\log [\text{Zn(II)}]_{(\text{o},\text{eq})}$ plot at constant equilibrium pH and extractant concentration is a horizontal straight line i.e. extraction ratio is not changed with equilibrium or initial Zn(II) concentration in the aqueous phase. The pH dependence of extraction ratio at constant equilibrium extractant concentration is found to be 2 i.e. 2 g ion H^+ is liberated during complexation of 1 g ion Zn(II). The $\log {}^cD$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o},\text{eq})}$ plots at constant equilibrium pH values are not straight lines but curves are obtained with asymptotic slopes of 1 and 2 at lcr and hcr of extractant, respectively. These results indicate that extraction at lcr of extractant occurs through the reaction: $\text{Zn}^{2+} + \text{H}_2\text{A}_{2(\text{o})} \rightleftharpoons [\text{ZnA}_2]_{(\text{o})} + 2 \text{H}^+$; but at hcr of extractant, it occurs via the reaction: $\text{Zn}^{2+} + 2\text{H}_2\text{A}_2 \rightleftharpoons [\text{Zn}(\text{HA}_2)_2]_{(\text{o})} + 2 \text{H}^+$. The extraction ratio, D is found to be an inverse function of $(1+2[\text{SO}_4^{2-}])$. The extraction equilibrium constants (K_{ex}) at lcr and hcr of extractant at 303 K are estimated to be $10^{-3.11}$ and $10^{-2.08}$, respectively. The extraction process is found to be endothermic but ΔH value increasing with increasing extractant concentration (~ 16 kJ/mol at 0.025 kmol/m^3 extractant being increased to ~ 46 kJ/mol at 0.30 kmol/m^3). The maximum loading capacity is estimated to be 11.5 g Zn(II) by 100 g extractant. At maximum loading, the species that exists in organic phase is ZnA_2 .

D) Kinetics of forward extraction of Mn(II) in $\text{Mn(II)-SO}_4^{2-}\text{-Ac}^-(\text{Na}^+, \text{H}^+)\text{-Cyanex 272-kerosene system}$

The rate of forward extraction of Mn(II) or flux (rate per unit area) of Mn(II)-transfer in the title system has been investigated thoroughly at 303 K using single falling

drop technique. In this technique, drop fall time taken as the reaction time. But there occurs some mass transfer during drop formation and coalescence. So this time has been evaluated as 0.5 s and this time has always been added to the drop fall time in calculating true flux values. The flux of Mn(II) transfer in the studied system is determined to be directly proportional to the initial Mn(II) concentration in the aqueous phase, directly proportional to the square root of the initial extractant concentration in the organic phase, inversely proportional to the initial hydrogen ion concentration in the aqueous phase, inversely proportional to the term $(1 + 1.58 [\text{SO}_4^{=}])$ and independent of acetate ion concentration in the aqueous phase. The rate constant (k_f) for the system at 303 K has been estimated to be $\sim 10^{-3.6}$. The activation energies (E_a) for the process at some parametric conditions have been estimated with the help of Arrhenius equation (using temperature dependence flux data). At high pH and low extractant concentration used, E_a is only ~ 15 kJ/mol, whereas, at low pH and high extractant concentration used, it is as high as ~ 52 kJ/mol. At intermediate conditions, E_a value in ltr is quite high but it is decreased to a low value in htr. On analyzing the rate or flux equation the mechanism has been proposed. Depending on extraction condition, either the chemical reaction step: $\text{Mn}^{2+} + \text{A}^- \xrightleftharpoons{\text{slow}} [\text{MnA}]^+$; or the diffusion of reactant or product species become the rate controlling. The $\Delta S^\ddagger$ value (highly negative) determined by applying the Activated Complex Theory to the temperature dependence flux data indicate that the slow chemical reaction step occurs via S_N2 mechanism; i.e. the attack or addition of the first anionic ligand (A^-) to the restricted coordination sphere of Mn(II) in forming higher co-ordinated activated complex is the rate determining.

E) Kinetic of forward extraction Ni(II)- $\text{SO}_4^{=}$ -Ac $^-(\text{Na}^+, \text{H}^+)$ - Cyanex 272-octanol-kerosene

For this system also the time for drop formation and coalescence time has been estimated to be $\Delta s = 0.5$ s. The slopes of $\log F_f$ vs. $\log [\text{Ni(II)}]$ plots at three experimental conditions are found to be unity; so that the reaction order with respect to Ni(II) concentration in the forward extraction is unity. The $\log F_f$ vs. pH plots are not straight lines; the experimental point-fitted curves can be expressed by equations. It is found that flux is inversely proportional to the factor $(1 + 10^{6.32} [\text{H}^+])$. The $\log F_f$ vs. $\log [\text{H}_2\text{A}_2]_{(o)}$ plots are straight lines with slopes ~ 0.50 . Therefore, the flux of Ni(II) transfer is directly proportional to the square root of the extractant concentration. Moreover, the Ni(II) transfer flux is also found to be inversely proportional to factors: $(1 + 6.3 [\text{SO}_4^{=}])$ and $(1 + 0.55 [\text{Ac}^-])$; this means that the rate is independent of $\text{SO}_4^{=}$ and Ac^- concentration in their lcr but

inversely proportional to $[\text{SO}_4^{=}]$ and $[\text{Ac}^-]$ at their hcr. The rate constant, k_f for Ni(II) extraction has been estimated to be $10^{-3.74}$. Analysis of the empirical flux equation shows that the extraction mechanism is changed with extraction condition. At low pH region, $\text{Ni}^{2+} + \text{A}^- \rightarrow [\text{NiA}]^+$ is the slow reaction step and this has been supported by high activation energy (~ 56 kJ/mol). But at higher pH region, the diffusion rather than the chemical reaction step mentioned above is the slow step which is supported by low activation energy of ~ 19 kJ/mol found at higher pH region. The temperature dependence flux data have also been treated by the Activated Complex Theory to evaluate the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The highly negative $\Delta S^\ddagger$ value indicates that the chemically controlled rate determining step occurs via $\text{S}_{\text{N}}2$ mechanism.

F) Kinetics of forward extraction of Zn(II) in Zn(II)- $\text{SO}_4^{=}$ (Na^+ , H^+) - Cyanex 272-kerosene system

In this case, drop fall time has been added to 0.4 s to estimate flux values. The $\log F_f$ vs. $\log [\text{Zn(II)}]_{(\text{ini})}$ plots at different experimental parameters are always straight lines with unity slope; so the reaction order with respect to Zn(II) concentration is unity in the forward extraction of Zn(II). The $\log F_f$ vs. $\log [\text{H}_2\text{A}_2]_{(\text{o,ini})}$ plots at different experimental parameters are not straight lines. The curves are obtained with limiting slopes of 0.5 and 1.0 at lcr and hcr of extractant respectively. The flux of Zn(II) transfer is found to be directly proportional to the term: $([\text{H}_2\text{A}_2]_{(\text{o})})^{1/2} + 1.07 [\text{H}_2\text{A}_2]_{(\text{o})}$. On the other hand, the $\log F_f$ vs. pH plots are straight lines in its lower region. It has been considered that at higher pH, the deviation from the unity sloped straight line is due to instantaneous interfacial pH change. The ΔpH ($= \text{pH}_{(\text{ini})} - \text{pH}_{(\text{int})}$) terms at various $\text{pH}_{(\text{ini})}$ have been calculated. It is concluded that the rate of Zn(II) extraction is inversely proportional to the interfacial pH rather than to initial pH. Zn(II) transfer flux in forward extraction is also found to be inversely proportional to the factor $(1 + 0.708 [\text{SO}_4^{=}])$. The value of rate constant, k_f for forward extraction of Zn(II) is found to be $10^{-8.26}$ and $10^{-7.44}$ at lcr and hcr of extractant, respectively. Activation energy is dependent of pH and extractant concentration. $\Delta H^\ddagger$ values are positive; whereas, $\Delta S^\ddagger$ values are always negative. Analysis of flux equation has been done to give extraction mechanism. The chemical reaction steps assigned as rate determining are $\text{Zn}^{2+} + \text{A}^- \rightarrow [\text{ZnA}]^+$ at lcr of extractant and $\text{Zn}^{2+}_{(\text{int})} + \text{HA}_2_{(\text{int})} \rightarrow [\text{ZnHA}_2]_{(\text{int})}^+$ at hcr of extractant.

G) Kinetics of backward extraction of Mn(II) in MnA_2 - H_2A_2 -kerosene - $\text{SO}_4^{=}$ - Ac^- (Na^+ , H^+) system

In flux calculation, drop formation and coalescence time of 0.5 s has been considered in studying this system. The $\log F_b$ vs. $\log [\text{Mn(II)}]_{(o)}$ plots are unity sloped straight lines indicating that the rate of stripping of Mn(II) from MnA_2 complex is directly proportional to the concentration of $[\text{MnA}_2]$ in the organic phase. The $\log F_b$ vs. $\text{pH}_{(ini)}$ plots are not straight lines. Curves with lower negative slope at lower pH region and higher negative slope at higher pH region are obtained. The flux is found to be inversely proportional to the factor: $(1 + 0.002 [\text{H}^+]^{-1})$. On the other hand, the extractant dependence rate plots ($\log F_b$ vs. $\log [\text{H}_2\text{A}_2]_{(o,ini)}$) are straight lines with slope of ~ -0.5 ; so that the stripping rate is inversely proportional to the extractant concentration. Sulphate ion concentration has an effect on the rate of stripping. The rate is found to be directly proportional to $(1 + 5.129 [\text{SO}_4^{=}])$. Acetate ion does not influence rate of stripping. The stripping rate constant, k_b has been estimated to be $10^{-4.88}$. Analysis of the stripping rate equation suggests the chemical reaction step: $\text{MnA}^+ \rightarrow \text{Mn}^{2+} + \text{A}^-$; occurring in the bulk aqueous phase is the rate determining. Activation energy, enthalpy of activation and entropy of activation have been determined from the temperature dependent flux data. Low activation energy at low pH region indicates that the diffusion rather than the above chemical reaction is rate determining; whereas high activation at high pH region supports that the process is chemically controlled at high pH region. High negative $\Delta S^\ddagger$ value indicates that the chemically controlled step occurs via $\text{S}_{\text{N}}2$ mechanism.

H) Kinetics of backward extraction of Ni(II) in Ni(II)-Cyanex 272 complex- H_2A_2 -kerosene - $\text{SO}_4^{=}$ - Ac^- (Na^+ , H^+) system

On considering drop formation and coalescence time of 0.5 s, this study has been performed. The $\log F_b$ vs. $\log [\text{Ni(II)}]_{(o,ini)}$ plot is a straight line with unity slope; i.e. the rate of stripping is directly proportional to the organic phase nickel(II) concentration. The $\log F_b$ vs. $\log \text{pH}_{(ini)}$ plots in backward extraction of Ni(II) are not straight lines. Curves are obtained with limiting slopes of zero and -1 at higher and lower pH regions, respectively. Flux of stripping of Ni(II) is found to be inversely proportional to $(1 + 10^{-3.42} [\text{H}^+])$. The log-log extractant concentration dependence flux plots are not straight lines too. The flux is found to be inversely proportional to $([\text{H}_2\text{A}_2]_{(o)}^{1/2} + 2.5 [\text{H}_2\text{A}_2]_{(o)})$. The rate of stripping of Ni(II) is found to be proportional to the factors: $(1 + 6 [\text{SO}_4^{=}])$ and $(1 + 3.2 [\text{Ac}^-])$. The

backward extraction rate (k_b) constant has been estimated to be $10^{-4.35}$. The values of activation energy, enthalpy of activation and entropy of activation have been calculated from the temperature dependence rate/flux data. The activation energy is found to be dependable on experimental parameters. Analysis of flux equation indicates that the dissociation of the second monomeric anion ligand (A^-) from NiA^+ in the bulk aqueous phase is rate controlling at low pH and extractant concentration region; whereas, that of the first dimeric anion ligand (HA_2^-) from $[Ni(HA_2)_2]$ at the interface is rate controlling. Activation energy has been used to identify the rate controlling steps at various experimental parameters. Depending on experimental conditions, the process may be chemical, diffusion or intermediate control. Here also, high negative $\Delta S^\ddagger$ value indicates that either of the chemical reaction steps mentioned above occurs through S_N2 mechanism.

I) Kinetics of backward extraction of Zn(II) in $ZnA_2/Zn(HA_2)_2$ - H_2A_2 -kerosene - $SO_4^{=}(Na^+,H^+)$ system

This system has also been investigated by the single falling drop technique considering drop formation and coalescence time of 0.4 s. It is found from unity slope of $\log F_b$ vs. $\log [Zn(II)]_{(o,ini)}$ plot that the reaction order with respect to the organic phase Zn(II) concentration is unity or the flux of Zn(II) transfer is directly proportional to ZnA_2 or $Zn(HA_2)_2$ concentration existing in the organic phase depending mainly on the concentration of free extractant prevailed in the system. Here the $\log F_b$ vs. $pH_{(ini)}$ and $\log F_b$ vs. $\log [H_2A_2]_{(o,ini)}$ plots are straight lines with slopes equaling to -1 and -0.5, respectively. These values indicate that the stripping rate of Zn(II) transfer is directly proportional to H^+ or inversely proportional to pH and also inversely proportional to the square root of free extractant concentration in the organic phase. It is also found from the $\log F_b$ vs. $\log [SO_4^{=}]$ plot that the stripping flux is directly proportional to the term $(1 + 1.5[SO_4^{=}])$. The value of the rate constant (k_b) for Zn(II) stripping has been evaluated to be $10^{-5.24}$. The temperature dependence flux data at only one set of experimental parameter has been considered for evolution of the values of E_a , $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The Arrhenius plot is a curve, whose limiting slopes give E_a of ~ 25 kJ/mol and ~ 54 kJ/mol at htr and ltr, respectively. From the treatment of temperature dependence data by the Activated complex theory, the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ have been calculated at htr and ltr. Analysis of the empirical flux equation at different extraction conditions has been done to propose mechanism. It is seen that either the chemical reaction $[ZnA]^+ \rightarrow Zn^{2+} + A^-$ (at ltr of $SO_4^{=}$) or $[ZnA]^+ + SO_4^{=} \rightarrow ZnSO_4 + A^-$ (at hcr of $SO_4^{=}$) occurring in the bulk aqueous phase, or the diffusion of species to or from the reaction site or both are rate controlling.

J) Correlation of kinetic data with equilibrium data

In case of Mn(II) extraction, the equilibrium constant ($K_{\text{ex}} = 10^{-6.17}$) derived from the equilibrium study does not match with that derived from the rate studies ($K_{\text{ex (rate)}} = k_f/k_b = 10^{-3.6}/10^{-4.88} = 10^{1.28}$). But the situation has reviewed otherwise. At hcr of H^+ , the k_f value shown above is changed to $10^{-8.33}$ and at lcr of H^+ , the k_b value is changed to $10^{-2.18}$; so that $K_{\text{ex (rate)}}$ appears as $10^{-8.33}/10^{-2.18} = 10^{-6.15}$; which is very close to $10^{-6.17}$, the equilibrium constant measured from equilibrium study. It should be mentioned here that at hcr of H^+ (low pH) the forward extraction is chemically controlled and at lcr of H^+ (high pH) the stripping rate is also chemically controlled; so the equilibrium constant obtainable from the rate studies at the parameter where extraction and stripping are both chemically controlled is comparable to the K_{ex} value obtained from the equilibrium study. All these statement are valid at 303 K.

The K_{ex} values derived from the equilibrium studies on Ni(II) extraction by Cyanex 272 at 303 K are $10^{-11.16}$ and $10^{-11.56}$ at lcr and hcr of extractant, respectively. The $K_{\text{ex (rate)}}$ at 303 K is found to be $10^{-3.7}/10^{-4.35} = 10^{0.65}$, which differs extensively from that obtained from the equilibrium study. However, at hcr of H^+ and SO_4^- and lcr of Ac^- , the k_f value is changed to $10^{-10.02}$; whereas, at lcr of H^+ and H_2A_2 , the k_b value is changed to $10^{-0.93}$. So the minimum possible $K_{\text{ex (rate)}}$ will be $10^{-10.82}/10^{-0.93} = 10^{-9.91}$; which is still more than 10 times greater than that obtained from the equilibrium study. The reason for this anomaly is not known, though one reason may be the loss of acetate buffer action in the some pH regions within the whole pH range used in the study, resulting in decrease in interfacial pH.

In Zn(II) extraction by Cyanex 272, the values of K_{ex} obtained from the equilibrium study are $10^{-3.11}$ and $10^{-2.08}$ at lcr and hcr of extractant, respectively at 303 K. The evaluated k_f value is $10^{-8.4}$, whereas k_b value of $10^{-5.24}$ giving $K_{\text{ex (rate)}} = 10^{-3.16}$; which is very close to that obtained from the equilibrium study for lcr of extractant.

So the kinetic data obtained in the Mn(II) and Zn(II) systems match well with the extraction equilibrium data and there exists some sort of discrepancy in Ni(II)-extraction system.

It has been shown that the values of separation factors $\beta_{\text{Zn/Mn}}$, $\beta_{\text{Mn/Ni}}$ and $\beta_{\text{Zn/Ni}}$ are 1148, 34673 and 39810717, respectively at $\text{pH}_{(\text{eq})} = 4$, $[\text{H}_2\text{A}_2]_{(\text{o,eq})} = 0.025 \text{ kmol/m}^3$, $\text{SO}_4^- = -0.10 \text{ kmol/m}^3$ and $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$. In this parametric condition, the percentage extractions of Mn(II), Ni(II) and Zn(II) are 58.55, 0.0041 and 99.94, respectively. Thus for the Zn(II)-Ni(II) system, separation factor of 39810717 together with Zn(II) and Ni(II)

extraction percentages of 99.94 and 0.0041, respectively direct that complete separation of Zn(II) from Ni(II) is possible in a single contact with 99.94% Zn(II) being extracted in the organic phase; whereas 99.996% Ni(II) is left in the aqueous phase. At the same experimental condition, the separation factor 1148 for Zn/Mn system together with respective Zn(II) and Mn(II) extraction percentages of 99.94 and 58.55 indicate that the complete separation is not possible in single-stage operation. So for better separation of Zn(II) from Mn(II), an alternative experimental condition should be chosen where the value of $\beta_{Zn/Mn}$ will be very high and extraction percentage of Mn(II) will be very low with high extraction % on Zn(II) (obviously less than 99.94%). This condition can be achieved by lowering the equilibrium pH. For example, on fixing $pH_{(eq)}$ value of 3 (maintaining other conditions unchanged), $\beta_{Zn/Ni}$ will be unchanged; but the extraction percentage of Zn(II) and Mn(II) will be 94.2 and 1.56%, respectively.

In case of Mn(II) - Ni(II) separation, $\beta_{Mn/Ni}$ is 34737. At equilibrium pH of 5, the extraction percentage of Mn(II) and Ni(II) are 99.3 and 0.406 %, respectively. Therefore, single stage extraction can provide clear-cut separation of Mn(II) from Ni(II).

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EXPERIMENTAL DATA

Table I. Data for the construction of calibration curve for the estimation of Mn(II) by spectrophotometric technique (Fig. 1).

Number of observation	Wavelength, nm	Concentration of Mn(II), g/L	Absorbance
		0.0000	0.000
1	545	0.0022	0.071
2		0.0033	0.120
3		0.0044	0.140
4		0.0055	0.182
5		0.0077	0.253
6		0.0100	0.335

Table II. Data for the construction of calibration curve for the estimation of Ni(II) by spectrophotometric technique (Fig. 2).

Number of observation	Wavelength, nm	Concentration of Ni(II), g/L	Absorbance
		0.000	0.00
1	445	0.002	0.08
2		0.004	0.16
3		0.006	0.24
4		0.008	0.32
5		0.010	0.40
6		0.012	0.47

Table III. Data for the construction of calibration curve for the estimation of Mn(II) by atomic absorption spectrophotometric technique (Fig. 3).

Number of observation	Wavelength, nm	Concentration of Mn(II), g/L	Absorbance
		0.0000	0.0000
1	279.5	0.0020	0.2520
2		0.0030	0.3950
3		0.0050	0.6830
4		0.0075	1.0020
5		0.0100	1.3199

Table IV. Data for the construction of calibration curve for the estimation of Ni(II) by atomic absorption spectrophotometric technique (Fig. 4).

Number of observation	Wavelength, nm	Concentration of Ni(II), g/L	Absorbance
		0.0000	0.0000
1		0.0005	0.0150
2		0.0010	0.0320
3	232.00	0.0015	0.0450
4		0.0020	0.0625
5		0.0030	0.0940
6		0.0040	0.1279

Table V. Data for the construction of calibration curve for the estimation of Zn(II) by atomic absorption spectrophotometric technique (Fig. 5).

Number of observation	Wavelength, nm	Concentration of Zn(II), g/L	Absorbance
0		0.00000	0.000
1		0.00025	0.112
2		0.00050	0.230
3	213.9	0.00075	0.335
4		0.00100	0.443
5		0.00150	0.654

Table VI. Effect of phase contact time on the extraction of Mn(II) from sulfate-acetato medium by Cyanex 272 in kerosene. $[\text{Mn(II)}]_{(\text{ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.60$, Temperature = $(303 \pm 0.50) \text{ K}$, O/A (Phase ratio) = 1 (Fig. 6).

Time, min	$[\text{Mn(II)}]_{\text{kg/m}^3}$	$[\text{Mn(II)}]_{(\text{o})}, \text{kg/m}^3$	Concentration ratio ($[\text{Mn(II)}]_{(\text{o})} / [\text{Mn(II)}]_{(\text{i})}$)
0.25	0.350	0.050	0.14
0.50	0.300	0.100	0.33
0.75	0.265	0.135	0.51
1.00	0.238	0.162	0.68
1.50	0.190	0.210	1.11
2.00	0.148	0.252	1.70
2.50	0.124	0.276	2.23
3.00	0.106	0.294	2.77
3.50	0.098	0.302	3.08
4.00	0.090	0.310	3.44
5.00	0.090	0.310	3.44
6.00	0.090	0.310	3.44

Table VII. Effect of metal ion concentration on the extraction of Mn(II) by Cyanex 272 in kerosene. $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.018 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.60$, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1, Equilibration time = 5 min (Fig. 7).

$[\text{Mn(II)}]_{(\text{ini})}, \text{kg/m}^3$	$[\text{Mn(II)}]_{(\text{ini})}, \text{kmol/m}^3$	$\log ([\text{Mn(II)}]_{(\text{ini})}, \text{kmol/m}^3)$	$\text{pH}_{(\text{eq})}$	$[\text{Mn(II)}]_{(\text{eq})}, \text{kg/m}^3$	$[\text{Mn(II)}]_{(\text{o,eq})}, \text{kg/m}^3$	D	$\log D$	* $\log {}^c D$ at $\text{pH}_{(\text{Const.})} = 4.60$ and $[\text{H}_2\text{A}_2]_{(\text{o, const.})} = 0.025 \text{ kmol/m}^3$
0.165	0.0030	-2.523	4.60	0.0106	0.1894	17.87	1.25	1.314
0.385	0.0070	-2.155	4.58	0.0250	0.3580	14.32	1.16	1.331
0.588	0.0107	-1.971	4.57	0.0256	0.5350	10.17	1.01	1.284
0.972	0.0177	-1.752	4.55	0.1330	0.8390	6.31	0.80	1.310
1.247	0.0227	-1.644	4.53	0.2460	1.0010	4.07	0.61	1.300
1.958	0.0356	-1.449	4.52	0.7470	1.2110	1.62	0.21	1.300

* $\log {}^c D_{[\text{H}_2\text{A}_2] = 0.025 \text{ kmol/m}^3}^{\text{pH} = 4.60} = \log D + 2 (\text{pH}_{(\text{const.})} - \text{pH}_{(\text{eq})}) + \{ \log [\text{H}_2\text{A}_2]_{(\text{const.})} - \log [\text{H}_2\text{A}_2]_{(\text{ini.})} - [\text{Mn(II)}]_{(\text{o,eq})} \}$ (all concentration terms are in kmol/m^3).

Table VIII. Effect of equilibrium pH on the extraction of Mn(II) by Cyanex 272 in kerosene. $[\text{Mn(II)}]_{(\text{ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, Temperature = $(303 \pm 0.50) \text{ K}$, Equilibration time = 5 min, O/A = 1 (Fig. 8).

$\text{pH}_{(\text{eq})}$	$[\text{Mn(II)}]_{(\text{aq})}$, kg/m^3	$[\text{Mn(II)}]_{(\text{o})}$, kg/m^3	Extraction ratio (D)	log D	* $\log {}^c\text{D}_{[\text{H}_2\text{A}_2] = 0.025 \text{ kmol/m}^3}$
<i>i) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3 = [\text{H}_2\text{A}_2]_{(\text{o,eq})} = \text{chosen as constant}$</i>					
4.64	0.0174	0.3826	21.980	1.342	1.484
4.49	0.0366	0.3660	10.000	1.000	1.135
4.35	0.0673	0.3330	4.950	0.694	0.815
4.22	0.0900	0.3100	3.440	0.537	0.648
4.20	0.0932	0.3068	3.290	0.517	0.627
4.18	0.1090	0.2910	2.670	0.430	0.525
4.05	0.1456	0.2544	1.750	0.242	0.331
3.90	0.2080	0.1920	0.923	-0.035	0.030
3.84	0.2332	0.1668	0.720	-0.146	-0.089
3.81	0.2560	0.1440	0.565	-0.250	-0.202
3.77	0.2626	0.1374	0.523	-0.281	-0.235
3.58	0.3200	0.0800	0.250	-0.602	-0.576
3.39	0.3625	0.0375	0.103	-0.985	-0.973
3.20	0.3815	0.0185	0.048	-1.314	-1.307
<i>ii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3 = [\text{H}_2\text{A}_2]_{(\text{o,eq})} = \text{chosen as constant}$</i>					
4.45	0.0084	0.3916	46.619	1.669	1.701
4.19	0.0282	0.3718	13.184	1.120	1.150
4.00	0.0515	0.3485	6.767	0.824	0.852
3.82	0.1176	0.2824	2.401	0.380	0.403
3.54	0.2252	0.1748	0.776	-0.110	-0.096
3.37	0.3046	0.0954	0.313	-0.505	-0.497
3.19	0.3506	0.0494	0.141	-0.853	-0.847

* $\log {}^c\text{D}_{[\text{H}_2\text{A}_2] = 0.025 \text{ kmol/m}^3} = \log D + \{ \log 0.025 - \log (0.025 - [\text{Mn(II)}]_{(\text{o})}) \}$; and

$\log {}^c\text{D}_{[\text{H}_2\text{A}_2] = 0.100 \text{ kmol/m}^3} = \log D + \{ \log 0.10 - \log (0.10 - [\text{Mn(II)}]_{(\text{o})}) \}$; all concentration terms are in kmol/m^3 since extractant dependence is found to be unity.

Table IX. Effect of extractant (Cyanex 272) concentration on the extraction ratio of Mn(II) from aqueous sulfate - acetato medium. $[\text{Mn(II)}]_{(\text{ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1 (Fig. 9).

$[\text{H}_2\text{A}_2]_{(\text{o,ini})}$ kmol/m ³	$\log ([\text{H}_2\text{A}_2]_{(\text{o,ini})})$ kmol/m ³	$\text{pH}_{(\text{eq})}$	$[\text{Mn(II)}]_{(\text{eq})}$ kg/m ³	$[\text{Mn(II)}]_{(\text{o,eq})}$ kg/m ³	D	$\log D$	* $\log {}^cD$	$[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ kmol/m ³	$\log [\text{H}_2\text{A}_2]_{(\text{o,eq})}$ kmol/m ³
<i>i) $\text{pH}_{(\text{ini})} = 3.75$, $\text{pH}_{(\text{eq})} = 3.74$, ${}^cD = D$ at const. equilibrium pH of 3.74</i>									
0.025	-1.602	3.74	0.3005	0.0995	0.33	-0.48	-0.48	0.0232	-1.635
0.030	-1.523	3.74	0.2665	0.1335	0.50	-0.30	-0.30	0.0276	-1.559
0.033	-1.481	3.74	0.2540	0.1460	0.57	-0.24	-0.24	0.0303	-1.518
0.051	-1.292	3.73	0.2092	0.1908	0.91	-0.04	0.06	0.0475	-1.323
0.054	-1.268	3.73	0.1954	0.2046	1.05	0.02	0.00	0.0503	-1.299
0.080	-1.097	3.73	0.1504	0.2496	1.66	0.22	0.20	0.0755	-1.122
0.100	-1.000	3.73	0.1255	0.2745	2.19	0.34	0.32	0.0950	-1.022
0.150	-0.824	3.72	0.0917	0.3083	3.36	0.56	0.52	0.1440	-0.841
0.200	-0.699	3.72	0.0746	0.3254	4.36	0.64	0.60	0.1941	-0.712
<i>ii) $\text{pH}_{(\text{ini})} = 4.15$, $\text{pH}_{(\text{eq})} = 4.13$, ${}^cD = D$ at const. equilibrium pH of 4.13</i>									
0.025	-1.602	4.13	0.1456	0.2544	1.75	0.244	0.24	0.0204	-1.690
0.030	-1.523	4.13	0.1047	0.2953	2.82	0.45	0.45	0.0246	-1.609
0.033	-1.481	4.12	0.0995	0.3005	3.02	0.48	0.50	0.0275	-1.561
0.051	-1.292	4.10	0.0774	0.3226	4.17	0.62	0.68	0.0451	-1.346
0.054	-1.268	4.09	0.0746	0.3254	4.36	0.64	0.72	0.0481	-1.318
0.080	-1.097	4.08	0.0505	0.3495	6.92	0.84	0.94	0.0736	-1.133
0.100	-1.000	4.07	0.0430	0.3570	8.31	0.92	1.04	0.0935	-1.029
0.150	-0.824	4.06	0.0318	0.3682	12.59	1.10	1.24	0.1433	-0.844
0.200	-0.699	4.06	0.0243	0.3757	15.49	1.19	1.33	0.1932	-0.714
<i>iii) $\text{pH}_{(\text{ini})} = 4.45$, $\text{pH}_{(\text{eq})} = 4.35$, ${}^cD = D$ at const. equilibrium pH of 4.35</i>									
0.025	-1.602	4.35	0.0569	0.3431	6.03	0.78	0.78	0.0188	-1.726
0.030	-1.523	4.34	0.0421	0.3579	8.50	0.93	0.95	0.0235	-1.629
0.033	-1.481	4.34	0.0412	0.3588	8.71	0.94	0.96	0.0265	-1.577
0.051	-1.292	4.33	0.0259	0.3741	14.44	1.16	1.20	0.0442	-1.355
0.054	-1.268	4.33	0.0237	0.3763	15.85	1.20	1.24	0.0471	-1.327
0.080	-1.097	4.33	0.0167	0.3833	22.95	1.36	1.40	0.0730	-1.137
0.100	-1.000	4.32	0.0134	0.3866	28.85	1.46	1.52	0.0930	-1.032
0.150	-0.824	4.32	0.0090	0.3910	43.44	1.64	1.70	0.1430	-0.845
0.200	-0.699	4.32	0.0075	0.3925	52.33	1.72	1.78	0.1929	-0.715

* $\log {}^cD = \log D + 2$ (constant $\text{pH}_{(\text{eq})}$ chosen - $\text{pH}_{(\text{eq})}$ experimental) and $[\text{H}_2\text{A}_2]_{(\text{o,eq})} = [\text{H}_2\text{A}_2]_{(\text{o,ini})} - [\text{Mn(II)}]_{(\text{o})}$; $[\text{Mn(II)}]_{(\text{o})}$ in kmol/m³.

Table X. Effect of temperature on the extraction ratio of Mn(II) being extracted by Cyanex 272. $[\text{Mn(II)}]_{(\text{ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, Equilibration time = 5 min, O/A = 1 (Fig. 10).

Temp., K	$(1/T) \times 10^3, \text{K}^{-1}$	$\text{pH}_{(\text{eq})}$	$[\text{Mn(II)}]_{(\text{aq})}, \text{kg/m}^3$	$[\text{Mn(II)}]_{(\text{o})}, \text{kg/m}^3$	D	log D	*log $^{\text{c}}\text{D}$
i) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.25$, Const. $\text{pH}_{(\text{eq})}$ Chosen = 4.20							
288	3.472	4.19	0.1563	0.2437	1.560	0.193	0.278
293	3.413	4.19	0.1270	0.2730	2.150	0.333	0.429
298	3.356	4.20	0.1140	0.2860	2.510	0.400	0.501
303	3.300	4.20	0.0932	0.3068	3.300	0.527	0.637
308	3.247	4.21	0.0727	0.3273	4.500	0.653	0.750
313	3.195	4.22	0.0561	0.3438	6.120	0.789	0.868
318	3.145	4.23	0.0462	0.3238	7.600	0.884	0.949
ii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 3.80$, const. $\text{pH}_{(\text{eq})}$ Chosen = 3.78							
288	3.472	3.78	0.3241	0.0759	0.234	-0.630	-0.605
293	3.413	3.78	0.3040	0.0960	0.316	-0.500	-0.468
298	3.356	3.78	0.2861	0.1139	0.398	-0.400	-0.362
303	3.300	3.79	0.2549	0.1451	0.569	-0.245	-0.214
308	3.247	3.79	0.2286	0.1714	0.750	-0.125	-0.087
313	3.195	3.79	0.2023	0.1977	0.977	-0.010	0.028
318	3.145	3.79	0.1844	0.2156	1.169	0.068	0.108
iii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 3.80$, const. $\text{pH}_{(\text{eq})}$ chosen = 3.80							
288	3.472	3.75	0.2320	0.1680	0.724	-0.140	-0.030
293	3.413	3.76	0.1908	0.2092	1.096	0.040	0.130
298	3.356	3.76	0.1591	0.2409	1.514	0.180	0.280
303	3.300	3.77	0.1336	0.2664	1.995	0.300	0.380
308	3.247	3.77	0.1030	0.2970	2.883	0.460	0.540
313	3.195	3.77	0.0864	0.3136	3.630	0.560	0.640
318	3.145	3.78	0.0691	0.3309	4.789	0.680	0.740

*log $^{\text{c}}\text{D} = \log D + 2 (\text{constant } \text{pH}_{(\text{eq})} \text{ chosen} - \text{pH}_{(\text{eq})} \text{ experimental}) + \{\log \{[\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - [\text{Mn(II)}]_{(\text{o,eq})}\}$; where all concentrations are in kmol/m^3 .

Table XI. Effect of added acetate ion concentration on the extraction equilibria of Mn(II) - Cyanex 272 system. $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1 (Fig. 11).

$[\text{Ac}^-]$, kmol/m^3	$\log([\text{Ac}^-]$, $\text{kmol/m}^3)$	$\text{pH}_{(\text{eq})}$	$[\text{Mn(II)}]_{(\text{ini})}$, kg/m^3	$[\text{Mn(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Mn(II)}]_{(\text{o,eq})}$, kg/m^3	D	$\log D$	$^*\log {}^cD$
i) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 3.70$, Const. $\text{pH}_{(\text{eq})}$ Chosen = 3.69								
0.10	-1.00	3.69	0.415	0.2950	0.1200	0.407	-0.390	-0.35
0.25	-0.602	3.69	0.408	0.2918	0.1162	0.398	-0.400	-0.36
0.40	-0.400	3.69	0.411	0.2935	0.1175	0.400	-0.398	-0.36
0.70	-0.155	3.69	0.398	0.2827	0.1153	0.408	-0.390	-0.35
1.00	0.000	3.69	0.405	0.2882	0.1168	0.405	-0.392	-0.35
2.00	0.300	3.69	0.403	0.2887	0.1143	0.396	-0.402	-0.36
ii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.25$, Const. $\text{pH}_{(\text{eq})}$ Chosen = 4.22								
0.10	-1.00	4.18	0.415	0.0880	0.3270	3.720	0.571	0.76
0.25	-0.602	4.19	0.408	0.0820	0.3260	3.980	0.599	0.77
0.40	-0.400	4.20	0.411	0.0810	0.3300	4.090	0.610	0.76
0.70	-0.155	4.21	0.398	0.0770	0.3210	4.170	0.620	0.75
1.00	0.000	4.21	0.405	0.0780	0.3270	4.190	0.622	0.75
2.00	0.300	4.22	0.403	0.0750	0.3280	4.370	0.641	0.75
iii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 3.70$, Const. $\text{pH}_{(\text{eq})}$ Chosen = 3.70								
0.10	-1.00	3.68	0.415	0.1700	0.2450	1.441	0.159	0.215
0.25	-0.602	3.68	0.408	0.1714	0.2366	1.380	0.140	0.196
0.40	-0.400	3.69	0.411	0.1740	0.2470	1.506	0.178	0.214
0.70	-0.155	3.69	0.398	0.1624	0.2356	1.450	0.160	0.196
1.00	0.000	3.70	0.405	0.1630	0.2420	1.485	0.170	0.186
2.00	0.300	3.70	0.403	0.1580	0.2450	1.551	0.190	0.206

$^*\log {}^cD = \log D + 2 (\text{const. } \text{pH}_{(\text{eq})} \text{ chosen} - \text{pH}_{(\text{eq})} \text{ experimental}) + \{ \log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log ([\text{H}_2\text{A}_2]_{(\text{o,ini})} - [\text{Mn(II)}]_{(\text{o,eq})}) \}$; where all concentrations are in kmol/m^3 .

Table XII. Effect of co-existing sulfate ion in the aqueous phase on extraction equilibria of Mn(II) by Cyanex 272. $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, Temperature = $(303 \pm 0.50) \text{ K}$, Equilibration time = 5 min, O/A = 1 (Fig. 12).

$[\text{SO}_4^{2-}]$, kmol/m^3	$\log [\text{SO}_4^{2-}]$, kmol/m^3	$\text{pH}_{(\text{eq})}$	$[\text{Mn(II)}]_{(\text{ini})}$, kg/m^3	$[\text{Mn(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Mn(II)}]_{(\text{o,eq})}$, kg/m^3	D	$\log D$	$\log {}^cD$
<i>i) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.30$, Const. $\text{pH}_{(\text{eq})}$ Chosen = 4.22</i>								
0.008	-2.10	4.22	0.412	0.1060	0.3060	2.887	0.40	0.570
0.025	-1.60	4.22	0.398	0.1049	0.2931	2.793	0.446	0.550
0.500	-1.30	4.22	0.408	0.1083	0.2997	2.767	0.442	0.548
0.100	-1.00	4.22	0.405	0.1155	0.2895	2.506	0.399	0.501
0.300	-0.52	4.23	0.410	0.1388	0.2712	1.954	0.291	0.401
0.500	-0.30	4.23	0.400	0.1554	0.2446	1.574	0.197	0.279
1.000	0.00	4.24	0.402	0.2017	0.2003	0.993	-0.003	0.101
1.500	0.18	4.24	0.395	0.2188	0.1762	0.805	-0.094	0.001
2.000	0.30	4.25	0.404	0.2390	0.1649	0.690	-0.160	-0.050
<i>ii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 3.82$, Const. $\text{pH}_{(\text{eq})}$ Chosen = 3.80</i>								
0.008	-2.10	3.80	0.410	0.2667	0.1433	0.537	-0.270	-0.220
0.025	-1.60	3.80	0.394	0.2576	0.1383	0.537	-0.270	-0.220
0.500	-1.30	3.80	0.406	0.2705	0.1355	0.501	-0.300	-0.250
0.100	-1.00	3.80	0.403	0.2785	0.1245	0.447	-0.350	-0.300
0.300	-0.52	3.81	0.408	0.3030	0.1050	0.347	-0.460	-0.400
0.500	-0.30	3.81	0.397	0.3114	0.0856	0.275	-0.560	-0.500
1.000	0.00	3.82	0.400	0.3373	0.0627	0.186	-0.730	-0.670
1.500	0.18	3.82	0.392	0.3424	0.0496	0.145	-0.840	-0.800
2.000	0.30	3.82	0.401	0.3580	0.0430	0.120	-0.920	-0.880

$\log {}^cD = \log D + 2 (\text{const. } \text{pH}_{(\text{eq})} \text{ chosen} - \text{pH}_{(\text{eq})}) + \{ \log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - [\text{Mn(II)}]_{(\text{o,eq})} \}$;
where all concentration are in kmol/m^3 .

Table. XIII. Loading of Cyanex 272 with Mn(II). $\text{Mn(II)}_{(ini)} = 1.05 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.019 \text{ kmol/m}^3$, $\text{pH}_{(ini)} = 6.00$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A (Phase ratio) = 1 (Fig. 13).

Contact numbers	$\text{pH}_{(eq)}$	$[\text{Mn(II)}]_{(eq), \text{ kg/m}^3}$	$[\text{Mn(II)}]_{(o,eq), \text{ kg/m}^3}$	Cumulative $[\text{Mn(II)}]_{(o), \text{ kg/m}^3}$
i) $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3 (\blacktriangle)$				
1	5.14	0.197	0.853	0.853
2	5.40	0.696	0.354	1.207
3	5.67	0.948	0.102	1.309
4	5.84	1.010	0.040	1.349
5	5.96	1.031	0.019	1.368
6	5.99	1.040	0.010	1.378
7	6.01	1.050	0.000	1.378
ii) $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.05 \text{ kmol/m}^3 (\blacksquare)$				
1	5.15	0.069	0.981	0.981
2	5.20	0.254	0.796	1.777
3	5.27	0.470	0.580	2.357
4	5.49	0.668	0.382	2.739
5	5.65	1.019	0.031	2.760
6	5.80	1.050	0.000	2.760
7	5.86	1.050	0.000	2.760

Table XIV. Correlation between distribution ratios of Mn(II) in different diluents and the cross-sectional area of BTMPPA molecules at the interfaces. $[\text{Mn(II)}]_{(\text{ini})} = 0.45 \text{ kg/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$ in different diluents, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.50$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, $\text{O/A} = 1$ (Fig. 14).

Name of diluent	*A, Å ²	log (A, Å ²)	D	log D
CCl ₄	157	2.20	0.784	-0.1055(4)
Cl CH ₂ - CH ₂ Cl	174	2.24	0.500	-0.3010(7)
C ₆ H ₆	262	2.42	0.730	-0.1367(6)
C ₇ H ₈	211	2.32	0.670	-0.1740(5)
CHCl ₃	335	2.53	0.350	-0.4560(8)
Cyclo C ₆ H ₁₄	166	2.22	0.875	-0.0580(3)
n- C ₇ H ₁₆	176	2.25	1.885	0.2750(1)
Kerosene	211	2.32	1.310	0.1165(2)
C ₆ H ₁₃ OH	734	2.87	0.364	-0.4400(9)
C ₇ H ₁₅ OH	532	2.73	0.154	-0.8130 (10)

*A = cross-sectional area of BTMPPA as adsorbed at the interface [115].

Table XV. Data for the estimation of extraction equilibrium constant (K_{ex}) of Mn(II) by Cyanex 272; plotted as $\log {}^C D$ vs. $\log f(R)$ at Temp. 303 K (Fig. 15).

pH _(eq)	[H ₂ A ₂], kmol/m ³	[SO ₄ ⁼], kmol/m ³	[2 pH + log [H ₂ A ₂] - log (1 + 1.9 [SO ₄ ⁼])] = log f(R)	log ^C D
4.64	0.025	0.008	7.671388	1.484
4.49	0.025	0.008	7.371388	1.135
4.35	0.025	0.008	7.091388	0.815
4.22	0.025	0.008	6.831388	0.648
4.20	0.025	0.008	6.791388	0.627
4.18	0.025	0.008	6.751388	0.535
4.05	0.025	0.008	6.491388	0.331
3.90	0.025	0.008	6.191388	0.030
3.84	0.025	0.008	6.071388	-0.089
3.81	0.025	0.008	6.011388	-0.202
3.77	0.025	0.008	5.931388	-0.235
3.58	0.025	0.008	5.551388	-0.576
3.39	0.025	0.008	5.171388	-0.973
3.20	0.025	0.008	4.791388	-1.307
4.45	0.100	0.008	7.893448	1.701
4.19	0.100	0.008	7.373448	1.150
4.00	0.100	0.008	6.993448	0.852
3.82	0.100	0.008	6.633448	0.403
3.54	0.100	0.008	6.073448	-0.096
3.37	0.100	0.008	5.733448	-0.497
3.19	0.100	0.008	5.373448	-0.847
3.74	0.025	0.008	5.871388	-0.480
3.74	0.030	0.008	5.950570	-0.300
3.74	0.033	0.008	5.991962	-0.240
3.74	0.051	0.008	6.181019	-0.060
3.74	0.054	0.008	6.205842	0.000
3.74	0.080	0.008	6.376538	0.200
3.74	0.100	0.008	6.473448	0.320
3.74	0.150	0.008	6.649540	0.520
3.74	0.200	0.008	6.774478	0.600
4.13	0.025	0.008	6.651388	0.240
4.13	0.030	0.008	6.730570	0.450
4.13	0.033	0.008	6.771962	0.500

Continued...

pH _(eq)	[H ₂ A ₂], kmol/m ³	[SO ₄ ⁼], kmol/m ³	2 pH + log [H ₂ A ₂] - log (1 + 1.9 [SO ₄ ⁼]) = log f(R)	log ^c D
4.13	0.051	0.008	6.961019	0.680
4.13	0.054	0.008	6.985842	0.720
4.13	0.080	0.008	7.156538	0.940
4.13	0.100	0.008	7.253448	1.040
4.13	0.150	0.008	7.429540	1.240
4.13	0.200	0.008	7.554478	1.330
4.35	0.025	0.008	7.091388	0.780
4.35	0.030	0.008	7.170570	0.950
4.35	0.033	0.008	7.211962	0.960
4.35	0.051	0.008	7.401019	1.200
4.35	0.054	0.008	7.425842	1.240
4.35	0.080	0.008	7.596538	1.400
4.35	0.100	0.008	7.693448	1.520
4.35	0.150	0.008	7.869540	1.700
4.35	0.200	0.008	7.994478	1.780
4.30	0.025	0.008	6.991388	0.570
4.30	0.025	0.025	6.977786	0.550
4.30	0.025	0.050	6.958526	0.548
4.30	0.025	0.100	6.922393	0.501
4.30	0.025	0.300	6.802040	0.401
4.30	0.025	0.500	6.707905	0.279
4.30	0.025	1.000	6.535542	0.101
4.30	0.025	1.500	6.412479	0.001
4.30	0.025	2.000	6.316699	-0.050
3.82	0.025	0.008	6.031388	-0.220
3.82	0.025	0.025	6.017786	-0.220
3.82	0.025	0.050	5.998526	-0.250
3.82	0.025	0.100	5.962393	-0.300
3.82	0.025	0.300	5.842040	-0.400
3.82	0.025	0.500	5.747905	-0.500
3.82	0.025	1.000	5.575542	-0.670
3.82	0.025	1.500	5.452479	-0.800
3.82	0.025	2.000	5.356699	-0.880

Table XVI. Data for the determination of equilibrium time in the extraction of Ni(II) by Cyanex 272 in kerosene. $[\text{Ni(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.034 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 7.00$, de-emulsifier = 3% (v/v) octan-1-ol, Temperature = (303 ± 0.50) , O/A (Phase ratio) = 1 (Fig. 16).

Time of shaking, min	$[\text{Ni(II)}]_{(\text{ini})}$, kg/m^3	$[\text{Ni(II)}]_{(\text{o})}$, kg/m^3	$\log \{ [\text{Ni(II)}]_{(\text{o})} / [\text{Ni(II)}]_{(\text{i})} \}$
0.25	0.74	0.26	-0.46
0.50	0.61	0.39	-0.19
0.75	0.50	0.50	0.00
1.00	0.42	0.58	0.14
1.25	0.36	0.64	0.25
1.50	0.32	0.68	0.33
1.75	0.29	0.71	0.39
2.00	0.29	0.71	0.39
2.50	0.29	0.71	0.39

Table XVII. Effect of Ni(II) concentration on the extraction ratio of Ni(II) being extracted by Cyanex 272. $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.034 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 7.40$, de-emulsifier = 3% (v/v) octan-1-ol, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1, Equilibration time = 2 min (Fig. 17).

$[\text{Ni(II)}]_{(\text{ini})}$, kmol/m^3	$\log [\text{Ni(II)}]_{(\text{ini})}$, kmol/m^3	$\text{pH}_{(\text{eq})}$	$[\text{Ni(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Ni(II)}]_{(\text{o,eq})}$, kg/m^3	D	$\log D$	* $\log {}^cD_{6.95/0.025}$	$\log [\text{Ni(II)}]_{(\text{eq})}$, kmol/m^3
0.00340	-2.47	6.95	0.0155	0.1885	16.40	1.21	1.31	-3.70
0.00626	-2.20	6.92	0.0271	0.3409	12.58	1.10	1.28	-3.34
0.00850	-2.07	6.90	0.0410	0.4590	11.20	1.05	1.30	-3.15
0.01250	-1.90	6.82	0.1110	0.6240	5.62	0.75	1.25	-2.72
0.01700	-1.77	6.75	0.2028	0.7972	3.93	0.59	1.33	-2.31
0.02500	-1.60	6.68	0.5900	0.9100	1.54	0.19	1.31	-2.00
0.03400	-1.47	6.67	0.8500	1.1500	1.35	0.13	1.36	-1.84

* ${}^cD_{6.95/0.025}$ indicates the corrected D value at constant equilibrium pH of 6.95 and constant equilibrium extractant concentration of 0.025 kmol/m^3 and calculated as follows:
 $\log {}^cD_{6.95/0.025} = \log D + x (6.95 - \text{pH}_{(\text{eq})}) + y [\log 0.025 - \log (0.025 - y[\text{Ni(II)}]_{(\text{o,eq})})]$ in kmol/m^3 ,
 where $x = \text{pH dependence}$ (taken as 2) and $y = \text{extractant dependence}$ (taken as 1).

Table XVIII. Effect of extractant concentration on the extraction ratio of Ni(II) being extracted by Cyanex 272. $[\text{Ni(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.017 \text{ kmol/m}^3$, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1 (Fig. 17).

$[\text{H}_2\text{A}_2]_{(\text{o,ini})}$ kmol/m^3	$\log\{[\text{H}_2\text{A}_2]_{(\text{o,ini})}\}$ kmol/m^3	$\text{pH}_{(\text{eq})}$	$[\text{Ni(II)}]_{(\text{eq})}$ kg/m^3	$[\text{Ni(II)}]_{(\text{o,eq})}$ kg/m^3	D	log D	$\log {}^c\text{D}_{\text{const. pH}}$	$\log$ $([\text{H}_2\text{A}_2]_{(\text{o,eq})})$ kmol/m^3
<i>i) $\text{pH}_{(\text{ini})} = 5.98$, constant $\text{pH} = 5.90$ (chosen)</i>								
0.0250	-1.60	5.90	0.7576	0.2424	0.32	-0.495	-0.495	-1.6800
0.0300	-1.52	5.90	0.7143	0.2857	0.40	-0.398	-0.398	-1.600
0.0375	-1.43	5.90	0.6667	0.3333	0.50	-0.301	-0.301	-1.497
0.0500	-1.30	5.87	0.5952	0.4048	0.68	-0.167	-0.107	-1.365
0.0600	-1.22	5.83	0.5495	0.4505	0.82	-0.086	0.054	-1.281
0.0750	-1.12	5.78	0.5025	0.4975	0.99	-0.004	0.236	-1.177
0.0900	-1.05	5.67	0.4831	0.5169	1.07	0.0290	0.489	-1.090
0.1000	-1.00	5.63	0.4673	0.5327	1.14	0.0570	0.600	-1.041
0.1250	-0.90	5.49	0.4484	0.5516	1.23	0.090	0.910	-0.937
0.1500	-0.82	5.38	0.4292	0.5708	1.33	0.128	1.108	-0.853
<i>ii) $\text{pH}_{(\text{ini})} = 6.30$, constant $\text{pH} = 6.10$ (chosen)</i>								
0.0250	-1.60	6.10	0.5600	0.4400	0.79	-0.105	-0.105	-1.756
0.0300	-1.52	6.08	0.5181	0.4819	0.93	-0.030	0.010	-1.660
0.0375	-1.43	6.07	0.4575	0.5425	1.18	0.074	0.134	-1.549
0.0500	-1.30	6.05	0.3750	0.6250	1.67	0.232	0.322	-1.405
0.0600	-1.22	6.01	0.3290	0.6710	2.04	0.310	0.490	-1.310
0.0750	-1.12	5.96	0.2875	0.7125	2.48	0.394	0.674	-1.201
0.0900	-1.05	5.85	0.2670	0.7330	2.75	0.440	0.990	-1.110
0.1000	-1.00	5.80	0.2500	0.7500	3.00	0.477	1.077	-1.059
0.1250	-0.90	5.61	0.2320	0.7680	3.31	0.520	1.500	-0.916
0.1500	-0.82	5.55	0.2198	0.7802	3.55	0.550	1.650	-0.864
<i>iii) $\text{pH}_{(\text{ini})} = 7.08$, constant $\text{pH} = 6.55$ (chosen)</i>								
0.0250	-1.60	6.55	0.1664	0.8336	5.01	0.700	0.700	-1.965
0.0300	-1.52	6.50	0.1511	0.8489	5.62	0.750	0.850	-1.808
0.0375	-1.43	6.47	0.1265	0.8735	6.92	0.840	1.000	-1.645
0.0500	-1.30	6.42	0.1030	0.8970	8.71	0.940	1.200	-1.459
0.0600	-1.22	6.38	0.0800	0.9284	11.48	1.060	1.400	-1.353
0.0750	-1.12	6.30	0.0716	0.9200	12.56	1.100	1.600	-1.228
0.0900	-1.05	6.20	0.0658	0.9342	14.12	1.150	1.850	-1.130
0.1000	-1.00	6.12	0.0594	0.9406	15.85	1.200	2.060	-1.076

* $\log {}^c\text{D}_{\text{constant pH}} = \log D + x (\text{constant eq. pH chosen} - \text{pH}_{(\text{eq})})$; where $x = \text{pH dependence} = 2$; and $[\text{H}_2\text{A}_2]_{(\text{o,eq})} = [\text{H}_2\text{A}_2]_{(\text{o,ini})} - y [\text{Ni(II)}]_{(\text{o,eq})}$; where $y = \text{extractant dependence} = 1$; all concentration terms are in kmol/m^3 .

Table XIX. Effect of equilibrium pH on the extraction of Ni(II) by Cyanex 272 in kerosene. $[\text{Ni(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.017 \text{ kmol/m}^3$, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1 (Fig. 18).

$\text{pH}_{(\text{ini})}$	$\text{pH}_{(\text{eq})}$	$[\text{Ni(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Ni(II)}]_{(\text{o,eq})}$, kg/m^3	D	log D	*log $^{\text{c}}\text{D}$
i) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, constant $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.025 kmol/m^3 (■, □)						
5.98	5.90	0.7576	0.2424	0.32	-0.495	-0.416
6.25	6.05	0.6250	0.3750	0.60	-0.222	-0.092
6.30	6.10	0.5600	0.4400	0.79	-0.105	0.050
6.65	6.30	0.4270	0.5730	1.34	0.128	0.342
6.70	6.33	0.3500	0.6500	1.86	0.269	0.522
6.75	6.35	0.2875	0.7125	2.48	0.394	0.681
7.00	6.55	0.1660	0.8340	5.02	0.701	1.070
7.15	6.60	0.1500	0.8500	5.67	0.750	1.125
7.45	6.80	0.0713	0.9287	13.04	1.115	1.549
ii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.05 \text{ kmol/m}^3$, constant $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.05 kmol/m^3 (●, ○)						
5.80	5.75			0.45	-0.350	
5.98	5.87	0.5952	0.4048	0.68	-0.167	-0.103
6.10	5.91	0.5405	0.4595	0.85	-0.070	0.004
6.30	6.05	0.3750	0.6250	1.67	0.222	0.326
6.41	6.10	0.3497	0.6503	1.86	0.270	0.379
6.80	6.30	0.1727	0.8273	4.79	0.680	0.824
7.08	6.42	0.1030	0.8970	8.71	0.940	1.098
7.15	6.49	0.0832	0.9168	10.98	1.040	1.203
7.58	6.73	0.0321	0.9679	30.15	1.480	1.653
iii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, constant $[\text{H}_2\text{A}_2]_{(\text{o,eq})}$ chosen = 0.10 kmol/m^3 (▲, △)						
5.45	5.40	0.6610	0.3390	0.513	-0.290	-0.042
5.60	5.53	0.5402	0.4598	0.851	-0.070	0.279
5.98	5.63	0.4673	0.5327	1.140	0.057	0.471
6.15	5.70	0.3600	0.6400	1.778	0.250	0.766
6.30	5.80	0.2500	0.7500	3.000	0.477	1.107
6.60	5.90	0.1830	0.8170	4.467	0.650	1.354
7.10	6.00	0.1368	0.8632	6.310	0.800	1.558

*log $^{\text{c}}\text{D} = \log \text{D}$ at constant equilibrium extractant concentration (chosen)

$= \log \text{D} + y (\log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log ([\text{H}_2\text{A}_2]_{(\text{o,ini})} - y [\text{Ni(II)}]_{(\text{o,eq})})$; where y = extractant concentration dependence (1 for 0.025 and 0.05 kmol/m^3 systems and 3 for 0.1 kmol/m^3 system) : all concentration terms are in kmol/m^3 .

Table XX. Effect of co-existing sulfate ion concentration on the aqueous extraction of Ni(II) by Cyanex 272. $[\text{Ni(II)}]_{(\text{ini})} = \sim 1.00 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, Temperature = $(303 \pm 0.50) \text{ K}$, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, O/A = 1 (Fig. 20).

$[\text{SO}_4^{2-}]$, kmol/m^3	$\log$ $[\text{SO}_4^{2-}]$, kmol/m^3	$\text{pH}_{(\text{ini})}$	$\text{pH}_{(\text{eq})}$	$[\text{Ni(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Ni(II)}]_{(\text{o,eq})}$, kg/m^3	D	$\log D$	* $\log {}^cD$
0.017	-1.77	6.75 ± 0.05	6.08	0.575	0.425	0.739	-0.131	0.018
0.030	-1.53		6.10	0.570	0.430	0.734	-0.123	-0.012
0.050	-1.30		6.12	0.582	0.418	0.718	-0.144	-0.078
0.100	-1.00		6.16	0.572	0.428	0.748	-0.126	-0.136
0.200	-0.70		6.22	0.568	0.432	0.761	-0.119	-0.248
0.300	-0.52		6.29	0.575	0.425	0.739	-0.131	-0.402
0.500	-0.30		6.35	0.578	0.422	0.730	-0.137	-0.530
1.00	0.00		6.50	0.580	0.420	0.724	-0.140	-0.834
1.500	0.18		6.57	0.582	0.418	0.718	-0.144	-0.998

* $\log {}^cD$ = corrected D at constant eq. pH of 6.08 and constant equilibrium free extractant concentration of 0.025 kmol/m^3 calculated as follows:

* $\log {}^cD = \log D + x (6.08 - \text{pH}_{(\text{eq})}) + y (\log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - y [\text{Ni(II)}]_{(\text{o,eq})})$; where, x = pH dependence (2) and y = extractant dependence (1 in the used concentration region). All concentrations are in kmol/m^3 .

Table XXI. Effect of acetate ion concentration on the extraction of Ni(II) by Cyanex 272. $[\text{Ni(II)}] = 1.00 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.017 \text{ kmol/m}^3$, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A = 1 (Fig. 21).

$[\text{Ac}^-]$, kmol/m^3	$\log[\text{Ac}^-]$, kmol/m^3	$\text{pH}_{(\text{ini})}$	$\text{pH}_{(\text{eq})}$	$[\text{Ni(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Ni(II)}]_{(\text{o,eq})}$, kg/m^3	D	$\log D$	* $\log {}^cD$
0.10	-1.00	6.65 ± 0.05	6.05	0.485	0.515	1.062	0.026	0.214
0.25	-0.60		6.15	0.510	0.490	0.980	-0.017	-0.044
0.40	-0.40		6.20	0.518	0.482	0.931	-0.031	-0.258
0.50	-0.30		6.29	0.522	0.478	0.916	-0.038	-0.347
0.700	-0.15		6.35	0.528	0.472	0.894	-0.049	-0.487
1.00	0.00		6.44	0.535	0.465	0.869	-0.061	-0.676
1.50	0.18		6.50	0.540	0.460	0.852	-0.070	-0.807
2.00	0.30		6.55	0.552	0.448	0.812	-0.091	-0.933

* cD = corrected D at constant equilibrium pH of 6.05 and constant equilibrium free extractant concentration of 0.025 kmol/m^3 calculated as follows:

* $\log {}^cD = \log D + x (6.05 - \text{pH}_{(\text{eq})}) + y (\log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - y [\text{Ni(II)}]_{(\text{o,eq})})$; where, x = pH dependence (2) and y = extractant dependence (1). All concentrations are in kmol/m^3 .

Table XXII. Effect of temperature on the extraction of Ni(II) by Cyanex 272.

$[\text{Ni(II)}] = 1.00 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.60$,
de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, O/A = 1 (Fig. 22).

Temp., K	$\{(1/T) \times 10^3\}$, K^{-1}	$\text{pH}_{(\text{eq})}$	$[\text{Ni(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Ni(II)}]_{(\text{o,eq})}$, kg/m^3	D	log D	*log ^cD
293	3.413	6.28	0.4854	0.5146	1.06	0.025	0.092
298	3.356	6.34	0.4575	0.5425	1.18	0.074	0.274
303	3.300	6.32	0.4270	0.5730	1.34	0.128	0.383
308	3.246	6.28	0.3922	0.6078	1.55	0.190	0.559
313	3.195	6.24	0.3597	0.6403	1.78	0.250	0.690
318	3.144	6.21	0.3333	0.6667	2.00	0.300	0.805

* ^cD = corrected D at constant eq. pH of 6.34 and constant free extractant concentration of 0.025 kmol/m^3 calculated as given in Table XXI.

Table XXIII. Loading of Cyanex 272 with Ni(II). $[\text{Ni(II)}]_{(\text{ini})} = 1.95 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 6.85$,

de-emulsifier = 3%(v/v) octan-1-ol, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, equilibration time in each stage = 2 min; Temperature = $(303 \pm 0.50) \text{ K}$; phase ratio = 1:1, organic phase recycled (Fig. 23).

Contact numbers	$\text{pH}_{(\text{eq})}$	$[\text{Ni(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Ni(II)}]_{(\text{o,eq})}$, kg/m^3	Cumulative $[\text{Ni(II)}]_{(\text{o})}$, kg/m^3
i) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3 (\blacktriangle)$				
1.	6.51	0.690	1.260	1.260
2.	6.80	1.365	0.585	1.845
3.	7.04	1.530	0.420	2.265
4.	7.10	1.650	0.300	2.565
5.	7.15	1.732	0.218	2.783
6.	7.25	1.805	0.145	2.928
7.	7.25	1.860	0.090	3.018
8.	7.28	1.935	0.015	3.033
9.	7.28	1.935	0.000	3.033
ii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.05 \text{ kmol/m}^3 (\triangle)$				
1.	5.98	0.750	1.200	1.2000
2.	6.20	0.835	1.115	2.3150
3.	6.50	1.0265	0.9235	3.2385
4.	6.68	1.1885	0.7615	4.0000
5.	6.86	1.2886	0.6614	4.6614
6.	6.93	1.3865	0.5635	5.2249
7.	7.02	1.5149	0.4351	5.6600
8.	7.14	1.6000	0.3500	6.0100
9.	7.20	1.8250	0.1250	6.1350
10.	7.23	1.9136	0.0364	6.1714
11.	7.23	1.9500	0.0000	6.1714

Table XXIV. Data for the estimation of extraction equilibrium constant (K_{ex}) of Ni(II) by Cyanex 272 (Fig. 24).

$pH_{(eq)}$	$[H_2A_2], \text{ kmol/m}^3$	$[Ac^-], \text{ kmol/m}^3$	$[SO_4^{2-}], \text{ kmol/m}^3$	$[\log [H_2A_2]_{(o,eq)} + 2 pH_{(eq)} - \log [Ac^-] - \log (1 + 6.92 [SO_4^{2-}])] = \log f(R)$	$\log {}^cD$
5.90	0.0250	0.25	0.017	10.75170	-0.416
6.05	0.0250	0.25	0.017	11.05170	-0.092
6.10	0.0250	0.25	0.017	11.15170	0.050
6.30	0.0250	0.25	0.017	11.55170	0.342
6.33	0.0250	0.25	0.017	11.61170	0.522
6.35	0.0250	0.25	0.017	11.65170	0.681
6.55	0.0250	0.25	0.017	12.05170	1.070
6.60	0.0250	0.25	0.017	12.15170	1.125
6.80	0.0250	0.25	0.017	12.55170	1.549
5.75	0.0500	0.25	0.017	10.75273	-0.275
5.87	0.0500	0.25	0.017	10.99273	-0.103
5.91	0.0500	0.25	0.017	11.07273	0.004
6.05	0.0500	0.25	0.017	11.35273	0.326
6.10	0.0500	0.25	0.017	11.45273	0.379
6.30	0.0500	0.25	0.017	11.85273	0.824
6.42	0.0500	0.25	0.017	12.09273	1.098
6.49	0.0500	0.25	0.017	12.23273	1.203
6.73	0.0500	0.25	0.017	12.71273	1.653
5.40	0.1000	0.25	0.017	10.35376	-0.042
5.53	0.1000	0.25	0.017	10.61376	0.279
5.63	0.1000	0.25	0.017	10.81376	0.471
5.70	0.1000	0.25	0.017	10.95376	0.766
5.80	0.1000	0.25	0.017	11.15376	1.107
5.90	0.1000	0.25	0.017	11.35376	1.354
6.00	0.1000	0.25	0.017	11.55376	1.558
5.90	0.0250	0.25	0.017	10.75170	-0.495
5.90	0.0300	0.25	0.017	10.83088	-0.398
5.90	0.0375	0.25	0.017	10.92779	-0.301
5.90	0.0500	0.25	0.017	11.05273	-0.107
5.90	0.0600	0.25	0.017	11.13191	0.054
5.90	0.0750	0.25	0.017	11.22882	0.236
5.90	0.0900	0.25	0.017	11.30800	0.489
5.90	0.1000	0.25	0.017	11.35376	0.600
5.90	0.1250	0.25	0.017	11.45067	0.910
5.90	0.1500	0.25	0.017	11.52985	1.108

Continued...

$\text{pH}_{(\text{eq})}$	$[\text{H}_2\text{A}_2], \text{ kmol/m}^3$	$[\text{Ac}^-], \text{ kmol/m}^3$	$[\text{SO}_4^{2-}], \text{ kmol/m}^3$	$\log [\text{H}_2\text{A}_2]_{(\text{o,eq})} + 2 \text{ pH}_{(\text{eq})}$ $-\log [\text{Ac}^-] - \log (1 + 6.92$ $[\text{SO}_4^{2-}]) = \log f(\text{R})$	$\log {}^c\text{D}$
6.10	0.0250	0.25	0.017	11.15170	-0.105
6.10	0.0300	0.25	0.017	11.23088	0.010
6.10	0.0375	0.25	0.017	11.32779	0.134
6.10	0.0500	0.25	0.017	11.45273	0.322
6.10	0.0600	0.25	0.017	11.53191	0.490
6.10	0.0750	0.25	0.017	11.62882	0.674
6.10	0.0900	0.25	0.017	11.70800	0.900
6.10	0.1000	0.25	0.017	11.75376	1.077
6.10	0.1250	0.25	0.017	11.85067	1.500
6.10	0.1500	0.25	0.017	11.92985	1.650
6.55	0.0250	0.25	0.017	12.05170	0.700
6.55	0.0300	0.25	0.017	12.13088	0.850
6.55	0.0375	0.25	0.017	12.22779	1.000
6.55	0.0500	0.25	0.017	12.35273	1.200
6.55	0.0600	0.25	0.017	12.43191	1.400
6.55	0.0750	0.25	0.017	12.52882	1.600
6.55	0.0900	0.25	0.017	12.60800	1.850
6.55	0.1000	0.25	0.017	12.65376	2.060
6.05	0.0250	0.10	0.017	11.44964	0.214
6.05	0.0250	0.25	0.017	11.05170	-0.044
6.05	0.0250	0.40	0.017	10.84758	-0.258
6.05	0.0250	0.50	0.017	10.75067	-0.347
6.05	0.0250	0.70	0.017	10.60454	-0.487
6.05	0.0250	1.00	0.017	10.44964	-0.676
6.05	0.0250	1.50	0.017	10.27355	-0.807
6.05	0.0250	2.00	0.017	10.14861	-0.933
6.08	0.0250	0.25	0.017	11.11170	0.018
6.08	0.0250	0.25	0.030	11.07808	-0.012
6.08	0.0250	0.25	0.050	11.03095	-0.078
6.08	0.0250	0.25	0.100	10.93160	-0.136
6.08	0.0250	0.25	0.200	10.78269	-0.248
6.08	0.0250	0.25	0.300	10.67201	-0.402
6.08	0.0250	0.25	0.500	10.51067	-0.530
6.08	0.0250	0.25	1.000	10.26127	-0.834
6.08	0.0250	0.25	1.500	10.10386	-0.998

Table XXV. Determination of extraction equilibration time in the case of Zn(II) extraction by Cyanex 272. $[\text{Zn(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.0153 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.00$, Temperature = $(303 \pm 0.50) \text{ K}$, O/A (Phase ratio) = 1 (Fig. 25).

Time, min	$[\text{Zn(II)}]_{\text{kg/m}^3}$	$[\text{Zn(II)}]_{(\text{o})}, \text{kg/m}^3$	$[\text{Zn(II)}]_{(\text{o})}/[\text{Zn(II)}]$	$\log ([\text{Zn(II)}]_{(\text{o})}/[\text{Zn(II)}])$
0.25	0.909	0.091	0.10	-1.00
0.50	0.848	0.152	0.18	-0.74
0.75	0.795	0.205	0.26	-0.59
1.00	0.760	0.240	0.32	-0.49
1.50	0.695	0.305	0.44	-0.36
2.00	0.630	0.370	0.59	-0.23
2.50	0.592	0.408	0.69	-0.16
3.00	0.565	0.435	0.77	-0.11
3.50	0.550	0.450	0.82	-0.09
4.00	0.545	0.455	0.83	-0.08
4.50	0.542	0.458	0.85	-0.07
5.00	0.542	0.458	0.85	-0.07

Table XXVI. Effect of Zn(II) concentration on its extraction ratio when extracted by Cyanex 272. $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.046 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.00$, $\text{pH}_{(\text{eq})} = 2.50$, Temperature = $(303 \pm 0.50) \text{ K}$, O/A (Phase ratio) = 1, Equilibration time = 5 min (Fig. 26).

$[\text{Zn(II)}]_{(\text{ini})}, \text{kg/m}^3$	$[\text{Zn(II)}]_{(\text{ini})}, \text{kmol/m}^3$	$\log [\text{Zn(II)}]_{(\text{ini})}, \text{kmol/m}^3$	$\text{pH}_{(\text{eq})}$	$[\text{Zn(II)}]_{(\text{eq})}, \text{kg/m}^3$	$[\text{Zn(II)}]_{(\text{g,eq})}, \text{kg/m}^3$	D	$\log D$	$^*\log {}^cD$	$\log [\text{Zn(II)}]_{(\text{eq})}, \text{kmol/m}^3$
0.20	0.00358	-2.515	2.50	0.080	0.120	1.50	0.180	0.213	-2.91
0.35	0.00535	-2.272	2.48	0.155	0.195	1.26	0.100	0.195	-2.63
0.50	0.00764	-2.116	2.44	0.250	0.250	1.00	0.00	0.192	-2.42
0.70	0.0107	-1.970	2.41	0.380	0.320	0.84	-0.075	0.200	-2.21
1.00	0.0153	-1.816	2.40	0.572	0.428	0.75	-0.123	0.206	-2.10
1.50	0.0229	-1.640	2.35	0.980	0.520	0.53	-0.275	0.192	-1.82
2.00	0.0305	-1.515	2.30	1.420	0.580	0.41	-0.390	0.201	-1.66
3.00	0.0458	-1.338	2.26	2.290	0.710	0.31	-0.510	0.192	-1.45

* $\log {}^cD = \log D + x(2.50 - \text{pH}_{(\text{eq})}) + y(\log 0.025 - \log (0.025 - y[\text{Zn(II)}]_{(\text{o,eq})}))$ for calculating corrected D (cD) at constant equilibrium pH of 2.50 and equilibrium extractant concentration of 0.025 kmol/m³. In 0.025 kmol/m³ extractant concentration may be taken as 1 (as will be seen in the following section) and x may be taken as 2 (as will be seen later).

Table XXVII. Effect of extractant concentration on the extraction ratio of Zn(II) being extracted by Cyanex 272. $[\text{Zn(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.0153 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.00$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A (Phase ratio) = 1 (Fig. 27A and 27B).

$[\text{H}_2\text{A}_2]_{(\text{o,ini})}$ kmol/m^3	$\log [\text{H}_2\text{A}_2]_{(\text{o,ini})}$ kmol/m^3	$\text{pH}_{(\text{eq})}$	$[\text{Zn(II)}]_{(\text{eq})}$ kg/m^3	$[\text{Zn(II)}]_{(\text{o,eq})}$ kg/m^3	D	$\log D$	* $\log {}^cD$	$\log ([\text{H}_2\text{A}_2]_{(\text{o,eq})})$ kmol/m^3
<i>i) constant $\text{pH}_{(\text{eq})}$ chosen = 2.40 (o)</i>								
0.02500	-1.600	2.40	0.5720	0.4280	0.748	-0.126	0.007	-1.734 (1)
0.3750	-1.426	2.33	0.4513	0.5487	1.216	0.085	0.205	-1.536(1)
0.0500	-1.301	2.30	0.4000	0.6000	1.500	0.176	0.376	-1.389(1)
0.0750	-1.125	2.28	0.3139	0.6861	2.180	0.340	0.560	-1.205(1.2)
0.1000	-1.000	2.26	0.2551	0.7449	2.920	0.465	0.750	-1.075(1.4)
0.1500	-0.824	2.21	0.1695	0.8305	4.900	0.690	1.070	-0.887(1.6)
0.2000	-0.699	2.18	0.1289	0.8711	6.760	0.830	1.270	-0.754(1.8)
0.3000	-0.523	2.15	0.0705	0.9295	13.180	1.120	1.620	-0.566(2)
0.5000	-0.301	2.10	0.0313	0.9687	30.950	1.491	2.091	-0.327(2)
<i>ii) constant $\text{pH}_{(\text{eq})}$ chosen = 2.70 (●)</i>								
0.02500	-1.600	2.70	0.2200	0.7800	3.545	0.550	0.550	-1.884(1)
0.3750	-1.426	2.64	0.1728	0.8272	4.787	0.680	0.800	-1.605(1)
0.0500	-1.301	2.60	0.1510	0.8490	5.623	0.750	0.950	-1.432(1)
0.0750	-1.125	2.55	0.1238	0.8762	7.078	0.850	1.150	-1.230(1.2)
0.1000	-1.000	2.50	0.1009	0.8991	8.911	0.950	1.350	-1.093(1.4)
0.1500	-0.824	2.44	0.0854	0.9146	10.710	1.030	1.550	-0.894(1.6)
0.2000	-0.699	2.40	0.0532	0.9468	17.797	1.250	1.850	-0.760(1.8)
0.3000	-0.523	2.35	0.0383	0.9617	25.110	1.400	2.100	-0.568(2)
<i>iii) constant $\text{pH}_{(\text{eq})}$ chosen = 2.05 (□)</i>								
0.02500	-1.600	2.05	0.8065	0.1955	0.240	-0.620	-0.620	-1.657(1)
0.3750	-1.426	2.04	0.7337	0.2663	0.363	-0.440	-0.420	-1.496(1)
0.0500	-1.301	2.04	0.6761	0.3239	0.479	-0.320	-0.300	-1.346(1)
0.0750	-1.125	2.02	0.5800	0.4200	0.724	-0.140	-0.100	-1.194(1.2)
0.1000	-1.000	2.00	0.500	0.5000	1.000	0.000	0.100	-1.035(1.4)
0.1500	-0.824	1.98	0.3600	0.6400	1.778	0.250	0.350	-0.853(1.6)
0.2000	-0.699	1.98	0.2575	0.7425	2.884	0.460	0.600	-0.724(1.8)
0.3000	-0.523	1.97	0.1395	0.8605	6.168	0.790	0.950	-0.562(2)
0.5000	-0.301	1.95	0.0593	0.9407	15.869	1.200	1.400	-0.326(2)
<i>iv) constant $\text{pH}_{(\text{eq})}$ chosen = 1.85 (Δ)</i>								
0.02500	-1.600	1.85	0.9147	0.0853	0.093	-1.030	-1.030	-1.625(1)
0.3750	-1.426	1.85	0.8711	0.1289	0.148	-0.830	-0.830	-1.449(1)
0.0500	-1.301	1.85	0.8333	0.1667	0.200	-0.700	-0.700	-1.324(1)
0.0750	-1.125	1.84	0.7680	0.2320	0.302	-0.520	-0.500	-1.150(1.2)
0.1000	-1.000	1.84	0.6761	0.3239	0.479	-0.320	-0.300	-1.031(1.4)
0.1500	-0.824	1.83	0.5516	0.4484	0.813	-0.090	-0.050	-0.857(1.6)
0.2000	-0.699	1.83	0.4082	0.5918	1.450	0.160	0.200	-0.736(1.8)
0.3000	-0.523	1.83	0.2358	0.7642	3.240	0.510	0.550	-0.558(2)
0.5000	-0.301	1.82	0.1030	0.8970	8.710	0.940	1.00	-0.326(2)

* Figures within bracket in the right most columns indicate the corresponding extractant dependence obtained by trial and error method.

Table XXVIII. Effect of aqueous equilibrium pH on the extraction of Zn(II) by Cyanex 272. $[\text{Zn(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.0153 \text{ kmol/m}^3$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A (Phase ratio) = 1 (Fig. 28 A and 28B).

pH _(eq)	[Zn(II)] _(eq) , kg/m ³	[Zn(II)] _(g,eq) , kg/m ³	D	log D	*log ^c D	Extractant dependence(y) considered
i) [H ₂ A ₂] _(o,ini) = constant [H ₂ A ₂] _(o,eq) chosen = 0.025 kmol/m ³						
3.48	0.0196	0.9804	50.020	1.700	2.100	1.00
3.45	0.0294	0.9706	33.010	1.518	1.913	
3.40	0.0327	0.9673	29.580	1.481	1.860	
3.28	0.0491	0.9509	19.366	1.287	1.669	
3.17	0.0654	0.9346	14.290	1.155	1.524	
3.00	0.1177	0.8823	7.500	0.875	1.215	
2.75	0.2000	0.8000	4.000	0.600	0.700	
2.70	0.2200	0.7800	3.545	0.550	0.834	
2.45	0.5388	0.4612	0.856	-0.068	0.079	
2.40	0.5720	0.4280	0.750	-0.125	0.007	
2.28	0.7153	0.2847	0.398	-0.400	-0.317	
2.25	0.7521	0.2479	0.330	-0.481	-0.411	
2.05	0.8065	0.1935	0.240	-0.620	-0.680	
1.85	0.9147	0.0853	0.093	-1.030	-1.005	
ii) [H ₂ A ₂] _(o,ini) = constant [H ₂ A ₂] _(o,eq) chosen = 0.05 kmol/m ³						
3.20	0.0155	0.9845	63.516	1.803	1.959	1.00
3.03	0.0315	0.9685	30.740	1.488	1.641	
2.80	0.0657	0.9343	14.221	1.153	1.239	
2.70	0.1009	0.8991	8.912	0.950	1.090	
2.55	0.2044	0.7936	3.846	0.585	0.706	
2.40	0.2961	0.7039	3.377	0.376	0.481	
2.25	0.4851	0.5143	1.059	0.025	0.100	
2.05	0.6662	0.3338	0.501	-0.300	-0.257	
1.95	0.7520	0.2480	0.330	-0.482	-0.448	
1.85	0.8333	0.1667	0.200	-0.700	-0.677	
iii) [H ₂ A ₂] _(o,ini) = constant [H ₂ A ₂] _(o,eq) chosen = 0.10 kmol/m ³						
2.83	0.0257	0.9743	37.910	1.3579	1.721	1.40
2.70	0.0425	0.9575	22.530	1.353	1.492	
2.50	0.1009	0.8991	8.911	0.950	1.040	
2.26	0.2551	0.7449	2.920	0.465	0.571	
2.00	0.5000	0.5000	1.000	0.000	0.069	
1.84	0.6761	0.3239	0.479	-0.320	-0.276	
1.65	0.8265	0.1735	0.210	-0.678	-0.665	
1.45	0.9120	0.0880	0.096	-1.018	-1.006	
iv) [H ₂ A ₂] _(o,ini) = [H ₂ A ₂] _(o,eq) chosen = 0.30 kmol/m ³						
2.38	0.0265	0.9735	36.740	1.565	1.656	2.00
2.35	0.0383	0.9617	25.110	1.400	1.490	
2.15	0.0705	0.9295	13.180	1.120	1.206	
1.97	0.1395	0.8605	6.168	0.790	0.870	
1.83	0.2358	0.7642	3.240	0.510	0.580	
1.55	0.5208	0.4792	0.920	-0.036	0.008	
1.35	0.7056	0.2944	0.417	-0.380	-0.354	
1.15	0.8390	0.1610	0.192	-0.717	-0.703	

* ^cD is the corrected D values at constant equilibrium extractant concentration same as initial extractant concentration (chosen at all cases) and the values of the log ^cD have been calculated by:
 $\log {}^cD = \log D + y (\log [\text{H}_2\text{A}_2]_{(\text{o,ini})} - \log ([\text{H}_2\text{A}_2]_{(\text{o,ini})} - y [\text{Zn(II)}]_{(\text{o,eq})})$; where all concentration terms are in kmol/m³ and y is the extractant dependence chosen as shown in table.

Table XXIX. Effect of co-existing sulfate ion concentration on the extraction of Zn(II) by Cyanex 272. $[\text{Zn(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.00$, Equilibration time = 5 min, O/A (Phase ratio) = 1, Temperature = $(303 \pm 0.50) \text{ K}$ (Fig. 29).

$[\text{SO}_4^{2-}]$, kmol/m^3	$\log [\text{SO}_4^{2-}]$, kmol/m^3	$\text{pH}_{(\text{eq})}$	$[\text{Zn(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Zn(II)}]_{(\text{g,eq})}$, kg/m^3	D	$\log D$	* $\log {}^cD$
0.0153	-1.815	2.45	0.5422	0.4578	0.844	-0.074	0.067
0.0500	-1.301	2.48	0.5346	0.4654	0.870	-0.060	0.030
0.1000	-1.000	2.50	0.5200	0.4800	0.923	-0.035	0.018
0.1500	-0.824	2.52	0.5088	0.4912	0.965	-0.015	-0.035
0.2000	-0.700	2.60	0.4678	0.5322	1.140	0.0570	0.072
0.3000	-0.523	2.67	0.4421	0.5579	1.260	0.1000	-0.157
0.5000	-0.301	2.71	0.4250	0.5750	1.352	0.1310	-0.200
0.7500	-0.125	2.79	0.3924	0.6076	1.550	0.1900	-0.290
1.0000	0.0000	2.86	0.3698	0.6302	1.700	0.2300	-0.375
1.4000	0.1460	2.94	0.3270	0.6730	2.060	0.3130	-0.440
1.5500	0.1900	3.05	0.2650	0.7350	2.770	0.4420	-0.500

* cD is the corrected D value at constant equilibrium pH of 2.45 (chosen) and constant equilibrium extractant concentration of 0.025 kmol/m^3 (chosen) and the values of $\log {}^cD$ have been calculated using the following equation: $\log {}^cD = \log D + 2 (2.45 - \text{pH}_{(\text{eq})}) + (\log 0.025 - \log (0.025 - [\text{Zn(II)}]_{(\text{o,eq})}))$, where $[\text{Zn(II)}]_{(\text{o,eq})}$ is in kmol/m^3 .

Table XXX. Effect of temperature on the extraction of Zn(II) by Cyanex 272.

$[\text{Zn(II)}]_{(\text{ini})} = 1.00 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.0153 \text{ kmol/m}^3$, Equilibration time = 5 min, O/A = 1
(Fig. 30).

Temp., K	$(1/T) \times 10^3$, K^{-1}	$\text{pH}_{(\text{eq})}$	$[\text{Zn(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Zn(II)}]_{(\text{g,eq})}$, kg/m^3	D	log D	$\log {}^cD$
i) $\text{pH}_{(\text{ini})} = 6.00$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$: ${}^cD = D$ at $\text{pH}_{(\text{eq})} = 2.45$ and $[\text{H}_2\text{A}_2]_{(\text{o,eq})} = 0.025 \text{ kmol/m}^3$ (○)							
293	3.413	2.45	0.5720	0.4280	0.748	-0.126	0.006
298	3.356	2.45	0.5588	0.4412	0.790	-0.102	0.034
303	3.300	2.44	0.5422	0.4578	0.836	-0.078	0.085
308	3.247	2.44	0.5232	0.4768	0.911	-0.040	0.130
313	3.195	2.43	0.5101	0.4899	0.960	-0.017	0.177
318	3.145	2.42	0.4975	0.5029	1.010	0.004	0.224
ii) $\text{pH}_{(\text{ini})} = 7.00$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$: ${}^cD = D$ at $\text{pH}_{(\text{eq})} = 2.45$ and $[\text{H}_2\text{A}_2]_{(\text{o,eq})} = 0.10 \text{ kmol/m}^3$ (Δ)							
293	3.413	2.47	0.1764	0.8236	4.670	0.650	0.730
298	3.356	2.47	0.1422	0.8578	6.030	0.780	0.860
303	3.300	2.45	0.1368	0.8632	6.310	0.800	0.920
308	3.247	2.45	0.1189	0.8811	7.410	0.870	0.990
313	3.195	2.43	0.1095	0.8905	8.130	0.910	1.08
318	3.145	2.43	0.1009	0.8991	8.910	0.950	1.120
iii) $\text{pH}_{(\text{ini})} = 6.00$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ kmol/m}^3$: ${}^cD = D$ at $\text{pH}_{(\text{eq})} = 2.35$ and $[\text{H}_2\text{A}_2]_{(\text{o,eq})} = 0.30 \text{ kmol/m}^3$ (●)							
293	3.413	2.36	0.0801	0.9199	11.480	1.060	1.130
298	3.356	2.35	0.0520	0.9479	18.200	1.260	1.350
303	3.300	2.35	0.0383	0.9617	25.110	1.400	1.490
308	3.247	2.34	0.0307	0.9693	31.570	1.500	1.600
313	3.195	2.34	0.234	0.9766	41.730	1.620	1.720
318	3.145	2.33	0.0171	0.9821	54.860	1.740	1.850

$\log {}^cD$ values are calculated as specified before.

Table XXXI. Data on the loading of Cyanex 272 with Zn(II). $[\text{Zn(II)}]_{(\text{ini})} = 0.9502$ kg/m^3 , $[\text{SO}_4^{2-}] = 0.015 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 5.00$, Equilibration time = 5 min, Temperature = $(303 \pm 0.50) \text{ K}$, O/A ($\phi = 100 \text{ cm}^3$) = 1 (Fig. 31); organic phase recycled.

Contact numbers	$\text{pH}_{(\text{eq})}$	$[\text{Zn(II)}]_{(\text{eq})}$, kg/m^3	$[\text{Zn(II)}]_{(\text{o,eq})}$, kg/m^3	Cumulative $[\text{Zn(II)}]_{(\text{o})}$, kg/m^3
<i>i) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, pH uncontrolled ($\blacktriangle$)</i>				
1.	2.32	0.5820	0.3681	0.3681
2.	2.39	0.6471	0.3031	0.6712
3.	2.47	0.7162	0.2340	0.9052
4.	2.67	0.7742	0.1760	1.0812
5.	2.78	0.8032	0.1470	1.2282
6.	2.90	0.8243	0.1259	1.3541
7.	3.00	0.8410	0.1092	1.4633
8.	3.10	0.8724	0.0778	1.5411
9.	3.17	0.8835	0.0667	1.6078
10.	3.40	0.9250	0.0252	1.6633
11.	3.50	0.9480	0.0022	1.6655
12.	3.55	0.9502	0.0000	1.6655
13.	3.55	0.9502	0.0000	1.6655
<i>ii) $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$, pH controlled ($\bullet$)</i>				
1.	3.0	0.0250	0.9252	0.9252
2.	3.2	0.0240	0.9262	1.8514
3.	3.1	0.0260	0.9242	2.7756
4.	2.9	0.1025	0.8477	3.6233
5.	3.1	0.1065	0.8437	4.4670
6.	3.5	0.0865	0.8637	5.3307
7.	3.2	0.5087	0.6415	5.9722
8.	3.0	0.6015	0.3487	6.3209
9.	3.1	0.7250	0.2252	6.5461
10.	3.2	0.8359	0.1143	6.6604
11.	3.5	0.9250	0.0252	6.6856
12.	3.5	0.9502	0.0000	6.6856

Table XXXII. Data for the estimation of extraction equilibrium constant (K_{ex}) for Zn(II) extraction by Cyanex 272 at 303 K (Fig. 32).

$[H_2A_2]$, kmol/m ³	pH _(eq)	$[SO_4^{=}]$, kmol/m ³	$[(1-2) \log [H_2A_2]_{(o,eq)} + 2$ $pH_{(eq)} - \log (1 + 2 [SO_4^{=}]) =$ $\log f(R)$	$\log {}^cD$
0.0250	2.40	0.0153	3.184850	0.007
0.0375	2.40	0.0153	3.360941	0.205
0.0500	2.40	0.0153	3.485880	0.376
0.0750	2.40	0.0153	3.661971	0.560
0.1000	2.40	0.0153	3.786910	0.750
0.1500	2.40	0.0153	3.963001	1.070
0.2000	2.40	0.0153	4.087940	1.270
0.3000	2.40	0.0153	4.264031	1.620
0.5000	2.40	0.0153	4.485880	2.091
0.0250	2.70	0.0153	3.784850	0.550
0.0375	2.70	0.0153	3.960941	0.800
0.0500	2.70	0.0153	4.085880	0.950
0.0750	2.70	0.0153	4.261971	1.150
0.1000	2.70	0.0153	4.386910	1.350
0.1500	2.70	0.0153	4.563001	1.550
0.2000	2.70	0.0153	4.687940	1.850
0.3000	2.70	0.0153	4.864031	2.100
0.0250	2.05	0.0153	2.484850	-0.620
0.0375	2.05	0.0153	2.660941	-0.420
0.0500	2.05	0.0153	2.785880	-0.300
0.0750	2.05	0.0153	2.961971	-0.100
0.1000	2.05	0.0153	3.086910	0.100
0.1500	2.05	0.0153	3.263001	0.350
0.2000	2.05	0.0153	3.387940	0.600
0.3000	2.05	0.0153	3.564031	0.950
0.5000	2.05	0.0153	3.785880	1.400
0.0250	1.85	0.0153	2.084850	-1.030
0.0375	1.85	0.0153	2.260941	-0.830
0.0500	1.85	0.0153	2.385880	-0.700
0.0750	1.85	0.0153	2.561971	-0.500
0.1000	1.85	0.0153	2.686910	-0.300
0.1500	1.85	0.0153	2.863001	-0.050
0.2000	1.85	0.0153	2.987940	0.200
0.3000	1.85	0.0153	3.164031	0.550
0.5000	1.85	0.0153	3.385880	1.000
0.0250	3.48	0.0153	5.344850	2.100
0.0250	3.45	0.0153	5.284850	1.913
0.0250	3.40	0.0153	5.184850	1.860
0.0250	3.28	0.0153	4.944850	1.669
0.0250	3.17	0.0153	4.724850	1.524
0.0250	3.00	0.0153	4.384850	1.150
0.0250	2.75	0.0153	3.884850	0.700
0.0250	2.70	0.0153	3.784850	0.834
0.0250	2.45	0.0153	3.284850	0.079
0.0250	2.40	0.0153	3.184850	0.007
0.0250	2.28	0.0153	2.944850	-0.317
0.0250	2.25	0.0153	2.884850	-0.411

Continued...

$[\text{H}_2\text{A}_2],$ kmol/m^3	$\text{pH}_{(\text{eq})}$	$[\text{SO}_4^{2-}], \text{kmol/m}^3$	$[(1-2) \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} + 2$ $\text{pH}_{(\text{eq})} - \log (1 + 2 [\text{SO}_4^{2-}]) =$ $\log f(\text{R})$	$\log {}^c\text{D}$
0.0250	2.05	0.0153	2.484850	-0.680
0.0250	1.85	0.0153	2.084850	-1.005
0.0500	3.20	0.0153	5.085880	1.959
0.0500	3.03	0.0153	4.745880	1.641
0.0500	2.80	0.0153	4.285880	1.239
0.0500	2.70	0.0153	4.085880	1.090
0.0500	2.55	0.0153	3.785880	0.706
0.0500	2.40	0.0153	3.485880	0.481
0.0500	2.25	0.0153	3.185880	0.100
0.0500	2.05	0.0153	2.785880	-0.257
0.0500	1.95	0.0153	2.585880	-0.448
0.0500	1.85	0.0153	2.385880	-0.677
0.1000	2.83	0.0153	4.646910	1.721
0.1000	2.70	0.0153	4.386910	1.492
0.1000	2.50	0.0153	3.986910	1.040
0.1000	2.26	0.0153	3.506910	0.571
0.1000	2.00	0.0153	2.986910	0.069
0.1000	1.84	0.0153	2.666910	-0.276
0.1000	1.65	0.0153	2.286910	-0.665
0.1000	1.45	0.0153	1.886910	-1.006
0.3000	2.38	0.0153	4.224031	1.656
0.3000	2.35	0.0153	4.164031	1.490
0.3000	2.15	0.0153	3.764031	1.206
0.3000	1.97	0.0153	3.404031	0.870
0.3000	1.83	0.0153	3.124031	0.580
0.3000	1.55	0.0153	2.564031	0.008
0.3000	1.35	0.0153	2.164031	-0.354
0.3000	1.15	0.0153	1.764031	-0.703
0.0250	2.45	0.0153	3.284850	0.067
0.0250	2.45	0.0500	3.256547	0.030
0.0250	2.45	0.1000	3.218759	0.018
0.0250	2.45	0.1500	3.183997	-0.035
0.0250	2.45	0.2000	3.151812	-0.072
0.0250	2.45	0.3000	3.093820	-0.157
0.0250	2.45	0.5000	2.996910	-0.200
0.0250	2.45	0.7500	2.900000	-0.290
0.0250	2.45	1.0000	2.820819	-0.375
0.0250	2.45	1.4000	2.718156	-0.440
0.0250	2.45	1.5500	2.685156	-0.500

Table XXXIII. Data for the determination of time needed for drop formation and coalescence in a single drop experiment in Mn(II) extraction by Cyanex 272. $[\text{Mn(II)}]_{(\text{ini})} = 0.437 \text{ kg/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.80$, Temperature = 303 K, Number of drops collected = 100 (Fig. 33).

Height of column, m	Volume of 100 drops, cm^3	Drop fall time, s	[Mn(II)] in collected drops, kg/m^3	$a_{\text{Mn(II)}}$ transferred from a drop	
				$\times 10^3$, mg	$\times 10^{11}$, kmol
0.27	2.23	2.40	0.3804	1.26	2.30
0.40	2.27	3.50	0.3601	1.75	3.18
0.60	2.25	5.20	0.3269	2.48	4.51
0.66	2.24	5.70	0.3172	2.70	4.90
0.90	2.32	7.80	0.2808	3.63	6.60

Table XXXIV. Effect of column height on the flux of Mn(II)- transfer in a single drop experiment of Mn(II) extraction by Cyanex 272. $[\text{Mn(II)}]_{(\text{ini})} = 0.437 \text{ kg/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.008 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.80$, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$ (Fig. 34).

Height of column, m	Drop fall time, s	Vol. of 100 drops, cm^3	Surface area of a drop $(A) \times 10^5$, m^2	$a_{\text{Mn(II)}}$ transferred from a drop $\times 10^{11}$, kmol/drop	$*F_f' \times 10^7$, kmol/ m^2s	$*F_f \times 10^7$, kmol/ m^2s	$\log F_f'$, kmol/ m^2s	$\log (F_f)$, kmol/ m^2s
0.27	2.40	2.23	3.82	2.30	2.50	2.07	-6.60	-6.68
0.40	3.50	2.27	3.88	3.18	2.34	2.04	-6.63	-6.69
0.60	5.20	2.25	3.85	4.51	2.25	2.06	-6.65	-6.69
0.66	5.70	2.24	3.84	4.90	2.24	2.06	-6.65	-6.69
0.90	7.80	2.32	3.93	6.60	2.15	2.02	-6.67	-6.69

* $F_f' = a_{\text{Mn(II)}} / A \times t$; $F_f = a_{\text{Mn(II)}} / A \cdot (t + \Delta t)$

Table XXXVI. Effect of initial extractant concentration in the organic phase on the flux of Mn(II) transfer in its forward extraction by Cyanex 272. $[\text{Mn(II)}]_{(\text{ini})} = 0.437 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.60 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$ (Fig. 36).

[H ₂ A ₂] _(o,ini) , kmol/m ³	log [H ₂ A ₂], kmol/m ³	Drop fall time, s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Mn(II)] in collected drops, kg/m ³	a _{Mn(II)} transferred from a drop × 10 ³ , mg		F _r × 10 ⁷ , kmol/m ² s	log (F _r), kmol/m ² s
						× 10 ¹¹ , kmol			
i) pH _(ini) = 4.80									
0.025	-1.60	6.12	2.47	4.10	0.337	2.46	4.47	1.78	-6.75
0.030	-1.52	6.13	2.47	4.10	0.333	2.57	4.67	1.86	-6.73
0.040	-1.40	6.14	2.46	4.09	0.314	3.02	5.50	2.19	-6.66
0.050	-1.30	6.18	2.42	4.05	0.294	3.45	6.28	2.51	-6.60
0.060	-1.22	6.18	2.43	4.06	0.277	3.89	7.08	2.82	-6.55
0.080	-1.10	6.20	2.05	3.62	0.247	3.90	7.09	3.16	-6.50
0.100	-1.00	6.22	2.10	3.68	0.229	4.36	7.94	3.47	-6.46
0.150	-0.82	6.25	2.15	3.74	0.170	5.74	10.45	4.47	-6.35
0.200	-0.70	6.26	2.20	3.80	0.140	6.53	11.89	5.00	-6.30
0.300	-0.52	6.28	2.20	3.80	0.062	8.26	15.03	6.30	-6.20
ii) pH _(ini) = 4.00									
0.025	-1.60	6.05	2.52	4.16	0.398	0.98	1.79	0.71	-7.15
0.040	-1.40	6.07	2.48	4.11	0.388	1.22	2.22	0.89	-7.05
0.060	-1.22	6.10	2.48	4.11	0.381	1.38	2.51	1.00	-7.00
0.080	-1.10	6.10	2.45	4.08	0.366	1.73	3.14	1.26	-6.90
0.100	-1.00	6.12	2.48	4.11	0.358	1.95	3.55	1.41	-6.85
0.150	-0.82	6.18	2.46	4.09	0.337	2.47	4.50	1.78	-6.75
0.200	-0.70	6.22	2.42	4.05	0.335	2.46	4.48	1.78	-6.75
0.300	-0.52	6.24	2.47	4.10	0.291	3.53	6.42	2.51	-6.60

Table XXXVII. Effect of initial pH of the aqueous phase on the flux of Mn(II) transfer in the forward extraction of Mn(II) by

Cyanex 272. $[\text{Mn(II)}]_{(\text{ini})} = 0.437 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.60 m, Temperature = 303 K,Number of drops collected = 100, $\Delta t = 0.50 \text{ s}$ (Fig. 37).

pH _(ini)	Drop fall time, s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Mn(II)] in collected drops, kg/m ³	a _{Mn(II)} transferred from a drop		F _r × 10 ⁷ , kmol/ m ² s	log (F _r , kmol/ m ² s)
					× 10 ³ , mg	× 10 ¹¹ , kmol		
i) [H ₂ A ₂] _(o, ini) = 0.025 kmol/m ³								
3.74	6.11	2.05	3.622	0.412	0.52	0.945	0.427	-7.37
3.98	6.13	2.07	3.646	0.397	0.83	1.511	0.676	-7.17
4.26	6.12	2.09	3.669	0.381	1.18	2.144	0.955	-7.02
4.52	6.09	2.12	3.704	0.365	1.52	2.775	1.230	-6.91
4.75	6.13	2.08	3.657	0.336	2.09	3.806	1.698	-6.77
5.00	6.10	2.07	3.646	0.322	2.38	4.337	1.950	-6.71
5.24	6.12	2.09	3.669	0.299	2.89	5.263	2.344	-6.63
5.48	6.14	2.10	3.680	0.285	3.19	5.807	2.570	-6.59
ii) [H ₂ A ₂] _(o, ini) = 0.10 kmol/m ³								
3.74	6.22	2.14	3.72	0.378	1.27	2.310	1.000	-7.00
3.98	6.24	2.09	3.67	0.342	1.99	3.620	1.580	-6.80
4.26	6.20	2.11	3.69	0.304	2.81	5.120	2.240	-6.65
4.52	6.25	2.15	3.74	0.248	4.06	7.390	3.160	-6.50
4.75	6.18	2.14	3.72	0.228	4.48	8.160	3.550	-6.45
5.00	6.20	2.12	3.70	0.139	6.31	11.49	5.010	-6.30
5.24	6.23	2.14	3.72	0.133	6.50	11.84	5.110	-6.29
5.48	6.20	2.15	3.74	0.104	7.16	13.03	5.620	-6.25

Table XXXVIII. Effect of sulfate ion concentration of the aqueous phase on the flux of Mn(II) transfer in its forward extraction by Cyanex 272. $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.80$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.05 \text{ kmol/m}^3$, Column height = 0.60 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$ (Fig. 38).

$[\text{SO}_4^{2-}]$, kmol/m^3	$\log ([\text{SO}_4^{2-}])$, kmol/m^3	Drop fall time (t), s	Vol. of collected 100 drops, cm^3	Surface area of a drop (A) $\times 10^{-5}$, m^2	$[\text{Mn(II)}]_{(\text{ini})}$, kg/m^3	$[\text{Mn(II)}]$ in collected drops, kg/m^3	$a_{\text{Mn(II)}}$ transferred from a drop		$F_r \times 10^7$, $\text{kmol/m}^2\text{s}$	$\log (F_r \text{ kmol/}$ $\text{m}^2\text{s})$
							$\times 10^3$, mg	$\times 10^{11}$, kmol		
0.015	-1.82	6.05	1.96	3.52	0.4372	0.3076	2.560	4.660	2.188	-6.66
0.060	-1.22	5.96	2.00	3.56	0.4425	0.3205	2.440	4.440	2.093	-6.68
0.120	-0.92	5.86	2.00	3.56	0.4394	0.3277	2.234	4.066	1.949	-6.71
0.250	-0.60	5.78	1.98	3.52	0.4412	0.3491	1.823	3.319	1.622	-6.79
0.400	-0.40	5.65	1.97	3.53	0.4438	0.3670	1.513	2.754	1.380	-6.86
0.700	-0.16	5.44	1.96	3.52	0.4395	0.3793	1.180	2.148	1.122	-6.75
1.000	00	5.30	1.96	3.52	0.4375	0.3876	0.978	1.780	0.954	-7.02
1.250	0.10	4.90	1.93	3.48	0.4385	0.4000	0.743	1.352	0.793	-7.10
1.600	0.20	4.76	1.92	3.47	0.4406	0.4101	0.586	1.066	0.645	-7.19

Table XXXIX. Effect of acetate ion concentration of the aqueous phase on the flux of Mn(II) transfer in its forward extraction by Cyanex 272. $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 4.80$, Column height = 0.60 m, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$, Temperature = 303 K (Fig. 39).

[Ac ⁻], kmol/m ³	log {[Ac ⁻], kmol/m ³ }	Drop fall time, s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) $\times 10^5$, m ²	[Mn(II)] _(ini) , kg/m ³	[Mn(II)] in collected drops, kg/m ³	a _{Mn(II)} transferred from a drop		F _r $\times 10^7$, kmol/m ² s	log (F _s kmol/m ² s)
							$\times 10^3$, mg	$\times 10^{11}$, kmol		
0.125	-0.903	6.00	1.98	3.54	0.425	0.3177	2.124	3.866	1.82	-6.74
0.250	-0.600	6.10	2.08	3.65	0.437	0.3275	2.275	4.411	1.86	-6.73
0.500	-0.300	6.06	2.05	3.62	0.452	0.3374	2.350	4.278	1.95	-6.71
1.000	0.000	5.88	1.97	3.54	0.443	0.3330	2.173	3.955	1.90	-6.72
1.500	0.176	5.73	2.00	3.56	0.420	0.3130	2.140	3.896	1.91	-6.72
2.000	0.301	5.92	2.03	3.60	0.448	0.3327	2.330	4.241	1.99	-6.70

Table XL. Effect of temperature on the flux of Mn(II) transfer in its forward extraction by Cyanex 272. $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{Mn(II)}]_{(\text{ini})} = 0.437 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.60 m, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$ (Fig. 40).

Temp. $^{\circ}\text{C}$	Temp., K	$\{(1/T) \times 10^3\} \text{ K}^{-1}$	Drop fall time, s	Vol. of collected 100 drops, cm^3	Surface area of a drop (A) $\times$ $10^5, \text{m}^2$	[Mn(II)] in collected drops, kg/m^3	$a_{\text{Mn(II)}} \times 10^3, \text{mg}$	transferred from a drop $\times 10^{11}, \text{kmol}$	$F_f \times 10^7,$ $\text{kmol/m}^2 \text{ s}$	$\log (F_f, \text{kmol/}$ $\text{m}^2 \text{ s})$
i) $pH_{(\text{ini})} = 5.50$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$										
15	288	3.472	6.35	2.205	3.59	0.320	2.28	4.15	1.82	-6.74
20	293	3.412	6.28	2.064	3.64	0.313	2.56	4.66	2.04	-6.69
25	298	3.356	6.25	2.072	3.65	0.292	3.00	5.47	2.40	-6.62
30	303	3.300	6.20	2.060	3.63	0.286	3.10	5.65	2.51	-6.60
35	308	3.247	6.18	2.058	3.63	0.264	3.55	6.46	2.88	-6.54
40	313	3.195	6.16	2.050	3.62	0.257	3.70	6.73	3.02	-6.52
45	318	3.145	6.15	2.056	3.63	0.240	4.06	7.39	3.31	-6.48
ii) $pH_{(\text{ini})} = 4.80$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$										
15	288	3.472	6.32	2.058	3.63	0.395	0.87	1.58	0.69	-7.16
20	293	3.412	6.27	2.055	3.63	0.370	1.37	2.50	1.10	-6.96
25	298	3.356	6.24	2.050	3.62	0.349	1.80	3.27	1.45	-6.84
30	303	3.300	6.20	2.054	3.62	0.324	2.32	4.22	1.88	-6.72
35	308	3.247	6.18	2.052	3.62	0.300	2.81	5.12	2.29	-6.64
40	313	3.195	6.16	2.056	3.63	0.287	3.08	5.61	2.51	-6.60
45	318	3.145	6.14	2.057	3.63	0.261	3.61	6.57	2.95	-6.53
iii) $pH_{(\text{ini})} = 3.75$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ kmol/m}^3$										
15	288	3.472	6.30	2.065	3.64	0.416	0.44	0.80	0.35	-7.45
20	293	3.412	6.28	2.063	3.64	0.408	0.60	1.10	0.48	-7.32
25	298	3.356	6.27	2.066	3.64	0.394	0.89	1.62	0.71	-7.15
30	303	3.300	6.25	2.060	3.63	0.376	1.25	2.27	1.00	-7.00
35	308	3.247	6.22	2.063	3.64	0.354	1.71	3.12	1.38	-6.86
40	313	3.195	6.20	2.058	3.63	0.317	2.47	4.50	2.00	-6.70
45	318	3.145	6.18	2.055	3.62	0.280	3.23	5.88	2.63	-6.58

Table XLI. Data on the effect of temperature on the rate forward of extraction of Mn(II) by BTMPPA in kerosene to be treated by the Activated Complex Theory using single drop technique, $h = 6.6252 \times 10^{-37}$ kJ s, $k = 1.38 \times 10^{-26}$ kJ/deg (Fig. 41).

Temp., K	$(1/T) \times 10^3, K^{-1}$	$F_f \times 10^{-7},$ (kmol/m ² s)	$\log \{(F_f h / kT),$ (kmol /m ²)}
<i>i) $pH_{(ini)} = 5.50, [H_2A_2]_{(o,ini)} = 0.025$ kmol/m³</i>			
288	3.472	1.82	-19.5180
293	3.412	2.04	-19.4759
298	3.356	2.40	-19.4127
303	3.300	2.51	-19.4004
308	3.247	2.88	-19.3478
313	3.195	3.02	-19.3342
318	3.145	3.31	-19.3013
<i>ii) $pH_{(ini)} = 4.80, [H_2A_2]_{(o,ini)} = 0.025$ kmol/m³</i>			
288	3.472	0.69	-19.9392
293	3.412	1.10	-19.7442
298	3.356	1.45	-19.6315
303	3.300	1.88	-19.5260
308	3.247	2.29	-19.4474
313	3.195	2.51	-19.4146
318	3.145	2.95	-19.3513
<i>iii) $pH_{(ini)} = 3.75, [H_2A_2]_{(o,ini)} = 0.10$ kmol/m³</i>			
288	3.472	0.35	-20.2340
293	3.412	0.48	-20.1043
298	3.356	0.71	-19.9416
303	3.300	1.00	-19.8001
308	3.247	1.38	-19.6674
313	3.195	2.00	-19.5132
318	3.145	2.63	-19.4012

Table XLII. Data for the estimation of rate constant (k_f) in the forward extraction of Mn(II) by Cyanex 272 at 303 K; plotted as $\log F_f$ vs. $\log f(R)$; where, $\log f(R) = (\log [\text{Mn(II)}] + 0.5 \log [\text{H}_2\text{A}_2] - \log (1 + 31623 [\text{H}^+]) - \log (1 + 1.58 [\text{SO}_4^{2-}]))$ (Fig. 42).

$[\text{Mn(II)}],$ kmol/m^3	$[\text{H}_2\text{A}_2],$ kmol/m^3	$[\text{H}^+], \text{kmol/m}^3$	$[\text{SO}_4^{2-}],$ kmol/m^3	$[\log [\text{Mn(II)}] + 0.5 \log$ $[\text{H}_2\text{A}_2] - \log (1 + 31623$ $[\text{H}^+]) - \log (1 + 1.58$ $[\text{SO}_4^{2-}])] = \log f(R)$	$\log (F_f,$ $\text{kmol/m}^2\text{s})$
0.005752	0.025	0.00001995	0.040	-3.28027	-6.85
0.007936	0.025	0.00001995	0.040	-3.14047	-6.70
0.009337	0.025	0.00001995	0.040	-3.06984	-6.64
0.013487	0.025	0.00001995	0.040	-2.91014	-6.48
0.020896	0.025	0.00001995	0.040	-2.72001	-6.26
0.035475	0.025	0.00001995	0.040	-2.49014	-6.06
0.005752	0.200	0.00001995	0.040	-2.82872	-6.40
0.007936	0.200	0.00001995	0.040	-2.68892	-6.30
0.009337	0.200	0.00001995	0.040	-2.61829	-6.18
0.013487	0.200	0.00001995	0.040	-2.45859	-6.04
0.020896	0.200	0.00001995	0.040	-2.26847	-5.82
0.035475	0.200	0.00001995	0.040	-2.03860	-5.64
0.007954	0.025	0.00001585	0.010	-3.08369	-6.75
0.007954	0.030	0.00001585	0.010	-3.04410	-6.73
0.007954	0.040	0.00001585	0.010	-2.98163	-6.66
0.007954	0.050	0.00001585	0.010	-2.93318	-6.60
0.007954	0.060	0.00001585	0.010	-2.89359	-6.55
0.007954	0.080	0.00001585	0.010	-2.83112	-6.50
0.007954	0.100	0.00001585	0.010	-2.78266	-6.46
0.007954	0.150	0.00001585	0.010	-2.69462	-6.35
0.007954	0.200	0.00001585	0.010	-2.63215	-6.30
0.007954	0.300	0.00001585	0.010	-2.54410	-6.20
0.007954	0.025	0.00010000	0.010	-3.52658	-7.15
0.007954	0.040	0.00010000	0.010	-3.42452	-7.05
0.007954	0.060	0.00010000	0.010	-3.33647	-7.00
0.007954	0.080	0.00010000	0.010	-3.27400	-6.90
0.007954	0.100	0.00010000	0.010	-3.22555	-6.85
0.007954	0.150	0.00010000	0.010	-3.13750	-6.75
0.007954	0.200	0.00010000	0.010	-3.07503	-6.75
0.007954	0.300	0.00010000	0.010	-2.98699	-6.60
0.007954	0.025	0.00018200	0.010	-3.73690	-7.37
0.007954	0.025	0.00010470	0.010	-3.54182	-7.17

Continued...

[Mn(II)], kmol/m ³	[H ₂ A ₂], kmol/m ³	[H ⁺], kmol/m ³	[SO ₄ ⁼], kmol/m ³	log [Mn(II)] + 0.5 log [H ₂ A ₂] - log (1 + 31623 [H ⁺]) - log (1 + 1.58 [SO ₄ ⁼]) = log f(R)	log F _f
0.007954	0.025	0.00005495	0.010	-3.34463	-7.02
0.007954	0.025	0.00003020	0.010	-3.19839	-6.91
0.007954	0.025	0.00001778	0.010	-3.10102	-6.77
0.007954	0.025	0.00001000	0.010	-3.02658	-6.71
0.007954	0.025	0.00000575	0.010	-2.97985	-6.63
0.007954	0.025	0.00000331	0.010	-2.95048	-6.59
0.007954	0.100	0.00018200	0.010	-3.43587	-7.00
0.007954	0.100	0.00010500	0.010	-3.24174	-6.80
0.007954	0.100	0.00005500	0.010	-3.04385	-6.65
0.007954	0.100	0.00003020	0.010	-2.89737	-6.50
0.007954	0.100	0.00001780	0.010	-2.80014	-6.45
0.007954	0.100	0.00001000	0.010	-2.72555	-6.30
0.007954	0.100	0.00000575	0.010	-2.67877	-6.29
0.007954	0.100	0.00000331	0.010	-2.64945	-6.25
0.008191	0.050	0.00001585	0.015	-2.92381	-6.66
0.008191	0.050	0.00001585	0.060	-2.95297	-6.68
0.008191	0.050	0.00001585	0.120	-2.98904	-6.71
0.008191	0.050	0.00001585	0.250	-3.05821	-6.79
0.008191	0.050	0.00001585	0.400	-3.12636	-6.86
0.008191	0.050	0.00001585	0.700	-3.23710	-6.95
0.008191	0.050	0.00001585	1.000	-3.32526	-7.02
0.008191	0.050	0.00001585	1.250	-3.38712	-7.10
0.008191	0.050	0.00001585	2.000	-3.53273	-7.19

Table XLIII. Determination of time needed for drop formation and coalescence in a single drop experiment in the case of extraction of Ni(II) by Cyanex 272. $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{Ni(II)}]_{(\text{ini})} = 1.3405 \text{ kg/m}^3$, $[\text{Ac}] = 0.25 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.70$, $[\text{SO}_4^{2-}] = 0.023 \text{ kmol/m}^3$, de-emulsifier = 3% (v/v) octan-1-ol, Temperature = 303 K, Number of drops collected = 100 (Fig. 43).

Column height, m	Vol. of collected 100 drops, cm^3	Drop fall time (t), s	[Ni(II)] in collected drops, kg/m^3	a _{Ni(II)} transferred from a drop	
				$\times 10^3$, mg	$\times 10^{11}$, kmol
0.27	2.5683	2.50	1.2542	2.216	3.776
0.40	2.5832	3.71	1.2224	3.051	5.199
0.60	2.5732	5.57	1.1683	4.431	7.550
0.66	2.5840	6.12	1.1520	4.871	8.300
0.90	2.5582	8.35	1.0858	6.515	11.101
1.20	2.5672	11.13	1.0028	8.669	14.771

Table XLIV. Effect of column height on rate of Ni(II) extraction by Cyanex 272 using single drop devices. $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{Ni(II)}]_{(\text{ini})} = 1.3405 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.023 \text{ kmol/m}^3$, $[\text{Ac}] = 0.25 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 6.70$, de-emulsifier = 3% (v/v) octan-1-ol, Temperature = 303 K, $\Delta t = 0.50 \text{ s}$, Number of collected drops = 100 (Fig. 44).

Column height, m	Vol. of collected 100 drops, cm^3	Surface area of a drop (A) $\times 10^5$, m^2	a _{Ni(II)} transferred from a drop $\times 10^{11}$, kmol	$\text{F}_f' \times 10^7$ ($\text{kmol/m}^2\text{s}$)	$\log \text{F}_f'$ ($\text{kmol/m}^2\text{s}$)	$\text{F}_f' \times 10^7$ ($\text{kmol/m}^2\text{s}$)	$\log (\text{F}_f)$ ($\text{kmol/m}^2\text{s}$)
0.27	2.5683	4.210	3.776	3.588	-6.445	2.990	-6.524
0.40	2.5832	4.226	5.199	3.316	-6.479	2.922	-6.534
0.60	2.5732	4.215	7.550	3.216	-6.493	2.951	-6.530
0.66	2.5840	4.227	8.300	3.208	-6.494	2.966	-6.528
0.90	2.5582	4.199	11.101	3.166	-6.499	2.987	-6.525
1.20	2.5672	1.208	14.771	3.154	-6.501	3.018	-6.520

* $\text{F}_f' = a_{\text{Ni(II)}} / A \cdot t$; $\text{F}_f = a_{\text{Ni(II)}} / A(t + \Delta t)$

Table XLV. Dependence of initial Ni(II) concentration on the flux of Ni(II) transfer in the system: Ni(II)-SO₄⁼-Ac⁻-(H⁺, Na⁺) - Cyanex 272-kerosene during aqueous drop fall in a single drop column. [Ac⁻] = 0.25 kmol/m³, Δt = 0.50 s, Temperature = 303 K, de-emulsifier = 3% (v/v) octan-1-ol, Number of collected drops = 100, Column height = 0.66 m (Fig. 45).

[Ni(II)] _(ini) , kg/m ³	[Ni(II)] _(ini) , kmol/m ³	log [Ni(II)] _(ini) , kmol/m ³	Drop fall time, s	Vol. of 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Ni(II)] in collected drops, kg/m ³	a _{Ni(II)} transferred from a drop		F _r × 10 ⁷ , kmol/m ² s	log (F _r , kmol/m ² s)
i) pH _(ini) = 6.70, [H ₂ A ₂] _(a,ini) = 0.025 kmol/m ³ (○)										
0.3552	6.052	-2.218	6.27	2.5923	4.236	0.3073	1.242	2.116	0.738	-7.132
0.4323	7.366	-2.133	6.26	2.5884	4.232	0.3750	1.483	2.526	0.883	-7.054
0.6255	10.658	-1.972	6.25	2.5848	4.228	0.5321	2.414	4.113	1.442	-6.841
0.9293	15.834	-1.800	6.21	2.5829	4.226	0.7900	3.598	6.131	2.162	-6.665
1.1870	20.225	-1.694	6.13	2.5874	4.231	1.0122	4.523	7.707	2.747	-6.561
1.3405	22.840	-1.641	6.12	2.5840	4.227	1.1520	4.871	8.300	2.966	-6.525
1.8437	31.414	-1.503	6.00	2.5818	4.224	1.5744	6.953	11.845	4.315	-6.365
2.4408	41.588	-1.381	6.03	2.5833	4.226	2.0817	9.277	15.807	5.725	-6.242
ii) pH _(ini) = 6.00, [H ₂ A ₂] _(a,ini) = 0.025 kmol/m ³ (●)										
0.3552	6.052	-2.218	6.22	2.5839	4.227	0.3322	0.594	1.012	0.356	-7.448
0.4323	7.366	-2.133	6.25	2.5798	4.222	0.4018	0.787	1.341	0.471	-7.327
0.6255	10.658	-1.972	6.20	2.5840	4.227	0.5854	1.036	1.765	0.623	-7.205
0.9293	15.834	-1.800	6.18	2.5812	4.224	0.8663	1.626	2.770	0.982	-7.008
1.1870	20.225	-1.694	6.15	2.5792	4.222	1.1105	1.973	3.362	1.197	-6.922
1.3405	22.840	-1.641	6.11	2.5820	4.227	1.2587	2.112	3.599	1.288	-6.890
1.8437	31.414	-1.503	6.02	2.5816	4.224	1.7326	2.868	4.887	1.774	-6.751
2.4408	41.588	-1.381	6.05	2.5845	4.227	2.2974	3.706	6.315	2.280	-6.642
iii) pH _(ini) = 6.70, [H ₂ A ₂] _(a,ini) = 0.30 kmol/m ³ (□)										
0.3552	6.052	-2.218	6.82	2.5933	4.237	0.1491	5.345	9.107	2.936	-6.532
0.4323	7.366	-2.133	6.78	2.5983	4.242	0.2002	6.031	10.276	3.328	-6.478
0.6255	10.658	-1.972	6.80	2.5976	4.242	0.2428	9.941	16.938	5.470	-6.262
0.9293	15.834	-1.800	6.72	2.5965	4.240	0.4338	12.866	21.922	7.161	-6.145
1.1870	20.225	-1.694	6.68	2.5980	4.242	0.4989	17.877	30.460	10.000	-6.000
1.3405	22.840	-1.641	6.60	2.5958	4.240	0.6145	18.846	32.111	10.667	-5.972
1.8437	31.414	-1.503	6.52	2.5974	4.241	0.7602	28.143	47.952	16.107	-5.793
2.4408	41.588	-1.381	6.50	2.5980	4.242	1.0869	35.174	59.932	20.204	-5.695

Table XLVI. Effect of aqueous pH on Ni(II) transfer flux in the system: Ni(II)-SO₄⁼-Ac⁻-(H⁺, Na⁺) - Cyanex 272-kerosene. [SO₄⁼] = 0.05 kmol/m³, [Ac⁻] = 0.25 kmol/m³, de-emulsifier = 3% (v/v) octan-1-ol, Temperature = 303 K, Δt = 0.50 s, Number of collected drops = 100 (Fig. 46).

Column height, m	pH _(ini)	Drop fall time (t), s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Ni(II)] _(ini) , kg/m ³	[Ni(II)] in collected drops, kg/m ³	a _{Ni(II)} transferred from a drop × 10 ⁶ , mg × 10 ¹¹ , kmol		F _r × 10 ⁷ , kmol/m ² s	log (F _r , kmol/m ² s)
ii) [H ₂ A ₂] _(o,ini) = 0.025 kmol/m ³ ; (○)										
1.20	4.8	11.18	2.6018	4.246	1.3385	1.3258	0.330	0.563	0.114	-7.945
1.20	5.0	11.15	2.6005	4.245	1.3390	1.3170	0.572	0.975	0.197	-7.705
1.20	5.2	11.12	2.5980	4.242	1.3388	1.3082	0.795	1.355	0.275	-7.561
0.90	5.4	8.38	2.5988	4.243	1.3397	1.3018	0.985	1.678	0.445	-7.351
0.90	5.6	8.36	2.5992	4.243	1.3392	1.2864	1.372	2.338	0.621	-7.207
0.90	5.8	8.36	2.5996	4.244	1.3385	1.2593	2.059	3.508	0.933	-7.030
0.90	6.0	8.34	2.6008	4.245	1.3378	1.2257	2.915	4.968	1.324	-6.878
0.90	6.2	8.35	2.6014	4.246	1.3372	1.1775	4.154	7.079	1.884	-6.725
0.90	6.4	8.37	2.6002	4.244	1.3380	1.1434	5.060	8.622	2.290	-6.640
0.66	6.6	6.14	2.5992	4.243	1.3394	1.1646	4.543	7.741	2.748	-6.561
0.66	6.7	6.12	2.5988	4.243	1.3396	1.1502	4.922	8.387	2.986	-6.525
0.66	6.8	6.13	2.5994	4.244	1.3384	1.1434	5.069	8.637	3.070	-6.513
0.66	7.0	6.15	2.5998	4.244	1.3397	1.1198	5.717	9.741	3.451	-6.462
iii) [H ₂ A ₂] _(o,ini) = 0.10 kmol/m ³ ; (●)										
1.20	4.8	11.32	2.6500	4.298	1.3385	1.3103	0.747	1.273	0.251	-7.601
1.20	5.2	11.26	2.6488	4.297	1.3388	1.2728	1.748	2.979	0.590	-7.230
0.90	5.6	8.47	2.6496	4.298	1.3392	1.2245	3.039	5.178	1.343	-6.872
0.90	6.0	8.44	2.6512	4.300	1.3378	1.0838	6.734	11.473	2.984	-6.525
0.90	6.4	8.49	2.6490	4.297	1.3380	0.9358	10.654	18.153	4.700	-6.328
0.66	6.8	6.30	2.6525	4.301	1.3384	0.9348	10.705	18.241	6.237	-6.205
iii) [H ₂ A ₂] _(o,ini) = 0.30 kmol/m ³ ; (□)										
1.20	4.8	11.58	2.6748	4.325	1.3385	1.2855	1.418	2.415	0.462	-7.335
1.20	5.2	11.60	2.6139	4.259	1.3388	1.2163	3.202	5.456	1.059	-6.975
0.90	5.4	8.70	2.6245	4.271	1.3397	1.1863	4.026	6.860	1.746	-6.758
0.90	5.6	8.66	2.6638	4.313	1.3392	1.0733	7.083	12.069	3.055	-6.615
0.90	5.8	8.68	2.6598	4.309	1.3385	1.0414	7.902	13.464	3.404	-6.468
0.66	6.0	6.40	2.6508	4.299	1.3378	0.9810	9.458	16.115	5.433	-6.265
0.66	6.2	6.36	2.6566	4.306	1.3372	0.8805	12.132	20.673	6.999	-6.155
0.66	6.6	6.38	2.6539	4.303	1.3394	0.6877	17.295	29.469	6.954	-6.002
0.66	7.0	6.37	2.6318	4.279	1.3397	0.4655	23.007	39.201	13.335	-5.815

Table XLVII. Effect of extractant concentration on Ni(II) transfer flux in the system: Ni(II)-SO₄²⁻-Ac⁻-(H⁺,Na⁺)-Cyanex 272-kerosene. [Ac⁻] = 0.25 kmol/m³, [SO₄²⁻] = 0.05 kmol/m³, de-emulsifier = 3% (v/v) octan-1-ol, Temperature = 303 K, Number of collected drops = 100, Δt = 0.50 s (Fig. 47).

[H ₂ A ₂] ₃ kmol/m ³	log ([H ₂ A ₂] ₃) kmol/m ³	Drop fall time (t), s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A)×10 ³ , m ²	[Ni(II)] in collected drops, kg/m ³	a _{Ni(II)} transferred from a drop		F _r ×10 ⁷ , kmol /m ² s	log (F _r , kmol /m ² s)
						×10 ³ , mg	×10 ¹¹ , kmol		
i) pH _(ini) = 6.70, [Ni(II)] _(ini) = 1.3396 kg/m ³ , Column height = 0.66 m (○)									
0.025	-1.602	6.12	2.5988	4.243	1.1502	4.922	8.387	2.986	-6.525
0.050	-1.301	6.18	2.5912	4.235	1.0792	6.747	11.498	4.046	-6.391
0.075	-1.125	6.20	2.5948	4.239	0.9767	9.417	16.045	5.649	-6.248
0.100	-1.000	6.24	2.6013	4.246	0.9340	10.550	17.976	6.281	-6.202
0.150	-0.824	6.25	2.6015	4.246	0.8260	13.361	22.765	7.943	-6.100
0.200	-0.699	6.30	2.5992	4.243	0.7589	15.094	25.718	8.914	-6.050
0.250	-0.602	6.36	2.5987	4.243	0.6822	17.084	29.109	10.001	-6.000
0.300	-0.522	6.41	2.5968	4.241	0.5913	19.432	33.110	11.298	-5.947
ii) pH _(ini) = 6.10, [Ni(II)] _(ini) = 1.3408 kg/m ³ , Column height = 0.90 m (●)									
0.025	-1.602	8.35	2.6058	4.251	1.2080	3.461	5.897	1.567	-6.805
0.050	-1.301	8.40	2.5988	4.243	1.1534	4.870	8.300	2.198	-6.658
0.075	-1.125	8.44	2.5964	4.240	1.0705	7.018	11.958	3.155	-6.650
0.100	-1.000	8.47	2.5998	4.244	1.0602	7.295	12.429	3.265	-6.486
0.150	-0.824	8.50	2.6012	4.246	0.9904	9.115	15.530	4.064	-6.391
0.200	-0.699	8.56	2.6017	4.246	0.9330	10.610	18.078	4.699	-6.328
0.250	-0.602	8.60	2.6025	4.247	0.8393	13.052	22.239	5.754	-6.240
0.300	-0.522	8.63	2.6088	4.254	0.8203	13.578	23.135	5.957	-6.225
iii) pH _(ini) = 5.20, [Ni(II)] _(ini) = 1.3388 kg/m ³ , Column height = 1.20 m (□)									
0.025	-1.602	11.12	2.5980	4.242	1.3082	0.795	1.355	0.275	-7.561
0.050	-1.301	11.18	2.5998	4.244	1.2944	1.154	1.966	0.397	-7.401
0.075	-1.125	11.21	2.6138	4.259	1.2871	1.351	2.302	0.462	-7.335
0.100	-1.000	11.26	2.6488	4.297	1.2728	1.748	2.979	0.590	-7.230
0.150	-0.824	11.34	2.6412	4.289	1.2572	2.155	3.672	0.723	-7.141
0.200	-0.699	11.48	2.6365	4.284	1.2481	2.391	4.074	0.794	-7.100
0.250	-0.602	11.52	2.6033	4.248	1.2326	2.765	4.711	0.923	-7.035
0.300	-0.522	11.60	2.6139	4.259	1.2163	3.202	5.456	1.059	-6.975

Table XLVIII. Effect of sulfate concentration on Ni(II) transfer flux in Ni(II)-SO₄²⁻-Ac⁻(H⁺, Na⁺) - Cyanex 272-kerosene system. [Ac⁻] = 0.25 kmol/m³, de-emulsifier = 3% (v/v) octan-1-ol, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50$ s, Column height = 0.66 m. (Fig. 48).

[SO ₄ ²⁻] ₃ kmol/m ³	log [SO ₄ ²⁻] ₃ , kmol/m ³	Drop fall time (t), s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Ni(II)] _(m) , kg/m ³	[Ni(II)] in collected drops, kg/m ³	a _{Ni(II)} transferred from a drop		Flux (F _d) × 10 ⁷ , kmol /m ² s	log (F _d) kmol /m ² s
							× 10 ³ , mg	× 10 ¹¹ , kmol		
i) pH _(m) = 6.70, [H ₂ A ₂] _(o,m) = 0.025 kmol/m ³ , (O)										
0.0230	-1.635	6.30	2.4778	4.110	1.3405	1.1415	4.391	8.401	3.006	-6.522
0.0500	-1.301	6.24	2.5062	4.142	1.3198	1.1418	4.461	7.601	2.723	-6.565
0.0680	-1.167	6.18	2.5136	4.150	1.3082	1.1502	3.971	6.766	2.441	-6.612
0.0850	-1.071	6.26	2.4882	4.122	1.3378	1.1902	3.673	6.258	2.246	-6.649
0.1700	-0.770	6.17	2.5321	4.170	1.2808	1.1668	2.887	4.918	1.768	-6.753
0.3000	-0.523	6.20	2.5188	4.155	1.3045	1.2270	1.952	3.326	1.195	-6.923
0.5000	-0.301	8.70	2.5265	4.164	1.3096	1.2372	1.829	3.116	0.813	-7.090
1.0000	0.000	11.75	2.5012	4.136	1.3109	1.2543	1.416	2.413	0.476	-7.322
ii) pH _(m) = 6.40, [H ₂ A ₂] _(o,m) = 0.30 kmol/m ³ , (●)										
0.0230	-1.635	6.35	2.5018	4.137	1.3402	0.6754	16.624	28.325	10.000	-6.000
0.0500	-1.301	6.32	2.4950	4.129	1.3195	0.7873	13.278	22.624	8.035	-6.095
0.0850	-1.071	6.38	2.5128	4.149	1.3373	0.8256	12.858	21.908	7.675	-6.115
0.1700	-0.770	6.30	2.5168	4.153	1.2802	0.9191	9.088	15.485	5.483	-6.261
0.3000	-0.523	6.25	2.4979	4.132	1.3037	1.0591	6.110	10.411	3.725	-6.429
0.5000	-0.301	6.22	2.5060	4.141	1.3090	1.1442	4.130	7.037	2.529	-6.597
1.0000	0.000	11.82	2.5108	4.147	1.3100	1.1220	4.720	8.042	1.574	-6.803
2.000	0.300	11.70	2.5065	4.142	1.3196	1.2241	2.394	4.079	0.807	-7.093

Table II. Effect of acetate ion concentration on the flux of Ni(II) transfer during its extraction by Cyanex 272. $[H_2A_2]_{(o,ini)} = 0.025$ kmol/m³, $pH_{(ini)} = 6.60$, Temperature = 303 K, $[SO_4^{2-}] = 0.023$ kmol/m³, de-emulsifier = 3% (v/v) octan-1-ol, Number of collected drops = 100, $\Delta t = 0.50$ s, Column height = 0.66 m. (Fig. 49).

[Ac], kmol/m ³	log ([Ac], kmol/m ³)	Drop fall time (t), s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) $\times 10^5$, m ²	[Ni(II)] _(ini) , kg/m ³	[Ni(II)] in collected drops, kg/m ³	a _{Ni(II)} transferred from a drop		Flux (F _i) $\times 10^7$, kmol/m ² s	log (F _i , kmol/m ² s)
							$\times 10^3$, mg	$\times 10^{11}$, kmol		
0.15	-0.824	6.16	2.6109	4.256	1.3402	1.1500	4.966	8.461	2.985	-6.525
0.25	-0.602	6.14	2.5992	4.243	1.3394	1.1646	4.543	7.741	2.748	-6.561
0.35	-0.456	6.18	2.6017	4.246	1.3398	1.1781	4.181	7.124	2.512	-6.600
0.50	-0.301	6.19	2.6311	4.278	1.3382	1.1797	4.170	7.105	2.483	-6.605
0.70	-0.155	6.15	2.5990	4.243	1.3380	1.1927	3.776	6.434	2.280	-6.642
1.00	-0.000	6.17	2.6087	4.254	1.3370	1.1957	3.686	6.280	2.213	-6.655
1.50	0.176	6.12	2.6098	4.254	1.3371	1.2186	3.093	5.270	1.871	-6.728
2.00	0.300	6.15	2.6233	4.270	1.3368	1.2428	2.466	4.200	1.480	-6.830

Table L. Effect of temperature on the extraction flux of Ni(II) during its extraction by Cyanex 272 in kerosene, $\Delta t = 0.50$ s, de-emulsifier = 3% (v/v) octan-1-ol, Number of collected drops = 100 (Fig. 50).

Column height, m	Temp. (T), K	$(10^3/T)$, K ⁻¹	Drop fall time (t), s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Ni(II)] in drops, kg/m ³	$a_{\text{Ni(II)}}$ transferred from a drop × 10 ³ , mg × 10 ¹¹ , kmol		Flux (F _F) × 10 ⁷ , kmol /m ² s	log (F _F kmol /m ² s)
<i>i) pH_(ini) = 6.70, [H₂A₂]_(a,ini) = 0.10 kmol/m³, [SO₄²⁻] = 0.05 kmol/m³, [Ac⁻] = 0.25 kmol/m³, [Ni(II)]_(ini) = 1.3396 kg/m³; (●)</i>										
0.66	288	3.472	6.18	2.5997	4.244	1.0650	7.139	12.164	4.291	-6.367
	293	3.413	6.20	2.6063	4.251	1.0417	7.764	13.229	4.645	-6.333
	298	3.356	6.21	2.6049	4.250	0.9800	9.367	15.960	5.597	-6.252
	303	3.300	6.24	2.6013	4.246	0.9340	10.550	17.976	6.281	-6.202
	308	3.247	6.25	2.6104	4.256	0.8813	11.963	20.383	7.095	-6.149
	313	3.195	6.28	2.6077	4.253	0.8300	13.289	22.643	7.852	-6.105
	318	3.145	6.30	2.6054	4.250	0.7250	16.013	27.284	9.441	-6.025
	288	3.472	6.18	2.5997	4.244	1.0650	7.139	12.164	4.291	-6.367
<i>ii) pH_(ini) = 5.20, [H₂A₂]_(a,ini) = 0.30 kmol/m³, [SO₄²⁻] = 0.05 kmol/m³, [Ac⁻] = 0.25 kmol/m³, [Ni(II)]_(ini) = 1.3388 kg/m³; (○)</i>										
1.20	288	3.472	11.52	2.6107	4.256	1.3057	0.864	1.472	0.288	-7.540
	293	3.413	11.55	2.6118	4.257	1.2794	1.551	2.643	0.515	-7.288
	298	3.356	11.57	2.6088	4.254	1.2616	2.014	3.432	0.668	-7.175
	303	3.300	11.60	2.6139	4.259	1.2163	3.202	5.456	1.059	-6.975
	308	3.247	11.62	2.6068	4.252	1.1583	4.705	8.017	1.556	-6.808
	313	3.195	11.65	2.6107	4.256	1.1079	6.025	10.271	1.986	-6.702
	318	3.145	11.70	2.6133	4.259	1.0137	8.496	14.476	2.786	-6.555

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Column height, m	Temp. (T), K	$(10^3/T)$, K ⁻¹	Drop fall time (t), s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) $\times 10^5$, m ²	[Ni(II)] in collected drops, kg/m ³	a _{Ni(II)} transferred from a drop	Flux (F _i) $\times 10^7$, kmol/m ² s	log (F _i kmol/m ² s)
iii) $pH_{(ini)} = 6.7$, $[H_2A_2]_{(o,ini)} = 0.30$ kmol/m ³ , $[SO_4^{2-}] = 1.00$ kmol/m ³ , $[Ac^-] = 0.25$ kmol/m ³ , $[Ni(II)]_{(ini)} = 1.310$ kg/m ³ ; (□)									
1.20	288	3.472	11.75	2.5078	4.143	1.2421	1.703	2.902	0.572
	293	3.413	11.76	2.5267	4.164	1.2110	2.501	4.261	0.835
	298	3.356	11.79	2.5235	4.161	1.1709	3.510	5.981	1.170
	303	3.300	11.82	2.5108	4.147	1.1220	4.720	8.042	1.574
	308	3.247	11.85	2.5178	4.154	1.0630	6.219	10.596	2.065
	313	3.195	11.87	2.5132	4.149	0.9911	8.015	13.656	2.661
	318	3.145	11.90	2.5166	4.153	0.9285	9.601	16.359	3.177
iv) $pH_{(ini)} = 6.6$, $[H_2A_2]_{(o,ini)} = 0.30$ kmol/m ³ , $[SO_4^{2-}] = 0.023$ kmol/m ³ , $[Ac^-] = 2.0$ kmol/m ³ , $[Ni(II)]_{(ini)} = 1.3368$ kg/m ³ ; (■)									
1.20	288	3.472	11.80	2.5839	4.227	1.1430	5.008	8.533	1.641
	293	3.413	11.84	2.5976	4.242	1.0243	8.118	13.832	2.642
	298	3.356	11.89	2.6087	4.254	0.8983	11.439	19.491	3.698
	303	3.300	11.95	2.6135	4.259	0.7289	15.887	27.069	5.105
	308	3.247	11.99	2.6055	4.250	0.5876	19.520	33.259	6.266
	313	3.195	12.05	2.6109	4.256	0.4570	22.971	39.140	7.828
	318	3.145	12.12	2.6165	4.262	0.2908	27.369	46.633	8.670

Table LI. Temperature dependence flux data in the forward extraction of Ni(II) by BTMPPA for the treatment by Activated Complex Theory, $h = 6.6252 \times 10^{-37}$ kJ s, $k = 1.38 \times 10^{-26}$ kJ/deg (Fig. 51).

Temp., K	$(1/T) \times 10^3, K^{-1}$	$F_f \times 10^{-7}, \text{kmol/m}^2\text{s}$	$\log \{(F_f h / kT) \text{ kmol/m}^2\}$
i) $pH_{(ini)} = 6.70, [H_2A_2]_{(o,ini)} = 0.10 \text{ kmol/m}^3, [SO_4^{2-}] = 0.05 \text{ kmol/m}^3, [Ac^-] = 0.25 \text{ kmol/m}^3$			
288	3.472	4.291	-19.1455
293	3.412	4.645	-19.1186
298	3.356	5.597	-19.0449
303	3.300	6.281	-19.0021
308	3.247	7.095	-18.9563
313	3.195	7.852	-18.9192
318	3.145	9.441	-18.8461
ii) $pH_{(ini)} = 5.20, [H_2A_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3, [SO_4^{2-}] = 0.05 \text{ kmol/m}^3, [Ac^-] = 0.25 \text{ kmol/m}^3$			
288	3.472	0.288	-20.3187
293	3.412	0.515	-20.0737
298	3.356	0.668	-19.9681
303	3.300	1.059	-19.7752
308	3.247	1.556	-19.6152
313	3.195	1.986	-19.5162
318	3.145	2.786	-19.3761
iii) $pH_{(ini)} = 6.70, [H_2A_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3, [SO_4^{2-}] = 1.00 \text{ kmol/m}^3, [Ac^-] = 0.25 \text{ kmol/m}^3$			
288	3.472	0.572	-20.0207
293	3.412	0.835	-19.8639
298	3.356	1.170	-19.7247
303	3.300	1.574	-19.6031
308	3.247	2.065	-19.4923
313	3.195	2.661	-19.3892
318	3.145	3.177	-19.3191
iv) $pH_{(ini)} = 6.60, [H_2A_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3, [SO_4^{2-}] = 0.023 \text{ kmol/m}^3, [Ac^-] = 2.00 \text{ kmol/m}^3$			
288	3.472	1.641	-19.5630
293	3.412	2.642	-19.3636
298	3.356	3.698	-19.2249
303	3.300	5.105	-19.0921
308	3.247	6.266	-19.0102
313	3.195	7.828	-18.9206
318	3.145	8.670	-18.8831

Table LII. Data for the estimation of forward extraction rate constant (k_f) of Ni(II) by Cyanex 272 by plotting $\log F_f$ vs. $\log f(R)$ at 303 K (Fig. 52).

[Ni(II)], kmol/m ³	[H ⁺], kmol/m ³	[H ₂ A ₂], kmol/m ³	[Ac ⁻], kmol/m ³	[SO ₄ ⁼], kmol/m ³	$[\log [\text{Ni(II)}]_{(o,mi)} + 0.5 \log$ $[\text{H}_2\text{A}_2] - \log (1 + 10^{6.32} [\text{H}^+])$ $- \log (1 + 6.3 [\text{SO}_4^{=}) - \log$ $(1 + 0.55 [\text{Ac}^-]) = \log f(R)$	$\log F_f$
0.006051	1.9953×10^{-7}	0.025	0.042	0.25	-3.32843	-7.132
0.007365	1.9953×10^{-7}	0.025	0.042	0.25	-3.24312	-7.054
0.010656	1.9953×10^{-7}	0.025	0.042	0.25	-3.08268	-6.841
0.015831	1.9953×10^{-7}	0.025	0.042	0.25	-2.91075	-6.665
0.020221	1.9953×10^{-7}	0.025	0.042	0.25	-2.80445	-6.561
0.022836	1.9953×10^{-7}	0.025	0.042	0.25	-2.75164	-6.525
0.031409	1.9953×10^{-7}	0.025	0.042	0.25	-2.61321	-6.365
0.041581	1.9953×10^{-7}	0.025	0.042	0.25	-2.49137	-6.242
0.006051	1.0000×10^{-6}	0.025	0.042	0.25	-3.66696	-7.448
0.007365	1.0000×10^{-6}	0.025	0.042	0.25	-3.58165	-7.327
0.010656	1.0000×10^{-6}	0.025	0.042	0.25	-3.42120	-7.205
0.015831	1.0000×10^{-6}	0.025	0.042	0.25	-3.24928	-7.008
0.020221	1.0000×10^{-6}	0.025	0.042	0.25	-3.14298	-6.922
0.022836	1.0000×10^{-6}	0.025	0.042	0.25	-3.09017	-6.890
0.031409	1.0000×10^{-6}	0.025	0.042	0.25	-2.95174	-6.751
0.041581	1.0000×10^{-6}	0.025	0.042	0.25	-2.82990	-6.642
0.006051	1.9953×10^{-7}	0.300	0.042	0.25	-2.78884	-6.532
0.007365	1.9953×10^{-7}	0.300	0.042	0.25	-2.70353	-6.478
0.010656	1.9953×10^{-7}	0.300	0.042	0.25	-2.54309	-6.262
0.015831	1.9953×10^{-7}	0.300	0.042	0.25	-2.37116	-6.145
0.020221	1.9953×10^{-7}	0.300	0.042	0.25	-2.26486	-6.000
0.022836	1.9953×10^{-7}	0.300	0.042	0.25	-2.21205	-5.972
0.031409	1.9953×10^{-7}	0.300	0.042	0.25	-2.07362	-5.793
0.041581	1.9953×10^{-7}	0.300	0.042	0.25	-1.95178	-5.695
0.022828	1.5800×10^{-5}	0.025	0.050	0.25	-4.15036	-7.945
0.022828	1.0000×10^{-5}	0.025	0.050	0.25	-3.95774	-7.705
0.022828	6.3100×10^{-6}	0.025	0.050	0.25	-3.76920	-7.561
0.022828	3.9800×10^{-6}	0.025	0.050	0.25	-3.58675	-7.351
0.022828	2.5100×10^{-6}	0.025	0.050	0.25	-3.41319	-7.207
0.022828	1.5900×10^{-6}	0.025	0.050	0.25	-3.25207	-7.030
0.022828	1.0000×10^{-6}	0.025	0.050	0.25	-3.10730	-6.878
0.022828	6.3100×10^{-7}	0.025	0.050	0.25	-2.98260	-6.725
0.022828	3.9800×10^{-7}	0.025	0.050	0.25	-2.88031	-6.640
0.022828	2.5100×10^{-7}	0.025	0.050	0.25	-2.80066	-6.561

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[Ni(II)], kmol/m ³	[H ⁺], kmol/m ³	[H ₂ A ₂], kmol/m ³	[Ac ⁻], kmol/m ³	[SO ₄ ⁼], kmol/m ³	{log [Ni(II)] _(o,ini) + 0.5 log [H ₂ A ₂] - log (1 + 10 ^{6.32} [H ⁺]) - log (1 + 6.3 [SO ₄ ⁼]) - log (1 + 0.55 [Ac ⁻])} = log f(R)	log F _f
0.022828	2.0000 × 10 ⁻⁷	0.025	0.050	0.25	-2.76877	-6.525
0.022828	1.5900 × 10 ⁻⁷	0.025	0.050	0.25	-2.74167	-6.513
0.022828	1.0000 × 10 ⁻⁷	0.025	0.050	0.25	-2.69984	-6.462
0.022828	1.5800 × 10 ⁻⁵	0.100	0.050	0.25	-3.84933	-7.601
0.022828	6.3100 × 10 ⁻⁶	0.100	0.050	0.25	-3.46817	-7.230
0.022828	2.5100 × 10 ⁻⁶	0.100	0.050	0.25	-3.11216	-6.872
0.022828	1.0000 × 10 ⁻⁶	0.100	0.050	0.25	-2.80627	-6.525
0.022828	3.9800 × 10 ⁻⁷	0.100	0.050	0.25	-2.57928	-6.328
0.022828	1.5900 × 10 ⁻⁷	0.100	0.050	0.25	-2.44064	-6.205
0.022828	1.5800 × 10 ⁻⁵	0.300	0.050	0.25	-3.61077	-7.335
0.022828	6.3100 × 10 ⁻⁶	0.300	0.050	0.25	-3.22961	-6.975
0.022828	3.9800 × 10 ⁻⁶	0.300	0.050	0.25	-3.04716	-6.758
0.022828	2.5100 × 10 ⁻⁶	0.300	0.050	0.25	-2.87360	-6.615
0.022828	1.5900 × 10 ⁻⁶	0.300	0.050	0.25	-2.71248	-6.468
0.022828	1.0000 × 10 ⁻⁶	0.300	0.050	0.25	-2.56771	-6.265
0.022828	6.3100 × 10 ⁻⁷	0.300	0.050	0.25	-2.44301	-6.155
0.022828	2.5100 × 10 ⁻⁷	0.300	0.050	0.25	-2.26107	-6.002
0.022828	1.0000 × 10 ⁻⁷	0.300	0.050	0.25	-2.16025	-5.875
0.022821	2.0000 × 10 ⁻⁷	0.025	0.050	0.25	-2.76888	-6.525
0.022821	2.0000 × 10 ⁻⁷	0.050	0.050	0.25	-2.61837	-6.391
0.022821	2.0000 × 10 ⁻⁷	0.075	0.050	0.25	-2.53032	-6.248
0.022821	2.0000 × 10 ⁻⁷	0.100	0.050	0.25	-2.46785	-6.202
0.022821	2.0000 × 10 ⁻⁷	0.150	0.050	0.25	-2.37981	-6.100
0.022821	2.0000 × 10 ⁻⁷	0.200	0.050	0.25	-2.31734	-6.050
0.022821	2.0000 × 10 ⁻⁷	0.250	0.050	0.25	-2.26888	-6.000
0.022821	2.0000 × 10 ⁻⁷	0.300	0.050	0.25	-2.22929	-5.947
0.022842	7.9400 × 10 ⁻⁷	0.025	0.050	0.25	-3.04200	-6.805
0.022842	7.9400 × 10 ⁻⁷	0.050	0.050	0.25	-2.89148	-6.658
0.022842	7.9400 × 10 ⁻⁷	0.075	0.050	0.25	-2.80344	-6.501
0.022842	7.9400 × 10 ⁻⁷	0.100	0.050	0.25	-2.74097	-6.486
0.022842	7.9400 × 10 ⁻⁷	0.150	0.050	0.25	-2.65292	-6.391
0.022842	7.9400 × 10 ⁻⁷	0.200	0.050	0.25	-2.59045	-6.328
0.022842	7.9400 × 10 ⁻⁷	0.250	0.050	0.25	-2.54200	-6.240
0.022842	7.9400 × 10 ⁻⁷	0.300	0.050	0.25	-2.50241	-6.225
0.022807	6.3100 × 10 ⁻⁶	0.025	0.050	0.25	-3.76959	-7.561
0.022807	6.3100 × 10 ⁻⁶	0.050	0.050	0.25	-3.61907	-7.401

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[Ni(II)], kmol/m ³	[H ⁺], kmol/m ³	[H ₂ A ₂], kmol/m ³	[Ac ⁻], kmol/m ³	[SO ₄ ⁼], kmol/m ³	$[\log [\text{Ni(II)}]_{(0,\text{ini})} + 0.5 \log$ $[\text{H}_2\text{A}_2] - \log (1 + 10^{6.32} [\text{H}^+])$ $- \log (1 + 6.3 [\text{SO}_4^{=}) - \log (1$ $+ 0.55 [\text{Ac}^-]) = \log f(\text{R})$	log F _r
0.022807	6.3100 × 10 ⁻⁶	0.075	0.050	0.25	-3.53103	-7.335
0.022807	6.3100 × 10 ⁻⁶	0.100	0.050	0.25	-3.46856	-7.230
0.022807	6.3100 × 10 ⁻⁶	0.150	0.050	0.25	-3.38051	-7.141
0.022807	6.3100 × 10 ⁻⁶	0.200	0.050	0.25	-3.31804	-7.100
0.022807	6.3100 × 10 ⁻⁶	0.250	0.050	0.25	-3.26959	-7.035
0.022807	6.3100 × 10 ⁻⁶	0.300	0.050	0.25	-3.23000	-6.975
0.022828	2.0000 × 10 ⁻⁷	0.025	0.023	0.25	-2.70907	-6.522
0.022828	2.0000 × 10 ⁻⁷	0.025	0.050	0.25	-2.76875	-6.565
0.022828	2.0000 × 10 ⁻⁷	0.025	0.068	0.25	-2.80468	-6.612
0.022828	2.0000 × 10 ⁻⁷	0.025	0.085	0.25	-2.83608	-6.649
0.022828	2.0000 × 10 ⁻⁷	0.025	0.170	0.25	-2.96601	-6.753
0.022828	2.0000 × 10 ⁻⁷	0.025	0.300	0.25	-3.11073	-6.923
0.022828	2.0000 × 10 ⁻⁷	0.025	0.500	0.25	-3.26788	-7.09
0.022828	2.0000 × 10 ⁻⁷	0.025	1.000	0.25	-3.51315	-7.322
0.022828	3.9800 × 10 ⁻⁷	0.300	0.023	0.25	-2.28056	-6.000
0.022828	3.9800 × 10 ⁻⁷	0.300	0.050	0.25	-2.34072	-6.095
0.022828	3.9800 × 10 ⁻⁷	0.300	0.085	0.25	-2.40804	-6.115
0.022828	3.9800 × 10 ⁻⁷	0.300	0.170	0.25	-2.53798	-6.261
0.022828	3.9800 × 10 ⁻⁷	0.300	0.300	0.25	-2.68269	-6.429
0.022828	3.9800 × 10 ⁻⁷	0.300	0.500	0.25	-2.83984	-6.597
0.022828	3.9800 × 10 ⁻⁷	0.300	1.000	0.25	-3.08512	-6.803
0.022828	3.9800 × 10 ⁻⁷	0.300	2.000	0.25	-3.35533	-7.093
0.022828	2.5100 × 10 ⁻⁷	0.025	0.023	0.15	-2.71897	-6.525
0.022828	2.5100 × 10 ⁻⁷	0.025	0.023	0.25	-2.74050	-6.561
0.022828	2.5100 × 10 ⁻⁷	0.025	0.023	0.35	-2.76100	-6.600
0.022828	2.5100 × 10 ⁻⁷	0.025	0.023	0.50	-2.79006	-6.605
0.022828	2.5100 × 10 ⁻⁷	0.025	0.023	0.70	-2.82600	-6.642
0.022828	2.5100 × 10 ⁻⁷	0.025	0.023	1.00	-2.87488	-6.655
0.022828	2.5100 × 10 ⁻⁷	0.025	0.023	1.50	-2.94581	-6.728
0.022828	2.5100 × 10 ⁻⁷	0.025	0.023	2.00	-3.00677	-6.830

Table LIII. Data for the determination of time needed for drop formation and coalescence in a single drop experiment in the case of extraction of Zn(II) by Cyanex 272. $[\text{Zn(II)}]_{(\text{ini})} = 1.15 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.0176 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = (6.00 \pm 0.01)$, Temperature = 303 K, Number of collected drops = 100 (Fig. 53).

Column height, m	Drop fall time (t), s	Vol. of 100 drops, cm^3	[Zn(II)] in collected drops, kg/m^3	a _{Zn(II)} transferred from a drop $\times 10^3$, mg	
				$\times 10^3$, mg	$\times 10^{11}$, kmol
0.27	2.45	3.6205	1.0030	5.322	8.138
0.40	3.64	3.6310	0.9420	7.552	11.547
0.51	4.66	3.6350	0.8925	9.360	14.311
0.60	5.45	3.6480	0.8510	10.910	16.680
0.66	6.00	3.6320	0.8200	11.986	18.327
0.90	8.18	3.6505	0.7090	16.099	24.616

Table LIV. Effect of column height on the rate of Zn(II) transfer in a Single Drop experiment in the case of extraction of Zn(II) by Cyanex 272. $[\text{Zn(II)}]_{(\text{ini})} = 1.15 \text{ kg/m}^3$, $[\text{SO}_4^{2-}] = 0.0176 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = (6.00 \pm 0.01)$, Temperature = 303 K, $\Delta t = 0.40 \text{ s}$, Number of collected drops = 100 (Fig. 54).

Column height, m	Surface area of drop (A) $\times 10^5$, m^2	a _{Zn(II)} transferred from a drop $\times 10^3$, mg		F' $\times 10^7$, kmol/m ² s	log (F' $\times 10^7$, kmol/m ² s)	F _r $\times 10^7$, kmol/m ² s	log F _r (kmol/ m ² s)
		$\times 10^3$, mg	$\times 10^{11}$, kmol				
0.27	5.293	5.322	8.138	6.276	-6.202	5.395	-6.268
0.40	5.303	7.552	11.547	5.978	-6.223	5.386	-6.269
0.51	5.307	9.360	14.311	5.812	-6.236	5.350	-6.272
0.60	5.319	10.910	16.680	5.754	-6.240	5.361	-6.271
0.66	5.304	11.986	18.327	5.760	-6.240	5.400	-6.268
0.90	5.322	16.099	24.616	5.651	-6.240	5.387	-6.269

* $F'_r = a_{\text{Zn(II)}}/A$, t ; $F_r = a_{\text{Zn(II)}}/A(t + \Delta t)$

Table LV. Effect of initial Zn(II) concentration of the aqueous phase on the Zn(II) transfer in the forward extraction of Zn(II) by Cyanex 272 in kerosene. $[\text{SO}_4^{2-}] = 0.05 \text{ kmol/m}^3$, Temperature = 303 K, $\Delta t = 0.40 \text{ s}$, Number of collected drops = 100 (Fig. 55).

[Zn(II)] _(ini) , kg/m ³	[Zn(II)] _(ini) , × 10 ³ , kmol/m ³	log ([Zn(II)] _(ini)), kmol/ m ³)	Drop fall time (t), s	Vol. of 100 drops, cm ³	Surface area of drop (A) × 10 ³ , m ²	[Zn(II)] in collected drops, kg/m ³	a _{Zn(II)} transferred from a drop		F _f × 10 ⁷ , kmol/ m ² s	log (F _f , kmol/m ² s)
							× 10 ³ , mg	× 10 ¹¹ , kmol		
i) [H ₂ A ₂] _(o,ini) = 0.025 kmol/m ³ , pH _(ini) = (6.00 ± 0.02), Column height = 0.66 m (■)										
0.100	1.53	-2.815	6.00	3.5860	5.259	0.0755	0.880	1.3460	0.400	-7.398
0.210	3.21	-2.493	5.98	3.6125	5.285	0.1491	2.200	3.3640	0.998	-7.00
0.320	4.90	-2.310	5.97	3.6020	5.274	0.2240	3.450	5.2870	1.573	-6.803
0.420	6.42	-2.192	5.95	3.6250	5.297	0.2990	4.386	6.7070	1.994	-6.700
0.750	11.09	-1.955	5.93	3.6120	5.285	0.510	7.766	11.857	3.550	-6.450
1.150	17.58	-1.755	6.00	3.6320	5.292	0.820	11.98	18.330	5.400	-6.268
1.610	24.62	-1.609	5.97	3.6400	5.311	1.160	16.38	25.050	7.406	-6.130
3.200	48.93	-1.310	5.90	3.6200	5.292	2.250	28.96	44.280	13.281	-5.876
ii) [H ₂ A ₂] _(o,ini) = 0.10 kmol/m ³ , pH _(ini) = (6.00 ± 0.02), Column height = 0.60 m (●)										
0.100	1.53	-2.815	6.02	3.5926	5.265	0.0511	1.757	2.687	0.794	-7.100
0.210	3.21	-2.493	6.00	3.6003	5.273	0.1010	3.924	6.000	1.778	-6.750
0.320	4.90	-2.310	6.03	3.6020	5.274	0.1297	6.855	10.482	3.091	-6.510
0.420	6.42	-2.192	5.98	3.6125	5.285	0.1879	8.385	12.821	3.802	-6.420
0.750	11.09	-1.955	5.98	3.6085	5.281	0.2927	15.600	23.851	7.079	-6.150
1.150	17.58	-1.755	5.97	3.6205	5.293	0.4974	23.627	36.127	10.715	-5.970
1.610	24.62	-1.609	5.96	3.6255	5.297	0.6468	34.921	53.396	15.850	-5.800
3.200	48.93	-1.310	5.96	3.6335	5.305	1.5275	60.770	92.920	27.540	-5.560

Continued...

[Zn(II)] _(ini) , kg/m ³	[Zn(II)] _(ini) , × 10 ³ kmol/m ³	log ([Zn(II)] _(ini)), kmol/ m ³	Drop fall time (t), s	Vol. of 100 drops, cm ³	Surface area of drop (A) × 10 ⁵ , m ²	[Zn(II)] in collected drops, kg/m ³	a _{zn(ii)} transferred from a drop		F _r × 10 ⁷ , kmol/ m ² s	log (F _f) kmol/m ² s
							× 10 ³ , mg	× 10 ¹¹ , kmol		
iii) [H ₂ A ₂] _(o,ini) = 0.30 kmol/m ³ , pH _(ini) = (6.00 ± 0.02), Column height = 0.40 m (▲)										
0.100	1.53	-2.815	4.68	3.5135	5.188	0.0209	2.779	4.249	1.612	-6.793
0.210	3.21	-2.493	4.70	3.5215	5.196	0.0572	5.381	8.228	3.105	-6.508
0.320	4.90	-2.310	4.71	3.5185	5.193	0.0756	8.599	13.148	4.955	-6.305
0.420	6.42	-2.192	4.72	3.5315	5.205	0.1123	10.866	16.614	6.234	-6.205
0.750	11.09	-1.955	4.68	3.5402	5.214	0.1835	19.170	29.312	11.067	-5.956
1.150	17.58	-1.755	4.72	3.5203	5.194	0.1867	33.911	51.852	19.498	-5.710
1.610	24.62	-1.609	4.68	3.5288	5.203	0.3962	43.009	65.763	24.881	-5.604
3.200	48.93	-1.310	4.65	3.5285	5.202	1.0500	75.863	115.998	44.156	-5.355
iv) [H ₂ A ₂] _(o,ini) = 0.025 kmol/m ³ , pH _(ini) = (5.00 ± 0.02), Column height = 0.66 m (▼)										
0.100	1.53	-2.815	6.05	3.6325	5.305	0.0877	0.447	0.684	0.200	-7.699
0.210	3.21	-2.493	6.00	3.6224	5.294	0.1849	0.908	1.389	0.410	-7.387
0.320	4.90	-2.310	5.98	3.6259	5.298	0.2802	1.443	2.207	0.653	-7.185
0.420	6.42	-2.192	6.00	3.6184	5.290	0.3679	1.884	2.881	0.851	-7.070
0.750	11.09	-1.955	5.96	3.6045	5.277	0.6380	3.136	4.796	1.429	-6.845
1.150	17.58	-1.755	5.95	3.6471	5.318	1.0113	5.059	7.735	2.291	-6.640
1.610	24.62	-1.609	5.85	3.6382	5.310	1.4205	6.896	10.544	3.177	-6.498
3.200	48.93	-1.310	5.78	3.6255	5.297	2.8680	12.038	18.407	5.623	-6.250
v) [H ₂ A ₂] _(o,ini) = 0.025 kmol/m ³ , pH _(ini) = (4.00 ± 0.02), Column height = 0.90 m (◆)										
0.210	3.21	-2.493	8.20	3.5825	5.255	0.1084	0.416	0.636	0.141	-7.851
0.320	4.90	-2.310	8.20	3.5785	5.252	0.3015	0.662	1.012	0.224	-7.650
0.420	6.42	-2.192	8.18	3.5792	5.352	0.3944	0.916	1.401	0.305	-7.516
0.750	11.09	-1.955	8.18	3.5805	5.353	0.6837	1.479	2.261	0.492	-7.308
1.150	17.58	-1.755	8.18	3.5804	5.353	1.0833	2.388	3.651	0.795	-7.100
1.610	24.62	-1.609	8.14	3.5830	5.356	1.5084	3.640	5.566	1.217	-6.915
3.200	48.93	-1.310	8.08	3.5824	5.255	3.0492	5.402	8.260	1.854	-6.732

Table LVI. Effect of extractant concentration of the organic on the Zn(II) transfer in the forward extraction of Zn(II) by Cyanex 272 in kerosene. $[Zn(II)]_{(ini)} = 1.15 \text{ kg/m}^3$, $[SO_4^{2-}] = 0.0176 \text{ kmol/m}^3$, Number of collected drops = 100, Temperature = 303 K, $\Delta t = 0.40 \text{ s}$ (Fig. 56).

$[H_2A_2]_{(o,ini)}$, kmol/m ³	log $[H_2A_2]_{(o,ini)}$, kmol/m ³	Column height, m	Drop fall time (t), s	Vol. of 100 drops, cm ³	Surface area of drop (A) × 10 ³ , m ²	[Zn(II)] in collected drops, kg/m ³	a _{Zn(II)} transferred from a drop × 10 ³ , mg	× 10 ¹¹ , mol	F _f × 10 ⁷ , kmol/m ² s	log (F _f , kmol/m ² s)
i) pH = (6.00 ± 0.02) (■)										
0.025	-1.602	0.66	6.00	3.6320	5.304	0.8202	11.977	18.314	5.395	-6.268
0.050	-1.300	0.66	6.20	3.5716	5.245	0.7033	15.954	24.395	7.047	-6.152
0.075	-1.125	0.66	6.26	3.5428	5.217	0.5849	20.020	30.611	8.810	-6.055
0.100	-1.000	0.66	6.42	3.5435	5.217	0.4624	24.365	37.256	10.411	-5.980
0.150	-0.825	0.66	6.70	3.5323	5.206	0.1749	34.447	52.671	14.125	-5.850
0.200	-0.699	0.40	4.27	3.5246	5.199	0.4194	25.752	39.376	16.218	-5.790
0.250	-0.600	0.40	4.54	3.5163	5.190	0.1985	33.457	51.157	19.953	-5.700
0.300	-0.523	0.30	3.61	3.5128	5.187	0.2831	30.454	40.565	22.387	-5.650
ii) pH = (5.00 ± 0.02) (●)										
0.025	-1.602	0.66	5.95	3.6471	5.318	1.0113	5.059	7.735	2.291	-6.640
0.050	-1.300	0.66	6.12	3.6450	5.316	0.9542	7.136	10.911	3.148	-6.502
0.075	-1.125	0.66	6.20	3.6272	5.299	0.9018	9.003	13.766	3.936	-6.405
0.100	-1.000	0.66	6.32	3.6385	5.310	0.8595	10.570	16.162	4.529	-6.344
0.150	-0.825	0.66	6.55	3.6455	5.317	0.7318	15.245	23.311	6.308	-6.200
0.200	-0.699	0.66	6.84	3.6512	5.322	0.5913	20.399	31.193	8.095	-6.095
0.250	-0.600	0.66	7.08	3.6414	5.313	0.5283	22.638	34.615	8.710	-6.060
0.300	-0.523	0.66	7.35	3.6477	5.319	0.4109	26.959	41.222	10.00	-6.000
iii) pH = (4.00 ± 0.01) (▲)										
0.025	-1.602	0.90	8.18	3.5804	5.353	1.0833	2.338	3.651	0.795	-7.100
0.050	-1.300	0.90	8.26	3.5998	5.272	1.0503	3.589	5.488	1.202	-6.920
0.075	-1.125	0.90	8.35	3.6025	5.275	1.0322	4.244	6.490	1.406	-6.852
0.100	-1.000	0.90	8.48	3.6145	5.287	1.0037	5.288	8.085	1.722	-6.764
0.150	-0.825	0.90	8.72	3.5950	5.268	0.9485	7.244	11.007	2.291	-6.640
0.200	-0.699	0.90	8.98	3.6090	5.281	0.8726	10.011	15.307	3.090	-6.510
0.250	-0.600	0.90	9.22	3.6058	5.278	0.8520	10.746	16.431	3.236	-6.490
0.300	-0.523	0.90	9.52	3.5928	5.266	0.8043	12.412	18.978	3.631	-6.440

Table LVII. Effect of initial aqueous pH of the flux of Zn(II) transfer in the forward extraction of Zn(II) by Cyanex 272 in kerosene. $[Zn(II)]_{(ini)} = 1.15 \text{ kg/m}^3$, $[SO_4^{2-}] = 0.0176 \text{ kmol/m}^3$, Number of collected drops = 100, Temperature = 303 K, $\Delta t = 0.40 \text{ s}$ (Fig. 57).

pH _(ini)	Column height, m	Drop fall time, s	Vol. of collected 100 drops, cm ³	Surface area of drop (A) × 10 ⁻⁵ , m ²	[Zn(II)] in collected drops, kg/m ³	a _{Zn(II)} transferred from a drop		F _F × 10 ⁷ , kmol/m ² s	log (F _F , kmol/m ² s)
						× 10 ³ , mg	× 10 ¹¹ , kmol		
i) [H ₂ A ₂] _(o,ini) = 0.025 kmol/m ³ (■)									
3.20	1.20	10.95	3.6025	5.275	1.1283	0.782	1.196	0.200	-7.700
3.40	0.90	8.20	3.6108	5.283	1.1240	0.932	1.436	0.316	-7.500
3.60	0.90	8.18	3.5938	5.266	1.1108	1.409	2.154	0.477	-7.321
3.80	0.90	8.16	3.5792	5.252	1.1016	1.732	2.648	0.589	-7.230
4.00	0.90	8.20	3.6090	5.281	1.0869	2.277	3.482	0.767	-7.115
4.30	0.90	8.18	3.5988	5.271	1.0678	2.958	4.523	1.000	-7.000
4.60	0.90	8.18	3.5920	5.265	1.0249	4.494	6.871	1.521	-6.818
5.00	0.90	8.17	3.5850	5.258	0.9668	6.568	10.040	2.228	-6.652
5.25	0.90	8.19	3.5820	5.255	0.8976	19.041	13.824	3.062	-6.514
5.50	0.66	5.95	3.5800	5.263	0.9080	8.662	13.244	3.963	-6.402
5.80	0.66	5.98	3.5875	5.260	0.8767	9.804	14.991	4.467	-6.350
6.00	0.66	6.00	3.6000	5.273	0.8170	11.988	18.331	5.432	-6.265
6.25	0.66	6.00	3.6080	5.280	0.7680	13.784	21.076	6.237	-6.205
6.50	0.66	5.95	3.5898	5.263	0.7551	14.176	21.676	6.486	-6.188
ii) [H ₂ A ₂] _(o,ini) = 0.10 kmol/m ³ (●)									
2.90	1.20	11.35	3.5920	5.265	1.1147	1.268	1.939	0.316	-7.504
3.05	1.20	11.32	3.5866	5.259	1.0998	1.800	2.752	0.446	-7.350
3.20	0.90	8.50	3.5825	5.255	1.0954	1.956	2.991	0.640	-7.194
3.40	0.90	8.48	3.5882	5.261	1.0696	2.885	4.411	0.944	-7.025
3.60	0.90	8.48	3.5810	5.254	1.0442	3.789	5.794	1.242	-6.906
3.80	0.90	8.47	3.5770	5.250	1.0205	4.632	7.083	1.521	-6.818
4.00	0.90	8.42	3.5868	5.260	0.9996	5.395	8.249	1.778	-6.750
4.30	0.90	8.45	3.5912	5.264	0.9320	7.829	11.971	2.570	-6.590
4.60	0.90	8.47	3.6003	5.273	0.8763	9.854	11.067	3.221	-6.492

Continued...

pH _(ini)	Column height, m	Drop fall time, s	Vol. of collected 100 drops, cm ³	Surface area of drop (A) × 10 ³ , m ²	[Zn(II)] in collected drops, kg/m ³	a _{Zn(II)} transferred from a drop		F _t × 10 ³ , kmol/m ² s	log (F _t ² , kmol/m ² s)
						× 10 ³ , mg	× 10 ¹¹ , kmol		
5.00	0.66	6.38	3.5866	5.259	0.8301	11.473	17.543	4.920	-6.308
5.25	0.66	6.40	3.5824	5.255	0.7932	12.782	19.544	5.469	-6.262
5.50	0.66	6.35	3.5798	5.253	0.6390	18.294	27.973	7.889	-6.103
5.80	0.66	6.33	3.5925	5.265	0.5124	22.906	35.024	9.884	-6.005
6.00	0.66	6.28	3.5808	5.254	0.4941	23.488	35.914	10.233	-5.990
6.25	0.66	6.40	3.5769	5.250	0.3321	29.255	44.736	12.531	-5.902
6.50	0.66	6.38	3.5885	5.261	0.3126	30.051	45.950	12.882	-5.890
iii) [H ₂ A ₂] _(a,ini) = 0.30 kmol/m ³ (▲)									
2.60	1.20	12.72	3.5866	5.259	1.0999	2.012	3.077	0.446	-7.352
2.90	0.90	9.54	3.5785	5.251	1.0591	3.253	4.974	0.953	-7.123
3.05	0.90	9.52	3.5686	5.242	1.0436	3.798	5.808	1.117	-6.952
3.20	0.90	9.48	3.5720	5.245	1.0155	4.804	7.345	1.429	-6.845
3.40	0.90	9.50	3.5860	5.259	0.9618	6.749	10.319	1.982	-6.703
3.60	0.66	7.05	3.5758	5.249	0.9662	6.573	10.050	2.570	-6.590
3.80	0.66	7.08	3.5820	5.255	0.9272	7.981	12.203	3.105	-6.508
4.00	0.66	7.12	3.5886	5.261	0.887	9.439	14.431	3.648	-6.438
4.30	0.66	7.10	3.5778	5.251	0.7958	12.672	19.376	4.920	-6.308
4.60	0.66	7.12	3.5806	5.254	0.6894	16.492	25.217	6.383	-6.195
5.00	0.66	7.15	3.5710	5.244	0.4978	23.291	35.613	8.995	-6.046
5.25	0.66	7.11	3.5695	5.243	0.2584	31.826	48.663	12.359	-5.908
5.50	0.40	4.32	3.5733	5.246	0.4828	23.841	36.454	14.723	-5.832
5.80	0.40	4.35	3.5702	5.243	0.2847	30.892	47.236	18.967	-5.722
6.00	0.40	4.36	3.5810	5.254	0.1576	35.538	54.339	21.728	-5.663
6.25	0.40	4.32	3.5883	5.261	0.0891	38.068	58.208	23.441	-5.630
6.50	0.40	4.33	3.5792	5.252	0.0177	40.527	61.968	24.945	-5.603

Table LVIII. Data for ΔpH ($\text{pH}_{(\text{ini})} - \text{pH}_{(\text{int})}$) of the aqueous film of interface as function of $\text{pH}_{(\text{ini})}$ at various extractant concentrations of Zn(II) . (Fig. 58).

$\text{pH}_{(\text{ini})}$	Estimated ΔpH at Cyanex 272 concentration of			$\log \Delta\text{pH}$ at Cyanex 272 concentration of		
	$0.025 \text{ kmol/m}^3 (\blacksquare)$	$0.10 \text{ kmol/m}^3 (\bullet)$	$0.30 \text{ kmol/m}^3 (\blacktriangle)$	$0.025 \text{ kmol/m}^3 (\square)$	$0.10 \text{ kmol/m}^3 (\circ)$	$0.30 \text{ kmol/m}^3 (\Delta)$
3.20	0.00	0.00	0.01	-----	-----	-2.00
3.40	0.00	0.05	0.08	-----	-1.30	-1.10
3.60	0.04	0.11	0.17	-1.40	-0.96	-0.77
3.80	0.13	0.23	0.29	-0.89	-0.64	-0.54
4.00	0.22	0.34	0.42	-0.66	-0.47	-0.38
4.30	0.40	0.50	0.59	-0.40	-0.30	-0.23
4.60	0.55	0.70	0.79	-0.25	-0.15	-0.10
5.00	0.74	0.92	1.02	-0.14	-0.04	0.01
5.25	0.88	1.06	1.16	-0.06	0.03	0.06
5.50	1.02	1.23	1.32	0.01	0.09	0.12
5.75	1.22	1.37	1.41	0.09	0.14	0.15
6.00	1.36	1.55	1.66	0.13	0.19	0.22
6.25	1.66	1.75	1.90	0.22	0.24	0.28
6.50	1.80	2.00	2.10	0.26	0.30	0.32

Table LIX. Effect of initial sulfate ion concentration of the aqueous phase on the flux of Zn(II) transfer in the forward extraction of Zn(II) by Cyanex 272 in kerosene. $[H_2A_2]_{(o,ini)} = 0.025 \text{ kmol/m}^3$, $pH_{(ini)} = (6.00 \pm 0.01)$, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.40 \text{ s}$, Column height = 0.66 m (Fig. 59).

$[SO_4^{2-}]$, kmol/m ³	$\log ([SO_4^{2-}])$, kmol/m ³	Drop fall time (t), s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) $\times 10^5$, m ²	$[Zn(II)]_{(ini)}$, kg/m ³	$[Zn(II)]$ in collected drops, kg/m ³	a _{Zn(II)} transferred from a drop		$F_r \times 10^7$, kmol/m ² s	$\log (F_r)$, kmol/m ² s
							$\times 10^3$, mg	$\times 10^{11}$, mol		
0.0176	-1.754	6.00	3.6320	5.303	1.1512	0.8212	11.996	18.343	5.405	-6.267
0.0350	-1.456	5.80	3.5630	5.236	1.0890	0.7790	11.045	16.888	5.202	-6.284
0.0700	-1.155	5.60	3.4568	5.132	1.1588	0.8688	9.997	15.286	4.964	-6.304
0.1400	-0.854	5.30	3.5460	5.220	1.1008	0.8908	9.220	14.098	4.738	-6.326
0.5600	-0.252	4.85	3.5560	5.229	1.1212	0.9215	7.101	10.858	3.995	-6.403
1.0000	0.0000	4.60	3.5624	5.236	1.1508	1.0005	5.354	8.187	3.127	-6.508
2.0000	0.3010	4.55	3.5824	5.255	1.1308	1.0206	3.948	6.037	2.320	-6.635

Table LX. Effect of temperature on the flux of Zn(II) transfer in the forward extraction of Zn(II) Cyanex 272 in kerosene.
 $[\text{Zn(II)}]_{(\text{ini})} = 1.15 \text{ kg/m}^3$, Number of collected drops = 100, $\Delta t = 0.40 \text{ s}$ (Fig. 60).

Temp., °C	Temp., K	(10 ³ /T), K ⁻¹	Drop fall time (t), s	Vol. of 100 drops, cm ³	Surface area of drop (A) × 10 ⁻⁵ , m ²	[Zn(II)] in collected drops, kg/m ³	a _{Zn(II)} transferred from a drop		F _f × 10 ⁷ , kmol/m ² s	log (F _f , kmol/m ² s)
							× 10 ³ , mg	× 10 ¹¹ , kmol		
i) pH _(ini) = 6.00, [H ₂ A ₂] _(o,ini) = 0.025 kmol/m ³ , [SO ₄ ²⁻] = 0.0176 kmol/m ³ , Column height = 0.66 m (■)										
15	288	3.472	5.95	3.5835	5.256	1.0136	4.887	7.473	2.239	-6.650
20	293	3.413	5.97	3.5085	5.183	0.9462	7.150	10.932	3.311	-6.480
25	298	3.356	5.93	3.6720	5.343	0.9093	8.839	13.515	4.571	-6.340
30	303	3.300	6.00	3.6320	5.304	0.8188	12.029	18.393	5.418	-6.266
35	308	3.247	5.91	3.6379	5.309	0.7280	13.532	20.691	6.176	-6.209
40	313	3.195	5.87	3.5211	5.195	0.7470	14.190	21.697	6.661	-6.176
45	318	3.145	5.85	3.5500	5.224	0.7185	15.232	23.291	7.134	-6.147
ii) pH _(ini) = 4.00, [H ₂ A ₂] _(o,ini) = 0.30 kmol/m ³ , [SO ₄ ²⁻] = 0.0176 kmol/m ³ , Column height = 0.90 m (●)										
15	288	3.472	9.48	3.5965	5.269	0.9128	8.531	13.044	2.506	-6.601
20	293	3.413	9.50	3.5982	5.271	0.8876	9.442	14.437	2.767	-6.558
25	298	3.356	9.52	3.5988	5.271	0.8169	11.988	18.330	3.351	-6.525
30	303	3.300	9.52	3.5928	5.266	0.8043	12.420	18.900	3.634	-6.459
35	308	3.247	9.54	3.5943	5.267	0.7708	13.630	20.841	3.981	-6.400
40	313	3.195	9.53	3.4944	5.267	0.7100	15.815	24.182	4.624	-6.335
45	318	3.145	9.54	3.5940	5.267	0.6670	17.359	26.543	5.070	-6.295
iii) pH _(ini) = 6.00, [H ₂ A ₂] _(o,ini) = 0.025 kmol/m ³ , [SO ₄ ²⁻] = 2.00 kmol/m ³ , Column height = 0.90 m (▲)										
15	288	3.472	6.31	3.5912	5.264	1.0796	2.527	3.864	1.054	-6.961
20	293	3.413	6.33	3.5938	5.266	1.0555	3.396	5.193	1.465	-6.834
25	298	3.356	6.34	3.5908	5.264	1.0263	4.442	6.792	1.914	-6.718
30	303	3.300	6.35	3.5824	5.255	1.0017	5.313	8.123	2.290	-6.640
35	308	3.247	6.37	3.5888	5.262	0.9707	6.435	9.839	2.762	-6.559
40	313	3.195	6.37	3.5882	5.261	0.9405	7.517	11.494	3.227	-6.491
45	318	3.145	6.38	3.5902	5.263	0.9034	8.853	13.537	3.794	-6.421

Table LXI. Data for the treatment of temperature dependent flux data of Zn(II) extraction by BTMPPA in kerosene by the Activated Complex

Theory: For the plots of $\log (F_f h/kT)$ vs. $1/T$, $h = 6.6252 \times 10^{-37}$ kJ s, $k = 1.38 \times 10^{-26}$ kJ/deg (Fig. 61).

Temp. K	$(1/T) \times 10^3, K^{-1}$	$F_f \times 10^{-7}, \text{kmol/m}^2\text{s}$	$\log \{(F_f h/kT) \text{ kmol/m}^2\}$
<i>i) $pH_{(ini)} = 6.00, [H_2A_2]_{(o)} = 0.025 \text{ kmol/m}^3, [SO_4^{=}] = 0.0176 \text{ kmol/m}^3$</i>			
288	3.472	2.239	-19.428
293	3.412	3.311	-19.266
298	3.356	4.571	-19.133
303	3.300	5.418	-19.066
308	3.247	6.176	-19.017
313	3.195	6.661	-18.991
318	3.145	7.134	-18.968
<i>ii) $pH_{(ini)} = 4.00, [H_2A_2]_{(o)} = 0.30 \text{ kmol/m}^3, [SO_4^{=}] = 0.0176 \text{ kmol/m}^3$</i>			
288	3.472	2.506	-19.379
293	3.412	2.767	-19.344
298	3.356	3.351	-19.268
303	3.300	3.634	-19.240
308	3.247	3.981	-19.207
313	3.195	4.624	-19.149
318	3.145	5.070	-19.116
<i>iii) $pH_{(ini)} = 6.00, [H_2A_2]_{(o)} = 0.025 \text{ kmol/m}^3, [SO_4^{=}] = 2.00 \text{ kmol/m}^3$</i>			
288	3.472	1.054	-19.755
293	3.412	1.465	-19.620
298	3.356	1.914	-19.511
303	3.300	2.29	-19.440
308	3.247	2.762	-19.360
313	3.195	3.227	-19.305
318	3.145	3.794	-19.242

Table LXII. Data for the estimation of forward extraction rate constant (k_f) of Zn(II) by Cyanex 272 (Fig. 62).

$[\text{Zn(II)}]_i$, kmol/m ³	pH _(ini)	$[\text{H}_2\text{A}_2]_i$, kmol/m ³	(pH _(ini) - ΔpH)	$[\text{SO}_4^{2-}]_i$, kmol/m ³	$[\log [\text{Zn(II)}] + \log ([\text{H}_2\text{A}_2]^{0.5} + 1.07 [\text{H}_2\text{A}_2]) + (\text{pH}_{(\text{ini})} - \Delta\text{pH}) - \log (1 + 0.708 [\text{SO}_4^{2-}])] = f(R)$	log F_f
0.001529	6	0.025	4.64	0.0500	1.076166	-7.398
0.003211	6	0.025	4.64	0.0500	1.398385	-7.001
0.004893	6	0.025	4.64	0.0500	1.581316	-6.803
0.006422	6	0.025	4.64	0.0500	1.699415	-6.700
0.011468	6	0.025	4.64	0.0500	1.951227	-6.450
0.017584	6	0.025	4.64	0.0500	2.136864	-6.268
0.024618	6	0.025	4.64	0.0500	2.282992	-6.130
0.048930	6	0.025	4.64	0.0500	2.581316	-5.876
0.001529	6	0.100	4.45	0.0500	1.245888	-7.100
0.003211	6	0.100	4.45	0.0500	1.568108	-6.750
0.004893	6	0.100	4.45	0.0500	1.751038	-6.510
0.006422	6	0.100	4.45	0.0500	1.869138	-6.420
0.011468	6	0.100	4.45	0.0500	2.120950	-6.150
0.017584	6	0.100	4.45	0.0500	2.306586	-5.970
0.024618	6	0.100	4.45	0.0500	2.452714	-5.800
0.048930	6	0.100	4.45	0.0500	2.751038	-5.560
0.001529	6	0.300	4.34	0.0500	1.448195	-6.793
0.003211	6	0.300	4.34	0.0500	1.770414	-6.508
0.004893	6	0.300	4.34	0.0500	1.953345	-6.305
0.006422	6	0.300	4.34	0.0500	2.071444	-6.205
0.011468	6	0.300	4.34	0.0500	2.323256	-5.956
0.017584	6	0.300	4.34	0.0500	2.508893	-5.710
0.024618	6	0.300	4.34	0.0500	2.655021	-5.604
0.048930	6	0.300	4.34	0.0500	2.953345	-5.355
0.001529	5	0.025	4.26	0.0500	0.696166	-7.699
0.003211	5	0.025	4.26	0.0500	1.018385	-7.387
0.004893	5	0.025	4.26	0.0500	1.201316	-7.185
0.006422	5	0.025	4.26	0.0500	1.319415	-7.070
0.011468	5	0.025	4.26	0.0500	1.571227	-6.845
0.017584	5	0.025	4.26	0.0500	1.756864	-6.640
0.024618	5	0.025	4.26	0.0500	1.902992	-6.498
0.048930	5	0.025	4.26	0.0500	2.201316	-6.250
0.003211	4	0.025	3.78	0.0500	0.538385	-7.851
0.004893	4	0.025	3.78	0.0500	0.721316	-7.650
0.006422	4	0.025	3.78	0.0500	0.839415	-7.316
0.011086	4	0.025	3.78	0.0500	1.076504	-7.308

Continued...

$[\text{Zn(II)}]_2$ kmol/m ³	pH _(ini)	$[\text{H}_2\text{A}_2]_2$ kmol/m ³	(pH _(ini) - ΔpH)	$[\text{SO}_4^{=}]_2$ kmol/m ³	$\{\log [\text{Zn(II)}] + \log ([\text{H}_2\text{A}_2]^{0.5} + 1.07 [\text{H}_2\text{A}_2]) + (\text{pH}_{(\text{ini})} - \Delta\text{pH}) - \log (1 + 0.708 [\text{SO}_4^{=}])\} = \log f(\text{R})$	log F _f
0.017584	4	0.025	3.78	0.0500	1.276864	-7.100
0.024618	4	0.025	3.78	0.0500	1.422992	-6.915
0.048930	4	0.025	3.78	0.0500	1.721316	-6.732
0.017584	6	0.025	4.64	0.0176	2.146594	-6.268
0.017584	6	0.050	4.55	0.0176	2.232389	-6.152
0.017584	6	0.075	4.50	0.0176	2.288882	-6.055
0.017584	6	0.100	4.45	0.0176	2.316316	-5.980
0.017584	6	0.150	4.40	0.0176	2.378363	-5.850
0.017584	6	0.200	4.38	0.0176	2.440084	-5.790
0.017584	6	0.250	4.36	0.0176	2.484820	-5.700
0.017584	6	0.300	4.34	0.0176	2.518623	-5.650
0.017584	5	0.025	4.26	0.0176	1.766594	-6.640
0.017584	5	0.050	4.17	0.0176	1.852389	-6.502
0.017584	5	0.075	4.15	0.0176	1.938882	-6.405
0.017584	5	0.100	4.08	0.0176	1.946316	-6.344
0.017584	5	0.150	4.05	0.0176	2.028363	-6.200
0.017584	5	0.200	4.02	0.0176	2.080084	-6.095
0.017584	5	0.250	4.00	0.0176	2.124820	-6.060
0.017584	5	0.300	3.98	0.0176	2.158623	-6.000
0.017584	4	0.025	3.78	0.0176	1.286594	-7.100
0.017584	4	0.050	3.72	0.0176	1.402389	-6.920
0.017584	4	0.075	3.70	0.0176	1.488882	-6.852
0.017584	4	0.100	3.66	0.0176	1.526316	-6.764
0.017584	4	0.150	3.64	0.0176	1.618363	-6.640
0.017584	4	0.200	3.62	0.0176	1.680084	-6.510
0.017584	4	0.250	3.60	0.0176	1.724820	-6.490
0.017584	4	0.300	3.58	0.0176	1.758623	-6.440
0.017584	6	0.025	4.64	0.0176	2.146594	-6.267
0.017584	6	0.025	4.64	0.0350	2.141342	-6.284
0.017584	6	0.025	4.64	0.0700	2.130965	-6.304
0.017584	6	0.025	4.64	0.1400	2.110927	-6.326
0.017584	6	0.025	4.64	0.5600	2.006937	-6.403
0.017584	6	0.025	4.64	1.0000	1.919484	-6.508
0.017584	6	0.025	4.64	2.0000	1.768875	-6.635

Table LXIII. Effect of Mn(II) concentration in the organic phase on the Mn(II) transfer flux in stripping of Mn(II)-Cyanex 272

complex by sulfate-acetato solution. $[H_2A_2]_{(o,ini)} = 0.11 \text{ kmol/m}^3$, $[Ac^-] = 0.25 \text{ kmol/m}^3$, $pH_{(ini)} = 2.70$, $[SO_4^{2-}] = 0.01 \text{ kmol/m}^3$, Columnheight = 0.66 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$ (Fig. 63).

[Mn(II)] _(o,ini) , kg/m ³	[Mn(II)] _(o,ini) , $\times 10^3$, kmol/m ³	log. ([Mn(II)] _(o,ini) , kmol /m ³)	Fall time + Δt , s	Vol. of 100 drops, cm ³	Surface area of a drop (A) $\times 10^5$, m ²	[Mn(II)] in collected drops, kg/m ³	a _{Mn(II)} transferred from a drop		$F_b \times 10^7$, kmol/m ² s	log (F _b , kmol/m ² s)
							$\times 10^3$, mg	$\times 10^{11}$, kmol		
0.10	1.82	-2.74	6.95	3.105	4.78	0.0235	0.73	1.32	0.398	-7.40
0.20	3.64	-2.44	6.92	3.285	4.96	0.0424	1.38	2.51	0.731	-7.13
0.30	5.46	-2.26	6.96	3.135	4.81	0.0690	2.16	3.93	1.175	-6.93
0.40	7.28	-2.14	6.93	3.082	4.75	0.0840	2.59	4.71	1.430	-6.84
0.60	10.92	-1.96	6.96	3.153	4.83	0.1373	4.33	7.89	2.340	-6.85
0.80	14.56	-1.84	7.04	3.474	5.15	0.1606	5.58	10.15	2.800	-6.55
1.00	18.20	-1.74	7.01	3.202	4.88	0.2230	7.14	13.00	3.800	-6.42
1.20	21.84	-1.66	7.06	3.249	4.92	0.2380	7.73	14.07	4.050	-6.39
1.50	27.30	-1.56	7.05	3.250	4.92	0.3295	10.71	19.49	5.620	-6.25

Table LXIV. Effect of pH of aqueous phase on the Mn(II) transfer in the stripping of Mn(II)-Cyanex 272 complex by sulfate-acetato solution. $[\text{Mn(II)}]_{(a,ini)} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{SO}_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.66 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$ (Fig. 64).

pH _(ini)	Drop fall time + Δt, s	Vol. of 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Mn(II)] in collected drops, kg/m ³	a _{Mn(II)} transferred from a drop × 10 ³ , mg		F _b × 10 ⁷ , kmol/m ² s	log (F _b , kmol/m ² s)
					× 10 ¹¹ , kmol			
i) [H ₂ A ₂] _(a,ini) = 0.025 kmol/m ³								
1.60	6.72	3.4256	5.100	0.3237	11.09	20.180	5.89	-6.23
2.00	6.74	3.3286	5.000	0.3058	10.18	18.535	5.40	-6.26
2.40	6.76	3.4385	5.115	0.2414	8.30	15.110	4.37	-6.36
2.70	6.73	3.3436	5.060	0.1747	5.91	10.761	3.16	-6.50
3.00	6.75	3.4058	5.080	0.1184	4.03	7.338	2.14	-6.67
3.20	6.72	3.4319	5.110	0.0715	2.66	4.842	1.41	-6.85
3.40	6.76	3.4426	5.120	0.0552	1.90	3.461	1.00	-7.00
ii) [H ₂ A ₂] _(a,ini) = 0.125 mol/m ³								
1.60	6.68	3.4098	5.09	0.1504	5.13	9.350	2.75	-6.56
2.00	6.70	3.2122	4.89	0.1441	4.63	8.420	2.57	-6.59
2.40	6.80	3.5360	5.20	0.1052	3.72	6.770	1.91	-6.71
2.70	6.85	3.3285	5.00	0.0720	4.20	4.360	1.31	-6.88
3.00	6.81	3.4090	5.08	0.0531	1.81	3.300	0.95	-7.02
3.20	6.70	3.4353	5.11	0.0361	1.24	2.250	0.66	-7.18
3.40	6.70	3.4503	5.13	0.0246	0.85	1.550	0.45	-7.35

Table LXV. Effect of free extractant concentration in the organic phase on the Mn(II) transfer flux in stripping of Mn(II)-Cyanex 272 complex by sulfate-acetate solution. $[Ac^-] = 0.25 \text{ kmol/m}^3$, $[Mn(II)]_{(o,ini)} = 0.40 \text{ kg/m}^3$, $[SO_4^{2-}] = 0.01 \text{ kmol/m}^3$, Column height = 0.66 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$ (Fig. 65).

[H ₂ A ₂] _(o, ini) , kmol/m ³	log [H ₂ A ₂] _(o, ini) , kmol/m ³	Drop fall time, s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Mn(II)] in collected drops, kg/m ³	a _{Mn(II)} transferred from a drop		F _b × 10 ⁷ , kmol/m ² s	log (F _b), kmol/m ² s
						× 10 ³ , mg	× 10 ¹¹ , kmol		
i) pH _(ini) = 2.00									
0.020	-1.700	6.73	3.4820	5.160	0.3457	12.037	21.910	6.310	-6.20
0.025	-1.602	6.71	3.4486	5.125	0.3010	10.382	18.897	5.495	-6.26
0.040	-1.400	6.69	3.4292	5.105	0.2619	8.980	16.345	4.786	-6.32
0.070	-1.155	6.69	3.4536	5.132	0.1809	6.246	11.368	3.311	-6.48
0.100	-1.000	6.68	3.4395	5.117	0.1538	5.291	9.630	2.818	-6.55
0.125	-0.903	6.68	3.4536	5.130	0.1401	4.839	8.807	2.570	-6.59
0.150	-0.824	6.68	3.4689	5.143	0.1305	4.528	8.242	2.399	-6.62
0.200	-0.700	6.70	3.4528	5.130	0.1117	3.856	7.019	2.041	-6.69
ii) pH _(ini) = 3.00									
0.020	-1.700	6.75	3.4425	5.120	0.1323	4.555	8.291	2.399	-6.62
0.025	-1.602	6.72	3.4472	5.122	0.1173	4.043	7.359	2.138	-6.67
0.040	-1.400	6.72	3.4327	5.110	0.0933	3.204	5.831	1.698	-6.77
0.070	-1.155	6.70	3.4330	5.110	0.0690	2.368	4.310	1.259	-6.90
0.100	-1.000	6.70	3.4520	5.300	0.0634	2.189	3.984	1.122	-9.95
0.125	-0.903	6.72	3.4485	5.250	0.5370	1.851	3.639	0.955	-7.02
0.150	-0.824	6.72	3.4465	5.122	0.0446	1.537	2.798	0.813	-7.09

Table LXVI. Effect of sulfate ion concentration in the aqueous phase on the Mn(II) transfer flux in stripping rate of Mn(II)-

Cyanex 272 complex by sulfate-acetate solution. $[\text{Mn(II)}]_{(0,\text{ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $[\text{H}_2\text{A}_2]_{(0,\text{ini})} = 0.025 \text{ kmol/m}^3$, $\text{pH}_{(\text{ini})} = 3.00$, Column height = 0.66 m, Temperature = 303 K, Number of collected drops = 100, $\Delta t = 0.50 \text{ s}$ (Fig. 66).

[SO ₄ ²⁻], kmol/m ³	log {[SO ₄ ²⁻], kmol/m ³ }	Drop fall time (t), s	Vol. of collected 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Mn(II)], kg/m ³	a _{Mn(II)} transferred from a drop		F _b × 10 ⁷ , kmol/m ² s	log (F _b , kmol/m ² s)
						× 10 ³ , mg	× 10 ¹¹ , kmol		
0.01	-2.00	6.72	3.4472	5.122	0.1173	4.0430	7.359	2.138	-6.670
0.02	-1.70	6.74	3.4492	5.124	0.1228	4.2356	7.701	2.223	-6.653
0.03	-1.52	6.70	3.4265	5.097	0.1264	4.3470	7.913	2.317	-6.635
0.05	-1.30	6.68	3.4280	5.099	0.1365	4.6781	8.515	2.500	-6.602
0.10	-1.00	6.70	3.4320	5.105	0.1826	5.3198	9.683	3.831	-6.548
0.20	-0.70	6.72	3.4532	5.129	0.2106	6.0987	11.102	3.221	-6.492
0.30	-0.52	6.74	3.4450	5.120	0.2758	9.5017	17.296	5.012	-6.300

Table LXVII. Effect of temperature on Mn(II) transfer flux in the stripping of Mn(II)-Cyanex 272 by sulfate-acetato solution.

$[\text{Mn(II)}]_{(\alpha, \text{ini})} = 0.40 \text{ kg/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, Number of collected drops = 100, Column height = 0.66 m, $\Delta t = 0.5 \text{ s}$. (Fig. 67).

Temp. K	(10 ³ /T), K ⁻¹	Drop fall time + Δt, s	Vol. of collected 100 drops, cm ³	Surface area of a drop × 10 ⁵ , m ²	[Mn(II)] in collected drops, kg/m ³	a _{Mn(II)} transferred from a drop		F _b × 10 ⁷ , kmol/m ² s	log (F _b , kmol/m ² s)
						× 10 ³ , mg	× 10 ¹¹ , kmol		
i) pH _(ini) = 3.50, [H ₂ A ₂] = 0.025 kmol/m ³ , [SO ₄ ²⁻] = 1.00 kmol/m ³ ; (Δ)									
288	3.472	6.70	3.48	5.155	0.0905	3.15	5.733	1.66	-6.78
293	3.413	6.68	3.45	5.125	0.1249	4.31	7.840	2.29	-6.64
298	3.356	6.71	3.47	4.145	0.1729	6.00	10.909	3.16	-6.50
303	3.300	6.65	3.49	5.165	0.2711	9.46	17.208	5.01	-6.30
308	3.247	6.68	3.50	5.174	0.3840	13.44	24.470	7.08	-6.15
313	3.195	6.70	3.50	5.174	0.5442	19.05	34.666	10.00	-6.00
318	3.145	6.69	3.52	5.194	0.7963	28.03	51.392	14.68	-5.83
ii) pH _(ini) = 1.50, [H ₂ A ₂] _(α, ini) = 0.025 kmol/m ³ , [SO ₄ ²⁻] = 0.05 kmol/m ³ ; (●)									
288	3.472	6.63	3.45	5.125	0.2652	9.15	16.650	4.90	-6.31
293	3.413	6.65	3.43	5.105	0.2991	10.26	18.672	5.55	-6.26
298	3.356	6.60	3.42	5.100	0.3412	11.67	21.239	6.31	-6.20
303	3.300	6.63	3.44	5.115	0.3837	13.20	24.010	7.08	-6.15
308	3.247	6.62	3.46	5.135	0.4491	15.54	28.283	8.32	-6.08
313	3.195	6.64	3.41	5.085	0.5076	17.31	31.502	9.33	-6.03
318	3.145	6.65	3.45	5.125	0.5684	19.61	35.683	10.47	-5.98
iii) pH _(ini) = 2.70, [H ₂ A ₂] _(α, ini) = 0.055 kmol/m ³ , [SO ₄ ²⁻] = 0.01 kmol/m ³ ; (o)									
288	3.472	6.66	3.50	5.174	0.0471	1.65	3.00	0.87	-7.06
293	3.413	6.62	3.50	5.174	0.0694	2.43	4.42	1.29	-6.89
298	3.356	6.65	3.46	5.135	0.0858	2.97	5.40	1.58	-6.80
303	3.300	6.64	3.47	5.145	0.1104	3.83	6.97	2.04	-6.69
308	3.247	6.60	3.49	5.165	0.1347	4.70	8.56	2.51	-6.60
313	3.195	6.63	3.48	5.155	0.1629	5.67	10.32	3.02	-6.62
318	3.145	6.65	3.47	5.145	0.1793	6.22	11.32	3.31	-6.48

Continued....

Continued....

Temp. K	$10^3/T, K^{-1}$	Drop fall time + $\Delta t, s$	Vol. of collected 100 drops, cm^3	Surface area of a drop $\times$ $10^5, m^2$	[Mn(II)] in collected drops, kg/m^3	$a_{Mn(II)}$ transferred from a drop $\times 10^3, mg$	$\times 10^{11}, kmol$	$F_b \times 10^7,$ $kmol/m^2 s$	$\log (F_b,$ $kmol/m^2 s)$
iv) $pH_{(ini)} = 3.50, [H_2A_2]_{(a, ini)} = 0.025 kmol/m^3, [SO_4^{2-}] = 0.05 kmol/m^3; (\square)$									
288	3.472	6.60	3.46	5.135	0.0199	0.60	1.26	0.37	-7.43
293	3.413	6.66	3.50	5.174	0.0283	0.98	1.79	0.52	-7.28
298	3.356	6.62	3.49	5.165	0.0387	1.35	2.46	0.72	-7.14
303	3.300	6.61	3.48	5.155	0.0566	1.96	3.58	1.05	-6.98
308	3.247	6.65	3.45	5.125	0.0684	2.36	4.29	1.26	-6.90
303	3.195	6.64	3.46	5.135	0.0786	2.72	4.94	1.45	-6.84
318	3.145	6.66	3.48	5.155	0.0856	2.98	5.42	1.58	-6.80
v) $pH_{(ini)} = 1.50, [H_2A_2]_{(a, ini)} = 0.20 kmol/m^3, [SO_4^{2-}] = 1.00 kmol/m^3; (\blacksquare)$									
288	3.472	6.68	3.50	5.174	0.2849	9.97	18.15	5.25	-6.28
293	3.413	6.65	3.48	5.155	0.4011	13.96	15.40	7.41	-6.13
298	3.356	6.66	3.46	5.135	0.5434	18.80	34.20	10.00	-6.00
303	3.300	6.62	3.48	5.155	0.6784	23.61	42.96	12.59	-5.90
308	3.247	6.65	3.47	5.145	0.8014	27.81	50.60	14.79	-5.83
313	3.195	6.67	3.45	5.125	0.9681	33.40	60.78	17.78	-5.75
318	3.145	6.66	3.48	5.155	1.1072	38.53	70.11	20.42	-5.69

Table LXVIII. Data for $\log (F_b h/kT)$ vs. $(1/T)$ plot in the backward extraction rate of Mn(II) in the Mn(II)-Cyanex 272 complex- H_2A_2 -kerosene - $(Na^+, H^+) SO_4^{2-}-Ac^-$ system, $h = 6.6252 \times 10^{-37}$ kJ s, $k = 1.38 \times 10^{-26}$ kJ/deg (Fig. 68).

Temp., K	$(1/T) \times 10^3, K^{-1}$	$F_b \times 10^{-7}, \text{kmol/m}^2\text{s}$	$\log \{(F_b h/kT) \text{ kmol/m}^2\}$
<i>i) $pH_{(ini)} = 3.50, [H_2A_2] = 0.025 \text{ kmol/m}^3, [SO_4^{2-}] = 1.00 \text{ kmol/m}^3$</i>			
288	3.472	1.66	-19.558
293	3.413	2.29	-19.4257
298	3.356	3.16	-19.2932
303	3.300	5.01	-19.1003
308	3.247	7.08	-18.9572
313	3.195	10.00	-18.8142
318	3.145	14.68	-18.6544
<i>ii) $pH_{(ini)} = 1.50, [H_2A_2]_{(o, ini)} = 0.025 \text{ kmol/m}^3, [SO_4^{2-}] = 0.05 \text{ kmol/m}^3$</i>			
288	3.472	4.90	-19.0879
293	3.413	5.55	-19.0413
298	3.356	6.31	-18.9929
303	3.300	7.08	-18.9501
308	3.247	8.32	-18.8871
313	3.195	9.33	-18.8443
318	3.145	10.47	-18.8012
<i>iii) $pH_{(ini)} = 2.70, [H_2A_2]_{(o, ini)} = 0.055 \text{ kmol/m}^3, [SO_4^{2-}] = 0.01 \text{ kmol/m}^3$</i>			
288	3.472	0.87	-19.8386
293	3.413	1.29	-19.675
298	3.356	1.58	-19.5942
303	3.300	2.04	-19.4905
308	3.247	2.51	-19.4076
313	3.195	3.02	-19.3342
318	3.145	3.31	-19.3013
<i>iv) $pH_{(ini)} = 3.50, [H_2A_2]_{(o, ini)} = 0.025 \text{ kmol/m}^3, [SO_4^{2-}] = 0.05 \text{ kmol/m}^3$</i>			
288	3.472	0.37	-20.2099
293	3.413	0.52	-20.0695
298	3.356	0.72	-19.9356
303	3.300	1.05	-19.7789
308	3.247	1.26	-19.7069
313	3.195	1.45	-19.6529
318	3.145	1.58	-19.6225
<i>v) $pH_{(ini)} = 1.50, [H_2A_2]_{(o, ini)} = 0.20 \text{ kmol/m}^3, [SO_4^{2-}] = 1.00 \text{ kmol/m}^3$</i>			
288	3.472	5.25	-19.0579
293	3.413	7.41	-18.9157
298	3.356	10.00	-18.7929
303	3.300	12.59	-18.7001
308	3.247	14.79	-18.6373
313	3.195	17.78	-18.5643
318	3.145	20.42	-18.5111

Table LXIX. Data for the estimation of rate constant (k_b) in backward extraction of Mn(II) in the Mn(II)-Cyanex 272 complex- H_2A_2 -kerosene - (Na^+ , H^+) SO_4^{2-} -Ac⁻ system at 303 K (Fig. 69).

$[Mn(II)]_{(o,ini)}$, kmol/m ³	$[H_2A_2]_3$, kmol/m ³	$[H^+]$, kmol/m ³	$[SO_4^{2-}]$, kmol/m ³	$[\log [Mn(II)]_{(o,ini)} - \log (1 + 0.002$ $[H^+]^{-1}) - 0.5 \log [H_2A_2] + \log$ $(1 + 5.129 [SO_4^{2-}])] = \log f(R)$	$\log F_b$
0.001820	0.110	501.1870	0.01	-2.5404	-7.400
0.003640	0.110	501.1870	0.01	-2.2394	-7.130
0.005461	0.110	501.1870	0.01	-2.0633	-6.930
0.007281	0.110	501.1870	0.01	-1.9383	-6.840
0.010921	0.110	501.1870	0.01	-1.7623	-6.650
0.014561	0.110	501.1870	0.01	-1.6373	-6.550
0.018202	0.110	501.1870	0.01	-1.5404	-6.420
0.021842	0.110	501.1870	0.01	-1.4612	-6.390
0.027303	0.110	501.1870	0.01	-1.3643	-6.250
0.007281	0.025	39.8110	0.01	-1.3483	-6.230
0.007281	0.025	100.0000	0.01	-1.3943	-6.260
0.007281	0.025	251.1890	0.01	-1.4919	-6.360
0.007281	0.025	501.1870	0.01	-1.6166	-6.500
0.007281	0.025	1000.0000	0.01	-1.7922	-6.670
0.007281	0.025	1584.8900	0.01	-1.9352	-6.850
0.007281	0.025	2511.8860	0.01	-2.0949	-7.000
0.007281	0.125	39.8110	0.01	-1.6978	-6.560
0.007281	0.125	100.0000	0.01	-1.7437	-6.590
0.007281	0.125	251.1886	0.01	-1.8413	-6.710
0.007281	0.125	501.1870	0.01	-1.9661	-6.880
0.007281	0.125	1000.0000	0.01	-2.1417	-7.020
0.007281	0.125	1584.8930	0.01	-2.2847	-7.180
0.007281	0.125	2511.8860	0.01	-2.4444	-7.350
0.007281	0.020	100.0000	0.01	-1.3458	-6.200
0.007281	0.025	100.0000	0.01	-1.3943	-6.260
0.007281	0.040	100.0000	0.01	-1.4963	-6.320
0.007281	0.070	100.0000	0.01	-1.6178	-6.480
0.007281	0.100	100.0000	0.01	-1.6953	-6.550
0.007281	0.125	100.0000	0.01	-1.7437	-6.590
0.007281	0.150	100.0000	0.01	-1.7833	-6.620
0.007281	0.200	100.0000	0.01	-1.8458	-6.690
0.007281	0.020	1000.0000	0.01	-1.7437	-6.620
0.007281	0.025	1000.0000	0.01	-1.7922	-6.670
0.007281	0.040	1000.0000	0.01	-1.8943	-6.770
0.007281	0.070	1000.0000	0.01	-2.0158	-6.900
0.007281	0.100	1000.0000	0.01	-2.0932	-6.950
0.007281	0.125	1000.0000	0.01	-2.1417	-7.020
0.007281	0.150	1000.0000	0.01	-2.1813	-7.090
0.007281	0.025	1000.0000	0.01	-1.7922	-6.670
0.007281	0.025	1000.0000	0.02	-1.7715	-6.653
0.007281	0.025	1000.0000	0.03	-1.7518	-6.635
0.007281	0.025	1000.0000	0.05	-1.7148	-6.602
0.007281	0.025	1000.0000	0.10	-1.6341	-6.548
0.007281	0.025	1000.0000	0.20	-1.5073	-6.492
0.007281	0.025	1000.0000	0.30	-1.4093	-6.300

Table LXX. Dependence of organic phase Ni(II) concentration on the flux of Ni(II) transfer during stripping by sulphuric acid
 - acetic acid mixture. $\text{pH}_{(\text{ini})} = 5.0$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ kmol/m}^3$, $[\text{SO}_4] = 0.1 \text{ kmol/m}^3$, $[\text{Ac}^-] = 0.25 \text{ kmol/m}^3$, $\Delta t = 0.5 \text{ s}$, Temp. = 303 K (Fig. 70).

[Ni(II)] _(o,ini) , kmol/m ³	log ([Ni(II)] _(o,ini) , kmol/m ³)	Column height, m	Drop fall time (t) + Δt , s	Vol. of 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Ni(II)] collected drops, kg/m ³	a _{Ni(II)} transferred to a drop		Flux (F _b × 10 ⁷ , kmol/m ² s)	log (F _b , kmol/m ² s)
							× 10 ³ , mg	× 10 ¹¹ , kmol		
0.0034	-2.468	1.20	12.40	3.552	5.226	0.0613	2.177	3.709	0.572	-7.243
0.0068	-2.167	1.20	12.43	3.518	5.192	0.1231	4.331	7.379	1.143	-6.942
0.0136	-1.865	0.90	9.51	3.547	5.221	0.1882	6.675	11.373	2.291	-6.640
0.0204	-1.689	0.90	9.54	3.568	5.241	0.2851	10.172	17.322	3.466	-6.460
0.0273	-1.564	0.66	7.22	3.572	5.245	0.2850	10.180	17.345	4.580	-6.339
0.0340	-1.467	0.66	7.26	3.588	5.261	0.3576	12.840	21.878	5.728	-6.242

Table LXXI. Dependence of the aqueous phase acidity on the Ni(II) transfer flux in stripping of Ni(II) by H₂SO₄- Acetic acid mixture.

[Ni(II)_(o,ini)] = 0.40 kg/m³, [SO₄²⁻] = 0.1 kmol/m³, [Ac⁻] = 0.25 kmol/m³, Number of collected drops = 100, Δt = 0.5s, Temp = 303 K (Fig. 71).

pH _(ini)	Column height, m	Drop fall time (t) + Δt, s	Vol. of 100 drops , cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Ni(II)] collected drops, kg/m ³	a _{Ni(m)} × 10 ³ , mg × 10 ¹¹ , kmol	Flux (F _b) × 10 ⁷ , kmol/m ² s	log (F _b , kmol/m ² s)
i) [H ₂ A ₂] _(o,ini) = 0.025 kmol/m ³ ; (○)								
6.0	1.20	12.37	3.555	5.229	0.0149	0.528	0.899	-7.857
5.5	1.20	12.40	3.524	5.198	0.0380	1.339	2.282	-7.451
5.0	1.20	12.38	3.568	5.241	0.1192	4.253	7.247	-6.952
4.5	1.20	12.38	3.549	5.223	0.3707	13.157	22.418	-6.460
4.0	0.40	4.34	3.542	5.216	0.3566	12.630	21.519	-6.022
3.5	0.40	4.32	3.539	5.213	0.5671	20.071	35.285	-5.805
3.0	0.20	2.36	3.529	5.203	0.4551	16.060	27.363	-5.652
2.5	0.20	2.35	3.536	5.210	0.5014	18.050	30.754	-5.600
2.0	0.20	2.35	3.551	5.225	0.5437	19.307	32.897	-5.572
ii) [H ₂ A ₂] _(o,ini) = 0.30 kmol/m ³ ; (●)								
5.0	1.20	12.52	3.547	5.221	0.0203	0.720	1.227	-7.725
4.5	1.20	12.48	3.541	5.215	0.0624	2.210	3.766	-7.237
4.0	1.20	12.51	3.546	5.220	0.1667	5.911	10.072	-6.812
3.5	0.66	7.11	3.551	5.225	0.2178	7.734	13.178	-6.450
3.0	0.66	7.13	3.549	5.223	0.3232	11.470	19.543	-6.280
2.5	0.40	4.50	3.539	5.213	0.2722	9.633	16.413	-6.155
2.0	0.40	4.51	3.542	5.216	0.2890	10.236	17.441	-6.130

Table LXXII. Dependence of organic phase free-extractant concentration on the stripping flux of Ni(II) in the system : Ni(II)-

complex-H₂A₂-kerosene - (Na⁺, H⁺) SO₄-Ac⁻. [Ni(II)_(o,ini)] = 0.40 kg/m³, [SO₄⁻] = 0.10 kmol/m³, [Ac⁻] = 0.25 kmol/m³, Δt = 0.5 s, Temp.

= 303 K (Fig. 72).

Free [H ₂ A ₂] _(o,ini) , kmol/m ³	log ([H ₂ A ₂] _(o,ini)), kmol/m ³	Column height, m	Drop fall time (t) + Δt, s	Vol. of 100 drops cm ³	Surface area of a drop (A) × 10 ³ , m ²	[Ni(II)] collected drops, kg/m ³	a _{Ni(II)} transferred to a drop		Flux (F _b) × 10 ⁷ , kmol/m ² s	log (F _b), kmol/m ² s
(i) pH _(ini) = 4.50 ; (○)										
0.005	-0.301	0.66	7.05	3.552	5.256	0.5457	19.383	33.026	8.913	-6.050
0.010	-2.000	0.66	7.08	3.556	5.229	0.3640	12.944	22.055	5.957	-6.225
0.025	-1.602	0.66	7.09	3.554	5.228	0.1990	7.072	12.050	3.251	-6.488
0.040	-1.398	0.66	7.12	3.552	5.226	0.1520	5.399	9.199	2.472	-6.607
0.075	-1.125	0.66	7.15	3.550	5.224	0.1054	3.742	6.376	1.707	-6.768
0.100	-1.000	1.20	12.60	3.489	5.164	0.1394	4.864	8.288	1.274	-6.895
0.200	-0.699	1.20	12.63	3.559	5.232	0.0894	3.182	5.422	0.821	-7.086
0.300	-0.523	1.20	12.65	3.557	5.230	0.0650	2.312	3.939	0.595	-7.225
0.500	-0.301	1.20	12.68	3.553	5.227	0.0433	1.538	2.621	0.395	-7.403
(ii) pH _(ini) = 4.00 ; (●)										
0.005	-0.301	0.20	2.39	3.493	5.168	0.4967	17.350	29.562	23.934	-5.621
0.010	-2.000	0.20	2.40	3.504	5.178	0.3431	12.022	20.484	16.482	-5.783
0.025	-1.602	0.40	4.32	3.498	5.172	0.3491	12.212	20.808	9.313	-6.031
0.040	-1.398	0.40	4.31	3.491	5.166	0.2626	9.167	15.619	7.015	-6.154
0.075	-1.125	0.66	7.14	3.508	5.182	0.2778	9.745	16.602	4.487	-6.348
0.100	-1.000	0.66	7.16	3.501	5.175	0.2229	7.804	13.297	3.589	-6.445
0.200	-0.699	0.66	7.19	3.522	5.196	0.1535	5.406	9.211	2.466	-6.608
0.300	-0.523	1.20	12.58	3.524	5.198	0.1707	6.015	10.249	1.567	-6.805
0.500	-0.301	1.20	12.62	3.519	5.193	0.1131	3.980	6.781	1.035	-6.985

Table LXXIV. Dependence of acetate ion concentration on the stripping flux of Ni(II) in the Ni(II)-H₂A₂complex-H₂A₂-kerosene

-(Na⁺, H⁺) SO₄⁻-Ac⁻ system. [Ni(II)]_(o,ini) = 0.40 kg/m³, pH_(ini) = 4.0, [H₂A₂]_(o,ini) = 0.30, kmol/m³, [SO₄⁻] = 0.10 kmol/m³ Δt = 0.5 s,

Number of collected drops = 100, Temp = 303 K (Fig. 74).

[Ac ⁻], kmol/m ³	log [Ac] _[o,ini] kmol/m ³	Column height, m	Drop fall time (t) + Δt, s	Vol. of 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Ni(II)] collected drops, kg/m ³	a _{Ni(II)} transferred to a drop	Flux (F _b) × 10 ⁷ , kmol/m ² s	log (F _b , kmol/m ² s)	
							× 10 ³ , mg × 10 ¹¹ , kmol			
0.05	-1.301	1.20	12.52	3.555	5.229	0.1218	4.330	7.378	1.127	-6.948
0.10	-1.000	1.20	12.51	3.541	5.215	0.1270	4.497	7.662	1.174	-6.930
0.20	-0.699	1.20	12.48	3.546	5.220	0.1613	5.720	9.476	1.496	-6.825
0.25	-0.602	1.20	12.49	3.551	5.225	0.1633	5.799	9.881	1.514	-6.820
0.50	-0.301	1.20	12.46	3.549	5.223	0.2410	8.553	14.573	2.239	-6.650
0.70	-0.155	1.20	12.45	3.518	5.192	0.3317	11.669	19.883	3.076	-6.512
1.00	0.000	1.20	12.42	3.547	5.221	0.3825	13.567	23.117	3.565	-6.448
1.50	0.176	0.40	4.44	3.539	5.213	0.1919	6.791	11.571	5.000	-6.301
2.00	0.301	0.40	4.43	3.536	5.210	0.2445	8.646	14.732	6.383	-6.195
3.00	0.477	0.40	4.40	3.539	5.213	0.3375	11.944	20.351	8.872	-6.052

Table LXXV. Effect of temperature on the stripping flux of Ni(II) in the Ni(II)-H₂A₂ complex-H₂A₂-kerosene - (Na⁺, H⁺)SO₄⁻ -Ac⁻ system. [Ni(II)]_(o,ini) = 0.40 kg/m³, Number of collected drops = 100, Δt = 0.5 s (Fig. 75).

Temp. (T), K	$\left\{\left(\frac{1}{T}\right) \times 10^3\right\}, K^{-1}$	Column height, m	Drop fall time (t) + Δt, s	Vol. of 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Ni(II)] collected, kg/m ³	$a_{Ni(II)}$ transferred to a drop × 10 ³ , mg × 10 ¹¹ , kmol	Flux (F _b) × 10 ⁷ , kmol/m ² s	log (F _b , kmol/m ² s)
(i) $pH_{(ini)} = 5.00$, $[H_2A_2]_{(o,ini)} = 0.01 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.01 \text{ kmol/m}^3$, $[Ac^-] = 0.10 \text{ kmol/m}^3$									
293	3.413	1.20	12.58	3.548	5.222	0.0526	1.866	3.179	0.484
298	3.356	1.20	12.58	3.546	5.220	0.0821	2.991	4.960	0.755
303	3.300	1.20	12.56	3.550	5.224	0.1141	4.051	6.902	1.052
308	3.247	1.20	12.55	3.526	5.200	0.1563	5.511	9.390	1.439
313	3.195	1.20	12.52	3.528	5.202	0.2437	8.598	14.650	2.249
318	3.144	1.20	12.50	3.512	5.186	0.3067	10.771	18.352	2.831
(ii) $pH_{(ini)} = 2.50$, $[H_2A_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.01 \text{ kmol/m}^3$, $[Ac^-] = 0.10 \text{ kmol/m}^3$									
293	3.413	0.90	9.66	3.555	5.229	0.1775	6.310	10.751	2.128
298	3.356	0.90	9.63	3.568	5.241	0.2042	7.286	12.414	2.460
303	3.300	0.90	9.62	3.529	5.203	0.2164	7.638	13.014	2.600
308	3.247	0.90	9.61	3.536	5.210	0.2369	8.377	14.273	2.851
313	3.195	0.66	7.18	3.542	5.216	0.2088	7.396	12.602	3.365
318	3.144	0.66	7.15	3.549	5.223	0.2431	8.628	14.701	3.937

Continued...

Temp., (T), K	$\left\{\left(\frac{1}{T}\right) \times 10^3\right\}$, K ⁻¹	Column height, m	Drop fall time (t) + Δt , s	Vol. of 100 drops, cm ³	Surface area of a drop (A) $\times$ 10 ⁵ , m ²	[Ni(II)] collected drops, kg/m ³	$a_{\text{Ni(II)}}$ transferred to a drop $\times 10^3$, mg $\times 10^{11}$, kmol	Flux (F _b) $\times 10^7$, kmol/m ² s	log (F _b , kmol/m ² s)
(iii) $pH_{(ini)} = 2.50$, $[H_2A_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3$, $[SO_4^{2-}] = 1.00 \text{ kmol/m}^3$, $[Ac^-] = 0.10 \text{ kmol/m}^3$									
293	3.413	0.20	2.60	3.554	5.228	0.1734	6.163	10.501	7.725
298	3.356	0.20	2.60	3.559	5.232	0.2108	7.502	12.782	9.397
303	3.300	0.20	2.58	3.504	5.178	0.2540	8.900	15.164	11.350
308	3.247	0.20	2.58	3.522	5.196	0.2799	9.858	16.796	12.529
313	3.195	0.20	2.57	3.524	5.198	0.3001	10.576	18.020	13.490
318	3.144	0.20	2.57	3.541	5.215	0.3152	11.161	19.017	14.189
(iv) $pH_{(ini)} = 2.50$, $[H_2A_2]_{(o,ini)} = 0.30 \text{ kmol/m}^3$, $[SO_4^{2-}] = 0.01 \text{ kmol/m}^3$, $[Ac^-] = 1.00 \text{ kmol/m}^3$									
293	3.413	0.40	4.59	3.557	5.230	0.1614	5.741	9.782	4.075
298	3.356	0.40	4.56	3.526	5.200	0.2081	7.338	12.503	5.273
303	3.300	0.40	4.58	3.508	5.182	0.2623	9.201	15.677	6.605
308	3.247	0.40	4.56	3.519	5.193	0.3173	11.166	19.025	8.034
313	3.195	0.20	2.55	3.556	5.229	0.1957	6.959	11.857	8.892
318	3.144	0.20	2.53	3.546	5.220	0.2087	7.401	12.610	9.550

Table LXXVI. Data for the $\log (F_b h/kT)$ vs. $(1/T)$ plot in the backward extraction of Ni(II) by sulfuric acid solution, $h = 6.6252 \times 10^{-37}$ kJ s, $k = 1.38 \times 10^{-26}$ kJ/deg (Fig. 76).

Temp., K	$(1/T) \times 10^3, K^{-1}$	$F_b \times 10^{-7}, \text{kmol/m}^2\text{s}$	$\log\{(F_b h/kT), \text{kmol/m}^2\}$
(i) $pH_{(m)} = 5.00, [H_2A_2] = 0.01 \text{ kmol/m}^3, [SO_4^{2-}] = 0.01 \text{ kmol/m}^3, [Ac^-] = 0.10 \text{ kmol/m}^3$			
293	3.413	0.484	-20.1007
298	3.356	0.755	-19.9149
303	3.300	1.052	-19.7781
308	3.247	1.439	-19.6492
313	3.195	2.249	-19.4622
318	3.145	2.831	-19.3692
(ii) $pH_{(m)} = 2.50, [H_2A_2] = 0.30 \text{ kmol/m}^3, [SO_4^{2-}] = 0.01 \text{ kmol/m}^3, [Ac^-] = 0.10 \text{ kmol/m}^3$			
293	3.413	2.128	-19.4576
298	3.356	2.460	-19.402
303	3.300	2.600	-19.3851
308	3.247	2.851	-19.3522
313	3.195	3.365	-19.2872
318	3.145	3.937	-19.2259
(iii) $pH_{(m)} = 2.50, [H_2A_2] = 0.30 \text{ kmol/m}^3, [SO_4^{2-}] = 1.00 \text{ kmol/m}^3, [Ac^-] = 0.10 \text{ kmol/m}^3$			
293	3.413	7.725	-18.8976
298	3.356	9.397	-18.8199
303	3.300	11.350	-18.7451
308	3.247	12.529	-18.7093
313	3.195	13.490	-18.6842
318	3.145	14.189	-18.6692
(iv) $pH_{(m)} = 2.50, [H_2A_2] = 0.30 \text{ kmol/m}^3, [SO_4^{2-}] = 0.01 \text{ kmol/m}^3, [Ac^-] = 0.10 \text{ kmol/m}^3$			
293	3.413	4.075	-19.1754
298	3.356	5.273	-19.0708
303	3.300	6.605	-18.9802
308	3.247	8.034	-18.9023
313	3.195	8.892	-18.8652
318	3.145	9.550	-18.8411

Table LXXVII. Data for the estimation of rate constant (k_b) in backward extraction of Ni(II) in the Ni(II)-Cyanex 272 complex- H_2A_2 -keroserine - (Na^+ , H^+) SO_4^{2-} - Ac^- system at 303 K (Fig. 77).

[Ni(II)], kmol/m ³	[H ⁺], kmol/m ³	[H ₂ A ₂], kmol/m ³	[SO ₄ ²⁻], kmol/m ³	[Ac ⁻], kmol/m ³	$[\log [Ni(II)]_{(o,ini)} - \log (1 + 10^{-3.42} [H^+]^{-1}) - \log (\sqrt{[H_2A_2]} + 2.5 [H_2A_2]) + \log (1 + 6 [SO_4^{2-}]) + \log (1 + 3.2 [Ac^-]) = \log f(R)$	log F_b
0.003400	100000.00	0.025	0.100	0.25	-2.94404	-7.243
0.006800	100000.00	0.025	0.100	0.25	-2.64301	-6.942
0.013600	100000.00	0.025	0.100	0.25	-2.34198	-6.640
0.020400	100000.00	0.025	0.100	0.25	-2.16589	-6.460
0.027300	100000.00	0.025	0.100	0.25	-2.03935	-6.339
0.034000	100000.00	0.025	0.100	0.25	-1.94404	-6.242
0.006814	1000000.00	0.025	0.100	0.25	-3.63198	-7.857
0.006814	316227.80	0.025	0.100	0.25	-3.13444	-7.451
0.006814	100000.00	0.025	0.100	0.25	-2.64211	-6.952
0.006814	31622.78	0.025	0.100	0.25	-2.16554	-6.460
0.006814	10000.00	0.025	0.100	0.25	-1.73225	-6.022
0.006814	3162.28	0.025	0.100	0.25	-1.39371	-5.805
0.006814	1000.00	0.025	0.100	0.25	-1.19078	-5.652
0.006814	316.23	0.025	0.100	0.25	-1.10014	-5.600
0.006814	100.00	0.025	0.100	0.25	-1.06704	-5.572
0.006814	100000.00	0.300	0.100	0.25	-3.41166	-7.725
0.006814	31622.78	0.300	0.100	0.25	-2.93509	-7.237
0.006814	10000.00	0.300	0.100	0.25	-2.50180	-6.812
0.006814	3162.28	0.300	0.100	0.25	-2.16326	-6.450
0.006814	1000.00	0.300	0.100	0.25	-1.96033	-6.280
0.006814	316.23	0.300	0.100	0.25	-1.86969	-6.155
0.006814	100.00	0.300	0.100	0.25	-1.83659	-6.130
0.006814	31622.78	0.005	0.100	0.25	-1.74208	-6.050
0.006814	31622.78	0.010	0.100	0.25	-1.91881	-6.225
0.006814	31622.78	0.025	0.100	0.25	-2.16554	-6.488
0.006814	31622.78	0.040	0.100	0.25	-2.29903	-6.607
0.006814	31622.78	0.075	0.100	0.25	-2.48595	-6.768
0.006814	31622.78	0.100	0.100	0.25	-2.5749	-6.895
0.006814	31622.78	0.200	0.100	0.25	-2.79835	-7.086
0.006814	31622.78	0.300	0.100	0.25	-2.93509	-7.225
0.006814	31622.78	0.500	0.100	0.25	-3.11352	-7.403
0.006814	10000.00	0.005	0.100	0.25	-1.30880	-5.621

Continued...

[Ni(II)], kmol/m ³	[H ⁺], kmol/m ³	[H ₂ A ₂], kmol/m ³	[SO ₄ ⁼], kmol/m ³	[Ac ⁻], kmol/m ³	{log [Ni(II)] _(o,ini) - log (1 + 10 ^{-3.42} [H ⁺] ⁻¹) - log (√[H ₂ A ₂] + 2.5 [H ₂ A ₂]) + log (1 + 6 [SO ₄ ⁼]) + log (1 + 3.2 [Ac ⁻])} = log f(R)	log F _b
0.006814	10000.00	0.010	0.100	0.25	-1.48553	-5.783
0.006814	10000.00	0.025	0.100	0.25	-1.73225	-6.031
0.006814	10000.00	0.040	0.100	0.25	-1.86574	-6.154
0.006814	10000.00	0.075	0.100	0.25	-2.05266	-6.348
0.006814	10000.00	0.100	0.100	0.25	-2.14161	-6.445
0.006814	10000.00	0.200	0.100	0.25	-2.36507	-6.608
0.006814	10000.00	0.300	0.100	0.25	-2.50180	-6.805
0.006814	10000.00	0.500	0.100	0.25	-2.68023	-6.985
0.006814	31622.78	0.300	0.001	0.25	-3.13661	-7.428
0.006814	31622.78	0.300	0.003	0.25	-3.13146	-7.428
0.006814	31622.78	0.300	0.010	0.25	-3.11390	-7.418
0.006814	31622.78	0.300	0.030	0.25	-3.06732	-7.365
0.006814	31622.78	0.300	0.100	0.25	-2.93509	-7.215
0.006814	31622.78	0.300	0.300	0.25	-2.69205	-6.990
0.006814	31622.78	0.300	1.000	0.25	-2.29411	-6.574
0.006814	31622.78	0.300	2.000	0.25	-2.02526	-6.352
0.006814	10000.00	0.300	0.001	0.25	-2.70332	-7.020
0.006814	10000.00	0.300	0.003	0.25	-2.69817	-7.000
0.006814	10000.00	0.300	0.010	0.25	-2.68061	-6.991
0.006814	10000.00	0.300	0.030	0.25	-2.63404	-6.920
0.006814	10000.00	0.300	0.100	0.25	-2.50180	-6.840
0.006814	10000.00	0.300	0.300	0.25	-2.25876	-6.542
0.006814	10000.00	0.300	1.000	0.25	-1.86082	-6.202
0.006814	10000.00	0.300	2.000	0.25	-1.59198	-5.903
0.006814	10000.00	0.300	0.100	0.05	-2.69261	-6.948
0.006814	10000.00	0.300	0.100	0.10	-2.63650	-6.930
0.006814	10000.00	0.300	0.100	0.20	-2.54223	-6.825
0.006814	10000.00	0.300	0.100	0.25	-2.50180	-6.820
0.006814	10000.00	0.300	0.100	0.50	-2.34210	-6.650
0.006814	10000.00	0.300	0.100	0.70	-2.24653	-6.512
0.006814	10000.00	0.300	0.100	1.00	-2.13382	-6.448
0.006814	10000.00	0.300	0.100	1.50	-1.99364	-6.301
0.006814	10000.00	0.300	0.100	2.00	-1.88784	-6.195
0.006814	10000.00	0.300	0.100	3.00	-1.73177	-6.052

Table LXXVIII. Data on the dependence of organic phase Zn(II) concentration on the flux of Zn(II) transfer during stripping of Zn-H₂A₂ complex by sulphuric acid solution. [H₂A₂]_(o,ini) = 0.05 kmol/m³, [SO₄²⁻] = 0.10 kmol/m³, pH_(ini) = 1, Δt = 0.4 s, Temp. = 303 K, Number of collected drops = 100, Column height = 0.90 m (Fig. 78).

[Zn(II)] _(o,ini) , kg/m ³	[Zn(II)] _(o,ini) × 10 ³ , kmol/m ³	log [Zn(II)] _(o,ini) , kmol/m ³	Drop fall time (t) + Δt, s	Vol. of 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Zn(II)] collected drops, kg/m ³	a _{Zn(II)} transferred to a drop		Flux (F _b) × 10 ⁷ , kmol/m ² s	log (F _b , kmol/m ² s)
							× 10 ³ , mg	× 10 ¹¹ , kmol		
0.4008	6.163	-2.210	9.50	3.452	5.178	0.0168	0.580	0.887	0.180	-7.745
0.6482	9.911	-2.004	9.52	3.521	5.175	0.275	0.968	1.480	0.299	-7.524
0.9965	15.237	-1.817	9.58	3.538	5.212	0.0425	1.504	2.300	0.461	-7.336
1.5022	22.969	-1.639	9.66	3.498	5.172	0.0664	2.253	3.444	0.689	-7.162
1.9991	30.569	-1.515	9.72	3.525	5.209	0.0835	2.952	4.514	0.892	-7.050

Table LXXIX. Dependence of the aqueous pH on the flux of Zn(II) transfer during stripping of Zn-H₂A₂ complex by sulphuric acid solution. [Zn(II)]_(o,ini) = ~1.00 kg/m³, [H₂A₂]_(o,ini) = 0.05 kmol/m³, [SO₄²⁻] = 1.00 kmol/m³, Δt = 0.4 s, Temp. = 303 K, Column height = 0.90 m (Fig. 79).

pH _(ini)	Drop fall time (t) + Δt, s	Vol. of 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Zn(II)] in collected drops, kg/m ³	[Zn(II)] _(o,ini) , kg/m ³	a _{Zn(II)} transferred to a drop		Flux (F _b) × 10 ⁷ , kmol/m ² s	log (F _b , kmol/m ² s)
						× 10 ³ , mg	× 10 ¹¹ , kmol		
1.75	9.57	3.498	5.172	1.0052	0.0159	0.556	0.850	0.172	-7.765
1.50	9.60	3.512	5.186	0.9978	0.0282	0.990	1.514	0.304	-7.517
1.25	9.58	3.538	5.212	0.9992	0.0512	1.811	2.770	0.555	-7.256
1.00	9.60	3.506	5.180	1.0083	0.0908	3.183	4.868	0.979	-7.009
0.75	9.63	3.496	5.170	1.0052	0.1574	5.503	8.414	1.690	-6.772
0.50	9.62	3.516	5.190	1.0012	0.2857	10.045	15.360	3.076	-6.512
0.25	9.62	3.522	5.196	1.0059	0.5100	17.962	27.465	5.495	-6.260

Table LXXX. Dependence of free extractant (H_2A_2) concentration in the organic phase on the flux of Zn(II) transfer during stripping of $\text{Zn-H}_2\text{A}_2$ complex by sulphuric acid solution. $[\text{Zn(II)}]_{(\text{o,ini})} = 1.0058 \text{ kg/m}^3$, $\text{pH}_{(\text{ini})} = 1$, $[\text{SO}_4^{2-}] = 0.1 \text{ kmol/m}^3$, $\Delta t = 0.4 \text{ s}$, Temp. = 303 K, Column height = 0.90 m (Fig. 80).

$[\text{H}_2\text{A}_2]_{(\text{o,ini})}$, kmol/m^3	$\log ([\text{H}_2\text{A}_2]_{(\text{o,ini})})$, kmol/m^3	Drop fall time (t) + Δt , s	Vol. of 100 drops, cm^3	Surface area of a drop (A) $\times 10^5$, m^2	$[\text{Ni(II)}]$ collected drops, kg/m^3	$a_{\text{Ni(II)}}$ transferred to a drop $\times 10^3$, mg $\times 10^{11}$, kmol		Flux (F_b) $\times 10^7$, $\text{kmol/m}^2\text{s}$	$\log (F_b)$, $\text{kmol/m}^2\text{s}$
						$\times 10^3$, mg	$\times 10^{11}$, kmol		
0.025	-1.602	9.62	3.522	5.196	0.0586	2.064	3.156	0.631	-7.200
0.050	-1.301	9.66	3.518	5.192	0.0422	1.485	2.270	0.453	-7.344
0.075	-1.125	9.68	3.526	5.200	0.0334	1.178	1.801	0.358	-7.446
0.100	-1.000	9.72	3.518	5.192	0.0296	1.047	1.592	0.315	-7.502
0.150	-0.824	9.70	3.520	5.194	0.0241	0.848	1.297	0.257	-7.590
0.200	-0.700	9.72	3.524	5.197	0.0209	0.737	1.127	0.223	-7.652

Table LXXXI. Dependence of sulphate ion concentration of the aqueous phase on the flux of Zn(II) transfer during stripping of Zn-H₂A₂ complex by sulphuric acid solution. [H₂A₂]_(o,ini) = 0.05 kmol/m³, [Zn(II)]_(o,ini) = ~1.00 kg/m³, pH_(ini) = 1.0, Δt = 0.4 s, , Number of collected drops = 100, Temp. = 303 K, Column height = 0.90 m (Fig. 81).

[SO ₄ ²⁻], kmol/m ³	log ([SO ₄ ²⁻], kmol/m ³)	Drop fall time (t) + Δt, s	Vol. of 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Ni(II)] _(o,ini) , kg/m ³	[Ni(II)] collected drops, kg/m ³	a _{Zn(II)} transferred to a drop		Flux (F _b) × 10 ⁷ , kmol/m ² s	log (F _b , kmol/m ² s)
							× 10 ³ , mg	× 10 ¹¹ , kmol		
0.1	-1.000	9.68	3.488	5.163	0.9922	0.0417	1.454	2.223	0.445	-7.352
0.2	-0.700	9.68	3.502	5.176	0.9986	0.0469	1.642	2.511	0.501	-7.300
0.3	-0.523	9.65	3.522	5.196	1.0012	0.0523	1.842	2.817	0.562	-7.250
0.5	-0.300	9.62	3.498	5.172	1.0008	0.0629	2.200	3.364	0.676	-7.170
0.7	-0.155	9.63	3.512	5.186	0.9996	0.0734	2.578	3.942	0.789	-7.103
1.0	0.000	9.60	3.504	5.178	1.0012	0.0886	3.105	4.748	0.955	-7.020
1.5	0.176	9.58	3.518	5.192	0.9990	0.1151	4.049	6.191	1.245	-6.905
2.0	0.301	9.55	3.520	5.194	0.9996	0.1411	4.967	7.595	1.531	-6.815

Table LXXXII. Effect of temperature on the stripping rate flux of Zn(II)-A₂-H₂A₂-kerosene / H₂SO₄-SO₄ system.

[H₂A₂]_(o,ini) = 0.05 kmol/m³, [Zn(II)]_(o,ini) = 1.00 kg/m³, pH_(ini) = 0.50, [SO₄²⁻] = 1.00 kmol/m³, Δt = 0.4 s, Number of collected drops = 100, Column height = 0.90 m (Fig. 82).

Temp., K	$\left\{\left(\frac{1}{T}\right) \times 10^3\right\}, K^{-1}$	Drop fall time (t) + Δt, s	Vol. of 100 drops, cm ³	Surface area of a drop (A) × 10 ⁵ , m ²	[Zn(II)] collected drops, kg/m ³	a _{Zn(II)} transferred to a drop		Flux (F _b × 10 ⁷ , kmol/m ² s)	log (F _b , kmol/m ² s)
						× 10 ³ , mg	× 10 ¹¹ , kmol		
288	3.472	9.52	3.585	5.258	0.0974	3.492	5.339	1.067	-6.972
293	3.413	9.54	3.576	5.249	0.1442	5.157	7.885	1.575	-6.803
298	3.356	9.56	3.567	5.240	0.2066	7.369	11.268	2.249	-6.648
303	3.300	9.62	3.516	5.190	0.2857	10.045	15.360	3.076	-6.512
308	3.247	9.76	3.531	5.205	0.3737	13.195	20.176	3.972	-6.401
313	3.195	9.88	3.532	5.206	0.4353	15.375	23.509	4.571	-6.340
318	3.145	9.99	3.528	5.202	0.5115	18.046	27.593	5.310	-6.275

$$\log f(R) = \log [Zn(II)]_{(o,ini)} - pH - 0.5 \log [H_2A_2] + \log (1 + 1.5 [SO_4^{2-}])$$

$$= \log 0.0153 - 0.5 - 0.5 \log 0.05 + \log (1 + 1.5 \times 1) = -1.815 - 0.5 + 0.651 + 0.398 = -1.266$$

Table LXXXIII. Data for the $\log (F_b h/kT)$ vs. $(1/T)$ plot in the backward extraction of Zn(II) by sulfuric acid solution, $h = 6.6252 \times 10^{-37}$ kJ s, $k = 1.38 \times 10^{-26}$ kJ/deg (Fig. 83).

Temp. K	$(1/T) \times 10^3, K^{-1}$	$F_b \times 10^{-7}, \text{kmol/m}^2\text{s}$	$\log \{(F_b h/kT) \text{ kmol/m}^2\}$
288	3.472	1.067	-19.7499
293	3.413	1.575	-19.5883
298	3.356	2.249	-19.4409
303	3.300	3.076	-19.3121
308	3.247	3.972	-19.2082
313	3.195	4.571	-19.1542
318	3.145	5.310	-19.0960

Table LXXXIV. Data for the estimation of rate constant (k_b) in the backward extraction of Zn(II)-H₂A₂ complex by sulfuric acid solution at 303 K (Fig. 84).

[Zn(II)], kmol/m ³	pH _(ini)	[H ₂ A ₂], kmol/m ³	[SO ₄ ⁼], kmol/m ³	$\frac{[[Zn(II)]_{(o,ini)} - pH_{(ini)} - 0.5 \log [H_2A_2] + \log (1 + 1.5 [SO_4^{=}])]}{\log f(R)}$	log F _b
0.006128	1.00	0.050	0.10	-2.50144	-7.745
0.009911	1.00	0.050	0.10	-2.29266	-7.524
0.015237	1.00	0.050	0.10	-2.10589	-7.336
0.022969	1.00	0.050	0.10	-1.92764	-7.162
0.030569	1.00	0.050	0.10	-1.80351	-7.050
0.015291	1.75	0.050	1.00	-2.51712	-7.765
0.015291	1.50	0.050	1.00	-2.26712	-7.517
0.015291	1.25	0.050	1.00	-2.01712	-7.256
0.015291	1.00	0.050	1.00	-1.76712	-7.009
0.015291	0.75	0.050	1.00	-1.51712	-6.772
0.015291	0.50	0.050	1.00	-1.26712	-6.512
0.015291	0.25	0.050	1.00	-1.01712	-6.260
0.015379	1.00	0.025	0.10	-1.95134	-7.200
0.015379	1.00	0.050	0.10	-2.10185	-7.344
0.015379	1.00	0.075	0.10	-2.18990	-7.446
0.015379	1.00	0.100	0.10	-2.25237	-7.502
0.015379	1.00	0.150	0.10	-2.34041	-7.590
0.015379	1.00	0.200	0.10	-2.40288	-7.652
0.015291	1.00	0.050	0.10	-2.10436	-7.352
0.015291	1.00	0.050	0.20	-2.05112	-7.300
0.015291	1.00	0.050	0.30	-2.00369	-7.250
0.015291	1.00	0.050	0.50	-1.92202	-7.170
0.015291	1.00	0.050	0.70	-1.85331	-7.103
0.015291	1.00	0.050	1.00	-1.76712	-7.020
0.015291	1.00	0.050	1.50	-1.65318	-6.905
0.015291	1.00	0.050	2.00	-1.56300	-6.815