

Some Physico-Chemical Properties of Cyanex 272 and Extraction of Some Metal Ions



A Dissertation Submitted to the University of Rajshahi, Rajshahi,
Bangladesh in Partial Fulfilment of the Requirement for the
Degree of Doctor of Philosophy

By

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University of Rajshahi
Rajshahi-6205, Bangladesh
May, 2006

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Ph.D. Thesis

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DECLARATION CERTIFICATE

The Undersigned certifies that all the research works presented in this dissertation are the original works of Hari Prosad Singha, 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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ABSTRACT

Using a reported technique for purifying organophosphorous extractants, the as-received Cyanex 272 extractant containing 85% bis-2,4,4-trimethylpentylphosphinic acid [BTMPPA] has been purified to a purity of about 99% BTMPPA. The purified reagent has been characterized and compared to the literature values.

A technique for the colorimetric estimation of purified Cyanex 272 has been developed. It consists of the digestion of pure sample or its aqueous solution (after evaporating out most of water) with concentrated HNO_3 (70%) - HClO_4 (70%) mixture at 2:1 ratio for 1 h. The oxidizing mixed acid quantitatively converts Cyanex 272 to a clear solution of orthophosphate which can be easily estimated by the molybdenum blue colorimetric method at 830 nm. The method is sensitive with a molar extinction coefficient of $\sim 2.6 \times 10^4$ and reproducible within $\pm 2\%$. Applying this technique of analysis, the dimerization constant (K_2), distribution or partition coefficient (K_d) and the ionization constant (K_a) of the purified Cyanex 272 i.e. BTMPPA have been estimated to be 190, 53 and 5.52×10^{-4} , respectively.

Interactions of BTMPPA + diluent (n-hexane / cyclohexane / benzene / toluene / chloroform / carbon tetrachloride / 1,2-dichloroethane (DCE) / 1-heptanol) binary mixtures have been studied in terms of density and viscosity measurements and also in terms of derived properties such as excess molar volumes (V_m^E), excess viscosities (η^E) and excess Gibbs free energy changes of activation of flow (ΔG^E). Variations of these values together with the variations of the Grunberg-Nissan interaction parameter (d) for BTMPPA - diluent binary systems show that BTMPPA interacts with the diluents in varying degrees. However, no correlation between d, ΔG^E , η^E or V_m^E and the Cu^{2+} / Fe^{3+} - extraction characteristics with BTMPPA could be noticed.

The interfacial adsorption property of Cyanex 272 (purified) at the 0.50 mol/dm³ H_2SO_4 (pH = 0.8) / BTMPPA - diluent (carbon tetrachloride / cyclohexane / DCE / n-hexane / toluene / kerosene / benzene / chloroform / 1-heptanol / 1-hexanol) interface have been investigated. Applying the Gibbs adsorption isotherm to the γ vs. log [BTMPPA] plots for each of the diluent used (γ being the interfacial tension, mN/m), the apparent cross-sectional areas (A in Å²) of BTMPPA molecules adsorbed at the interfaces have been estimated. A (Å²) is found to vary in the order : CCl_4 (157 Å²) < cy-C₆H₁₂ (166 Å²) < DCE (174 Å²) < n - C₆H₁₄ (176 Å²) < C₆H₅ - CH₃ (211 Å²)

= kerosene (211 Å²) < C₆H₆ (262 Å²) < CHCl₃ (335 Å²) < 1-C₇H₁₅OH (532 Å²) < 1-C₆H₁₃OH (734 Å²). When the measurements are done in identical conditions of interfaces, then the cross-sectional areas can be correlated with the metal extraction data.

The extraction characteristics of Fe³⁺ from 0.10 mol/dm³ (H⁺, Na⁺) SO₄²⁻ medium by BTMPPA in kerosene have been investigated. The equilibration time is less than 25 min. The [Fe³⁺] dependence curve at a constant equilibrium pH and concentrations of extractant and sulphate has a slope of -0.5 and zero at lower and higher concentration regions of Fe³⁺. The pH dependence at lower pH region is 2; whereas, the extractant and sulphate ion dependences are 1 and -1, respectively. The pH dependence is decreased at higher pH regions due to hydrolysis of Fe³⁺. The temperature dependence of distribution ratio (D) indicates that the extraction process is exothermic with an average ΔH value of 30 kJ/mol. The extraction equilibrium reaction is suggested to be: Fe (HSO₂)₂⁺ + H₂A_{2(o)} ⇌ Fe.HSO₄.A_{2(o)} + HSO₄⁻ + 2H⁺ at the lower pH region of investigation. At higher pH region, the hydrolytic Fe³⁺ species is involved. The extraction equilibrium constant (*K_{ex}*) has been evaluated to be 10^{-2.3}. The extracted complex can be stripped by 0.50 mol/dm³ H₂SO₄ solution; but a three-stage stripping (O/A = 1 in each stage) is needed for 99% Fe³⁺ removal from the organic phase.

The solvent extraction of Cu²⁺ from 0.10 mol/dm³ sulphate medium by BTMPPA dissolved in distilled kerosene has been investigated. The equilibration time is less than 15 min. The distribution ratio is found to decrease appreciably with equilibrium Cu²⁺ concentration in the aqueous phase, particularly, at its higher concentration region indicating some sort of association of Cu²⁺ species in either of the phases. The pH and the extractant concentration dependences on D are 1 and 1.2, respectively. D is almost independent of sulphate ion concentrations in the aqueous phase. The ΔH value is 27.3 ± 0.5 kJ/mol. The 60% extraction equilibrium reaction is suggested to be : CuHSO₄⁺ + H₂A_{2(o)} ⇌ CuHSO₄.A.0.5 H₂A_{2(o)} + H⁺ and some 40% reaction is likely to occur via the reaction: CuHSO₄⁺ + 1.5 H₂A_{2(o)} ⇌ CuHSO₄.A.H₂A_{2(o)} + H⁺ satisfying the extractant dependence of 1.2. The apparent extraction equilibrium constant (*K_{ex}*) is estimated to be 10^{-3.15}. The loading capacity of BTMPPA is 13.47 g Cu²⁺ / 100 g BTMPPA. Among H₂SO₄, HCl and HNO₃ solutions as stripping agent, 1 mol/dm³ H₂SO₄ solution is found to be the best ; 99.6% Cu²⁺ in the organic phase can be stripped off in three stages (O/A = 1 in each stage). The Cu²⁺ distribution ratio measured at pH = 4 in different diluents does not show good correlation with the cross - sectional area of BTMPPA - molecules at interfaces formed by different diluents at pH 0.80.

CHAPTER I

INTRODUCTION

A. a) Solvent extraction

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. Thus the liquid-liquid extraction is a technique in which a solution (generally aqueous) is brought into contact with a second solvent (usually organic) essentially immiscible with the first, in order to bring about a transfer of one or more solutes into the second solvent.

The distribution of which is studied at equilibrium may be called distribuend. The solvent used as organic phase (immiscible with aqueous phase) is capable of dissolving the distribuend to some extent. The extractant and diluent together act as a solvent. Sometimes 1-3% higher liquid alcohols (known as modifier) are used 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.

Solvent extraction is not a recent used process. It has been usually used in the purification of organic substances. Many organic substances have been purified using solvent extraction technique by the organic chemists [1]. As for example, a multistage extraction was proposed at the beginning of the 20th century by Traube [2] for the industrial purification of alcohol. French [3] provided the basis of the theoretical treatment in 1925. In 1934, Cornish *et al.* [4] described the separation of vitamins by a discontinuous multistage process.

Early it has been investigated that many inorganic substances can also be partitioned between two immiscible solvents depending on the relative solubilities in the individual phases. The chemical engineering aspects and equipments are available which can be used in metallurgical application. Also the applications of solvent extraction in analytical and metallurgical separation processes are very fruitful.

Peligot [5] observed that the organic solvents could extract metal ions. He in 1842 observed that uranyl nitrate was appreciably soluble in diethyl ether, and used this property for separating uranium from other constituents of pitchblende. Another worthy example to note is the extraction of iron(III) from hydrochloric acid solution with diethyl ether which was reported in 1892 by Rothe [6] and also by Hanroit [7]. Afterwards this method has been widely applied to the separation of this element from many other metal ions [8].

Nevertheless the wide spread application and improvement in solvent extraction technique in the extractive metallurgy and nuclear technology have been started during the Second World War. This has

stimulated research throughout the metallurgical world for the requirement of elements like uranium, thorium, the lanthanides and the actinides of high purity in the field of nuclear and atomic energy.

Although the solvent extraction technique of separation is very simple, rapid, convenient and applicable to both trace and large amount of materials, most equipments used now-a-days industrially were developed in the early sixties of the last century. Mixer-settlers [9], baffle-cup plate tower [10,11], sieve-plate tower [12], spray tower [13] etc. are in use industrially. But simple sort of apparatus like separatory funnels or reagent bottles of handy sizes are always used in the laboratory scale. Moreover, there are various techniques or cells to study liquid-liquid extraction kinetics. Some of them are as follows:

- i) The static constant interfacial area cell (Hahn cell) [14-17],
- ii) The stirred constant interfacial area cell (Lewis cell) [15-17, 18-21],
- iii) The stirred tank (AKUFVE apparatus) [22, 23],
- iv) The laminar jet [24],
- v) The rotating diffusion cell (RDC) [24-29],
- vi) The single drop technique (rising and falling) [30-36].

Each technique exhibits different hydrodynamics relating to the metal transferred 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,
- 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 [37].

b) The theoretical principles of solvent extraction

The theoretical principles of solvent extraction have been outlined by Calvin [38, 39]. The solvent extraction separation method of metal ions depends upon the formation of nonionised chelate compounds by reaction of metal ions with certain organic chelating agents (extractants), diluted with an organic phase. The overall reaction involved in the transfer of the element between the aqueous and organic phases may be represented by the following equation:



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. Now, the equilibrium constant, K_{Ex} for a given metal ion M^{n+} with a particular organic system 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 ratio or coefficient of the metal ion expressed as the total concentration of metal ion in the organic phase divided by the total concentration of the metal ion in the aqueous phase. Thus, for any given metal ion, M^{n+} with a particular organic 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 elements [40-43], it is clear how such a system may be used for the separation of elements.

The Eq. (2) involves the assumption that the concentration of the metal chelate, $\overline{MA}_n$ and the intermediate complexes in the aqueous phase is negligible compared to that of the metal ion, $\overline{MA}_n$ in the organic phase. But this is not always the case, particularly when the extraction of the metal ion is nearly complete. So, the introduction of another distribution coefficient, called true distribution coefficient is necessary and this differs from that obtained in Eq. (3). But the error in most cases is small. Kolthoff [44] described a modified form of the distribution coefficient equation which took into account the hydrolysis of the metal ion in the aqueous phase. His relationship was applied to the hydrolysis of divalent metal ion to base of the types $M(OH)^+$ and $M(OH)_2$. If hydrolysis occurs, it is seen that the distribution coefficient dependence on $[\overline{HA}]$ in the organic phase is not affected by the hydrolysis of the metal ion, but the exponent of $[H^+]$ which enters into 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 groups attached to the metal ion in the aqueous phase prior to extraction. In the hydrolysis of a highly charged ion, the metal is usually distributed among a number of forms and expression for D_M^o is greatly complicated. A general relationship for such system has been derived by Connick and McVey [45].

The approximate equations developed above for the distribution coefficient, D_M^o for the solvent extraction of a metal chelate, offer 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. Under the limiting condition for the derivation of Eq. (3), the values of “n” and formula of the chelate may be determined by studying the:

- i) Dependence of D_M^o on the concentration of uncombined chelating agent in the organic phase; and
- ii) Dependence of D_M^o on the aqueous pH in equilibrium condition.

Since, D_M^o is the experimentally measured quantity, it is convenient to use Eq. (4) in the form of Eq. (5):

$$K_{EX} = D_M^o \frac{[H^+]^m}{[\overline{HA}]^n} \quad (5)$$

and it is thus possible to select reasonable values of “n” and “m” which will render K_{EX} reasonably constant when H^+ and $\overline{HA}$ concentrations are varied. In this way, Furman [46] showed for various dithizonates that “n”

had a value of 2 and 4 for Cu(II) and U(IV), respectively, in agreement with previously determined formulae of these chelates. Thus copper(II) was suggested to be tetra co-ordinated and uranium(IV) is octa co-ordinated and dithizonate of Cu(II) is square planner, whereas that of U(IV) is dodecahedral.

The study 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 and is no longer looked upon as a curiosity or as a new-fangled process. With the coming of age and proven performance, further expansion in applications would be assured. The following few paragraphs narrate some of the established applications of solvent extraction processes:

The American Potash and Chemical Corporation has developed a process for boron recovery using solvent extraction. Boron is extracted from the lake water, where the boron content is 8-10%. At present 3000-4000 gal/min are treated by this method in full scale plant. Extraction is carried out by polyols dissolved in kerosene. The final product contains 99.9% H_3BO_3 , 0.05% SO_3 and 0.029% Na [47, 48].

The extraction of cesium from pollutic ore by a substituted phenol has been developed by Oak Ridge National Laboratory (ORNL, USA). This extractant is highly selective for cesium. The process was originally developed for extracting radioactive cesium from reactor waste solutions [49-51].

The extraction of copper in commercial scale is done at Blue Bird Randers Company in Miami, Arizona using the extractant LIX 64 N. This process has been developed on pilot stage at Bugdad and Duval Corporations, both in Arizona [52-54].

Gold and silver can be leached from their ores by cyanide solution and they exist as the anions $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$, respectively, in the leach solution. Such anions have been found to be extracted by amines, e. g., tri-octylamine [55, 56].

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 [57]. A flow sheet has been developed in Canada for cobalt and nickel separation using D2EHPA as extractant [58]. Nippon Mining in Japan has implemented this process in a commercial plant, but there the extractant is mono-(2-ethylhexyl)phosphoric acid (EHEHPA) because of its higher separation factor [59]. Very recently, as will be seen latter, for Co(II) –Ni(II) separation, Cyanex reagents particularly Cyanex 272 have been used in a commercial scale.

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 [60-61]. A flow sheet has been developed for producing yttrium and rare earths by a uranium recovery plant [62]. Yttrium recovery plants have been reported to be operating in Japan, Canada, Norway and France.

Indium is recovered in Japan using D2EHPA and tributylphosphate (TBP) as extractants [63-64]. Molybdenum is recovered in Finland from a copper shaft furnace residue by solvent extraction using D2EHPA and 1-dodecanol as phase modifier [65]. D2EHPA has been used in the USA to purify crude strontium-90.

Uranium is recovered from wet process phosphoric acid using two extraction circuits with D2EHPA extractant and a tri-(n-octyl) phosphine oxide (TOPO) extractant in both circuits [58]. Plants are currently operating in the USA, Sweden and reportedly also in Iraq [59, 66]. D2EHPA is also used to recover uranium from tailings from a copper refinery in the USA.

D2EHPA has been used with dibutyl butyl phosphonate (DBBP) as coextractant in the second cycle of plants recovering uranium from wet process phosphoric acid. Two plants have demonstrated the use of this extractant combination. A flow sheet based on the use of D2EHPA and DBBP in both cycles of a plant for recovery of uranium from wet process phosphoric acid has been demonstrated in a pilot plant in Taiwan [65].

D2EHPA has been used with tributyl phosphate (TBP) as a coextractant in the commercial operation for the recovery of uranium from uranium ore (DAPEX process) [67, 68]. These compounds have also been used in the operations for recovery of a vanadium by-product [67, 68]. Plants in Portugal and Spain use D2EHPA in the second cycle of a zinc recovery process which use the Zincex technology developed by Tecnicas Reunidas [69]. Zinc extraction with D2EHPA is also practiced in processing complex streams and waste streams. A company in Japan

removes zinc with D2EHPA prior to separating cobalt and nickel. It 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.

Iron has been separated from a cobalt and nickel containing stream in a US plant by extraction with D2EHPA [70]. Iron is stripped using a reducing sugar which reduces the iron to ferrous state and forms a complex with it in the aqueous phase, permitting the use of high concentrations without precipitation problems. The US Bureau of Mines has proposed similar processing in a flow sheet for cobalt recovery from copper leach solutions [71]. Nihon Solex in Japan has developed a process in which a high purity iron is recovered from waste acids from steel pickling. Ammonia and hydrogen fluoride (HF) are used for stripping the iron from the D2EHPA extractant. The iron extraction produces a high purity iron product and facilitates recovery of the waste acid for recycling. A plant in Japan uses this technology [72]. A modification of this technology has been developed for recycle of acid wastes from titanium dioxide (TiO_2) production. This process has not yet been demonstrated commercially, but will soon be piloted.

Another important application of solvent extraction is its use in separating a number of metals occurring together. This can usually be achieved by selecting the proper pH, adding a complexing agent in the aqueous phase, above all choosing a solvent that shows more selectivity for one metal than for other. For example, sulphuric acid leach solutions of monazite sand containing rare earths, thorium and uranium, the Eldorado Mining and Refining Company at Port Hope, Ontario developed a process for separation of these metals. The process involves the

treatment of a concentrate consisting mainly of fine hydroxides of uranium, copper, cobalt and nickel. After being leaching 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 etc. can be carried out by solvent extraction [73-77].

It is possible to separate titanium from its associates present in ilmenite (a heavy fraction of beach sand) via suitable leaching, extraction, stripping and precipitation processes. The associates are usually iron, chromium, manganese [78-79] etc. When ilmenite is leached by one of the reported methods [80-83], titanium together with the associates go into solution.

Titanium and iron(III) can be separated easily from Mn(II) and Cr(III) by single stage extraction by D2EHPA at around pH 1.0 [84-86]. Titanium can be removed from iron by extraction with methyl isobutyl ketone (MIBK) from 7.0 mol dm^{-3} HCl solution [87, 88].

B. Extractants

The classification of extracting reagents, i.e., extractants, 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 [89, 90]. 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, 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 behaviour, 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:

- a) acidic extractants,
- b) basic extractants and
- c) neutral extractants.

a) 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, $R_2O_2PO(OH)$, 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 type 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),
- 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),
- xii) β -diketones (acetyl acetone, benzoyl acetone, thenoyltrifluoro acetone, hexafluoroacetyl acetone etc).
- xiii) Hydroxyoximes (LIX-reagents)

b) Basic extractants

These are organic reagents which can easily form a salt when in contact with an aqueous acid solution. The only basic extractants which

have been studied in some detail from the point of view of the 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.

c) 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.

C) Cyanex 272 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 alkyl phosphoric acids, alkyl amines and neutral organophosphates are all familiar extractants, originally developed and used in the nuclear industry. Now-a-days, they are all in use in variety of processes (nuclear and non-nuclear). Carboxylic acids originally proposed as cheap alternative to the more

expensive alkyl phosphoric 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 [90-101] 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) [102-126].

Cyanex 272 extractant is a proprietary 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 Extractant

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

Chemical family : Dialkylphosphinic acid

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

Molecular Weight : 290

Purity : 80-87% (found 83%)

Impurity : Trialkylphosphine oxide

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

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

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

Specific Gravity : 0.92 at $20^{\circ}C$

Volatility : 0%

Solubility in water : 16 mg/dm³ at $20^{\circ}C$

Appearance and odor: Slightly amber colored viscous liquid

Hazardness: Causes eye and skin irritation on direct contact

Stability: Stable; does not polymerize

COD: 195000 ppm

Octanol-H₂O partition coefficient: $> 10^{2.65}$

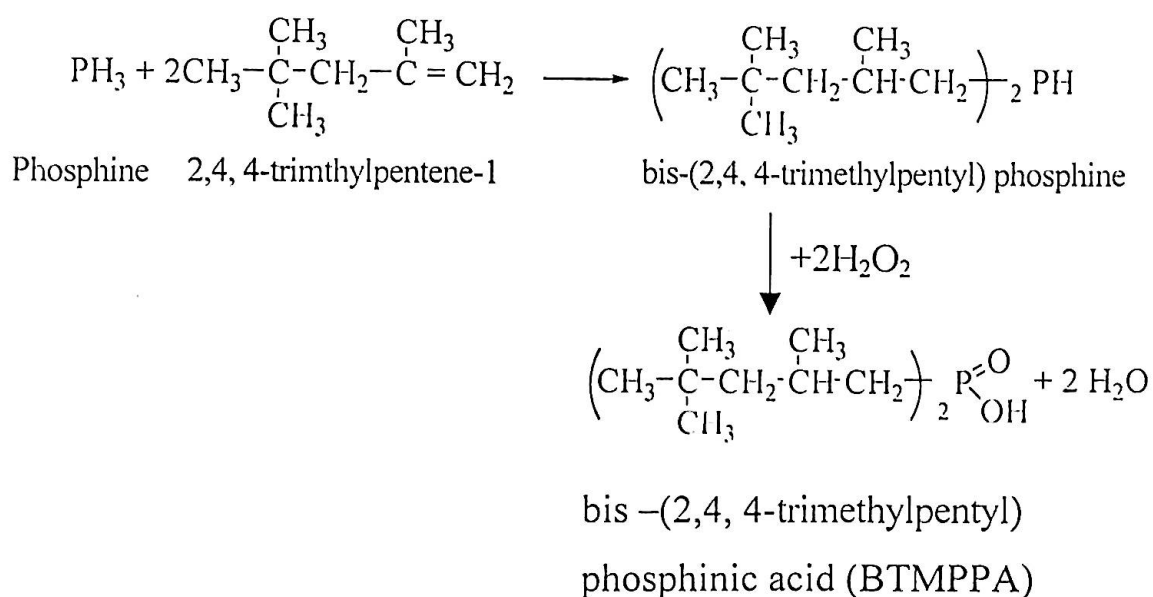
Bluegill, 96 h : 46 mg/dm³

Trout, 96 h : 22 mg/dm³

Daphnia, 48 h : 2.9 mg/dm³

WHMIS classification: Class D Division 2B Toxic

Cyanex 272 extractant is manufactured by reacting phosphine (PH₃) with 2,4,4-trimethylpentene-1 and then oxidising the intermediate with hydrogen peroxide as shown below [118]:

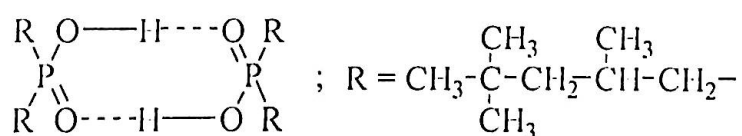


During this synthesis, tris-(2,4,4-trimethylpentyl)phosphine oxide (TOPO) is also formed to an extent of 10-17%. Sole and Hiskey [127] have found by ³¹P-NMR and GC-MS that the extractant supplied by Cyanamide Canada Inc. contains 87-88% BTMPPA, 10% TOPO and 2% unknown compounds. Paatero *et al.*, [128] 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 Cu²⁺ than purified Cyanex 272 (BTMPPA). So many researchers use as received

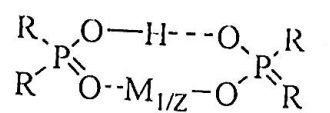
Cyanex 272 in metal extraction studies as TOPO in BTMPPA exhibits synergism. But in order to investigate on the mechanism of a metal extraction by Cyanex 272, from equilibrium and kinetic point of views, at least 99% BTMPPA should be used. It is therefore desirable to purify Cyanex 272 prior to its use 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 [129-132]. This method is time consuming and costly, consuming large quantities of acetone and ether. Zhengshui *et al.* [133] have developed a new purification method for dialkyl phosphoric / phosphonic / phosphinic acid extractants based on the principle that most of the surfactant molecules exist in the middle phase microemulsion. The later method of purification is easier and cheaper.

Like D2EHPA [134], BTMPPA - the active component of Cyanex 272 extractant may be represented by an eight-membered ring involving hydrogen bonding, similar to monocarboxylic acids:



If one of the acidic hydrogen atoms of this dimer 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 tetrahedra are joined at two corners by O-H····O bridges, so that they are effectively joined edge to edge.

CHAPTER II

LITERATURE REVIEWS

In the last seven 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 recent reports on :

- (A) The physico chemical properties of BTMPPA / Cyanex 272 extractant
- (B) The use of Cyanex 272 as an extractant for different metal ions and
- (C) Solvent extraction chemistry of Fe(III) and Cu(II) by different extractants.

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) 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 D2EHPA, the analysis of the aqueous phase for the extractant content has been done spectrophotometrically [135], colorimetrically [136, 137] and radiometrically with ^{32}P -labeled D2EHPA [138-140]. There are dozens of reports on K_2 , K_d and K_a for D2EHPA [135-143] in various aqueous / organic conditions using different analytical techniques. Considerable discrepancies among the values given by the authors are noticeable. It is observed that the anion present in the aqueous phase as well as the diluent used to constitute the organic phase affect the values of K_2 , K_d and K_a . Therefore, it is also expected for BTMPPA that the values of K_2 , K_d and K_a will depend on the aqueous condition and the diluent used in the organic phase. A very few report on the values of K_2 , K_d and K_a for BTMPPA could be found in the literature.

Ke-an *et al.* [144] 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 sulphate - acetate / chloroform - BTMPPA system at 298 K, they have reported that the values of K_{ab} , K_2 and K_a are 43.8 ± 1.8 , $184.3 \pm 16.1 \text{ dm}^3/\text{mol}$ and $(6.6 \pm 0.7) \times 10^{-4} \text{ mol/dm}^3$ ($\text{p}K_a = 3.18$), respectively.

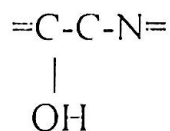
The dissociation equilibrium of BTMPPA together with three phosphinic acids have been studied in ethanol - water mixtures by potentiometric titration at 25°C [145]. Data have been analyzed both graphically and numerically using the program LETAGROP-ZETA. The obtained $\text{p}K_a$ values have been correlated with the corresponding value in water, determined both indirectly by means of extraction measurements

and by estimation using the suitable Hammett equation. They reported the pK_a value of BTMPPA as 5.42, 5.44 ± 0.02 , 3.38 and 3.51 ± 0.05 by graphical, LETAGROP-ZETA, Hammett equation and distribution measurements, respectively.

Using vapor pressure osmometry (VPO), Paatero *et al.* [146] 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/dm³.

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
$\begin{array}{c} > \text{P} = \text{O} \\ \\ \text{O} \text{H} \end{array}$	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



Oxines



1°, 2°, 3° amines

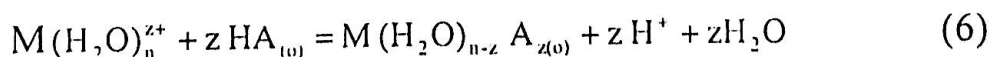


Quaternary ammonium salts

are responsible for the hydrophilic nature. The amphipathic characteristics is necessitated by the fact that an extractant must be able to interact with aqueous phase species while still maintaining a preferential organic phase solubility. The hydrophilic groups provide the functional groups which form the metal ligand bonds while the organic phase 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 [147] was insistent on that interfacial effects are of little importance in metal extraction. On the other hand, in another plenary lecture at the same conference, Hanson [148] 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 [149], 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 evidence derived from the interfacial and the bulk phase physico-chemical investigations is needed.

In 1967, two pioneering studies appeared in which interfacial tension measurements were used to elucidate metal extraction mechanisms: one by McDowell and Coleman [150-151] on the uranium-amine sulphate system and other by Scibona [152] 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.* [153-158], Van Dalen *et al.* [159-163], Flett *et al.*, [164-168], Yagodin *et al.* [169-171] and Osseo-Asare *et al.* [172-176], 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.

The density, viscosity and the excess properties, such as, excess molar volume, excess viscosity, excess enthalpy, excess Gibbs free energy change of activation of flow etc. afford valuable informations about the interactions between solute (extractant) and solvents (diluent). When BTMPPA as a solute is mixed with different diluents as solvents, it

interacts to some extent with the diluents. As a result, the different diluents cannot accommodate BTMPPA molecules in equal fashion. Consequently, the value of extraction ratio is expected to differ in different diluents when a metal ion is extracted from an aqueous phase keeping other experimental parameters unchanged. Although there are numerous experimental and theoretical studies on volumetric and thermodynamic behaviours of binary organic solutions in the literature, with the exception of very few studies can be applied to metallurgical problems. A few reports on these properties are pointed out below:

Treszczanowicz *et al.* [177] have shown that depending on the component or the ratio of the chain lengths of the components, the excess molar volumes of 1-alkanols + n-alkane binary systems vary from positive to negative value over the concentration range used. The excess volume behaviour is interpreted in terms of three effects: I) hydrogen bonding, ii) disruption of alkanol and alkane molecular order and iii) the negative effect due to interstitial accommodation.

Kimura and Benson [178] have measured excess molar volumes of binary mixtures of 1-hexanol with hexane isomers. Salamon and Patieories [179] have measured the viscosity of 1-propanol, 1-hexanol and 1-heptanol and their mixtures with n-alkanes and indicated that the degree of association of the alcohols has increased during dilution of the pure alcohol to mole fraction of 0.6 due to the dissociation of cyclic association present in the pure alcohol to give linear polymers.

Iwahashi *et al.* [180] have studied the dynamic structures of normal alcohols in their liquids as determined by viscosity and self-diffusion measurements. The conformation of molecules of normal alcohols in their

pure liquids is estimated through an analysis of their self-diffusion, coefficients of viscosities and molar volumes. The conformation of molecules of shorter chained alcohols is approximately spherical, while that for longer chain is of rodlike shape. In pure liquids of alcohols, rigid rod molecules, whose free rotating motion along their rod axes seem to be restricted, are randomly oriented and entangled with one another. The self-diffusion of long chain alcohols involves a longitudinal translation of rodlike molecules. Large apparent hydrodynamic radii suggest that the transport unit of normal alcohol is a dimer of alcohol molecules. The excess properties of methylisobutylketone (MIBK) with five diluents have also been reported [181].

There are some reports on the viscosities, density and excess properties of the binary and ternary mixtures of D2EHPA with hydrocarbon diluents. Swain *et al.* [182] have reported the viscosity and densities of the binary mixtures of D2EHPA with benzene, toluene and o-xylene at 30, 35, 40 and 45°C. They have fitted the mixture viscosity to a Redlich-Kister-Type equation. The excess molar volume, apparent viscosity and the excess Gibbs energy change of activation of flow have been calculated from the experimental data and are presented as functions of composition. The calculated excess quantities have been discussed in terms of the nature of binary interactions. Swain *et al.* [183] have also reported the viscosities and densities of the ternary liquid mixtures of D2EHPA + benzene + toluene which have been measured at 30, 35, 40 and 45°C. The mixture viscosity is fitted to a Redlich-Kister-type equation which includes the contribution of each constituent binary system along with a ternary contribution term. The non-idealities reflected in mixture viscosities are expressed and discussed in terms of

excess viscosities which are negative over the entire range of mole fraction. Negative values of excess viscosity and the nonlinear variation of viscosity and density with change of composition indicate molecular interaction between the polar extractant and non-polar diluents.

Furthermore, Swain *et al.* [184] have reported the viscosities and densities of the ternary mixtures of D2EHPA + benzene + o-xylene at 30, 35, 40 and 45°C. The non-idealities reflected in mixture viscosities are expressed in terms of excess viscosities. A Redlich-Kister-type equation is fitted to the η -X-T data which includes the contribution of each constituent binary system along with a ternary contribution term.

Swain *et al.* [185] have also reported the viscosities and densities of TBP + benzene + o-xylene at 30, 35, 40 and 45°C. The deviations in the viscosity from a mole fraction average are fitted in a Redlich-Kister-type equation, which includes the contribution of each constituent binary system along with a ternary contribution term. Viscosities and densities of the ternary liquid mixtures of TBP + benzene + toluene have been reported at 30, 35, 40 and 45°C [186]. Here also the deviations in the viscosity from a mole fraction average are fitted in a Redlich-Kister-type equation which includes the contribution of each constituent binary system along with a ternary contribution term. The viscosity deviations are negative in most of the case. Koekemoer *et al.*, [187] have reported the viscosity and density of D2EHPA + aliphatic kerosene. They have fitted the viscosity data to Kendal-Monroe equation to evaluate the average molecular weight of aliphatic kerosene used in the investigation.

Interactions of D2EHPA with n-hexane, n-octane, cyclohexane, carbon tetrachloride, toluene and nitrobenzene have been studied in terms

of densities viscosities, and derived excess properties (V_m^E , η^E , ΔG^E and also the interaction parameter d) by Biswas *et al.* [137]. Variation of these values for D2EHPA + diluent binary mixtures show that D2EHPA interacts with diluents in varying degrees. Correlation between d , ΔG^E , η^E , V_m^E and the metal extraction characteristics is noticed.

(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 [188] media and from sulphate media [182]. 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.* [103] 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 Extractant).

Fu and Golding [104] have reported the equilibrium and mass transfer (measured by Lewis cell) for the extraction of cobalt and nickel from sulphate 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 sulphate solution by

solvent extraction using Cyanex 272 Extractant has been patented by Chou and Beckstead [105]. Cho and Dai [106] 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 [107, 189-195]. There are also few reports on the cobalt-nickel separation on commercial plants [196-199].

Reports are also available on the use of Cyanex 272 as extractant for the extractive separations of Co(II) from Cu(II) [108, 109], Cu(II) from Zn(II) [110], Sc(III) from Fe(III) [111], Sc(III) from Th(IV), Fe(III) and Lu(III) [112], Zn(II) from Cd(II) [113], Al(III) from Co(II), Ni(II) and Mg(II) [200], Mn(II) from Co(II) [201], Mn(II) from Zn(II) [202] etc.

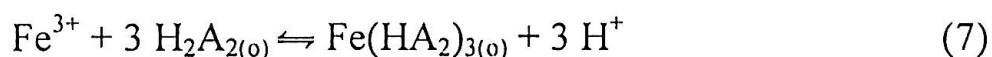
There are also some investigations on the extraction characteristics of several individual metal ions by Cyanex 272. Among them, the extractions of lanthanides [114, 115, 119, 120], Mo(IV) [116, 117], Zn(II) [118], Th(IV) [121], V(V) / V(IV) [122], Ag(I) [123], Cd(II) [124], Fe(III) [125, 126], Cu(II) [203] etc. can be mentioned. The Y(III) - Cyanex 272 [204, 205] and the La(III) - Cyanex 272 [206] systems have been investigated from the kinetic view points.

(C) Solvent extraction chemistry of Fe(III) by different extractants

Trivalent iron is one of the most easily extractable ion. For this reason, its masking or pre-extraction is an important step in separating other metal ions from it. Furthermore, the conversions of Fe(III) to Fe(II) and vice versa occur easily, but the distribution behaviour of the two ions is quite different.

The extractions of Fe(III) studied prior to 1976 by various extractants such as trioctylphosphine oxide (TOPO), ether, methylisobutylketone (MIBK), alcohols, esters, tributyl phosphate (TBP), various amines, quaternary ammonium salts, carboxylic acids, sulfonic acid, alkylphosphoric acid, acetyl acetone, benzoyl acetone, thenoyltrifluoro acetone, hexafluoroacetyl acetone, furoyltrifluoro acetone, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, β -isopropyltropolone, oxine, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, cupferron, N-benzoyl-N-phenylhydroxylamine, dithizone, diethyldithiocarbamate, xanthate, diethyldithiophosphate etc. have been summarized by Sekine and Hasegawa [207]. After that the following studies have been published for the extraction of Fe(III).

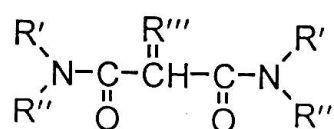
The solvent extraction of Fe(III) from acidic sulphate-acetate medium with D2EHPA in benzene has been reported [86]. The extraction reaction is suggested to be



which has an equilibrium constant of $10^{1.57}$. The forward extraction and the backward extraction kinetics of this system have been investigated and reported in references [208] and [209], respectively, by applying the shake-out method. The kinetics of Fe(III) extraction in the acidic chloride - D2EHPA - kerosene system using the constant interfacial area non-stirred cell technique (Hahn cell) have been reported by Biwsas *et al.* [17]. The extraction equilibrium of Fe(III) - Cl^- - D2EHPA - kerosene system has been thoroughly investigated by Biswas and Begum [210]. In this report it is shown that the species Fe^{3+} , FeCl^{++} , FeCl_2^+ , FeCl_3 and HFeCl_4 are all extracted by D2EHPA. The kinetics of the forward

extraction of Fe(III) from chloride medium by D2EHPA in kerosene using the single drop technique have also been reported [211]. The kinetics of stripping of Fe(III) - D2EHPA complexes from D2EHPA - kerosene phase by aqueous HCl - Cl⁻ phase using the single drop technique have also been investigated by Biswas and Begum [212].

Recently, malonamides of the following types:



(where, R' = usually -CH₃, R'' = n-alkyl, cycloalkyl or phenyl and R''' = H, C_nH_{2n+1} or oxoalkyl group) have been developed and used in the case of Fe(III) extraction. In ISEC'99, Costa *et al.* [213] presented the solvent extraction of base metal cations such as Fe(III) from HCl solutions using N-N' - tetra-substituted malonamides.

Costa and Paiva presented the solvent extraction of Fe(III) from HCl solutions using N,N'-dimethyl-N,N'-diphenyl malonamide in ISEC'02 [214]. The solvent extractions of iron(III) from HCl solutions using N,N'-dimethyl-N,N'-diphenyl malonamide and N,N'-dimethyl-N,N'-diphenyltetradecyl malonamide have been investigated by the same group of workers [215]. Costa, Martins and Paiva have also used N,N'-dimethyl-N,N'-dibutyl malonamide for the extraction of iron(III) from chloride medium [216]. Moreover, Costa and Paiva have reported the application of N,N'-tetrasubstituted malonamides to the recovery of Fe(III) for chloride solutions [217]. In these studies, it has been shown how the substituting groups change the minimum hydrochloric acid concentration for maximum extractions and also the extraction mechanism.

Three 3-phenyl-4-acyl-5-isoxazolones, namely, 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone (HFBPI), 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and 3-phenyl-4-(4-toluoyl)-5-isoxazolone (HTPI) have been used for the extraction of Fe(III) from 0.01-2.0 mol/dm³ HCl solutions. The equilibrium constants of the extracted complexes have been calculated by non-linear regression analysis by taking into account the aqueous phase complexation of metal ion with inorganic ligands (Cl⁻) and all plausible complexes extracted in the organic phase. The values are 4.35 ± 0.03 , 4.12 ± 0.04 and 4.07 ± 0.04 for HFBPI, HPBI and HTPI, respectively [218].

The mass transfer behaviours of Fe(III) together with Cd(II), Zn(II) and Eu(III) in sulphuric acid solution using microporous hollow fibre membrane (HFM) containing Cyanex 302 (bis-2,4,4-trimethylpentyl-monothiosphosphinic acid) have been investigated by Luo *et al.* [219]. It is shown that the mass transfer coefficients are increased with decrease of [H⁺] and increase of [Cyanex 302]. The order of mass transfer rate of metal ions at low pH is Cd > Zn > Fe > Eu. The interfacial activity of Cyanex 302 in sulphuric acid solution has been measured and treated by Gibbs adsorption isotherm.

Didi *et al.* [220] have prepared (1-hydroxo-1-phosphonohexadecyl) phosphonic acid [HPHPA] and (1-hydroxo-1-phosphonododecyl) phosphonic acid (HPDPA) by reaction of PCl₃ with palmitic and lauric acids, respectively, characterized them by elemental microanalysis, IR, ¹H and ³¹P NMR spectroscopies and used them in CCl₄ - octanol (10% v/v) solutions for extraction of Fe(III). The extracted complexes are Fe[C₁₁H₂₃C(OH)(PO₃H)]₂ · Cl · 3H₂O and Fe[C₁₅H₃₁C(OH)(PO₃H)]₂ · Cl · 3H₂O with HPDPA and HPHPA, respectively. HPHPA as ligand exhibits

stronger extracting power for Fe^{3+} and has a more hydrophobic character than HPDPA.

Principe and Demopoulos have made a comparative study of iron(III) separation from zinc sulphate - sulphuric acid solutions using the organophosphorous extractants - octylphenyl acid phosphate (OPAP) and D2EHPA [221] at 20 and 50°C. D2EHPA is found to coextract approximately 20 times the sulphate amount extracted by OPAP. Fe/Zn selectivity with OPAP at 20°C is found close to that of D2EHPA obtained at 50°C.

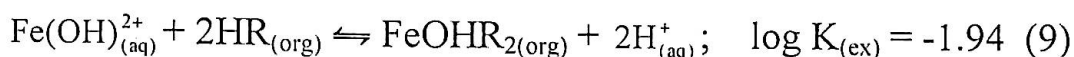
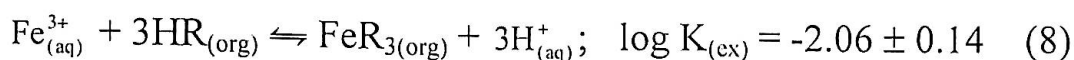
Six commercial cation exchange carboxylic resins [212] have been evaluated with respect to their ability to extract Fe(III) ions from acid sulphate media. It is found that these resins exhibit strikingly different characteristics, which depend on the matrix morphology and the acidity of the $-\text{COOH}$ group. Gel-type resins do not extract large amounts of Fe(III) and SEM studies show that the diffusion of Fe(III) ions into a gel-type matrix is severely hindered. By contrast, macroporous acrylic resins are efficient and selective extractants of Fe(III). The extraction rate is relatively slow, but it can be increased significantly by rising the temperature and decreasing the particle size. A macroporous methacrylic resin can also extract Fe(III) selectively, but the reaction is strongly dependant on pH. Both acrylic and methacrylic carboxylic resins can be readily eluted with relatively dilute H_2SO_4 . These characteristics make carboxylic resins useful for removing Fe(III) selectively from metallurgical solutions and effluents with the purpose of producing compact and stable iron products for safe disposal or marketing.

Distribution equilibria of approximately 0.01 mol/dm^3 Fe(III) together with Ga(III), Cd(II), Zn(II), Cu(II) + Pb(II) (0.10 mol/dm^3) from $1\text{-}4 \text{ mol/dm}^3$ HCl media have been studied using the commercial trialkylamine ADOGEN 364 (ADG) dissolved in kerosene as extractant [223]. Self-association of this reagent in the organic phase has been taken into account when analyzing the extraction reactions. Numerical analysis of the data with the LETAGROP-DISTR program allowed the evaluation of the equilibrium constants of the proposed equilibria. The dependence of the extraction constant values with ionic strength has been analysed using the specific interaction theory (SIT) treatment, from which the interaction coefficients of Ga(III), Cd(III), Fe(III), Zn(II), Cu(II) and Pb(II) with Cl^- ions have been estimated.

The extraction of Fe(III) from hydrochloric acid solutions has been investigated by Saji *et al.* [224] using Cyanex 923 (TRPO) in xylene. Extraction is found to increase with increasing concentration of both HCl and extractant. The extracted species is identified as $\text{HFeCl}_4 \cdot 2\text{TRPO}$. The stripping percentage of Fe(III) with HCl from loaded Cyanex 923 is found to decrease with an increase in acid concentration. A 100% stripping efficiency of Fe(III) can be achieved with 0.4 mol/dm^3 HCl in two counter-current stages at an aqueous / organic phase ratio of 3:1. The nature of the diluent on the extraction of iron(III) with Cyanex 923 has also been studied and correlated with dielectric constants.

Solvent extraction of iron(III) by means of the commercial aldoxime MOC-55 TD and its influence on Cu(II) extraction from H_2SO_4 solution has been investigated by Ocana and Alguacil [225]. Experiments are carried out varying the equilibration time, temperature, extractant concentration, aqueous pH and the Fe(III) and Cu(II) concentrations.

Fe(III) extraction is found to take place over pH value of 1 and the extraction process is endothermic ($\Delta H = 52.5$ kJ/mol). The extraction of the metal by MOC-55 TD can be represented by the equilibria



where HR represents the extractant molecule. It has also been concluded that, under the present experimental conditions, Cu(II) is extracted preferably to iron(III) and the presence of this element does not appreciably influence the equilibrium constant of the copper extraction by MOC-55 TD.

The solvent extractions of some metal ions (Cu(II), Fe(III), Ga(III), Ni(II), Co(II), Zn(II), Pb(II)) with LIX 984 dissolved in n-heptane have been studied [226]. The extraction order observed as the pH of the aqueous solution increases is $\text{Cu(II)} > \text{Fe(III)} > \text{Ga(III)} > \text{Ni(II)} > \text{Co(II)} > \text{Zn(II)} \approx \text{Pb(II)}$. The experimental data obtained have been explained considering hydroxyoxime association and metal complex solvation. Numerical analysis of the data with the LETAGROP-DISTR program suggested the presence of the CuR_2 , $\text{CuR}_2 \cdot 2\text{HR}$, FeR_3 , GaR_3 , NiR_2 , InR_3 , $\text{CoR}_2 \cdot \text{HR}$, $\text{ZnR}_2 \cdot 3\text{HR}$ and $\text{PbR}_2 \cdot \text{HR}$ species in the organic phase. The values of the equilibrium constants for the extraction reactions have been reported.

Iron(III) extraction has been carried out at about 1 mol/dm^3 concentration from HCl solutions using TBP, MIBK and their mixtures as solvents [227]. Extraction increases with increasing concentration of both acid and solvent. The species extracted to the organic phase appears to be

HFeCl₄ with 3 mole of the solvent. A solvent mixture consisting of 70% (v/v) TBP and 30% (v/v) MIBK has been found suitable to achieve faster phase separation with no third phase formation. When the two solvents are used together, a synergistic effect on iron extraction is observed. Extraction and stripping isotherms have been obtained with the above solvent mixture for a typical solution containing 56.4 g/dm³ of iron(III) and 73.7 g/dm³ of HCl. Greater than 99.4% extraction and 100% stripping efficiencies of the metal have been achieved in five stages.

Solvent extraction of iron(III) by means of the commercial salicylaldoxime LIX 860 and its influence on Cu(II) extraction from H₂SO₄ solutions has been reported [228]. Extraction experiments have been carried out varying the equilibration time, temperature, extractant concentration, aqueous pH and the ferric and cupric ions concentrations. Iron(III) extraction by LIX 860 can be represented by; $\text{Fe}^{3+} + 3\text{HR}_{(o)} \rightleftharpoons \text{FeR}_{3(o)} + 3\text{H}^+$. The extraction can be performed at pH above 1 and the extraction reaction is endothermic. The value of log K_{ex} is -1.196 and the value of ΔH° is 8.6 kJ/mol. It is concluded that under the experimental conditions, Cu(II) is extracted preferable to iron(III) and the presence of this ion does not appreciably influence the equilibrium constant of the copper extraction by LIX 860.

Metallic membranes with minipores have been tested in the Rotating Diffusion Cell, RDC for the quantitative study of the effect of diffusion on the kinetics of solvent extraction of iron(III) with a primary amine N1923 and TBP [229]. The results have showed that the rate-limiting steps in the extraction process are chemical reactions at the interface. The effects of various parameters on the rate of extraction have suggested that the reaction orders may be 1, 1, -1 and 0 with respect to

the concentrations of iron(III), amine sulphate, H^+ and TBP concentrations, respectively. Due to the change in the reaction mechanism, the rate of extraction is increased by one order of magnitude with the addition of TBP to the primary amine system.

Ogwuegbu and Oforka [230] have reported the extraction separation behavior Fe(III), Co(II), Ni(II) and Cu(II) from aqueous solutions of various pH values and complexing agents using 1-phenyl-3-methyl-4-(p-nitrobenzoyl)-5-pyrazolone. The possible extraction mechanism and the compositions of the extracted species have been determined. The separation factors have been given and the efficient methods for the separation of Fe(III) from Co(II), Cu(II) and Ni(II) have been proposed.

A study of the extraction of Fe(III) from aqueous sulphate media by the primary amine Primene 81R at 50°C has been made by Alguacil and Amer [231]. The compound extracted from the organic phase with Primene 81R sulphate in kerosene has been isolated and recrystallized from a methanol-acetone mixture and has been shown to have the stoichiometric formula $3(RNH_3)_2SO_4 \cdot Fe(OH)SO_4$. On the basis of the experimental data and spectral studies a dimeric structure is suggested for the extracted complex.

Demopoulos and Gefvert [232] have shown the use of a novel synergistic extractant mixture based on an alkylated derivative of 8-hydroxyquinoline (Kelex 100) and D2EHPA for the selective removal of iron(III) from strong H_2SO_4 solutions. Stripping of iron from the loaded organic phase is affected by reacting with hydrogen to reduce Fe(III) to Fe(II), which subsequently is easily stripped with a weak acid solution.

The applicability of the process for iron removal from an actual copper electrolyte is also demonstrated.

Besides the above studies, the solvent extraction of Fe(III) from sulphate solution by mono-(2-ethylhexyl)phosphoric acid has been reported by Demopoulos and Pouskouleli [233], whereas that of Fe(III) from aqueous solutions by D2EHPA has been reported by Sato *et al.* [234], and the synergistic extraction of iron(III) at higher concentrations in D2EHPA - TBP mixed solvent systems has been reported by Sahu and Das [235].

The extraction of iron(III) from aqueous nitrate solutions by bis-2,4,4-trimethylpentylphosphinic acid (Cyanex 272, HA) dissolved in Isopar H (a hydrocarbon liquid) has been studied at 25°C and 0.1 mol/dm³ ionic strength [125]. The distribution of metal has been measured as a function of pH and extractant concentration. The data have been analyzed both graphically and numerically to determine the stoichiometry of extracted species and their equilibrium constants. It is found that Fe(III) is extracted into the organic phase by the formation of species FeA_3 , $\text{FeA}_3 \cdot (\text{HA})_3$ and $\text{Fe}(\text{NO}_3)_3 \cdot (\text{HA})_3$.

The synergistic extraction of Fe(III) from H_2SO_4 solutions, with a maximum at 130-150 g/dm³ H_2SO_4 , is observed when using mixtures of Kelex 100 with dialkylphosphorous (HR) acids: D2EHPA, PC-88A or Cyanex 272 [126]. No synergism, however, is observed when Kelex 100 - M2EHPA mixture is used. Synergism is attributed to the formation of mixed metal - Kelex 100 - HR - sulphate complexes. Based on the experimental data (continuous variation method, acid analysis of feed and raffinate solutions), the likely molar metal: Kelex 100 : HR : SO_4^{2-} ratio in

the complex is 2 : 2 : 4 : 1. A reaction mechanism, rationalizing the observed synergism, together with the roles of Kelex 100 and HR, is suggested.

d) Solvent extraction chemistry of Cu(II) by different extractants

Copper(II) is more stable than Cu(I) and so this element is usually extracted as divalent complexes. The extraction of copper complexes with neutral extractants is not always effective except that of some Cu(I) complexes. Nevertheless, there are many reports on this subject.

The extractions of Cu(II) prior to 1976 by various extractants such as diethylether, methylisobutyl ketone, amyl alcohol, tributylphosphate, various amines (such as triisooctylamine, amberlite XE-204, trioctylamine etc.), quaternary ammonium salts, diantipyrylmethane, di-2-ethylhexylphosphoric acid, carboxylic acid, β -diketones like acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, benzoylacetone, dibenzoylmethane, thenoyltrifluoroacetone, and furoyltrifluoroacetone, β -isopropyltropone, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, oxine (8-hydroxyquinoline) and its derivatives (such as 2-methyloxine, 5,7-dichlorooxine, 5,7-dibromooxine), oximes (such as dimethylglyoxime, α -furyldioxime, α -benzoinoxime), cupferron, N-benzoyl-N-phenyl hydroxylamine, PAN, 1-(thiazolylazo)-2-naphthol, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, 2-nitroso-1-naphthol-4-sulfonic acid, cyclohexanedithiocarboxylic acid, diaryldithiophosphoric acid, dialkyldithiophosphoric acid, thiodibenzoylmethane, thio-TTA, thiooxine, dithizone, diethyldithiocarbamate, diethylammonium diethyldithiocarbamate etc. have been referenced nicely by Sekine and Hasegawa [236]. The following paragraphs summarize some of the works done on copper extraction after 1976:

Comparative experimental studies have been carried out on extraction of Cu(II) from aqueous acid nitrate media using four LIX-reagents, representative of different extractant classes: LIX 984 N-1, LIX 860N, LIX 84-1 and LIX 65N [237]. As a diluent, liquid hydrocarbon undecane has been used. The extraction behaviour of the LIX-reagents has been compared on an analysis of the influence of the main factors on the two-phase mass-transfer process: aqueous pH value, initial copper and extractant concentrations and temperature. The experimental data received have been used in the calculations of important parameters characterizing the efficiency of copper extraction from nitrate media with different LIX reagents : distribution ratio D , concentration constants K_{ex} , $pH_{0.5}$ -values and thermodynamic parameters such as enthalpy, entropy and free energy changes.

Suhendra, Yeen and Haron [238] have used a mixture of fatty hydroxamic acids (FHA), synthesized from a commercial palm olein, for the extraction of Cu(II) from aqueous media. The content of the hydroxamic acid groups in the FHA has been estimated by elemental analysis to be 3.52 mmol/g. In solvent extraction studies, octanol is used as an organic diluent. The extraction of Cu(II) is found to occur through the formation of 1 : 2 Cu(II) : FHA complex. The extraction is pH dependent and not affected by the presence of large amount of Co(II), Ni(II), Ca(II) and Zn(II) ions.

Tao and Nagaosa [239] have made an investigation on the extraction of Cu(II) by di-2-methylnonylphosphoric acid [DMNPA] in *n*-dodecane, toluene and 1-octanol as organic diluents at $(28 \pm 0.2) ^\circ\text{C}$. The extracted copper complexes are reported to be $\text{CuA}_2 \cdot 2\text{HA}$ in dodecane, $\text{CuA}_2 \cdot 3\text{HA}$ in toluene and CuA_2 in 1-octanol. The stoichiometry of the

extracted metal species has been compared with that of di-2-ethylhexylphosphoric acid (D2EHPA) under the same experimental conditions. UV - visible and FT - IR spectroscopic data on the extractants and their complexes indicate that the binding mode of the metal complexes varied with the polarity of the diluents.

Miguel *et al.* [226] have reported the solvent extraction of Cu(II) with LIX 984 dissolved in n-hexane. The experimental data obtained are explained considering hydroxyoxime association and metal complex solvation. Numerical analysis of the data with the LETAGROP-DISTR program has suggested the presence of CuR_2 and $\text{CuR}_2 \cdot 2\text{HR}$ species in the organic phase. Complex formation between Cu(II) and the buffers used has been considered in the calculations. The values of the extraction equilibrium constants for the extraction reactions are reported.

The solvent extraction of Cu(II) from acidic sulphate solutions has been carried out using the new oxime extractant, MOC 45 diluted in distilled kerosene [240]. It is found that the increase of aqueous phase pH, extractant concentration in the organic phase and temperature increase the percentage extraction of Cu(II); whereas, reverse is observed during stripping. The process has been tested for the recovery of copper from converter slag leach solution. The extraction and stripping efficiencies are >98% and 100%, respectively.

The distribution of 0.1 mmol/dm^3 Cu(II) from $1\text{--}4 \text{ mol/dm}^3$ HCl media has been reported [223] using the commercial trialkylamine ADOGEN 364 (ADG) dissolved in kerosene. In analyzing the extraction reaction, the self association of this extractant in the organic phase has been taken into account. Numerical analysis of the data with the

LETAGROP-DISTR program has allowed the evaluation of the equilibrium constant. The variation of K_{ex} with ionic strength has been considered using the specific interaction theory, from which the interaction coefficient of Cu(II) with Cl^- has been estimated.

A study [241] has been carried out on the use of S_{EX} to remove Cu(II) from concentrated $ZnSO_4$ solutions. In a series of experiments using a plant leach solution containing 2 g/dm³ Cu(II), 2 g/dm³ Fe(III), 173 g/dm³ Zn(II), 7.9 g/dm³ H_2SO_4 , 0.25 g/dm³ Cd(II), 0.015 g/dm³ Co(II) and LIX 622 in SX, upto 97-98% of the Cu(II) present in the $ZnSO_4$ leach solution is extracted with negligible co-extraction of Zn(II), Fe(III), Cd(II) and Co(II). Selectivity is very high. Copper(II) is selectively extracted at relatively low pH and the process does not need any pH-modification. The stripping can be done by 150 g/dm³ H_2SO_4 solution.

Miguel *et al.* [226] have reported the extraction of Cu(II) with LIX 984 dissolved in n-heptane. The species reported are CuR_2 and $CuR_2 \cdot 2HR$. Amores, Coedo and Alguacil [242] have reported the application of the new extractant MOC 45 (oxime derivative) as an extraction agent of Cu(II) from sulphate media. The system has been studied as functions of temperature, diluent of the organic phase, metal concentration, along with the copper stripping stage by sulfuric acid solutions. The data have been analyzed to determine the stoichiometry of extracted species and their equilibrium constants. The extracted species are CuR_2 ($\log K_{ex} = 0.62$) and $Cu(HR_2)_2$ ($\log K_{ex} = 4.00$). The system has been studied batch-wise and continuously.

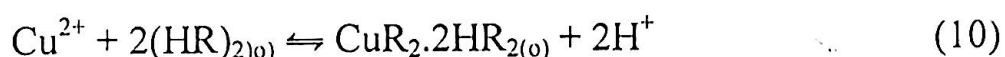
The mechanisms of copper(II) solvent extraction by Cyanex 272, Cyanex 302 and Cyanex 301 have been discussed by Sole and Hiskey [203]. Extraction from sulphate media is strongly dependant upon sulphur substitution in the phosphinic acid and complete extraction of copper(II) by Cyanex 302 and Cyanex 301 occurs below pH 0. Conventional stope analysis cannot be used for determining the complex stoichiometries. Electronic spectra, ^{31}P NMR and FAB-MS have been used for determining the complex stoichiometry and geometry. By sulfur containing ligands, Cu(II) is reduced to Cu(I), accompanied by corresponding oxidation of the extractant. It is shown that copper combines in a 1:1 stoichiometric ratio with these ligands to form multinuclear oligometric complexes, in which the ligands bridge between metal centers. The enhanced stabilities of the complexes formed with the sulphur containing ligands are explained in terms of the Hard – Soft Acid - Base, HSAB concept and pi-bonding between d-orbitals of the metal center and the donor atoms.

The ammoniacal leach liquor from the dissolution of polymetallic Indians Ocean sea-nodules has been treated using 25% LIX 64N in kerosene as extractant [243]. The co-extractions of Cu(II) and Ni(II) and their selective stripping produce metal-rich solutions. The nickel solution requires purification to remove copper using 10% LIX 64N. The effect of impurities such as Mn(II) and Fe(III) building up due to extraction and nickel winning is observed and controlled by bleeding-off the electrolyte to avoid cracking the deposit.

Bart *et al.* [244] have reported the factors that influence the extraction of copper in nitrate media by different ketooximes and aldoximes (together with modifiers). The effects of the composition of

the organic phase on the copper loading ability and transfer capacity are illustrated. Ketooximes are shown to be highly unstable in nitrate media compared to aldooximes especially with increasing acid strength. Ag/Cu selectivity is also better with aldooximes. Admixture of modifier causes rapid sludge formation in the organic phase, which is due to an enhanced support of nitration or degradation of the ion exchanger.

Measurements of the extraction equilibria of copper(II) have been carried out at 303 K with 2-buthylthiododecanoic acid (2-BTDA, HR), 2-bromododecanoic acid (2-BDA, HR) and naphthenic acid (NA, HR) in hexane by Baba and Inoue [245]. It is shown that Cu(II) is extracted according to the following stoichiometric relations;



for 2 - BTDA and 2 - BDA; and



for NA. Extraction equilibrium constants have been evaluated as $K_{\text{ex}} = 1.2 \times 10^{-5}$, 5.6×10^{-5} and 6.0×10^{-13} for 2-BDA, 2-BTDA and NA, respectively. The pK_a values of the acids have been determined by the measurement of pH titration curve and found to be in the order as follows:



From the experimental results, it has been concluded that there may be some intensive correlations between pK_a of the acidic extractants and the stoichiometric relations of the extraction reactions of metals and the extraction equilibrium constants.

Copper-loaded LIX 65N (Henkel Corporation) in decanol / kerosene solution has been hydrogen stripped to give metallic powder and regenerated extractant at between 160°C and 220°C using 0.63 MPa - 4.28 MPa hydrogen [246]. A semiempirical equilibrium model for copper(II) extraction from sulphuric acid solution by LIX 64N - Escaid 100 has been developed by Horng and Maa [247].

Inoue and Tsunomachi [248] have investigated on and reported the distribution equilibria in the extraction of copper and nickel from 1 mol/dm³ aqueous ammonium nitrate solution by anti-2-hydroxy-5-nonylacetophenone oxime, the active part of SME 529 in MSB 210 diluent at 30°C. Extraction equilibrium constants for copper and nickel are determined to be 19 and 3.2×10^5 , respectively. The aqueous solubility of the oxime is also examined, permitting the measurement of the partition coefficient of the monomeric oxime between the aqueous and organic phases, its dissociation constant in the aqueous phase and its dimerization constant in the organic phase as 2.2×10^{-4} , 0.53 mmol/dm³ and 31 dm³/mol, respectively. It has been found that the extraction of copper is decreased by the addition of p-nonylphenol due to adduct formation. The equilibrium constant of the adduct formation between the oxime and p-nonylphenol is determined to be 6.6 dm³/mol. It is observed that nickel is extracted by p-nonylphenol.

Paatero [249] has reported the interaction between syn- and anti-isomers of 2-hydroxy-5-nonylbenzophenone oxime in the extraction of copper(II) with LIX 65N and LIX 64N. Hudson and Shepherd [250] have reported the selective extraction and separation of metals especially silver and copper using poly (2-S-vinyl-1,3,4-biadiazole-5-thiol).

The solvent extractions of Cu(II) and Zn(II) with LIX 34 (HL) and mixtures of LIX 34 and Versatic 911 have been investigated and reported by Dukov and Guy [251]. The composition of extracted copper complex has been determined to be CuL_2 . No synergism is found when mixture of LIX 34 and Versatic 911 is used.

A liquid surfactant membrane process has been considered for the separation of copper ion from dilute aqueous solutions [252]. The process is shown to work effectively. Solutions ranging from 2000 ppm Cu(II) to 100 ppm Cu(II) as CuSO_4 have been successfully processed. In the case of the very dilute solutions, the Cu(II) concentration in the final raffinate can be taken down to less than 1 ppm in a single contact stage. The liquid membrane is made up of a chelating agent (Shell SME 529), organic diluent and emulsifying agent. Factors influencing mass transfer, such as membrane composition, O/A ratio, pH of the aqueous feed solution and acid content of the strip solution, contacting condition etc., have been studied. Providing membrane breakdown is low, the process can be represented as a pseudo first order rate process. It is shown that by using this form of facilitated transport transfer of Cu(II) against very adverse concentration gradients across the membrane can be achieved. Further pilot plant work is required to examine scale up features of this process. Compared with conventional S_{EX} , the amount of solvent (reagent + diluent) required in the contacting stage is very much reduced. In this work, it is shown that successful extraction of copper can be achieved using over two orders of magnitude less solvent than with solvent extraction.

Cognet *et al.* [253] have reported the thermodynamic data for distribution coefficients and maximum loading for cupric ion extraction

by LIX 64N solution in xylene. The influence of ionic strength and chloride ion concentration in the aqueous phase on distribution coefficients and measured pH is given and interpreted. The comparison of Cl^- and SO_4^{2-} aqueous solutions shows that if extraction seems higher in Cl^- solution at the same measured pH, it is of the same order of magnitude at the same true concentration of H^+ and it is higher in SO_4^{2-} solution at the same apparent concentration of acid.

A comparison has been made of the extraction of Cu(II) and Fe(III) from Cl^- and SO_4^{2-} solutions with LIX 64N in kerosene [254]. The effects on extraction of pH, anion concentration and temperature have been examined, and attention has been given to the ionic strength of the aqueous media, some of which contained aluminum and magnesium; extractions have been carried out under 'practical' rather than 'ideal' conditions. Extractions of both copper(II) and iron(III) are enhanced from chloride solutions compared with sulphate; although separation of Cu(II) from Fe(III) is slightly reduced, extraction of Cu(II) from chloride liquors appears to be applicable to commercial leach solutions.

CHAPTER III

OBJECTS OF PRESENT INVESTIGATION

From the literature review, it is found that bis-2,4,4-trimethylpentyl phosphinic acid (BTMPPA, active component of Cyanex 272) is an effective and a commercial extractant for the separation of Co(II) from Ni(II). Moreover, it has been used for the extraction of number of metal ions. In a solvent extraction plant for separation of Co(II) from Ni(II) using Cyanex 272, prior separation of Fe(III) is needed. The system also contains Cu(II). Since no data on the extraction of Fe(III) and Cu(II) from sulphate medium by Cyanex 272 are available; and also since the physico-chemical data on BTMPPA are not available, this study has been focussed on to investigate on the following outlines:

- 1) Determination of purity of Cyanex 272 and its purification by microemulsion formation method. Purified Cyanex 272 (BTMPPA) will then be subjected to some physical measurements.
- 2) A method for the colorimetric estimation of BTMPPA will be developed.
- 3) Distribution of BTMPPA in $0.1 \text{ mol/dm}^3 (\text{Na}^+, \text{H}^+)\text{Cl}^-$ - kerosene system will be investigated in order to estimate the partition or distribution coefficient (K_d), dimerization constant (K_2) and ionization constant (K_a) of BTMPPA.
- 4) Interfacial adsorption property of BTMPPA will be measured for $0.50 \text{ mol/dm}^3 \text{H}_2\text{SO}_4$ - BTMPPA in different diluent (n-hexane, kerosene, cyclohexane, benzene, toluene, 1,2-dichloroethane, chloroform, carbon tetrachloride, 1-hexanol, 1-heptanol) systems. Interfacial adsorption data will be correlated with Fe(III) and Cu(II) extraction equilibrium data with BTMPPA.

- 5) Interactions of BTMPPA + diluent (n-hexane / cyclohexane / benzene / toluene / chloroform / carbon tetrachloride / 1,2-dichloroethane / 1-heptanol) binary mixtures will be investigated in terms of densities, viscosities, excess molar volumes (V_m^E), excess viscosities (η^E), excess Gibbs free energy changes of activation of flow (ΔG^E) and Grungberg-Nissan interaction parameter (d) at 298.15 K and atmospheric pressure. Attempt will be taken to correlate d , ΔG^E , η^E or V_m^E with Cu(II) and Fe(III) extraction characteristics by BTMPPA in different diluents.
- 6) The extraction characteristics of Fe(III) from 0.10 mol/dm³ (Na⁺, H⁺) SO₄²⁻ medium by BTMPPA dissolved in kerosene will be investigated. The investigation will include the determinations of equilibration time together with the dependences of Fe(III) concentration, equilibrium pH, equilibrium extractant concentration, sulphate ion concentration and temperature on extraction ratio, loading capacity and stripping conditions. Extraction equilibrium constant will also be evaluated and a mechanism for Fe(III) extraction will be proposed.
- 7) The extraction characteristics of Cu(II) from 0.10 mol/dm³ (H⁺, Na⁺) SO₄²⁻ medium by BTMPPA dissolved in kerosene will be studied. The study will include the determinations of equilibration time together with the dependences of Cu(II) concentration, equilibrium pH, equilibrium extractant concentration, sulphate ion concentration and temperature on extraction ratio, loading capacity and stripping conditions. Extraction equilibrium constant will be estimated and the extraction mechanism (reaction) will be suggested.

CHAPTER IV

4.1 LIST OF CHEMICALS USED WITH THEIR SPECIFICATIONS AND SOURCES

SL.NO.	Name	Purity	Source
1.	Sulphuric acid	98%	E. Merck (Germany)
2.	Nitric acid	>70%	E. Merck (Germany)
3.	Hydrochloric acid	35.4%	BDH (England)
4.	Perchloric acid	>70%	E. Merck (India)
5.	Chromic oxide	99%	Loba Chemie (India)
6.	Sodium Molybdate	>99%	BDH (England)
7.	Hydrazinium sulphate	99%	BDH (England)
8.	Sodium hydroxide	97%	BDH (England), Fluka (Switzerland)
9.	Sodium carbonate (anhydrous)	99.5%	E. Merck (Germany)
10.	Potassium dichromate (analar)	99.9%	BDH (England)
11.	Potassium iodide (analar)	99.8%	BDH (England)
12.	Ammonium thiocyanate (GPR)	97%	BDH (England)
13.	Cupric sulphate (anhydrous)	98%	Loba Chemie (India)
14.	Ferric sulphate (technical)	-	BDH (England)
15.	Sodium thiosulphate pentahydrate (GPR)	99%	BDH (England)
16.	Di-potassium hydrogen phosphate (Aristar)	99.5%	BDH (England)
17.	Starch (soluble)	-	BDH (England)
18.	Ammonia solution	25%	E. Merck (Germany)
19.	2-propanol	99%	BDH (England)
20.	Acetone	99%	BDH (England)
21.	n-hexane 'Analar'	>99%	BDH (England)
22.	Benzene 'Analar'	>99%	BDH (England)
23.	Toluene 'Analar'	99.5%	BDH (England)
24.	Cyclohexane 'Analar'	99.50%	BDH (England)
25.	1, 2-Dichloroethane 'Analar'	>99.5%	BDH (England)
26.	Chloroform 'Analar'	>99.5%	BDH (England)
27.	Carbon tetrachloride 'Analar'	99.8%	BDH (England)
28.	1-Hexanol 'GPR'	98%	BDH (England)
29.	1-Heptanol 'GPR'	99%	BDH (England)
30.	Cyanex 272	-	Cytec Canada Inc. (as gift)
31.	Cyanex 302	-	Cytec Canada Inc. (as gift)
32.	Cyanex 301	-	Cytec Canada Inc. (as gift)
33.	Kerosene	-	Local Market
34.	Oxalic acid dihydrate	99.8%	BDH (England)

N. B. a) Cyanex 272, Cyanex 302 and Cyanex 301 were purified before use.

- b) Kerosene was distilled to collect colorless fraction consisting mainly of aliphatic hydrocarbons distilling over within 200-260°C.
- c) Other diluents (n-hexane, benzene, toluene, cyclohexane, 1, 2-dichloroethane, chloroform, carbon tetrachloride, 1-hexanol and 1-heptanol) were distilled before use.

4.2 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 thermostated 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 standardised by standard buffers of pH 4 and 7. After standardisation 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 minutes before taking the readings. The warm up time for the instrument was only fifteen minutes.

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 0.0001g. The calibration of the balance was checked time to time by the standard weights supplied by the Company.

d. Viscometer

Duran boro-silicate glass made Ostwald viscometers of three different calibration constants were used for viscosity measurements so that the measured efflux times were within 10 - 300s. The viscometers were of height 29 cm.

e. 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 in viscometric and other measurements wherever necessary. The separatory funnel or reagent bottle containing equal volumes of aqueous and organic phases was 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 upto three-fourth portions of the funnels or bottles. When the temperature gradient between the ambient and the experimental

temperatures was 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. In viscometric measurements, the viscometers as well as solutions in bottles or flasks were immersed in the thermostatic bath during measurements.

f. Tensiometer

A Du Nouy Tensiometer (Itoh Seisakusho Company, Tokyo; precision 0.1 mN/m) was used to measure the interfacial tension between two immiscible liquids. The apparatus comprises a platinum ring of a small known diameter (44 mm circumference) hung from the outer end of the balance arm. The other end of the arm is clamped to the middle of a torsion wire stretched between two clamps which can be rotated inside the frame of the instrument. A cylindrical evaporating dish containing the two immiscible liquids under test is placed on a platform which may be raised or lowered by means of a screw device. Two ends of the wire can be rotated independently by means of worm and gears actuated by Knurled Knobs. To the front clamp, is attached a vernier pointer, which moves over a scale graduated directly in mN per m (milliNewton per metre). Several evaporating flat bottomed circular dishes (6 cm id and 6 cm height) were used for the production of interface. A view of this tensiometer is shown in Fig. 1.

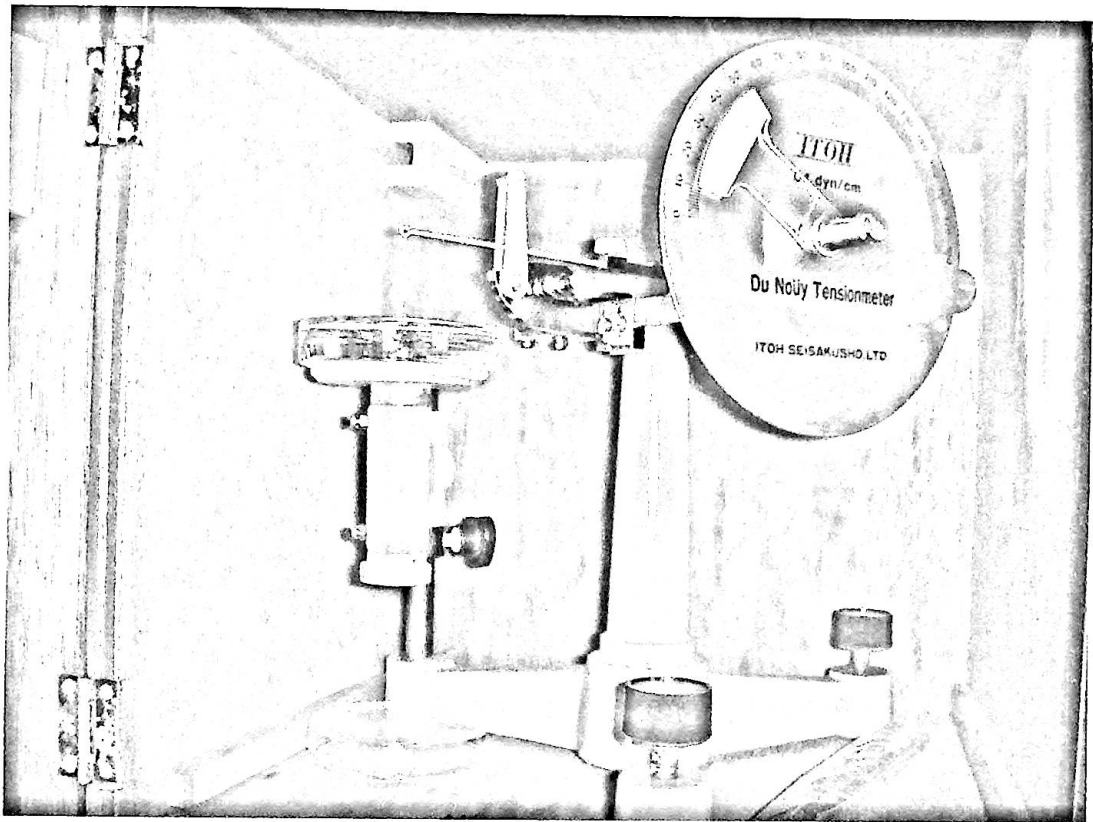


Fig. 1. Du Nouy Tensiometer.

g. Density meter

The densities of extractant, diluents and their mixtures were measured using a high precision vibrating tube digital density meter (DMA 5000, Anton Paar, Austria). The method is based on the principle of time lapse measurement for certain number of oscillations of a vibrating U-shaped sample tube filled with the sample liquid. At constant temperature, the natural vibration period of the U-tube is related to the density of liquid filling the tube. In DMA 5000, the natural vibration period is automatically converted into the density value and displayed directly on the LC display monitor of density meter. The DMA-5000 density measuring cell consists of a U-shaped oscillator glass cylinder (Fig. 2). The temperature of the sample tube is controlled by two integrated in-built Pt 100 platinum thermometers to a level of highest accuracy and traceable to national standards. The temperature of the sample can be controlled to $\pm 0.001\text{K}$.

The designs of the cell ensures identical volumes to be used for the measurement on different samples. Using a polyethylene syringe, the sample can be continuously and slowly injected to the upper part of the U-tube until the excess fluid flown out of the lower part. This ensures that the inner surface of the cell is completely wet and there is no micro-bubble inside the U-tube. The syringe is kept as such in plugged condition. After the measurement, the sample is removed and air is passed by built-in pump through the tube to remove excess liquid. The tube is then rinsed several times with the solutions whose density is to be determined next. All measurements are made starting from the lowest to the highest extractant concentration.

The density meter (Anton Paar DMA-5000) was checked or calibrated by the water supplied by the manufacturer ($\rho = 0.999707 \text{ g/cm}^3$ at 298.15 K). The apparatus automatically corrects the influence of viscosity upto 700 mPa.s on the measured density. Some technical data of the instrument are given below:

Measuring range:	1-3 g/cm^3
Repeatability (standard deviation):	
density:	$1 \times 10^{-6} \text{ g/cm}^3$
temperature:	0.001°C
Measuring temperature range:	0-90°C
Measuring pressure range:	1-10 bars
Amount of sample in measuring cell:	1 cm^3
Typical measuring time per sample:	40 s
Sample throughput:	10-30 h^{-1}
Dimension:	44×31.5×22 cm^3
Weight:	21 kg
Power:	50 VA

h. Refractometer

An ABBE refractometer (ATAGO Type-3, No. 21402, Japan) use used to measure the refractive index of BTMPPA.



Fig. 2a. Anton Paar DMA 5000 Density Meter.

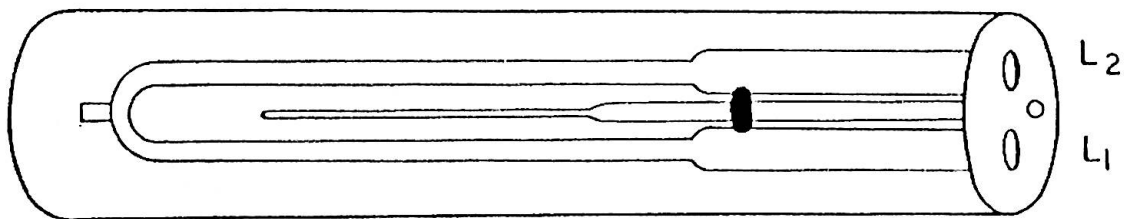


Fig. 2b. Anton Paar DMA 5000 Density Meter's density analyzing cell.

4.3 ANALYTICAL TECHNIQUES

a. Spectrophotometer

The spectrophotometer is used extensively for the determination of optical density or absorbance of the test solutions. The chief 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 methods.

The basic principle of most spectrophotometric measurement consists in comparing the colour produced by the substance in unknown amount with the same colour produced by a known amount of the material being determined, both being measured in terms of optical density or absorbance under well defined conditions. The quantitative comparison of these two solutions may in general, be carried out by one or more methods, one of which is based on the preparation of calibration curve by knowing the absorbance for the known concentrated solutions. The spectrophotometry is based on the Beer-Lambert law:

$$\log \frac{I_0}{I_t} = \epsilon ct \quad (12)$$

where I_0 and I_t represent the intensity of incident and transmitted light, and ϵ , c and t represent the molar extinction co-efficient, concentration in g-mol/dm^3 and thickness of solution medium (cm), respectively. The term in the left hand side of Eq. (12) is called absorbance (A) or optical density (O.D.), whereas I_t/I_0 is the transmittance (T).

The equation (12) 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 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 coloured solute ionizes, dissociates or associates in solution. Discrepancies may also occur when monochromatic light is not used. Throughout the whole investigation, concentrations of phosphorous and Fe(III) were determined by using a WPA S104 spectrophotometer (Made in UK).

i. Spectrophotometric estimation of phosphate (III)

Principle

Orthophosphate and molybdate ions condense in acidic solutions to give molybdophosphoric acid (phosphomolybdic acid), which upon selective reductions e.g., with hydrazine sulphate produces a blue colour [255] due to the formation of molybdenum blue of uncertain composition. The intensity of the blue colour is proportional to the amount of phosphate initially incorporated in the heteropoly acid. If the acidity at the time of reduction is 0.5 mol/dm^3 with respect to sulphuric acid and hydrazine sulphate is used as the reductant, the resulting blue complex exhibits maximum absorption at $820 \text{ nm} - 830 \text{ nm}$.

Interference

Ions which form heteropoly acids, such as silicate, arsenate, germanate and tungstate should be absent. Lead, antimony and copper also interfere, which may be removed by passage of the solution through a cation exchange column. Oxidising and reducing agents must be absent.

Construction of the calibration curve for phosphate(III)

Accurately weighed 0.2839 g of pre-dried (at 105°C) A. R. K_2HPO_4 was dissolved in de-ionised water and made upto 1.0 dm³, which gave the standard phosphate solution (1 cm³ $\equiv$ 0.05 mg phosphorous). 10.0 cm³ portion of the above prepared solution was taken into a 100.0 cm³ volumetric flask and diluted upto the mark with de-ionised water (1 cm³ $\equiv$ 0.005 mg phosphorous). Now, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 cm³ portions of this diluted solution were taken into six different 100 cm³ volumetric flasks, to each of which 5 cm³ of molybdate solution (12.5 g sodium molybdate per 500 cm³ of 5.0 mol/dm³ H₂SO₄) and 2 cm³ of hydrazine sulphate solution (0.75 g hydrazine sulphate per 500 cm³ de-ionised water) were added and diluted upto the marks with de-ionised water. The flasks with their contents were then heated by immersing the flasks in boiling water for 10 minutes, removed and cooled rapidly. The absorbances were then measured at 830 nm against a similarly treated reagent blank. The results are shown in Table I and in Fig. 3 as absorbance versus concentrations plot.

This calibration curve was used during the characterization of BTMPPA in chloride media.

ii. Spectrophotometric estimation of Fe(III)

Principle

Ferric ion reacts with thiocyanate to give a series of intensely red coloured compounds, which remain in true solution. Ferrous ion does not react. Depending upon the thiocyanate concentration, a series of complexes can be obtained. These complexes are red and can be formulated as $[\text{Fe}(\text{SCN})_n]^{3-n}$; where $n = 1, 2, \dots, 6$ [256]. At low thiocyanate concentration the predominant coloured species is $[\text{Fe}(\text{SCN})]^{2+}$ ($\text{Fe}^{3+} + \text{SCN}^- \rightarrow [\text{Fe}(\text{SCN})]^{2+}$), at 0.1 mol/dm^3 thiocyanate concentration it is largely $[\text{Fe}(\text{SCN}_2)]^+$ and at very high thiocyanate concentration it is $[\text{Fe}(\text{SCN})_6]^{3-}$. In the colorimetric determination a large excess of thiocyanate should be used since this increases the intensity and also the stability of the colour. Strong acid (hydrochloric or nitric acid of 0.5 mol/dm^3 concentration) should be present to suppress the hydrolysis.

Interference

Silver, copper, nickel, cobalt, titanium, uranium, molybdenum, mercury, zinc, cadmium and bismuth should be absent. Phosphates, arsenates, fluorides, oxalates and tartrates should also be absent.

Construction of the calibration curve for Fe(III)

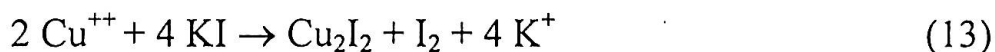
The standard solution of ferric ion was obtained by dissolving accurately weighed 0.4320 g of A. R. ferric ammonium sulphate in water and diluted to 1.0 dm^3 after adding 10 cm^3 of concentrated hydrochloric acid, so that 1 cm^3 of the resultant solution contained 0.05 mg of Fe(III).

The 1.0 cm³, 2.0 cm³, 3.0 cm³, 4.0 cm³, 5.0 cm³ and 6.0 cm³ portions of the standard solutions were taken into six different 50 cm³ volumetric flasks. To each flask, 3 cm³ of 4 mol/dm³ HNO₃ and 5 cm³ of 20% NH₄SCN solution were added. The flasks were then made up to the mark with distilled water and mixed well by thorough shaking. The absorbances of the samples were measured at 480 nm against a similarly treated reagent blank. The results are shown in Table II and in Fig. 4.

This calibration curve was used during the extraction equilibrium studies of Fe(III) by BTMPPA.

4.4. ESTIMATION OF COPPER(II) BY CONVENTIONAL METHOD

Copper(II) in nearly neutral solution liberates molecular iodine from an ionizable iodide (say, KI) according to the following reaction:



The liberated I₂ (equivalent to Cu⁺⁺ present) can be titrated by standard sodium thiosulphate solution following the reaction given below:



The end point of this titration can be detected by the use of 2 cm³ of starch solution. Starch forms a deep blue coloration with I₂ and so when I₂ is completely reacted, the blue coloration is disappeared.

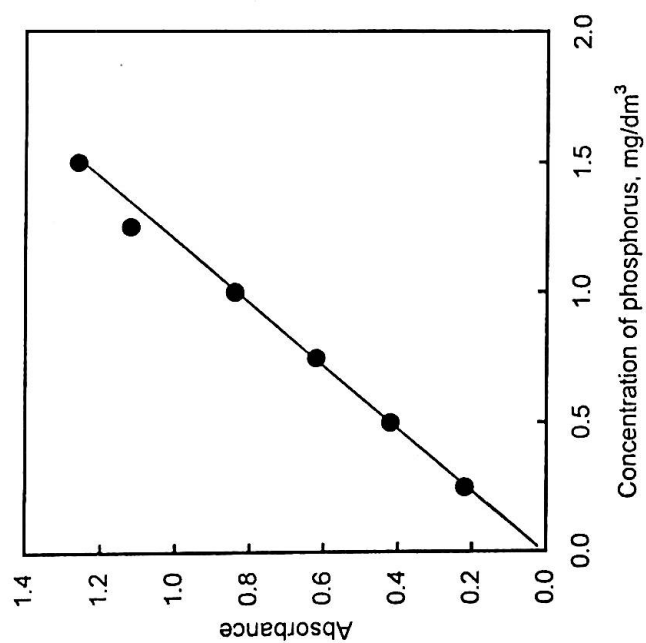


Figure 3. Calibration curve for the estimation of Phosphorous spectrophotometrically by the molybdenum blue method (Table I). $\lambda = 830$ nm.

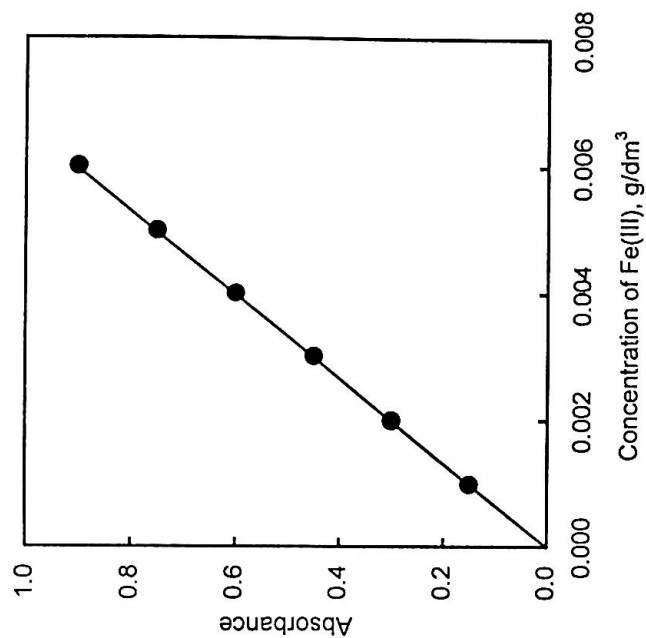


Figure 4. Calibration curve for the estimation of Fe^{3+} spectrophotometrically by the thiocyanate method (Table II). $\lambda = 480$ nm.

Sodium thiosulphate is not a primary standard substance and so prior standardization of sodium thiosulphate solution is needed. This is done by the titration of I_2 produced quantitatively from a solution of a primary standard oxidizing agent such as $K_2Cr_2O_7$.



Standardization of sodium thiosulphate solution

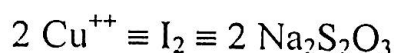
100 cm³ of cold distilled water is taken in a 500 cm³ conical flask. To it 10 cm³ standard dichromate solution, 2 g NaHCO₃ and 6 cm³ concentrated HCl are added, shaken and finally 1 g KI is added. The flask is stoppered and kept in dark for 5 min in order to ensure the completion of the reaction. The stopper and the wall of the flask are rinsed by water. The liberated I_2 is titrated with sodium thiosulphate solution (to be standardized) until the color of I_2 is faded. To this solution 2 cm³ of iodine solution is added to form blue coloration. Titration is continued drop-wise until 1 drop changes color from greenish-blue to light green. If V_1 (10 cm³) and S_1 are the volume and strength of $K_2Cr_2O_7$ solution used and V_2 is the volume of sodium thiosulphate solution required in titration, then the strength (S_2) of sodium thiosulphate solution will be given by :

$$S_2 = \frac{V_1 S_1}{V_2}.$$

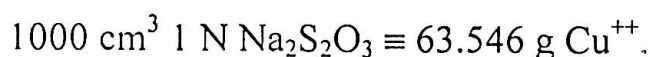
Titration of Cu^{++} solution

A definite aliquot of Cu^{++} solution is taken in a 250 cm³ conical flask. The solution is made neutral by adding NH_4OH and acetic acid solution. To this solution, 1 g KI is added, shaken, stoppered and kept the flask in dark for 5 min for completion of the reaction. The liberated I_2 is

titrated as above by previously standardized sodium thiosulphate solution with the exception that before adding the last one or two drops of thiosulphate solution, 1 g ammonium or sodium thiocyanate is added and the titration is completed rapidly. Copper(II) content is determined from the following relation:



or,



4.5 PREPARATION OF DIFFERENT SOLUTIONS

a. Preparations of aqueous solution

i. Molybdate solution

12.50 g of A. R. sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) was dissolved in $5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ and diluted to 500 cm^3 with $5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ solution. This solution was used during the construction of the calibration curve for phosphate(III) and the estimation of phosphorous in the aqueous phase by the Molybdenum blue method.

ii. Hydrazine sulphate solution

0.75 g of A. R. hydrazinium sulphate was dissolved in double-distilled de-ionised water (obtained by the passage of double-distilled water through a RALEIGH MIXED-BED LABORATORY DEIONISER) and diluted to 500 cm^3 . This solution was also used during the

construction of the calibration curve for phosphate(III) and the estimation of phosphorous in the aqueous phase by the Molybdenum blue method.

iii. *Starch solution*

A suspension of 1 g starch was made in 100 cm³ cold water and it was then poured into 900 cm³ boiling water with constant stirring. The mixture was boiled for 5 min cooled and filtered. To the filtrate 1 g KI was added as a preservative of starch solution. It was used as indicator in the iodometric estimation of copper (II).

iv. *Potassium dichromate solution*

1.2249 g primary standard K₂Cr₂O₇ was accurately weighed out by an electronic balance and taken into a 250 cm³ volumetric flask. 250 cm³ 0.10 N K₂Cr₂O₇ solution was prepared by dissolving the weighed out dichromate in distilled water and making the solution volume up to the mark by distilled water. This solution after making homogeneous was used in the standardization of Na₂S₂O₃ solution iodometrically.

v. *Sodium thiosulphate solution*

24.8 g Na₂S₂O₃·5H₂O was used to make 1 dm³ solution by distilled water. Its approximate strength was 0.10 N. Its actual strength was determined time to time by titration of 0.10 N K₂Cr₂O₇ solution iodometrically. This solution was used in the iodometric titration of Cu(II) solutions.

vi. *Sodium sulphate solution*

142.04 g of anhydrous Na_2SO_4 was dissolved into a 1 dm³ volumetric flask by double-distilled water to get 1 mol/dm³ Na_2SO_4 solution. This solution was used during (a) Purification of extractant and (b) Equilibrium studies of Fe^{3+} and Cu^{2+} in the same media, whenever necessary.

vii. *Hydrochloric acid solution*

6 mol/dm³ HCl solution was prepared by diluting concentrated acid with equal volume of distilled water. This solution was used in the purification work of Cyanex 272, Cyanex 302 and / or Cyanex 301 and also during the characterization of BTMPPA in chloride media.

viii. *Sulphuric acid solution*

1 dm³ of 1 mol/dm³ H_2SO_4 solution was prepared from the prediluted (>1 mol dm⁻³) H_2SO_4 which was standardized by carbonate-free standard NaOH solution. This solution was used during the equilibrium studies of Cu^{2+} and Fe^{3+} from the sulphate media.

ix. *Cu(II) sulphate stock and test solutions*

1 dm³ portion of stock solution of Cu(II) was prepared by dissolving and diluting the calculated amount of anhydrous cupric sulphate with distilled water after adding 10 cm³ of 1 mol/dm³ H_2SO_4 solution (to suppress hydrolysis of Cu(II)). The exact strength of the prepared stock solution was determined iodometrically and found to be 12.32 g Cu(II)/dm³. The sulphate content of the solution was ~ 0.19

mol/dm³. Definite amount of the stock solution was diluted with distilled water to prepare the test solutions containing the desired amount of Cu(II). The sulphate concentrations were adjusted at 0.1 mol/dm³ by adding calculated amount of 1 mol/dm³ Na₂SO₄ or H₂SO₄ solution. Then, pH of these solutions were adjusted by anhydrous Na₂CO₃ crystals and measured by a pH-meter. Finally, the copper(II) contents of these solutions were checked by iodometric titration method. These solutions were used as the aqueous phases in the equilibrium study of Cu(II) from sulphate media by BTMPPA.

x. Fe(III) sulphate stock and test solutions

1 dm³ portion of the stock solution of Fe(III) was prepared by dissolving and diluting the calculated amount of GPR grade Fe₂(SO₄)₃ with distilled water after adding 10 cm³ of 1 mol/dm³ H₂SO₄ solution (to suppress hydrolysis of Fe³⁺). The exact strength of the prepared stock solution was determined spectrophotometrically and found to be 11.82 g Fe(III)/dm³. The sulphate content of the stock solution was about 0.30 mol/dm³. Definit amount of the stock solution was diluted in volumetric flask with distilled water to prepare the test solution containing the desired amount of Fe(III). The sulphate concentrations were adjusted at 0.1 mol/dm³ always (otherwise started) by adding calculated amount of 1 mol/dm³ Na₂SO₄ or H₂SO₄ solution. Then the pH of these solutions were adjusted by anhydrous Na₂CO₃ crystals and measured by a pH-meter. Finally, the Fe(III) content of these solutions were checked by spectrophotometric method. These solutions were used as the aqueous phases in the equilibrium study of Fe(III) from sulphate media by BTMPPA.

xi. Sodium chloride solution

29.25 g A. R. grade NaCl was dissolved in a 500 cm³ volumetric flask by distilled water to get 1 mol/dm³ NaCl solution. This solution was used during the distribution study of BTMPPA in chloride media.

xii. Sodium hydroxide solution

About 10 g NaOH pellete was weighed out in a beaker. The pelletes were washed thrice with distilled water to remove the carbonates formed on the pelletes. The carbonate free pelletes were then dissolved by adding about 150 cm³ 75% (v/v) 2-propanol solution in water. The whole mass was the transferred into a 250 cm³ volumetric flask and made upto the mark with 75% (v/v) 2-propanol solution in water. This solution was standardized by standard oxalic acid solution potentiometrically and found to be 0.205 g eq/dm³. This solution after proper dilution with 75% (v/v) 2-propanol solution in water was used in the potentiometric titration of Cyanex 272 and BTMPPA. In the case of the preparation of standard carbonate free aqueous NaOH solution, a similar procedure was adapted except that in lieu of propanol solution water was used as solvent. This solution was also standardized by standard oxalic acid solution potentiometrically.

xiii. Oxalic acid solution

1.575 g oxalic acid (C₂O₄H₂.2H₂O) was accurately weighed out into a 250 cm³ volumetric flask. The solid was dissolved in distilled water and made up to the mark. After making the solution homogeneous of

strength 0.10 g eq/dm^3 (N), it was used in the standardization of NaOH solutions prepared above.

b. Preparation of organic solution

i. Preparation of organic solution for pH-metric titration

2 g as received Cyanex 272 was dissolved in 20 cm^3 75% (v/v) 2-propanol in water and used for the pH-metric (potentiometric) titration of as-received Cyanex 272. Similarly, 2.63 g purified Cyanex 272 i.e. BTMPPA was dissolved in 20 cm^3 75% (v/v) 2-propanol in water and used for the potentiometric titration of BTMPPA. These solutions were equilibrated with equal volumes of 1 mol/dm^3 H_2SO_4 for 1 h at 303 K before being used in titrations.

ii. Preparation of stock solution of BTMPPA

The molecular weight of dimeric BTMPPA is 580. Therefore, 290 g BTMPPA was weighed out into a dry 500 cm^3 volumetric flask, made upto the mark by distilled kerosene (colorless, distilling over $200\text{-}260^\circ\text{C}$) and shaken well to constitute the stock solution of concentration 1 mol/dm^3 of BTMPPA.

iii. Preparation of organic phase for Cu^{2+} and Fe^{3+} extractions

The above stock solution was used to prepare other solutions of lower concentrations in kerosene which were used in the extraction equilibrium studies of Cu^{2+} and Fe^{3+} .

iv. *Preparation of organic phases for distribution studies of BTMPPA*

The organic phases used in the distribution studies of BTMPPA were of concentrations 0.25, 0.20, 0.125, 0.10, 0.0625, 0.05, 0.0313, 0.0158, 0.0079, 0.0040, 0.0020, 0.0012, 0.0006, 0.0003, 0.45, 0.251, 0.116, 0.055, 0.028, 0.018, 0.008, 0.003, 0.0015, 0.00076 and 0.00035 mol/dm³ in kerosene and these solutions were prepared by proper dilution of the stock solution of BTMPPA made above by kerosene. Among these solution, 0.05, 0.10 and 0.20 mol/dm³ BTMPPA solutions were used in the distribution study of BTMPPA between aqueous 0.10 mol/dm³ (Na⁺, H⁺) Cl⁻ solution and kerosene in relation to [H⁺]. Other solutions were used in the study of distribution relating to the BTMPPA concentration in the aqueous phase.

v. *Preparation of BTMPPA - diluent binary mixtures for density and viscosity measurements*

For each diluent considered (n-hexane, cyclohexane, benzene, toluene, chloroform, carbon tetrachloride, 1,2-dichloroethane, n-1-heptanol), sets of sixteen binary mixtures of BTMPPA with each diluent were prepared by volume with increasing mole fraction of BTMPPA. Although these solutions were prepared by volume, they were weighed by a digital Mettler Toledo Electronic Balance (precision 0.0001 g) and the mole fractions were calculated. In each case, 50 cm³ solution was prepared and used for the density and viscosity measurements.

vi. *Preparation of BTMPPA - diluent mixture of different concentrations for interfacial tension measurements*

For each diluent considered (kerosene, cyclohexane, n-hexane, benzene, toluene, chloroform, carbon tetrachloride, 1, 2-dichloroethane, n-1-heptanol and n-1-hexanol), 100 cm³ portion of 1 mol/dm³ BTMPPA solution was made in distilled diluent. 50 cm³ portion of this solution was used for the interfacial tension measurement and the rest portion was diluted to make 100 cm³ portion of 0.50 mol/dm³ BTMPPA solution with proper diluent. 50 cm³ portion of this solution was used for the interfacial tension measurement and the rest was used for preparation of next dilute solution (0.20 mol/dm³) and so on.

4.6. PROCEDURES

i. *Procedure for titration of Cyanex 272 and BTMPPA*

Titration of the as-received and purified Cyanex 272 (BTMPPA) were carried out as suggested in the technical brochure of Cyanex 272 Extractant supplied by Cytec Canada Inc. Sodium hydroxide solution (in 75% (v/v) 2-propanol – 25% (v/v) water) was taken in a burette. The sample to be titrated was taken in 100 cm³ beakers and to it sodium hydroxide solution was added slowly after immersing the electrode of the Mettler Toledo 320 pH meter in the contents of the beaker. The stirring during titration was done by a magnetic stirrer. During titration in the alkaline region nitrogen was passed through the contents of the beaker. Extractant solutions were first equilibrated with 1 mol/dm³ H₂SO₄ solution for 1 h at 303 K prior to using them in titrations. Titrations were continued until pH values reached ~ 13.

ii. *Procedure for distribution of BTMPPA*

Several aqueous solutions (50 cm^3 each), each containing variable amounts of NaCl and HCl, were prepared so that they contained 0.10 mol/dm^3 (Na^+ , H^+) Cl^- . The organic phase was 0.05 , 0.10 and 0.20 mol/dm^3 BTMPPA in kerosene. Kerosene was saturated with water prior to equilibration (prior to BTMPPA solution preparation) to avoid change in volumes of the aqueous and organic phases due to saturation of the organic phase by water during equilibration. Equal volumes (20 cm^3) of the organic and aqueous phases were taken into a 125 cm^3 separating funnel and agitated for at least 12 h by an electrical shaking machine at ambient temperature of $(30\pm 1)^\circ\text{C}$. After equilibration, the separatory funnels were left for at least 72 h for complete phase separation by allowing the small organic droplets in the aqueous phase to enter in the organic phases. The phases were then disengaged very carefully. The equilibrium hydrogen ion concentration in the aqueous phase (pH) was measured. The concentration of BTMPPA in the aqueous phase was determined by estimating colorimetrically the amount of orthophosphate produced by applying a developed technique.

In order to determine the distribution ratio at constant equilibrium pH of 4.0 and 3.0 organic solutions containing different amounts of BTMPPA ($0.0003 - 0.45\text{ mol/dm}^3$) were prepared. Two sets of 250 cm^3 aqueous phase containing 0.10 mol/dm^3 (Na^+ , H^+) Cl^- were prepared and their pH values were adjusted to pH 4 and 3 by anhydrous Na_2CO_3 powder. Aliquots of 20 cm^3 of each phase were taken, agitated, settled and disengaged as above. The pH of the aqueous phase during equilibration was checked and adjusted from time to time.

iii. *Procedures for density and viscosity measurements*

The Anton Paar density meter-model DMA-5000 was calibrated with the calibrating water supplied by the manufacturer and also checked by deionized double distilled water. At 298.15 K, the meter was adjusted to read the density of water as 0.99707 g/cm^3 . The precision of density measurement was 0.0001 g/cm^3 . Acetone was used as the solvent for cleaning the sample cell of the density meter.

Depending on the fall time of the liquids/mixtures, Ostwald viscometers of three different calibrations constant were used. The selected viscometer filled with the liquid/mixture was kept immersed in the thermostatic water bath consisting of a large glass vessel for about 1 h prior to take reading. The temperature variation of the bath was maintained within $\pm 0.1 \text{ K}$. The flow of the liquid/mixture between two marks of the viscometer was determined with the help of a stop watch capable of reading up to 0.05 second. For each solution, the efflux time was measured until at least three observations agreed to within ± 0.05 second. The final value of the efflux time was taken as an average of these readings. Before each measurement, the inside wall of the viscometer was thoroughly cleaned with warm chromic acid so that there was no obstruction due to grease or any other impurity in the capillary and the liquid could move freely without leaving drops behind. It was then rinsed thoroughly with distilled water, followed by rectified spirit and acetone and finally dried.

iv. *Procedure for interfacial tension measurement*

Interfacial tension was measured with the help of a Du Nouy Tensiometer (precision 0.10 mN/m) at (298 ± 0.5) K using a platinum ring. Before measuring the interfacial tension, the aqueous (0.50 mol/dm^3 (Na^+ , H^+) SO_4^{2-} , $\text{pH} = 0.8$) and organic (BTMPPA solution of definite concentration in a particular diluent) phases were equilibrated for 1 h and settled for 24 h. Evaporating discs of 6 cm i.d. and 6 cm height were used as the container of phases in tension measurement. Proper cares were given to clean the rings and the discs. For this, the rings and discs were kept immersed in a chromic acid jar over-night. Next day, they were taken out with the help of a long sized tong, rinsed several times with distilled water, finally with acetone and dried. The accuracy of interfacial tension measurement was $\pm 0.20 \text{ mN/m}$.

v. *Procedures for extractions (distributions) of Fe^{3+} and Cu^{2+}*

In the cases of extraction, an aliquot of the aqueous phase (25 cm^3) containing Fe^{3+} or Cu^{2+} and SO_4^{2-} at definite concentrations and at definite pH (1.5 - 2.5 for Fe^{3+} and 4.0 - 5.5 for Cu^{2+}) was agitated with an equal aliquot of the organic phase consisting of BTMPPA and kerosene (taken in a 125 cm^3 separating funnel) for a predetermined time (30 min for Fe^{3+} and 15 min for Cu^{2+}) at (298 ± 1) K. The phase agitation was made effective by a Stuart Flask Shaker (220 V, 50 Hz, shaking speed controlled at 300 strokes/min). The temperature was controlled by putting the agitating flasks in a thermostatic water bath. After equilibration, phases were allowed to settle within the water bath and then disengaged. Separated aqueous solutions were subjected to equilibrium pH-measurements and Fe^{3+} or Cu^{2+} - concentration determinations. The

concentrations of Fe^{3+} or Cu^{2+} in the organic phases at equilibrium was calculated by difference. Then the extraction or distribution ratio (D) was calculated on dividing the concentration of Fe^{3+} or Cu^{2+} in the organic phase by that in the aqueous phase at equilibrium. In the case of Cu^{2+} extraction, anhydrous sodium carbonate powder was added intermittently to the shaking flask on monitoring the pH of the aqueous phase before final equilibrium being reached.

In the cases of loading of the organic phase by Fe^{3+} or Cu^{2+} and stage-wise stripping, a definite amount of the organic phase was repeatedly contacted with equal volumes of fresh aqueous solutions. In the case of stripping, 25 cm³ of an organic phase containing Fe^{3+} or Cu^{2+} and free BTMPPA of definite concentrations (diluent being kerosene) was equilibrated for 30 min for Fe^{3+} or 15 min for Cu^{2+} at 298 K with an equal volume of mineral acid (H_2SO_4 , HNO_3 , HCl) solution of a definite strength. Stripping ratio (S) was calculated on dividing Fe^{3+} or Cu^{2+} concentration in the aqueous phase by that in the organic phase at equilibrium.

CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the experimental results obtained by investigations will be given and the results will be discussed on the fundamental theories of chemistry and compared to the similar works reported earlier. Results and discussion will be provided here on the following head-lines:

1. Purification of Cyanex 272 and some physical properties of purified Cyanex 272 (BTMPPA)
2. Development of a spectrophotometric colorimetric method for quantitative estimation of phosphinic acid derivatives
3. Distribution studies of BTMPPA between the aqueous NaCl solution and kerosene
4. Densities (ρ), viscosities (η) and some derived properties like excess molar volume (V_m^E), excess viscosity (η^E), excess Gibbs free energy change for the activation of flow (ΔG^E) and the Grunberg-Nissan interaction parameter (d) of BTMPPA + various diluent systems
5. Interfacial adsorption of BTMPPA at various diluent / 0.50 mol/dm³ (Na^+ , H^+) $\text{SO}_4^{=}$ interfaces
6. Extraction equilibrium of Fe(III) by BTMPPA in kerosene
7. Extraction equilibrium of Cu(II) by BTMPPA in kerosene

5.1 Purification of Cyanex 272 and some physical properties of purified Cyanex 272 (BTMPPA):

The purity of as-received Cyanex 272 has been determined by the pH – metric titration using standard NaOH solution. The titration data is shown in Table III. During titration N₂ gas was purged through the sample holders.

Figure 5(a) shows the pH-metric titration curve of Cyanex 272 as received from Cytec Canada Inc. The curve shows three inflexions. The first inflexion in lower pH region is for H₂SO₄ neutralization, the second is for neutralization of Cyanex 272 (BTMPPA) and the first proton of organophosphorous acid (R-PO(OH)₂) and the third one is for the neutralization of the second proton of RPO(OH)₂. The volume of NaOH solution at the equivalence points are determined by the second derivative method as shown below.

Let T₁, T₂ and T₃ are the volumes of NaOH solution at the first, second and third inflexions. Then for determinations of T₁, T₂ and T₃, the second derivatives are determined first as shown in Table A.

The volume - strength product of NaOH solution required for neutralization of BTMPPA can be calculated from the following relation:

$$\begin{aligned}
 V_{\text{NaOH}} \times S_{\text{NaOH}} &= \{T_2 - (T_3 - T_2) - T_1\} \times 0.2 \\
 &= \{33.6625 - (36.26 - 33.662) - 1.96\} \times 0.2 \\
 &= 5.821 \text{ cm}^3 \text{ mol/dm}^3
 \end{aligned}$$

Table A. Data for determining T_1 , T_2 and T_3 by the second derivative method for as-received Cyanex 272

Vol. Of NaOH added, cm^3	pH	First derivative	Second derivative	$T_1, T_2 / T_3$
1.4	4.20			
1.6	4.24	4	0	$T_1 = 1.8 + 0.2 \left(\frac{8}{8+2} \right)$ $= 1.96 \text{ cm}^3$
1.8	4.28	4	8	
2.0	4.40	12	-2	
2.2	4.50	10	-5	
2.4	4.55	5		
33.2	68.4			
33.4	6.88	4	8	$T_2 = 33.6 + 0.2 \left(\frac{5}{5+11} \right)$ $= 33.6625 \text{ cm}^3$
33.6	7.00	12	5	
33.8	7.17	17	-11	
34.0	7.23	6	-2	
34.2	7.27	4		
35.50	7.48			
35.70	7.55	7	38	$T_3 = 36.10 + 0.2 \left(\frac{40}{40+10} \right)$ $= 36.26 \text{ cm}^3$
35.90	8.00	45	35	
36.10	8.80	80	40	
36.30	10.00	120	-10	
36.50	11.10	110	-20	
36.70	12.00	90	-60	
36.90	12.30	30		

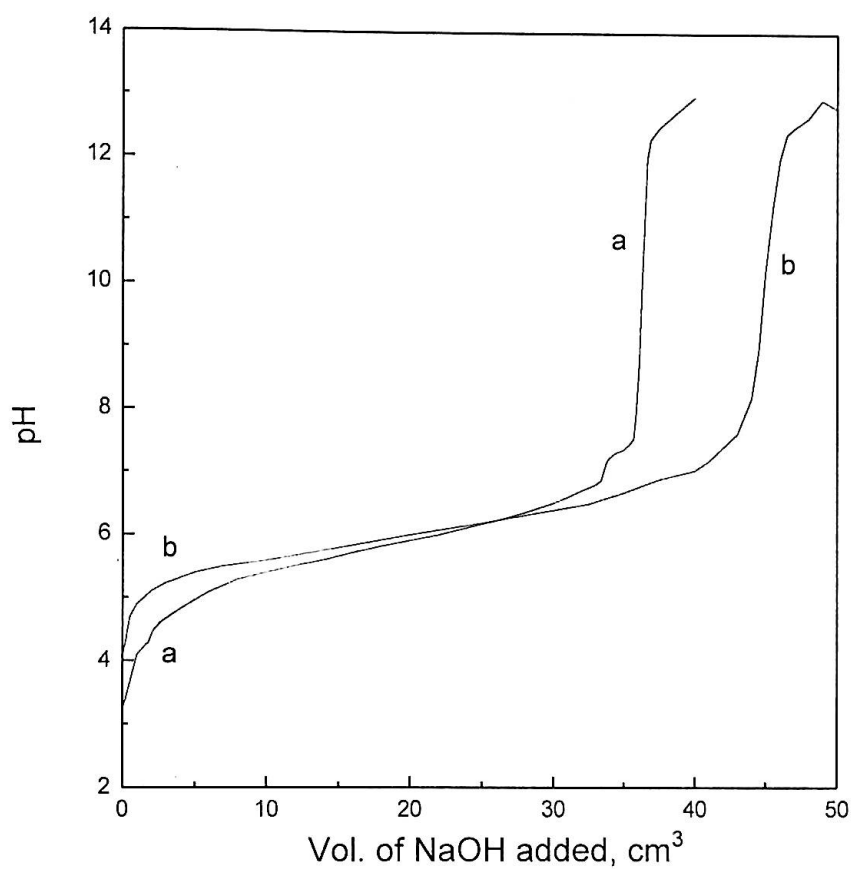


Figure 5. Potentiometric (pH-metric) titration curves of Cyanex 272 in 75% (v/v) propanol in water. $[\text{NaOH}] = 0.20 \text{ mol/dm}^3$ in 75% propanol solution, Cyanex solution = 20 cm^3 ; (a), as-received Cyanex 272 (2 g); (b), purified Cyanex 272 (2.63 g) (Table III).

This volume - strength product of NaOH solution will be equal to the volume - strength product of BTMPPA present in as-received Cyanex 272. Therefore,

$$\frac{\text{wt. of Cyanex 272 taken, g}}{\text{specific gravity}} \times S_{\text{BTMPPA}} = 5.821$$

$$\text{or, } \frac{2}{0.92} \times S_{\text{BTMPPA}} = 5.821$$

$$\therefore S_{\text{BTMPPA}} = 2.678 \text{ mol/dm}^3$$

If Cyanex 272 would contain 100% BTMPPA, then its molarity would be $(100 \times 0.92) \div 290 = 3.1724 \text{ mol/dm}^3$. Therefore, the percentage of BTMPPA in as-received Cyanex 272 is found to be $(2.678 \div 3.1724) \times 100 = 84.4\%$.

The volume - strength product of NaOH solution required for neutralization of the dibasic acid present in the as-received sample can be calculated from the following relation:

$$\begin{aligned} V'_{\text{NaOH}} \times S'_{\text{NaOH}} &= (T_3 - T_2) \times 0.2 \\ &= (36.26 - 33.6625) \times 0.2 \\ &= 0.5195 \text{ cm}^3 \text{ mol/dm}^3 \end{aligned}$$

This volume - strength product of NaOH solution will be equal to the volume - strength product of dibasic acid (assumed to be 2,4,4-trimethylpentylphosphonic acid, Mol. Wt = 194) present in as-received Cyanex 272. Therefore,

$$\frac{\text{wt. of Cyanex 272 taken, g}}{\text{specific gravity}} \times S_{\text{RPO(OH)}_2} = 0.5195$$

$$\text{or, } \frac{2}{0.92} \times S_{\text{RPO(OH)}_2} = 0.5195$$

$$\therefore S_{\text{RPO(OH)}_2} = 0.2389 \text{ mol/dm}^3$$

If Cyanex 272 would contain 100 % RPO(OH)₂, then its molarity would be $(100 \times 0.92) \div 194 = 4.74 \text{ mol/dm}^3$. Therefore, the percentage of RPO(OH)₂ in as-received Cyanex 272 is found to be $(0.2389 \div 4.74) \times 100 = 5.05 \%$ by weight. Otherwise, 1 dm³ of 0.2383 M RPO(OH)₂ is equivalent to $194 \times 0.2383 = 46.27 \text{ g}$. Therefore, Cyanex 272 contains 4.627 % RPO(OH)₂ by volume. So the sample contains 11% non-acidic impurities.

As-received Cyanex 272 has been purified by the micro-emulsion formation method of Zhengshui *et al.* [133]. A solution of Cyanex 272 in n-hexane has been made so that it contained 20% (v/v) Cyanex 272. Two litres of this solution have been agitated with two litres of an aqueous solution containing 51 g NaOH and 0.22 mol/dm³ sodium sulphate in a 5 litre reagent bottle for 2 h (occasionally) and stood overnight for equilibration and phase settling. A three phase system is formed. The middle phase contains about all BTMPPA in its sodium salt form. The middle phase is separated from the upper organic and lower aqueous phases. It is stripped with equal volume of 6 mol/dm³ hydrochloric acid solution. The extractant is returned to the organic phase in the acid form. The organic phase is washed with distilled water until no chloride ion can be detected in water (washing). The organic phase is dried with anhydrous sodium sulphate. It is then distilled to recover part (~80%) of the diluent (n-hexane). The residual n-hexane is separated in a vacuum oven at a pressure of 10 mm Hg and a temperature of ~80°C for 8 hours.

To ensure complete removal of n-hexane from the purified product, the last operation has been repeated for 5 days.

The titration curve of purified Cyanex 272 (BTMPPA) under similar titration condition is shown in Fig. 5(b). The titration data is given in Table III. The curve b of Fig. 5 shows only one inflexion and the volume NaOH solution of the mid point of inflexion is determined to be 44.84 cm^3 by the second derivative method as shown in Table B. The volume - strength product of NaOH required for neutralization of 2.63 g BTMPPA is $8.968 \text{ cm}^3 \text{ mol/dm}^3$ which will be equal to volume - strength product of BTMPPA; ie. $(2.63 \div 0.92) \times S_{\text{BTMPPA}} = 8.968$ giving $S_{\text{BTMPPA}} = 3.1371 \text{ mol/dm}^3$. 100% BTMPPA should have a strength of $(1000 \times 0.92) \div 290 = 3.1724 \text{ mol/dm}^3$; so that the purity of the purified Cyanex 272 is calculated to be $(3.1371 \div 3.1724) \times 100 = 98.9\%$ based on mono-acid content.

Table B. Data for determining the volume of NaOH solution (T) at the equivalence point in the titration of purified Cyanex 272 (BTMPPA)

Vol. of NaOH solution added, cm^3	pH	First derivative	Second derivative	T
44.0	8.20			$T = 44.5 + 0.5 \left(\frac{40}{40+20} \right)$ $= 44.84 \text{ cm}^3$
44.5	9.00	80	40	
45.0	10.20	120	-20	
45.5	11.20	100	-20	
46.0	12.00	80	-40	
46.5	12.40	40		

Some physical characteristics of as-received and purified Cyanex 272 are compared in Table C. The solubility of BTMPPA (purified Cyanex 272) in water at 25°C has been determined following the procedure of Fu *et al.* [257, 258]. Ten aliquots of 50 cm³ portion of distilled water (pH 6.7) have been taken in ten reagent bottles. To them 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 cm³ portions of 0.001 mol/dm³ BTMPPA solution in acetone are added. The solutions are agitated for 10 min at 25°C in a thermostatic water bath. The pH value of the resulted solutions have been measured by a standardized Mettler Toledo 320 pH Meter (Standardized by double buffers of pH 4 and 7). As the concentration of BTMPPA is increased, gradual flouring (cloudiness) formation is observed. The experimental data is given in Table IV and displayed in Fig. 6, as H⁺ activity (mol/dm³) vs. apparent concentration of BTMPPA in the aqueous solution. The plot is similar to that reported by Fu *et al.* [257], but in this case the H⁺ activity values are of rather lower values. A curve is obtained. The asymptotic lines intercepts at apparent BTMPPA concentration of 4.65×10^{-5} mol/dm³. It is concluded that the solubility of BTMPPA in water at 25°C is 4.65×10^{-5} g mol/dm³ (13.5 mg/dm³), compared to the solubilities of D2EHPA in water at 25°C being 3.53×10^{-4} g mol/dm³ [258] and of mono-2-ethylhexylphosphonic acid 2-ethyl hexyl ester (HEHEHP) in water at 25°C being 1.22×10^{-4} g mol/dm³ as reported by Li *et al.* [259] or 8.65×10^{-5} g mol/dm³ as reported by Gao *et al.* [260]. Therefore, the solubility of BTMPPA is less than the solubilities of D2EHPA and HEHEHP.

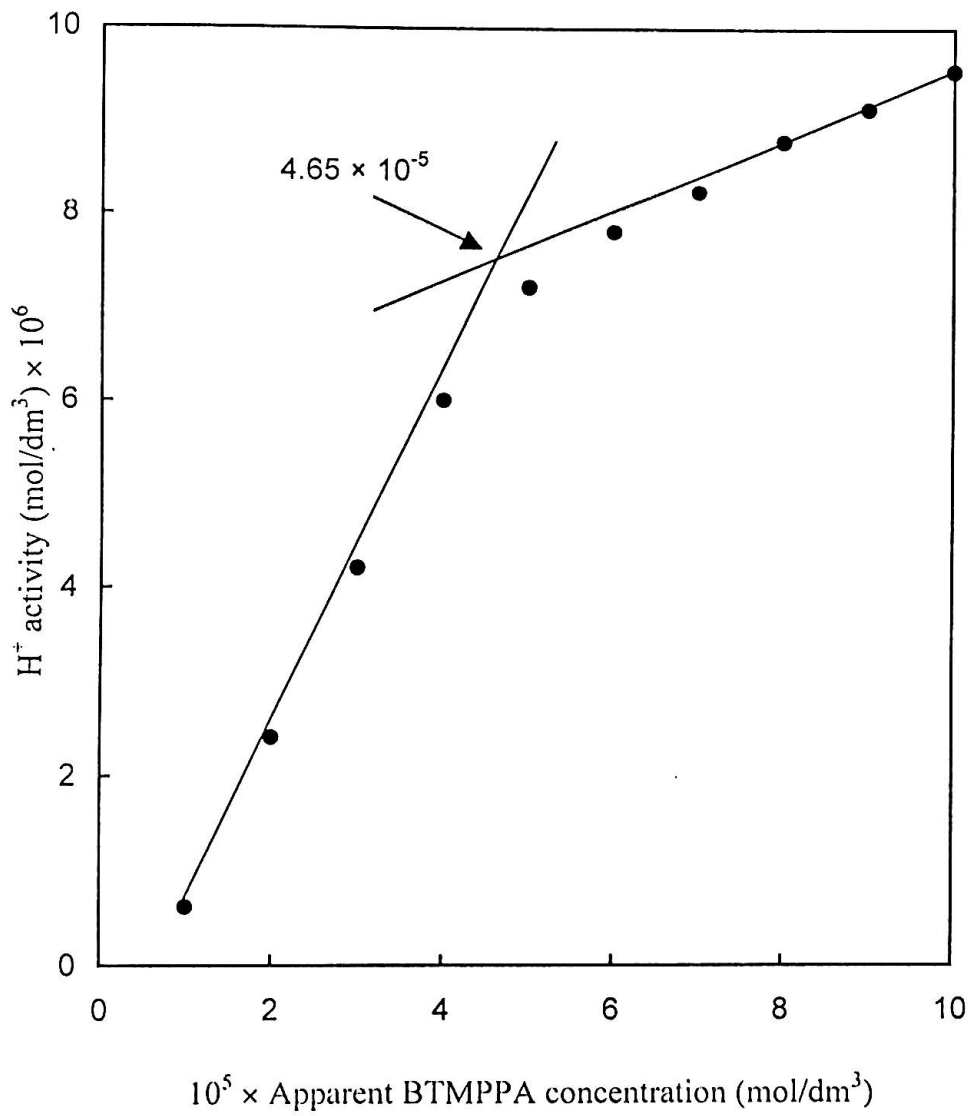


Figure 6. Determination of solubility of BTMPPA in water at 298 K

Table C shows that on purification amber color of Cyanex 272 is disappeared. The density at 25°C (0.9152 g/cm³), refractive index (1.4566) and viscosity at 25°C (120.02 cp) are taken as the criterion for the purified Cyanex 272 in subsequent purification steps.

Compared to the expensive copper salt purification method using triple crystallization [261-262], the method used in this work give higher recovery percentage (~88% recovery compared to ~80%). The used method is convenient over the copper salt method because it consumes less chemicals and less time.

Table C. Physical characteristics of as-received and purified Cyanex 272.

Property	As-received Cyanex 272		Purified Cyanex 272		
	This work	Brochure of CCI	This work	Zhengshui <i>et al.</i> (133)	Fu <i>et al.</i> (257)
Colour	Amber coloured	Amber coloured to colourless	Colourless	Colourless	-
Density ²⁵ , g/cm ³	0.9215	0.92	0.9152	0.9199	-
Refractive Index	1.4575	-	1.4566	1.4568	-
Viscosity ²⁵ , cp	140.02	142.00	120.02	-	-
Solubility ²⁵ _{H₂O} , mol/dm ³	5.48 × 10 ⁻⁵	5.52 × 10 ⁻⁵	4.65 × 10 ⁻⁵	-	4.58 × 10 ⁻⁵

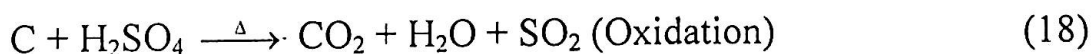
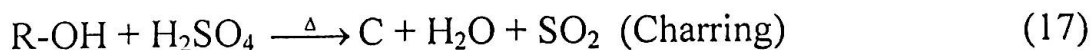
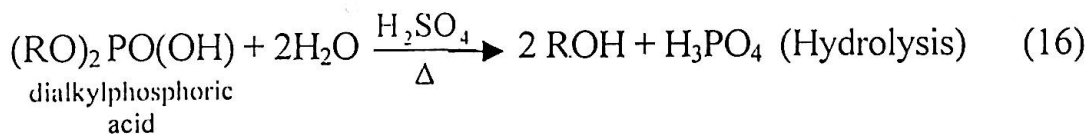
5.2 Development of a spectrophotometric/colorimetric method for the quantitative estimation of phosphinic acid derivatives

In order to determine dimerization constant (K_2), partition coefficient (K_d) and acid dissociation constant (K_a) values of BTMPPA, a technique has been developed for the conversion of organo-derivatives of

phosphinic acid into orthophosphate followed by its easy colorimetric estimation using the well-known molybdenum-blue method.

Organo-phosphoric acids such as D2EHPA, di-octylphosphoric acid (DOPA) and triesters of phosphoric acid like TBP can be easily estimated by a nonsophisticated colorimetric method after digestion with concentrated sulphuric acid [136, 263]. On digestion, orthophosphate is formed, which can be estimated by the molybdenum-blue method at 830 nm [255]. This sort of handy analytical technique permits the determination of dimerization, partition and ionization constants of organophosphoric acids [137, 143].

But it is found by preliminary experiments that the organo-phosphinic acids cannot be quantitatively converted to orthophosphate even on digestion for 6 h with concentrated sulphuric acid. It appears, therefore, that concentrated sulphuric acid can easily eliminate alkyl group of organo-phosphoric acid in which it is bonded to oxygen atom and consequently orthophosphate is formed by hydrolysis. During the latter period of digestion, the alkyl group is charred and oxidized by concentrated sulphuric acid to form a clear solution. The probable reactions during the digestion of a dialkylphosphoric acid with concentrated sulphuric acid are as follows:



In the case of organo-phosphinic acid, hydrolysis cannot take place because of the fact that alkyl radical is directly bonded to phosphorous

atom in this type of compound. In other words, there are only two oxygen atoms in phosphinic acid and so to convert it to orthophosphate, a very strong oxidizing environment is needed. To develop a new technique, a known amount of purified Cyanex 272 is heated in a beaker covered with a watch glass on a sand bath for a definite period with concentrated H_2SO_4 , HCl , HNO_3 , HClO_4 or $\text{HNO}_3 - \text{HClO}_4$ mixture, and the heated mass is used for phosphate estimation. Results are given in Table D. It is found that the concentrated H_2SO_4 and HCl are ineffective (< 4% conversion). On the

Table D. Digestion of BTMPPA with various concentrated acids and mixtures of HNO_3 and HClO_4 .

Acid	Amount of acid, cm^3	Ratio, (v/v)	Wt. of BTMPPA taken, g	Digestion time, h	% Orthophosphate conversion
H_2SO_4	5	-	0.0325	1	2.5
			0.0317	2	2.9
			0.0328	4	3.1
			0.0330	6	3.2
HCl	5	-	0.0324	1	1.0
			0.0328	2	1.2
HNO_3	5	-	0.0322	1	10.5
			0.0326	2	12.4
			0.0320	6	15.2
HClO_4	5	-	0.0333	1	7.5
			0.0322	2	9.6
			0.0326	4	10.5
			0.0325	6	11.3
$\text{HNO}_3/\text{HClO}_4$	9	1/8	0.0326	1	97.0
		2/7	0.0320	1	97.5
		3/6	0.0325	1	98.0
		4/5	0.0328	1	98.0
		5/4	0.0330	1	99.5
		6/3	0.0328	1	100.2
		7/2	0.0334	1	96.8
		8/1	0.0329	1	90.0

other hand, the concentrated HNO_3 and HClO_4 are better than H_2SO_4 and HCl . It is found that the mixture of concentrated (70%) HNO_3 and 70% HClO_4 can convert phosphinic acid to orthophosphoric acid. To get quantitative conversion, the ratio HNO_3 to HClO_4 equaling to 2 is needed. This mixture of HNO_3 and HClO_4 converts not only Cyanex 272 (BTMPPA) but also Cyanex 301 (2,4,4-trimethylpentylidithiophosphinic acid) and Cyanex 302 (2,4,4-trimethylpentylthiophosphinic acid) to orthophosphate which can be easily colorimetrically estimated by the molybdenum-blue method. .

Table E. Error analysis in estimation by the developed technique.

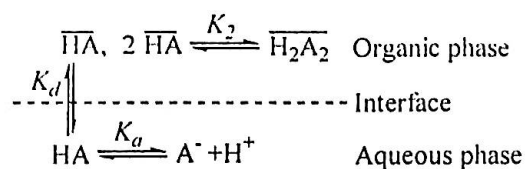
Digestion time = 1 h, Digestion acid = 70% HNO_3 (6 cm^3) + 70% HClO_4 (3 cm^3).

Purified reagent	No. of Expt.	Wt. of sample taken, g	Amount of P, mg		% Error	Stand. dev.
			Theoretical	Estimated		
Cyanex 272	1	0.0205	2.19	2.23	2.0	1.89%
	2	0.0395	4.22	4.16	-1.4	
	3	0.0577	6.17	6.01	-2.5	
	4	0.0790	8.44	8.46	0.1	
	5	0.1072	11.46	11.72	2.3	
	6	0.1373	14.68	14.58	-0.7	
Cyanex 301	1	0.0222	2.14	2.19	2.3	1.78%
	2	0.0233	2.24	2.19	-2.5	
	3	0.0430	4.14	4.06	-1.2	
	4	0.0442	4.26	4.26	0.1	
	5	0.0658	6.34	6.33	-0.2	
	6	0.0662	6.37	3.34	-0.5	
Cyanex 302	1	0.0176	1.72	1.76	2.6	1.72%
	2	0.0253	2.47	2.50	1.1	
	3	0.0460	4.50	4.39	-2.3	
	4	0.0472	4.61	4.54	-1.4	
	5	0.0720	7.03	7.09	0.8	
	6	0.0728	7.11	7.13	0.3	

To get an idea on the reproducibility in estimation by the developed technique, the error analyses in estimations have been done for purified Cyanex 272, Cyanex 301 and Cyanex 302. Results are shown in Table E. It is found that the percentage error is within $\pm 2.5\%$ and for six estimations, the standard deviations are 1.89, 1.78 and 1.72 % for Cyanex 272, Cyanex 302 and Cyanex 302. It is, therefore, concluded that the technique developed can be used successfully for the estimation of organo-derivatives of phosphinic acid.

5.3. Distribution studies of BTMPPA between the aqueous (H^+ , Na^+) Cl^- solution and kerosene

Cyanex 272 containing more than 98% BTMPPA is subjected to estimate the physico-chemical constants such as dimerization constant, K_2 ; partition coefficient, K_d and the ionization constant, (K_a) of BTMPPA (HA). HA may be dimerized through hydrogen bonding in the organic phase. The dimer cannot enter the aqueous phase, but it can be ionized at the interface (on interfacial adsorption). The monomer can be distributed to the aqueous phase and ionized. A scheme for these equilibria is depicted below:



where, the species with bars represent organic species and

$$\text{dimerization constant, } K_2 = \frac{[\overline{H_2A_2}]}{[\overline{HA}]^2} \quad (19)$$

$$\text{distribution constant, } K_d = \frac{[\overline{HA}]}{[HA]} \quad (20)$$

$$\text{and, ionization constant, } K_a = \frac{[H^+][A^-]}{[HA]} \quad (21)$$

Now, the net distribution ratio of HA can be defined as

$$D = \frac{\overline{C_{HA}}}{C_{HA}} = \frac{[\overline{HA}] + 2[\overline{H_2A_2}]}{[HA] + [A^-]} \quad (22)$$

Equation (22) is based on the consideration that the aqueous phase dose not contain appreciable amount of dimeric extractant, H_2A_2 . Now, if $\overline{C_{HA}} \gg \frac{1}{K_2}$, the concentration of the monomeric BTMPPA in the organic phase will be far less than that of the dimeric form, ie, $[\overline{HA}] \ll [\overline{H_2A_2}]$. Thus, in a practical situation, on gets:

$$\overline{C_{HA}} = 2[\overline{H_2A_2}] \quad (23)$$

so that the Eq. (22) takes the form :

$$D = \frac{2[\overline{H_2A_2}]}{[A^-] + [HA]} \quad (24)$$

Thus on putting the value of $[A^-]$ from Eq. (21), the following equation is obtained:

$$D = \frac{\sqrt{2}\sqrt{[\overline{H_2A_2}]} \cdot \sqrt{2}\sqrt{[\overline{H_2A_2}]}}{\frac{[HA]K_a}{[H^+]} + [HA]} \quad (25)$$

Equation (19) follows that $\sqrt{[\overline{H_2A_2}]} = \sqrt{K_2}[\overline{HA}]$ and from Eq.(23) one gets $\sqrt{2[\overline{H_2A_2}]} = \sqrt{\overline{C_{HA}}}$. Therefore, the equation (25) takes the form:

$$D = \frac{\sqrt{2}\sqrt{K_2}[\overline{HA}]\sqrt{\overline{C_{HA}}}}{[HA]\left(1 + \frac{K_a}{[H^+]}\right)} \quad (26)$$

From Eq. (20), one gets $[\overline{HA}] = K_d [HA]$ and on putting the value of $[\overline{HA}]$ in Eq. (26), one gets:

$$D = \frac{\sqrt{2}\sqrt{K_2}K_d\sqrt{\bar{C}_{HA}}}{1 + \frac{K_a}{[H^+]}} = \frac{1.41K_d\sqrt{K_2}\sqrt{\bar{C}_{HA}}}{1 + \frac{K_a}{[H^+]}} \quad (27)$$

On taking logarithm of the both sides of Eq. (27), the following equation is obtained:

$$\log D = \log (1.41)\sqrt{K_2} K_d \sqrt{\bar{C}_{HA}} - \log \left(1 + \frac{K_a}{[H^+]} \right) \quad (28)$$

Equation (28) indicates that the log-log plot of D vs $[H^+]$ has two asymptotes:

$$\text{when } [H^+] \rightarrow \infty, \text{ then } \log D = \log (1.41\sqrt{K_2} K_d \sqrt{\bar{C}_{HA}}) \quad (29)$$

and,

when $[H^+] \rightarrow 0$, then

$$\log D = \log (1.41\sqrt{K_2} K_d \sqrt{\bar{C}_{HA}}) - \log K_a + \log [H^+] \quad (30)$$

At the point of intersection of two asymptotes, the following relationship holds :

$$-\log K_a + \log [H^+] = 0 \quad (31)$$

Therefore, the value of K_a can be easily obtained from the abscissa of the point of intersection of two asymptotes.

The experimental data for the distribution of BTMPPA between aqueous 0.10 mol/dm^3 (H^+ , Na^+) Cl^- and kerosene in relation to $[H^+]$ at $(303 \pm 1) \text{ K}$ is given in Table V for $\bar{C}_{HA}$ values of 0.05, 0.10 and 0.20 mol/dm^3 monomeric BTMPPA systems. The $\log D$ vs $\log [H^+]$ plots for 0.05, 0.10 and 0.20 mol/dm^3 BTMPPA are shown in Fig. 7. In all cases, the experimental points form a curve. According to Eq. (29), the

asymptotic $\log D$ values at higher $[H^+]$ region equals to $\log D = \log (1.41 \sqrt{K_2} K_d \sqrt{\bar{C}_{HA}})$ and these values are 2.40, 2.50 and 2.65 for 0.05, 0.10 and 0.20 mol/dm³ extractant systems, respectively, and are shown by dashed lines. The dashed with dotted lines represent asymptotes at lower $[H^+]$ region. At the point of intersection of respective two asymptotes, abscissae are -3.20, -3.30 and -3.28 which give K_a value (cf. Eq. (31)) as 6.31×10^{-4} , 5.01×10^{-4} and 5.25×10^{-4} for 0.05, 0.10 and 0.20 M BTMPPA systems, respectively. So, the average value of K_a for BTMPPA can be taken as 5.52×10^{-4} ($pK_a = 3.26$). This value of K_a for BTMPPA is comparable to those reported earlier [144, 145, 257]. As from Eq. (29), the asymptotes of $\log D$ vs. $\log [H^+]$ plots at higher $[H^+]$ regions is equal to $\log (1.41 \sqrt{K_2} K_d \sqrt{\bar{C}_{HA}})$, the following relationships will hold :

$$\log (1.41 \sqrt{K_2} K_d \sqrt{\bar{C}_{HA}}) = 2.38 \text{ (for 0.05 mol/dm}^3 \text{ BTMPPA)} \quad (32)$$

$$\log (1.41 \sqrt{K_2} K_d \sqrt{\bar{C}_{HA}}) = 2.48 \text{ (for 0.10 mol/dm}^3 \text{ BTMPPA)} \quad (33)$$

$$\log (1.41 \sqrt{K_2} K_d \sqrt{\bar{C}_{HA}}) = 2.62 \text{ (for 0.20 mol/dm}^3 \text{ BTMPPA)} \quad (34)$$

The above three equations yield a common equation on substituting the value of $\bar{C}_{HA}$ in each equation as follows:

$$\log (\sqrt{K_2} K_d) = 2.84 \quad (35)$$

In the case of D2EHPA, the partition study between kerosene / 0.10 mol/dm³ (H^+ , Na^+) Cl^- yielded pK_a value of 1.70 [143]. It therefore appears that BTMPPA is a weaker acid than D2EHPA.

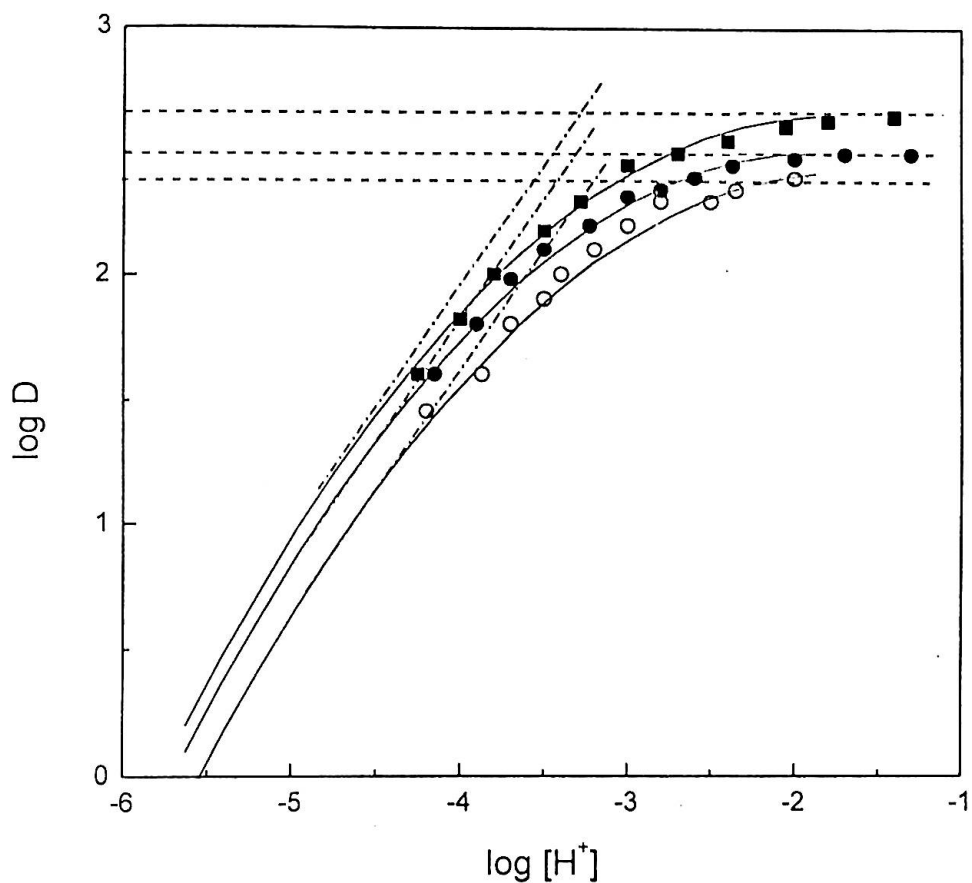


Figure 7. Distribution of BTMPPA between aqueous NaCl solution and kerosene in relation to $[H^+]$. $\mu = 0.10 \text{ mol/dm}^3$ (Na^+ , H^+) Cl^- , Temp. = $(303 \pm 1) \text{ K}$, $[BTMPPA] = 0.05 \text{ mol/dm}^3$ ($\circ$), 0.10 mol/dm^3 ($\bullet$) and 0.20 mol/dm^3 ($\blacksquare$). Points are experimental and curves are theoretical (Table V).

Again with the help of Eqs. (19-21), the Eq. (22) takes the form [143].

$$\begin{aligned}
 D &= \frac{K_d[HA] + 2K_2[\overline{HA}]^2}{[HA] + [HA]\frac{K_a}{[H^+]}} \\
 &= \frac{K_d[HA] + 2K_2K_d^2[HA]^2}{[HA] + [HA]\frac{K_a}{[H^+]}} \\
 &= \frac{K_d(1 + 2K_2K_d[HA])}{1 + \frac{K_a}{[H^+]}} \quad (36)
 \end{aligned}$$

On defining $1 + \frac{K_a}{[H^+]} = \phi$, Eq. (36) takes the form:

$$D = \frac{K_d}{\phi} (1 + 2K_2K_d[HA]) \quad (37)$$

Now,

$$\begin{aligned}
 C_{HA} &= [HA] + [A^-] \\
 &= [HA] + [HA]\frac{K_a}{[H^+]} \\
 &= [HA] \left(1 + \frac{K_a}{[H^+]}\right) \\
 &= [HA] \phi \quad (38)
 \end{aligned}$$

or,

$$[HA] = C_{HA} / \phi \quad (39)$$

Equation (39) converts the Eq. (37) into the following form :

$$D = \frac{K_d}{\phi} \{1 + (2K_2K_d C_{HA} / \phi)\} \quad (40)$$

On taking logarithm of both the sides of Eq. (40), Eq.(41) is obtained :

$$\log D = \log (K_d/\varphi) + \log \{(2 K_2 K_d C_{HA}/\varphi) + 1\} \quad (41)$$

Above equation indicates that the $\log D$ vs $\log C_{HA}$ plot at a particular φ ie. $[H^+]$ will have the following two asymptotes:

$$\text{when } C_{HA} \rightarrow 0, \text{ then } \log D = \log (K_d/\varphi) \quad (42)$$

and, when $C_{HA} \rightarrow \infty$, then

$$\log D = \log (K_d/\varphi) + \log (2 K_2 K_d/\varphi) + \log C_{HA} \quad (43)$$

Therefore, at the point of intersection of Eqs. (42) and (43), the following relationship holds:

$$\log (2 K_2 K_d/\varphi) + \log C_{HA} = 0 \quad (44)$$

Data for the distribution of BTMPPA between aqueous 0.10 mol/dm³ (Na⁺, H⁺) Cl⁻ and kerosene in relation to the concentration of BTMPPA in the aqueous phase at constant equilibrium pH values of 4 and 3 at (303 ± 1) K are given in Table VI.

The $\log D$ vs $\log C_{HA}$ plots for constant equilibrium pH values of 3 and 4 are shown in Fig. 8. Experimental points in each case form a curve. In the lower concentration region of the aqueous phase, the curve has an asymptotic $\log D$ value of 1.55 and 0.90 at pH 3 and 4, respectively. These values equal $\log (K_d/\varphi)$. The value of φ at pH 3 and 4 are 6.52 and 1.55 respectively. Consequently, Eq. (42) gives K_d values of 55.0 and 51.5 for pH 3 and 4 systems, respectively. Therefore, the estimated distribution ratio of BTMPPA for kerosene - 0.1 mol/dm³ (Na⁺, H⁺)Cl⁻ system is ~53 in comparison to 44 for chloroform - water system [144].

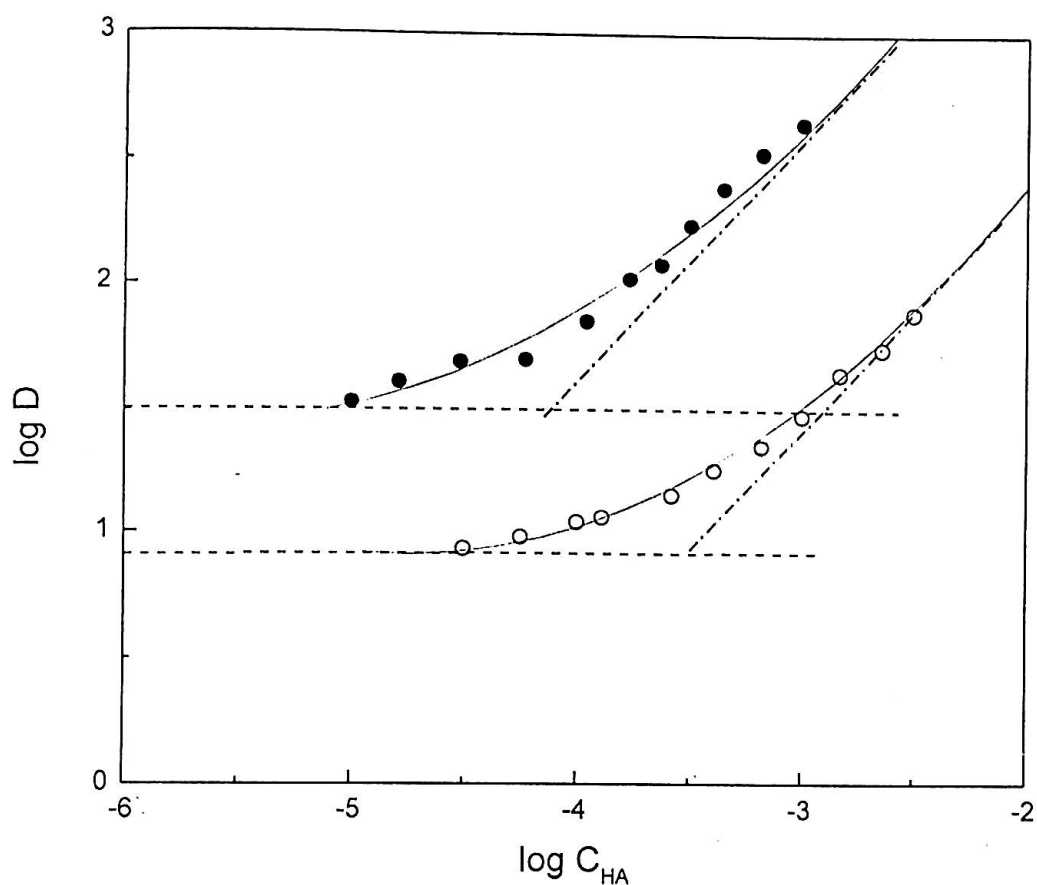


Figure 8. Distribution of BTMPPA between aqueous NaCl solution and kerosene in relation to its concentration in the aqueous phase $\mu = 0.10 \text{ mol/dm}^3 (\text{Na}^+, \text{H}^+)\text{Cl}^-$, Temp. = (303 ± 1) K. $\text{pH}_{\text{eq}} = 4$ ($\circ$) and 3 ($\bullet$). Points are experimental and curves are theoretical (Table VI).

The abscissae of the point of intersection of two asymptotes represented by Eqs. (42) and (43) are -4.1 and -3.5 for pH 3 and 4 systems, respectively. So, Eq. (44) yields the respective K_2 value of 186 and 195. Hence, the average K_2 value is 190 which is comparable to 184 ± 16 as reported by Ke-an *et al.* [144] for chloroform - water system.

Using the values of $K_2 = 190$ and $K_d = 53$, the value of $\log \left(1.41 \sqrt{K_2} K_d \sqrt{C_{HA}} \right)$ is found to be 2.36, 2.51 and 2.66 for 0.05, 0.10 and 0.20 mol/dm³ BTMPPA systems, respectively, which are almost identical to the corresponding asymptotic log D values at lower concentration region of H^+ in Fig. 7 and given in Eqs. (32 – 34). This coincidence proves that the experimental results are correct and the values of $K_2 = 15848$ and $K_d = 933$ reported by Fu *et al.* [257] using the conductivity measurements are not true.

5.4 Density (ρ), viscosities (η) and some derived properties like excess molar volume (V_m^E), excess viscosity (η^E), excess Gibbs free energy change for the activation of flow (ΔG^E) and the Grunberg-Nissan interaction parameter (d) of BTMPPA (2) + various diluents (1) systems

The knowledge of the solution properties for mixed solvents of two or more components is frequently required in the understanding of transport phenomena in the industrial chemical processes. These properties include density, viscosity and other common physical parameters such as dielectric constant, refractive index and any related quantity. According to Duncan *et al.* [264] and McKinnon and Williamson [265], excess thermodynamic functions can be used to predict the extent of interactions in a binary liquid mixture of non-electrolytes.

However, precise conclusion can hardly be drawn about the molecular interactions in liquid mixtures from the nature of the mixture components, though suggestion can be given about the interactions from the studied physical properties, deviations from additivity and other related phenomena. As for example, when the liquids are mixed together, there may be either contraction or expansion in volume from additivity. The volume contraction i.e. increase in density suggests that association may take place, compounds may be formed or other factors enter the phenomena. On the other hand, the volume expansion i.e. decrease in density suggests that the degree of association is decreased, molecular distance is increased or other factors play a role. Thus excess properties can give valuable information about molecular interactions between extractant (BTMPPA) and the diluent used.

The densities and viscosities of BTMPPA and the diluents used in this study are given in Table F at 298.15 K and atmospheric pressure. It is found in most cases that the measured values are of similar order as given in literatures. Mixture densities, viscosities, excess properties and interaction parameters are given in Table VII.

Densities in g/dm^3 of the binary mixtures of BTMPPA and eight different diluents at 298.15 K and atmospheric pressure are given in the third column of Table VII and in Figs. 9 - 12. It is generally accepted that the density of an ideal mixture (ρ_m) of two liquid non-electrolytes is given by the sum of the density of the components (ρ_i) multiplied by volume fraction ($x_{i,\text{vol}}$) of the respective components [187]:

$$\rho_m = \sum_{i=1}^2 x_{i,\text{vol}} \cdot \rho_i \quad (45)$$

Table F. Comparison of experimental densities, ρ and viscosities, η of BTMPPA and distilled diluents with literature values at 298.15 K and atmospheric pressure

BTMPPA/ diluent	$\rho \times 10^{-3}, \text{g/dm}^3$			$\eta, \text{mPa s}$		
	this work*	literature	$\epsilon, \%$	this work*	literature	$\epsilon, \%$
BTMPPA	0.9152	0.9152 ^a	-	120.0000	120.02 ^a	-
n-Hexane	0.6552	0.6549 ^b	+0.046	0.2970	0.2968 ^b 0.3000 ^c	0.067 -1.000
Cyclohexane	0.7738	0.7739 ^b	-0.013	0.8950	0.8923 ^b 0.8940 ^c	0.300 0.112
Benzene	0.8736	0.8737 ^b	-0.011	0.6045	0.6010 ^b 0.6040 ^c	0.582 0.083
Toluene	0.8626	0.8622 ^b	+0.046	0.5570	0.5500 ^b 0.5600 ^c	1.270 -0.536
CHCl ₃	1.4784	1.4797 ^b	-0.088	0.5390	0.5387 ^b 0.5570 ^c	0.056 0.372
CCl ₄	1.5838	1.5846 ^b	-0.050	0.9088	0.9092 ^b 0.9080 ^c	-0.044 0.088
1,2-DCE	1.2456	1.2464 ^b	-0.064	0.7808	0.7805 ^b 0.7790 ^c	0.038 0.231
1-Heptanol	0.8191	0.8186 ^b	+0.061	5.8082	5.8100 ^c	-0.031

Average of three readings, a Reference [this work], b Reference [137], c Reference [266]

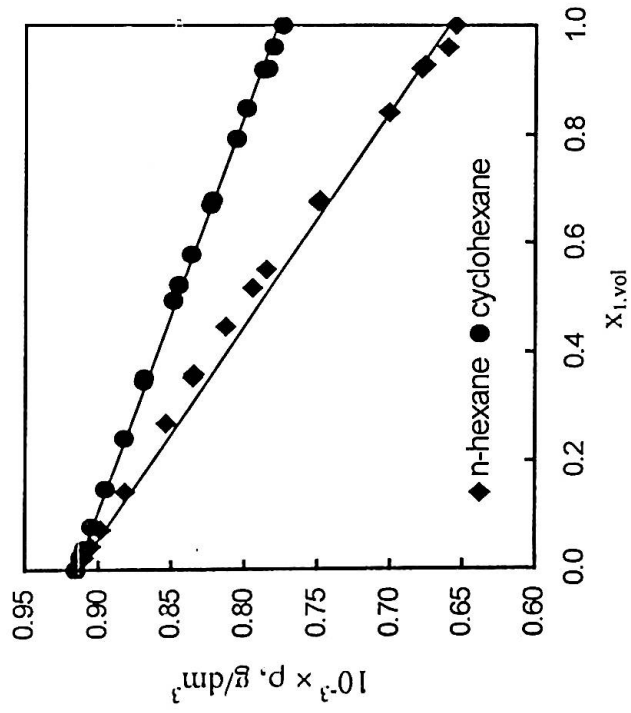


Figure 9. Densities of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for n-hexane and cyclohexane systems (Table VII).

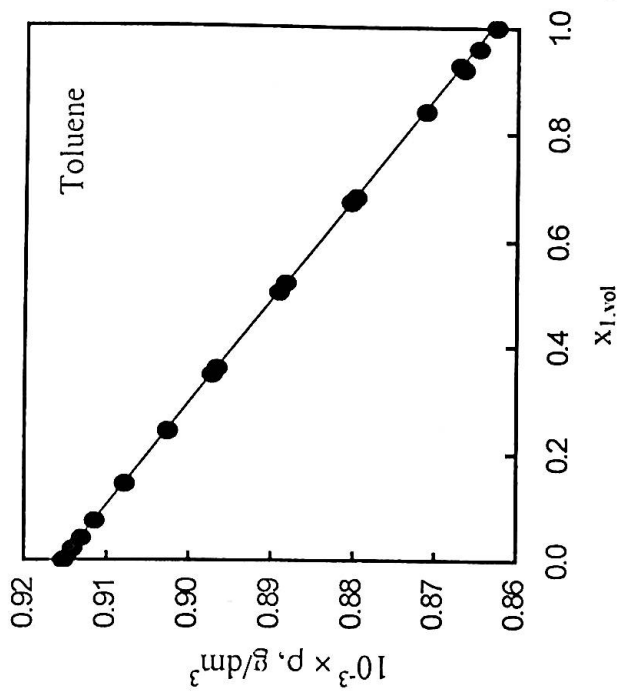


Figure 10. Densities of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for toluene system (Table VII).

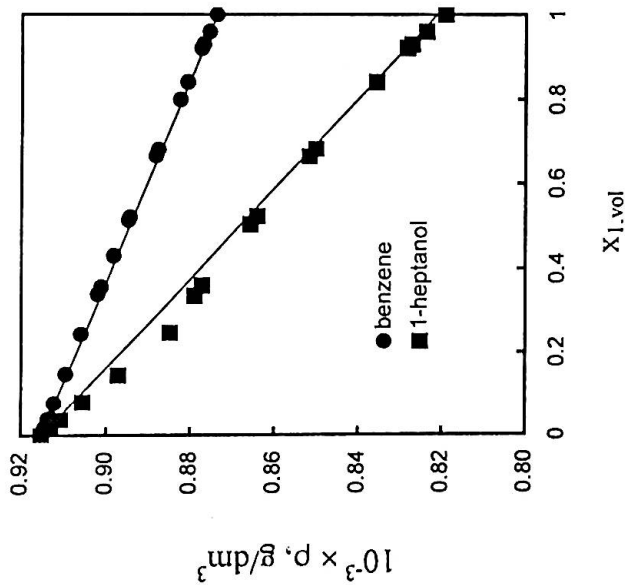


Figure 11. Densities of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for benzene and 1-heptanol systems (Table VII).

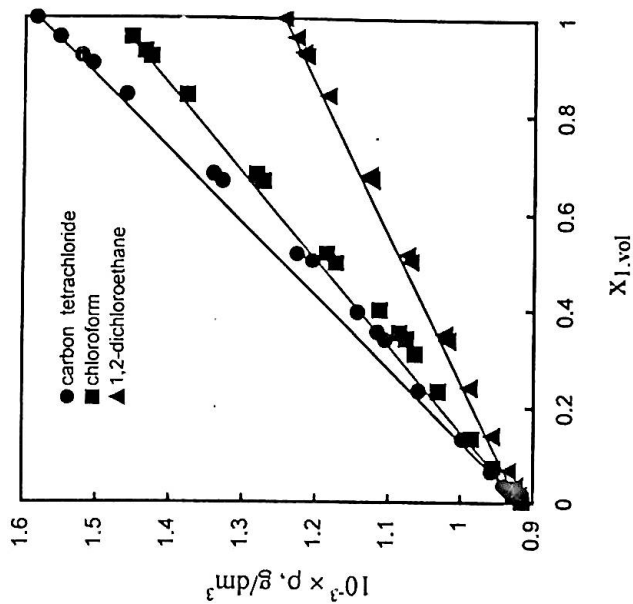


Figure 12. Densities of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for carbon tetrachloride, chloroform and 1,2-dichloroethane systems (Table VII).

The straight lines in Figs. 9 - 12 (Fig. 9 for n-hexane & cyclohexane system, Fig. 10 for toluene, Fig. 11 for benzene and 1-heptanol and Fig. 12 for carbon tetrachloride, chloroform and 1,2-dichloroethane) are drawn theoretically with the help of the above equation. The points are experimental mixture viscosities. In most of the cases under investigation, the experimental densities (except in cases of toluene and cyclohexane) differ significantly from the theoretical values indicating the non-ideality of the mixtures due to extractant - diluents interactions. These density differences are obviously related to excess molar volumes. When the experimental density becomes less than the theoretical density calculated by Eq. (45), then the excess molar volume (V_m^E) will be positive and the vice versa.

The fourth column of Table VII represents the viscosities in mPa s of the binary mixtures of BTMPPA and diluents used in this investigation at 298.15 K and atmospheric pressure. Theoretical viscosities of binary mixtures (η_m) are usually predicted with the help of Kendal-Monroe equation [187, 267]:

$$\eta_m = \sum_{i=1}^2 (x_{i,mol}^{di} \cdot \eta_i^{1/3})^3 \quad (46)$$

where, $x_{i,mol}^{di}$ is the mole fraction of a component based on dimeric BTMPPA and η_i is the component viscosity. The Kendal-Monroe (theoretical) viscosities of BTMPPA (2) + diluent mixtures of various mole fraction of different diluents (1) used in this study calculated on the basis of Eq. (46) are given in Table VIII. Equation (46) virtually gives mixture viscosities for ideal binary solutions. The continuous curves in Fig. 13 ($\ln \eta$ vs. $x_{i,mol}^{di}$) are drawn with the help of Eq. (46). These curves

represent the ideal viscosities i.e. if there remains no interaction between BTMPPA and the diluent used provided Kendal Monroe equation is valid for ideal mixtures. The experimental mixture viscosities are also shown in Fig. 13 as points. In most cases, the experimental viscosities (points) of the mixtures do not coincide with the Kendal-Monroe viscosities (curves). Deviations indicate the presence of some sort of interaction in the mixtures.

The molar volume of a mixture, V_m (dm^3/mol) can be defined as follows [268]:

$$V_m = (x_{1,\text{mol}}^{\text{di}} \cdot M_1 + x_{2,\text{mol}}^{\text{di}} \cdot M_2) / \rho_m \quad (47)$$

where, $x_{1,\text{mol}}^{\text{di}}$, $x_{2,\text{mol}}^{\text{di}}$, M_1 and M_2 are the mole fraction of diluent, mole fraction of BTMPPA, molecular weight of diluent expressed in g and molecular weight of BTMPPA expressed in g, respectively; whereas ρ_m is the experimental mixture density in g/dm^3 . The mole fractions $x_{1,\text{mol}}^{\text{di}}$ and $x_{2,\text{mol}}^{\text{di}}$ are calculated on the basis that BTMPPA in nonpolar diluents are dimeric [This work ($K_2 = 190$), 144, 145]. If V_1 and V_2 are the molar volumes (dm^3/mol) of a diluent and BTMPPA, respectively, then the excess molar volume (V_m^{E} in dm^3/mol) of the mixture can be defined as follows [268]:

$$V_m^{\text{E}} = V_m - (x_{1,\text{mol}}^{\text{di}} \cdot V_1 + x_{2,\text{mol}}^{\text{di}} \cdot V_2) \quad (48)$$

Excess molar volumes (V_m^{E} , dm^3/mol) of mixtures of BTMPPA in various diluents at various mole fractions of diluent considering BTMPPA as dimer ($x_{1,\text{mol}}^{\text{di}}$) are shown in the 6th column of Table VII. The V_m^{E} vs $x_{1,\text{mol}}^{\text{di}}$ plots at 298.15 K and atmospheric pressure for BTMPPA (2) - n-hexane / cyclohexane / toluene / chloroform / carbon tetrachloride

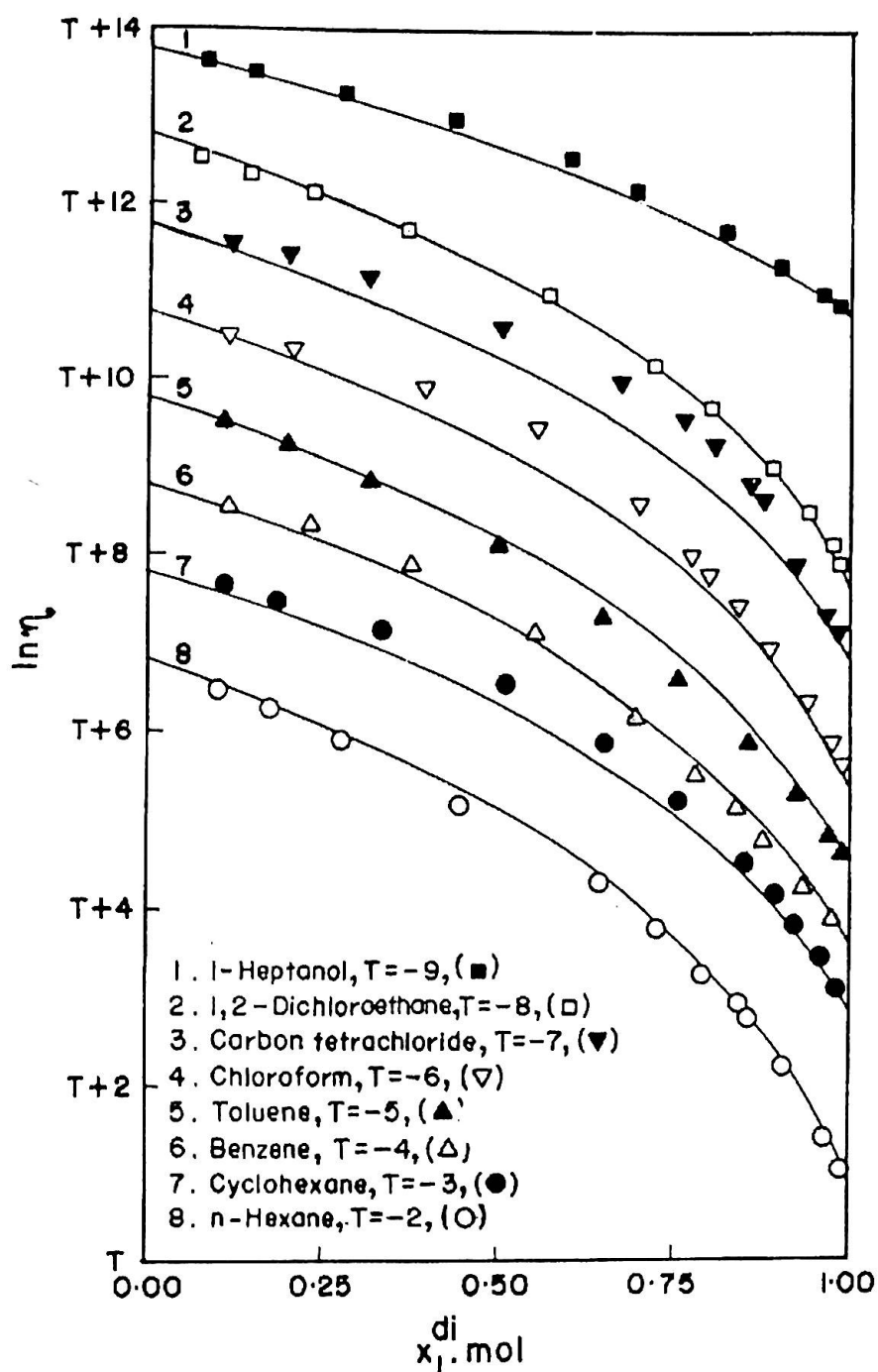
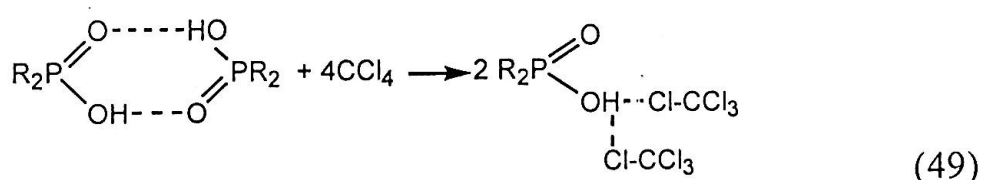
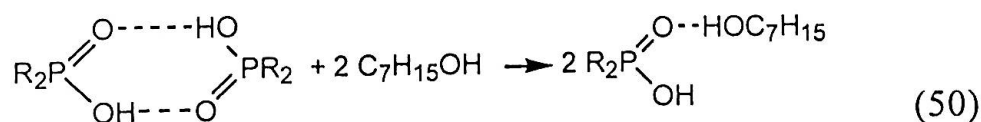


Figure 13. Viscosities of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure. Curves represent the Kendal – Monroe viscosities from Table VIII, whereas points represent experimental viscosities from Table VII.

/ 1,2-dichloroethane (1) systems are given in Fig. 14; whereas for BTMPPA (2) – benzene / 1-heptanol systems are given in Fig. 15. It is found that the excess molar volumes in the cases of 1,2-DCE, CHCl_3 and CCl_4 are positive over the whole mole fraction regions of these diluents. In the case of D2EHPA - CCl_4 system [137], V_m^E (dm^3/mol) values are reported to be slightly negative (not less than $-0.1 \times 10^{-3} \text{ dm}^3/\text{mol}$) in comparison to high positive values for the BTMPPA - CCl_4 system reporting here. Positive excess molar volume is the indicative of breaking of hydrogen bonding of BTMPPA and/or formation of a weak monomeric BTMPPA - diluent (under consideration) bond [269] and of the presence of dispersive forces leading to volume expansion upon mixing [270]. V_m^E values for CHCl_3 and CCl_4 systems are maximum within mole fraction of 0.75 - 0.80 indicating the formation of monomeric BTMPPA and diluent bonds as shown below for CCl_4 :



The above type of dissociation of extractant and reassociation with diluent might be responsible for volume expansion or decrease in density. In the case of 1-heptanol, the maximum V_m^E value is obtained at $x_{1,\text{mol}}^{\text{di}}$ value of 0.60 and this indicates the following type of changes:



Virtually for 1-heptanol, V_m^E vs $x_{1,\text{mol}}^{\text{di}}$ plot passes through a maximum and a minimum at $x_{1,\text{mol}}^{\text{di}}$ values of 0.60 and 0.98, respectively. The minimum

or, the negative V_m^E might be due to coiling of the hydrocarbon chain of 1-heptanol.

In the case of toluene, V_m^E is almost zero (slightly negative) at all $x_{l,mol}^{di}$ values indicating that no appreciable interaction exists between extractant under consideration and toluene. Similar result was also obtained for the D2EHPA - toluene system [137]. Therefore, toluene behaves similarly in both cases of BTMPPA and D2EHPA.

For benzene and n-hexane systems, V_m^E values are negative over the entire mole fraction regions of these diluents. On the other hand, for cyclohexane, it is positive at lower mole fraction (<0.2) and negative at higher mole fraction region (>0.2) of diluent. The largest negative V_m^E value ($-4.2 \times 10^{-3} \text{ dm}^3/\text{mol}$) is obtained for n-hexane system at its mole fraction of 0.73. This value ($-0.95 \text{ dm}^3/\text{mol}$) is obtained for cyclohexane at mole fraction of 0.87, whereas, it ($-0.23 \text{ dm}^3/\text{mol}$) is obtained for benzene at its mole fraction of 0.70. Negative V_m^E values for cyclohexane, n-hexane and benzene may arise [271 - 277] either due to (i) increased interaction between BTMPPA and cyclohexane / n-hexane / benzene, (ii) the very large difference in the molar volumes of pure components allowing interstitial accommodation, (iii) association through hydrogen bonding between molecules of cyclohexane / n-hexane / benzene and BTMPPA, (iv) enhanced coiling of hydrocarbon chain of n-hexane, (v) interconversion of chair and boat forms of cyclohexane, (vi) interaction of π -electron of benzene with H^+ of $-OH$ group of BTMPPA monomer, or (vii) differences in the sizes and shapes of the component molecules allowing them to fit into each others structure. However, the exact reason cannot be sorted. Comparison of V_m^E values for BTMPPA- and D2EHPA

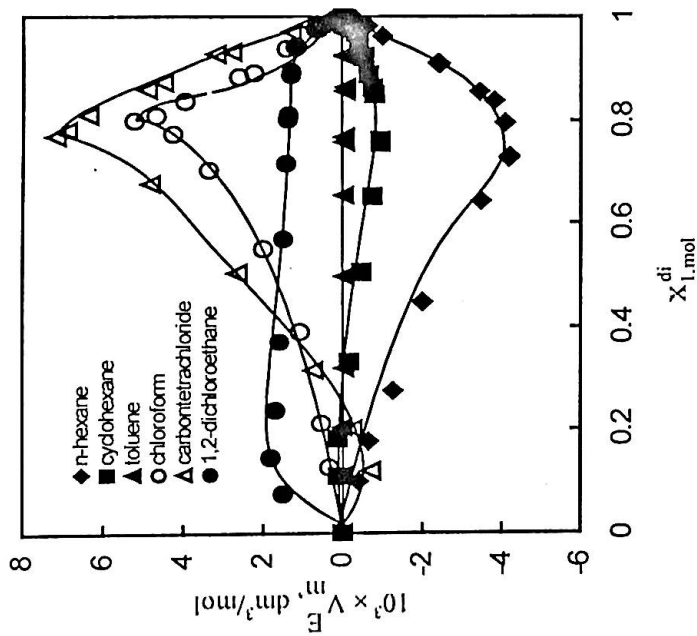


Figure 14. Excess molar volumes of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for n-hexane, cyclohexane, toluene, chloroform, carbon tetrachloride and 1,2-dichloroethane systems (Table VII).

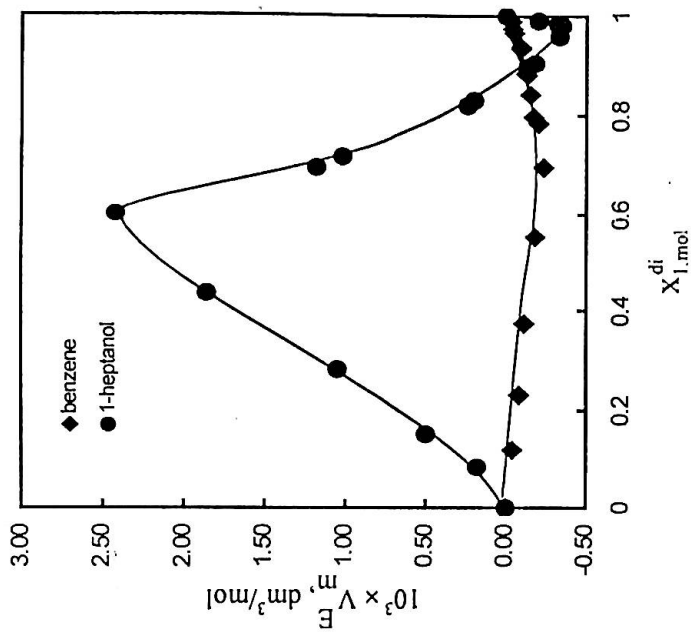


Figure 15. Excess molar volumes of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for benzene and 1-heptanol system (Table VII)

[137] - n-hexane / toluene / cyclohexane / carbon tetrachloride systems indicates that stronger interactions exist in cases of BTMPPA than those existing in cases of D2EHPA.

Following Liu *et al.*, [268], the excess viscosity, η^E in mPa s can be defined as follows:

$$\eta^E = \eta - (x_{1,\text{mol}}^{\text{di}} \cdot \eta_1 + x_{2,\text{mol}}^{\text{di}} \cdot \eta_2) \quad (51)$$

where, η , η_1 and η_2 are the experimentally determined viscosities of mixture, first component (diluent) and second component (BTMPPA), respectively. The variations of η^E for eight binary mixtures (BTMPPA + a diluent) at 298.15 K and atmosphere pressure with the mole fraction of the diluents (n-hexane, cyclohexane, benzene, CCl_4 , CHCl_3 , 1,2-DCE, toluene and 1-heptanol) are shown in the 7th column of Table 7. The η^E vs. $x_{1,\text{mol}}^{\text{di}}$ plots for n-hexane, benzene, cyclohexane, carbon tetrachloride and 1-heptanol systems are displayed in Fig. 16; whereas, Fig. 17 represents the same plots for toluene, chloroform and 1,2-dichloroethane. The value of η^E is negative over the entire composition region for all binary systems under investigation. η^E value gives an estimation of intermolecular interaction [278]. The magnitude of the negative value of η^E for the mixture at any composition approximately follows the order : BTMPPA – n-hexane > –toluene > –1,2-DCE $\approx$ –benzene > –cyclohexane > – $\text{CHCl}_3 \approx$ – CCl_4 > –1-heptanol. High negative value of η^E for n-hexane indicates the involvement of strong dispersive force possibly for the coiling of n-hexane chain [278]. The η^E vs $x_{1,\text{mol}}^{\text{di}}$ plots show minimum at about 0.37, 0.43, 0.45, 0.497, 0.50, 0.505, 0.55 and 0.552 mole fraction of diluent for 1,2-DCE, 1-heptanol, n-hexane, toluene,

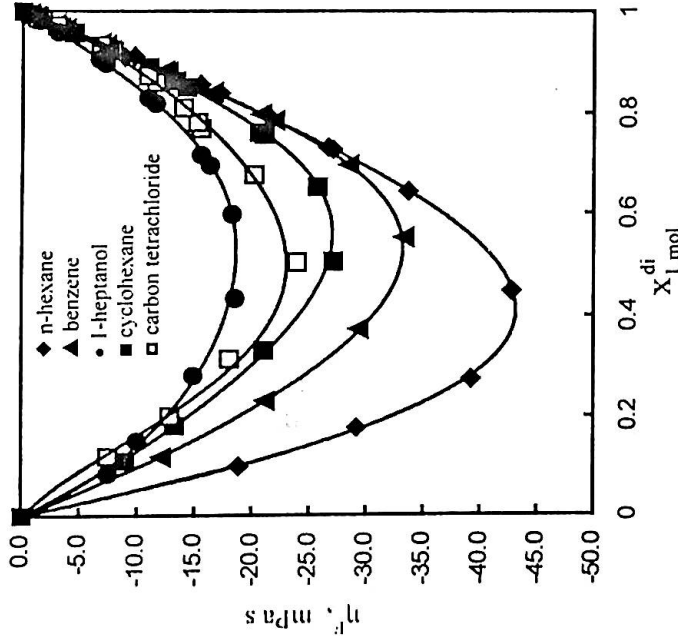


Figure 16. Excess viscosities of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for n-hexane, benzene, 1-heptanol, cyclohexane and carbon tetrachloride systems (Table VII).

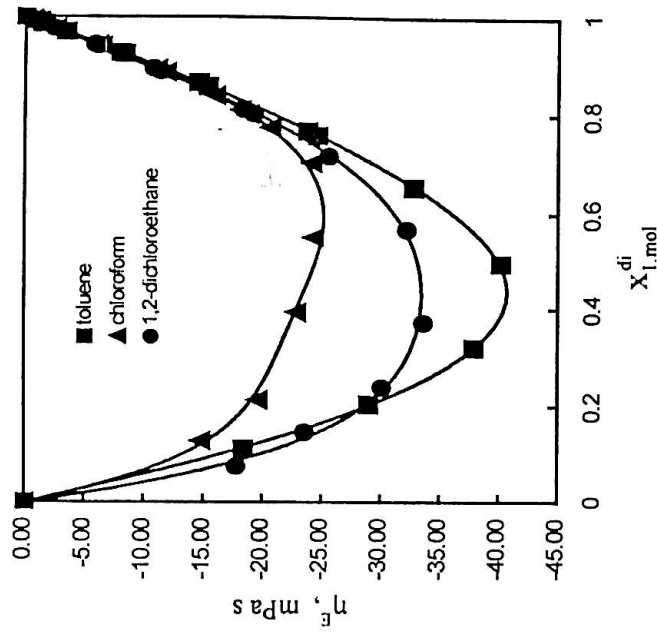


Figure 17. Excess viscosities of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for toluene, chloroform and 1,2-dichloroethane systems (Table VII).

CCl_4 , cyclohexane, CHCl_3 and benzene, respectively. This is related to the breakage of associated structure of BTMPPA accompanying the addition of diluents.

The excess Gibbs' free energy change of activation of flow (ΔG^E in kJ/mol) of a binary mixture can be calculated on the basis of the following equation [279]:

$$\Delta G^E = RT [\ln(\eta V_m) - x_{1,\text{mol}}^{\text{di}} \ln(\eta_1 V_1) - x_{2,\text{mol}}^{\text{di}} \ln(\eta_2 V_2)] \quad (52)$$

where, R is the molar gas constant (0.00832 kJ/deg/mol), T is the absolute temperature and the other symbols have their usual significances. The variations of ΔG^E with mole fraction of the diluents under investigation are displayed in the 8th column of Table VII and in Fig. 18 for n -hexane, benzene, carbon tetrachloride and 1,2-dichloroethane systems as well as in Fig. 19 for cyclohexane, toluene chloroform and 1-heptanol systems. It is seen that the values of ΔG^E are always positive for all diluent systems. The BTMPPA - CHCl_3 mixture at $x_{1,\text{mol}}^{\text{di}} = 0.55$ exhibits maximum with the highest ΔG^E value of 5.106 kJ/mol, whereas, the BTMPPA - 1-hexanol mixture at $x_{1,\text{mol}}^{\text{di}} = 0.598$ exhibits maximum with the lowest ΔG^E value of 2.00 kJ/mol. The positive ΔG^E for all systems under investigation suggests the presence of some dispersive type of forces between the component liquids of the binary mixtures [182].

The Grungberg-Nissan interaction parameter (d) is usually taken as a measure of strength of interaction between the components in a mixture. According to Grungberg and Nissan [180] and Yadava *et al.*, [181], d can

be calculated from the following relationship (symbols have their usual significances) :

$$d = (\ln \eta - x_{1,\text{mol}}^{\text{di}} \ln \eta_1 - x_{2,\text{mol}}^{\text{di}} \ln \eta_2) / x_1 x_2 \quad (53)$$

The variations of d with the mole fractions of diluents in mixture with BTMPPA are given in the last column of Table VII and shown graphically in Fig. 20 for cyclohexane, toluene, carbon tetrachloride and 1-heptanol system, as well as in Fig. 21 for n-hexane, benzene, chloroform and 1,2-dichloroethane systems. In all cases under investigation, d is increased with increasing mole fraction of diluent upto its value of $\sim 0.90 - 0.98$ and after that it is decreased sharply. The working concentration of BTMPPA ($0.50 \text{ mol/dm}^3 - 0.05 \text{ mol/dm}^3$) is within the diluent's mole fraction of $0.91 - 0.995$. At diluent's mole fraction of 0.91 ($\sim 0.5 \text{ mol/dm}^3$ BTMPPA), d value decreases in the following order: n-hexane (10.7) $>$ CHCl_3 (9.6) $>$ CCl_4 (9.0) $>$ 1,2- (7.3) $>$ cyclohexane (7.1) $>$ benzene (6.6) $>$ toluene (5.5) $>$ 1-heptanol (2.85); whereas at diluent's mole fraction of 0.99 ($\sim 0.05 \text{ mol/dm}^3$ BTMPPA), d value decreases in order : 1,2-dichloroethane (10.2) $>$ CHCl_3 (9.5) $>$ n-hexane (6.25) $>$ CCl_4 (4.8) $>$ cyclohexane (4.0) $>$ toluene (3.65) $>$ benzene (2.5) $>$ 1-heptanol (1.15). The maximum d values for chloroform ($d = 12.4$), 1,2-dichloroethane (11.43), n-hexane ($d = 10.68$), CCl_4 ($d = 9.90$), benzene ($d = 7.81$), cyclohexane ($d = 7.35$), toluene ($d = 5.76$) and 1-heptanol ($d = 2.86$) are obtained at mole fractions of 0.9762 , 0.9893 , 0.9111 , 0.86 , 0.9656 , 0.9513 , 0.9269 and 0.9056 , respectively. Increased d -value decreases the thermodynamic activity of BTMPPA and so at a particular concentration of BTMPPA, activity of BTMPPA varies with the diluent used to make up the solution.

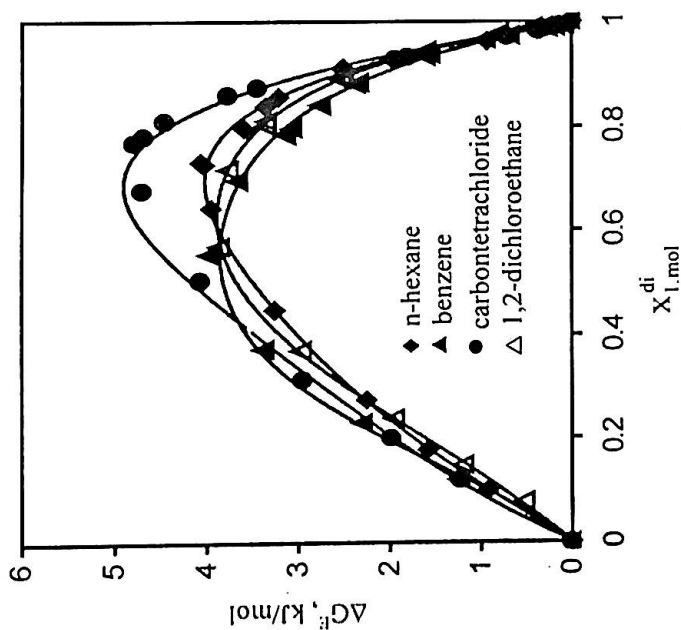


Figure 18. Excess Gibbs free energy changes of activation of flow of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for n-hexane, benzene, carbon tetrachloride and 1,2-dichloroethane systems (Table VII).

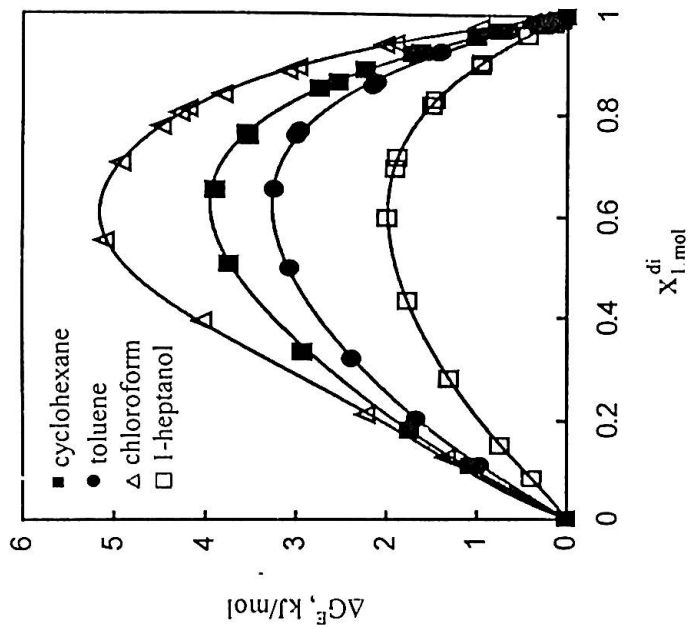


Figure 19. Excess Gibbs free energy changes of activation of flow of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for cyclohexane, toluene, chloroform and 1,2-dichloroethane systems (Table VII).

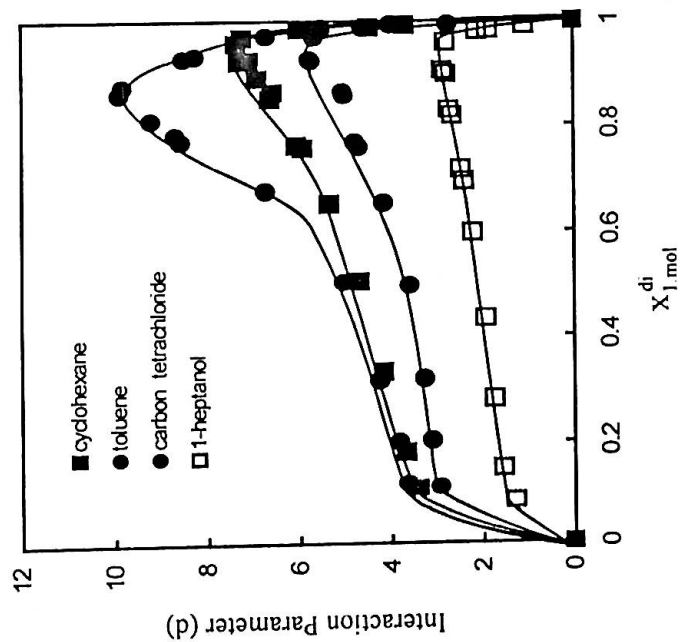


Figure 20. The Grunberg-Nissan interaction parameters for BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for cyclohexane, toluene, carbon tetrachloride and 1-heptanol systems (Table VII).

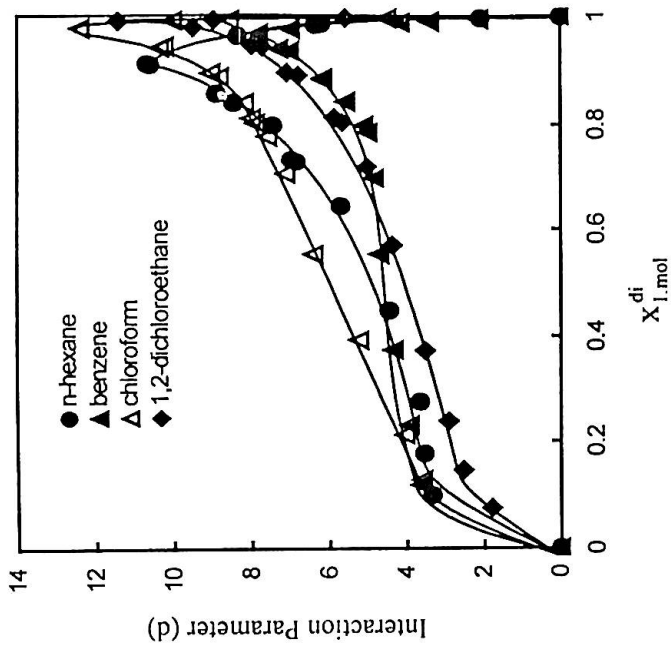


Figure 21. Grunberg – Nissan interaction parameters for BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure for n-hexane, benzene, chloroform and 1,2-dichloroethane systems (Table VII)

According to Fort and Moore [278] and Nigam and Mahl [282], (i) if $\eta^E > 0$ and $d > 0$, then strong specific interaction occurs, (ii) if $\eta^E < 0$ and $d > 0$, then weak specific interaction would be present and (iii) if $\eta^E < 0$ and $d < 0$, then specific interaction would be absent. This work fall in the second category. So it can be concluded that a weak specific interaction is in operation with the binary systems under investigation. According to Vora and Dodwood [283], the negative ΔG^E is for dispersive force or breaking of bonds of associated compounds, and the positive ΔG^E is for specific interaction of size difference of the components of the mixtures. Hence the excess properties of BTMPPA - diluent mixtures indicate that BTMPPA interacts with diluents in varying degree for size difference of components. Comparison of this work with those reported for D2EHPA - diluent systems [137] indicates that BTMPPA interacts stronger than D2EHPA does with diluents.

For 0.3 mol/dm^3 BTMPPA in n-hexane, cyclohexane, benzene, toluene, CHCl_3 , CCl_4 , 1,2-DCE and 1-heptanol, the mole fractions of the respective diluents are 0.9533, 0.9614, 0.9676, 0.9620, 0.9708, 0.9652, 0.9714 and 0.9502, respectively. At these respective mole fractions, the value of d decreases in the following order : CHCl_3 ($d = 12.3$) $>$ 1,2-dichloroethane ($d = 9.5$) $>$ n-hexane ($d = 9.0$) $>$ cyclohexane $\approx$ benzene ($d = 7.3$) $>$ CCl_4 ($d = 7.0$) $>$ toluene ($d = 5.6$) $>$ 1-heptanol ($d = 2.81$). The thermodynamic activity of BTMPPA will be expected to decrease in the reverse order and so it is expected that the distribution ratio (D) of a metal ion extracted by 0.3 mol/dm^3 would be the highest for the 1-heptanol system and the lowest for the chloroform system. Virtually, when Cu^{++} (initial concentration being 1 g/dm^3) is extracted from 0.5 mol/dm^3 sulphate medium at pH 4 by 0.3 mol/dm^3 BTMPPA dissolved in various

diluents, then the value of D is decreased in the following order : 1,2-dichloroethane ($D = 0.92$) > CCl_4 ($D = 0.64$) > n-hexane ($D = 0.53$) > CHCl_3 ($D = 0.48$) > toluene ($D = 0.44$) > cyclohexane ($D = 0.39$) > 1-heptanol ($D = 0.35$) > benzene ($D = 0.31$) > kerosene ($D = 0.28$) > 1-hexanol ($D = 0.24$). Hence no correlation between the D and d -values in respective different diluent systems are obtained for the extraction of Cu^{++} by BTMPPA.

On the other hand, when Fe^{3+} (initial concentration being 1.0 g/dm^3) is extracted from 0.50 mol/dm^3 H_2SO_4 solution at pH 2 by 0.05 mol/dm^3 BTMPPA dissolved in different diluents, then the value of distribution ratio (D) is found to decrease in the following order : CCl_4 ($D = 0.92$) > 1,2-dichloroethane ($D = 0.87$) > kerosene ($D = 0.81$) > CHCl_3 ($D = 0.74$) > toluene ($D = 0.70$) $\approx$ n-hexane ($D = 0.70$) > cyclohexane ($D = 0.65$) > 1-heptanol ($D = 0.50$) > 1-hexanol ($D = 0.47$) $\approx$ benzene ($D = 0.47$). In 0.05 mol/dm^3 BTMPPA system, the interaction parameter (d) decreases in the following order : 1,2-dichloroethane ($d = 4.5$) > CHCl_3 ($d = 4.0$) > n-hexane ($d = 3.6$) > CCl_4 ($d = 3.2$) > cyclohexane ($d = 3.0$) > toluene ($d = 2.0$) > benzene ($d = 1.5$) > 1-heptanol ($d = 0.88$). So in this case also, no correlation exists between D and d -values.

It is therefore realized that the excess properties may characterize the organic phase only, but the metal ions and other coexisting anions present in the aqueous phase can change the thermodynamic activity of an extractant in a diluent when the aqueous phase being brought into contact with the organic phase. It is concluded that the extraction behaviour of a metal ion by an extractant (BTMPPA) depends not only on

single parameter like interaction parameter but also on the details of each chemical problem.

5.5. Interfacial adsorption of BTMPPA at various diluent / 0.50 mol/dm³ (Na⁺, H⁺) SO₄⁼ interfaces:

As pointed out in the Literature Survey Section, it is now well established that hydrometallurgical liquid-liquid extraction reagents (mostly acidic and basic) can be usually considered as surface active agents [147-176]. 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 carboxylic acid phosphoric acid, sulphonic acid, amino etc groups are responsible for the hydrophilic nature. The amphipathic characteristic of extractants predicts that an extractant must be able to interact with aqueous phase species while still maintaining a preferential organic phase solubility. The hydrophilic groups provide the functional groups which form the metal-ligand bonds while the organic phase radicals ensure the desired organic phase solubility.

Liquid-liquid extraction involves liquid exchange processes whereby metal-organic bonds substitute for the metal-oxygen bonds present in the hydrated aqueous species. In general, extractant molecules possess extremely low aqueous solubilities. Thus, it is not unreasonable to expect that the locale of the extraction reaction should 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 evidence derived from interfacial and bulk phase physic-chemical investigations is needed.

Below the boiling point, the molecules present in a liquid do not fly off because they are held together by intermolecular attractive forces (e.g., London dispersion, dipole-dipole, dipole-induced dipole, hydrogen-bond) which are large enough to oppose the thermal forces which tend to destroy the liquid state. When an aqueous solution is brought into contact with an immiscible organic liquid, the molecules present at the phase boundary are in contact with unlike molecules on adjacent sides of the interface.

In general, the interfacial molecules will not experience the same degree of attraction from the foreign molecules as they would if they were present in their respective bulk regions. A system consisting of a layer of oil in contact with water may be considered. Then three possibilities can be imagined at the phase boundary according to whether the attraction of the water molecules for the oil phase molecules is:

- a) greater than the attraction of H_2O for H_2O ;
- b) equal to the attraction of H_2O for H_2O ;
- c) less than the attraction of H_2O for H_2O .

In the case of (a) and (b), it would be expected that the oil and aqueous phases would be completely miscible. On the otherhand, in the case of (c), the water molecules present at the phase boundary would not

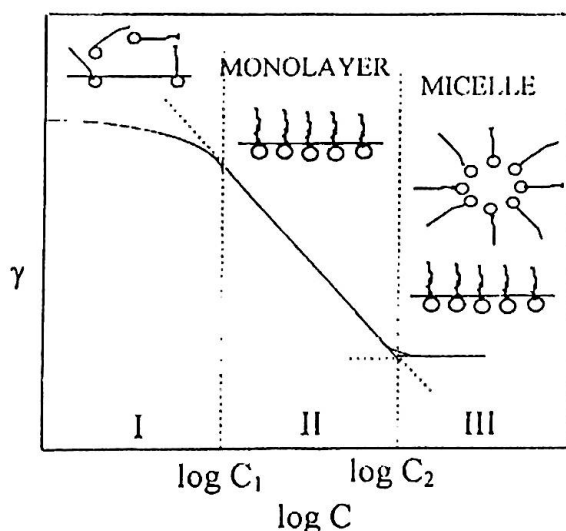
enjoy as much attractive interaction as those molecules in the bulk phase. Thus the interfacial molecules would possess a higher interfacial energy. The interfacial energy or interfacial tension is the most common property which is used to characterize the interfacial state of two-phase systems.

In view of the above discussion, it would be expected that the interfacial tension (γ) would decrease with increase in the strength of the attractive forces experienced by the dissimilar molecules. For example, the interfacial tensions of n-octane and n-octanol are 50.8 and 8.5 mN/m respectively against water [284]. Therefore, it should be concluded that the attractive forces between water and octanol molecules are greater than those between water and octane molecules. The interaction of water with alkanes such as n-octane is derived mainly from dispersion forces. On the other hand, in the case of the alkanols, hydrogen bonding provides an additional means of interaction with water. This hydrogen bonding is made possible by the presence of the polar hydroxyl group in the alkanol structure. In fact, the presence of polar and non-polar properties in the same molecule allows the octanol molecules at the oil/water interface to act as a bridge between the two phases, with the polar group dipping into the water while the non-polar organic portion is kept immersed in the organic phase. Thus, at the oil/water interface there is a certain amount of interfacial packing and orientation of octanol molecules.

If a three component system e.g., water in contact with a benzene solution of n-octanol is considered, the octanol molecules, through their hydroxyl groups, will again interact strongly with the water molecules at the oil/water interface. However, the presence of the water-insoluble hydrocarbon chains will discharge complete immersion of octanol molecules in water. Thus the polar hydroxyl and non-polar organic

portions will be immersed in the opposite sides of the interface. The possibility of interaction with water draws octanol molecules from the bulk organic phase to the interfacial region. This population of octanol molecules at the phase boundary represents adsorption, since it corresponds to an increased concentration of solute molecules in the interface relative to the bulk organic phase.

The adsorption of a solute at the oil/water interface leads to decrease in interfacial tension, as shown schematically below:



The γ versus $\log C$ curve can be divided into three parts. In region I, $C < C_1$, the liquid/liquid interface is sparsely populated by surfactant molecules and there is very little effect of concentration on interfacial tension. In region II, $C_1 \leq C \leq C_2$, the interfacial tension varies linearly with $\log C$ and the interface is characterized by a monolayer of adsorbed molecules. In region III, $C > C_2$, there is a change in slope of the γ versus $\log C$ curve, increase in surfactant concentration now has a less dramatic effect on interfacial tension. This region corresponds to the situation where the surfactant undergoes aggregation or micellization in the bulk

organic phase, and C_2 is termed as the critical micelle concentration or CMC.

The interfacial activity of an extractant is a function of its structure and properties of its hydrophobic and hydrophilic groups. In addition, the nature of the organic diluent and the aqueous phase is also important. The value of C_1 can be used as a measure of the efficiency of adsorption since it presents the minimum bulk phase concentration required to produce a saturated interface. If C_1 is small, it means that interfacial saturation occurs at relatively low extractant concentration and eventually indicating a strong interfacial activity. The value of C_1 for an extractant varies well with the diluent used. In general, for a particular diluent the value of C_1 increases with the decrease of the pK_a value of the extractant. For the common hydrophilic groups used in the extractant, the pK_a value increases in the order: sulphonic acid < phosphoric acid < carboxylic acid.

The interfacial tension will also be influenced by the aqueous phase composition i.e., the acidity and the metal ion present. Therefore, in this part of the work, the variation of BTMPPA + diluents / $H_2O - H_2SO_4$ interfacial tension on various associated parameters have been measured to find out any correlation if there present at all with the efficiency of this extractant to extract various metal ions.

The Gibbs adsorption equation provides a means of calculating the number of adsorbed molecules per unit area (Γ) or the interfacial molecular area (A) from the interfacial tension (γ) versus concentration (C) data. For a given temperature (T) the general form of the Gibbs equation [285] is:

$$\Gamma = \frac{1}{A} = - \frac{1}{kT} \frac{d\gamma}{d \ln C} = - \frac{1}{2.303 kT} \frac{d\gamma}{d \log C} \quad (54)$$

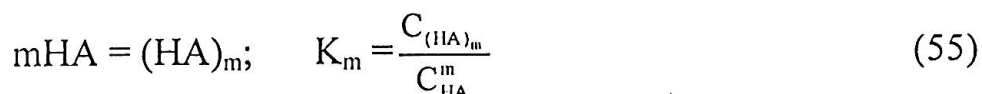
where, k is the Boltzman constant. Since usually $\frac{d\gamma}{d \ln C}$ has a positive or negative value, Γ is not zero. That is, the concentration in the interface is different from that in the bulk. When $\frac{d\gamma}{d \ln C}$ is negative, the Γ is positive i.e. there is positive adsorption. In solutions for which $\frac{d\gamma}{d \ln C}$ is positive, Γ will be negative, there would occur negative adsorption, sometimes called desorption.

The equation [54] suggests that the interfacial tension decreases with the increase in the extractant concentration. The slope of γ versus $\log C$, i. e., $\frac{d\gamma}{d \ln C}$, provides a method for the evaluation of interfacial area (A) of the solute. In the monolayer region, the value of $\frac{d\gamma}{d \ln C}$ is constant at a maximum value. Since γ decreases with $\ln C$, the value of the slope $\frac{d\gamma}{d \ln C}$ is negative. This slope value divided by $-kT$ is a positive quantity. This quantity is equal to Γ , the number of adsorbed molecules per unit area (m^2) of the interface. If the interfacial molecular area or the cross-sectional area is expressed by A in $\text{\AA}^2$, then A will be equal to $\frac{10^{20}}{\Gamma}$. At lower concentration region of the extractant, the slope of $\frac{d\gamma}{d \ln C}$ will be smaller. Therefore, Γ values in this region will be smaller and eventually

the cross-sectional area of the extractant molecule at the interface will be higher.

The interfacial tension (γ) versus $\ln C$ plot provides the concentration of the extractant (C_1) at which monolayer adsorption is completed. This type of plot also provides the concentration of the extractant (C_2) at which the micelles formation starts. Therefore, Eq. (54) can be used for calculating Γ or A at any C value in the region $C < C_2$ in the schematic diagram given above. Referring to this schematic diagram, this would imply that in the region $C > C_1$, there is negligible adsorption. However, obviously this cannot be the case since the low interfacial tension in region III indicate significant adsorption.

In order to explain this paradox, the aggregation of the solute molecules must be considered. Let an organic phase solute HA aggregates according to Eq. [55]:



where K_m is the equilibrium constant for the aggregation reaction. Let C_A be the total analytical concentration of A in the organic phase. Then

$$C_A = C_{HA} + m C_{(HA)_m} \quad (56)$$

Therefore, when $C_{HA} \gg C_{(HA)_m}$, i. e., at low concentration of A where aggregation is not significant, $C_A \cong C_{HA}$ and

$$\frac{d\gamma}{d \ln C_A} = \frac{d\gamma}{d \ln C_{HA}} \quad \{57\}$$

At higher concentrations of A, $C_A \cong m C_{(HA)}$ and therefore,

$$\frac{d\gamma}{d \ln C_A} = \frac{d\gamma}{d \ln C_{(HA)_m}} \quad (58)$$

Furthermore, according to Eq.(55)

$$C_{(HA)_m} = K_m C_{HA}^m \quad (59)$$

Thus it follows from Eqs. (58) and (59) that in region III of the above schematic diagram:

$$\frac{d\gamma}{d \ln C_A} = \frac{d\gamma}{m d \ln C_{HA}} \quad (60)$$

The right hand side of Eq. (60) approaches zero as the aggregation number, m becomes infinitely large. This is the reason why the variation of γ with extractant concentration is very small above the CMC.

Interfacial tensions for 0.01 - 1.00 mol/dm³ H₂SO₄ ([SO₄²⁻] = 1.00 mol/dm³) – 0.06 mol/dm³ BTMPPA in kerosene system have been measured at (298 ± 0.5) K for equilibrated conditions. The experimental data is given in Table IX. The interfacial tension, γ (mN/m) vs. $-\log([H_2SO_4], \text{mol/dm}^3)$ plot is shown in Fig. 22. It is seen that the interfacial tension decreases with decreasing H₂SO₄ concentration. A similar trend has been reported by Flett *et al.* [165,166], Al-Diwan *et al.* [286] and Biswas *et al.* [137] for D2EHPA. It can be explained by the following ways:

- (i) At higher acid concentration in the aqueous phase, the adsorbed extractant molecules cannot be ionized and so they do not exist in closed packed condition. On the other hand, at lower acid concentration in the aqueous phase, the extractant molecules can exist in a more regular packed way to yield lower interfacial tension.

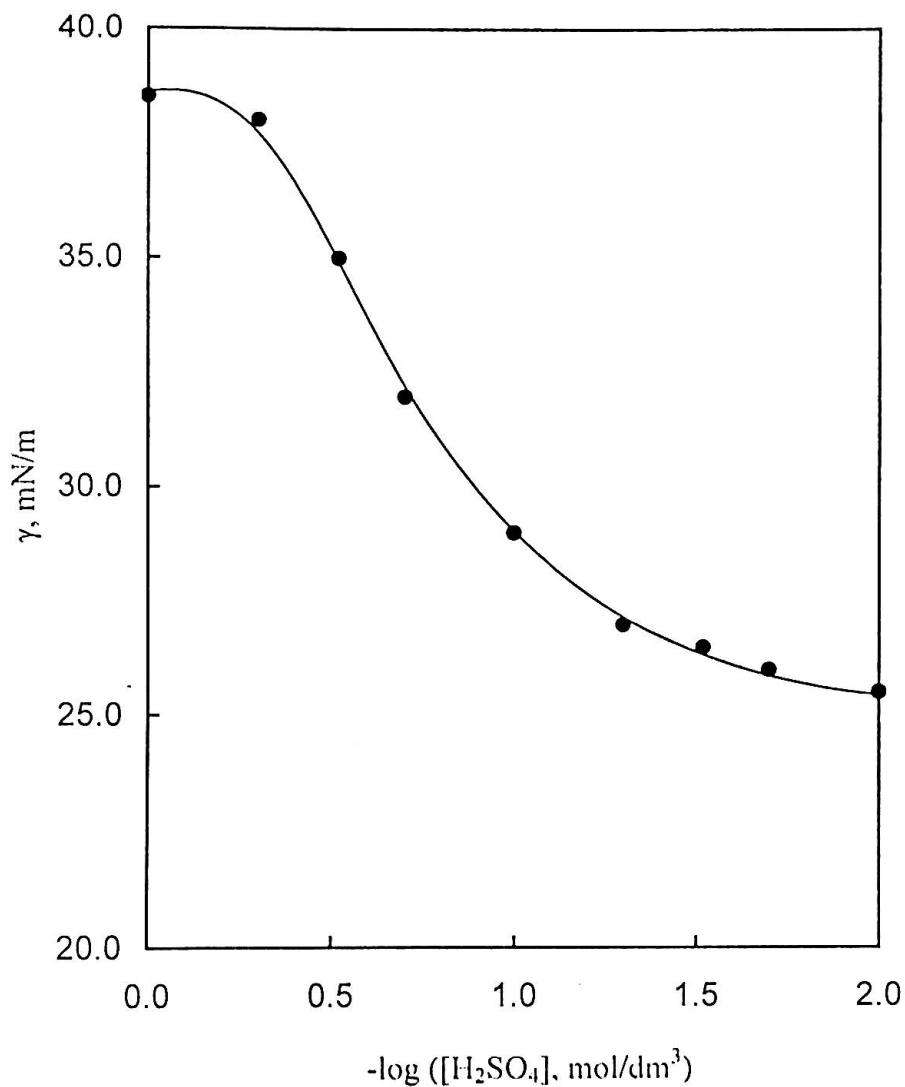


Figure 22. Effect of H_2SO_4 concentration on interfacial tension. $[\text{BTMPPA}]_{(\text{o})} = 0.06 \text{ mol/dm}^3$ in kerosene, temperature = $(293 \pm 0.5) \text{ K}$; aqueous phase: $[\text{H}_2\text{SO}_4] = \text{variable}$, $[\text{SO}_4^{2-}] = 1.00 \text{ mol/dm}^3$; equilibration time = 1 h, settling time = 24 h (Table IX).

- (ii) It is apparent that more molecules of BTMPPA at the interface results in a lower interfacial tension. But when the same number of molecules of BTMPPA exist at the interface, then it is expected that the interfacial tension would decrease as the number of ionized molecules of BTMPPA at the interface increases with increasing pH. This is due to the fact that the ionized BTMPPA is more polar than that is not ionized.
- (iii) From the dynamic nature of adsorption - desorption at the interface, it is expected that the desorption rate (per unit area at a moment) is decreased with increasing pH because of the inability of ionized BTMPPA to desorb whose number is increased with increasing pH. Consequently, the number of population (ionized and non-ionised BTMPPA) at the interface at any moment is increased with increasing pH which results in lowering of interfacial tension.

Table X shows the variation of interfacial tension (γ) with BTMPPA concentration in kerosene – 0.50 mol/dm³ H₂SO₄ system at (298±0.5) K. The γ (mN/m) vs. log ([BTMPPA], mol/dm³) plot for 0.50 mol/dm³ H₂SO₄ (pH = 0.8) – kerosene system at (298 ± 0.5) K is represented in Fig. 23. Tensions have been measured after equilibration for 1 h and settling for 24 h. It is found that the γ -value decreases gradually with increasing BTMPPA concentration after 2.0×10^{-6} mol/dm³ in the organic phase. At $C_1 = 6.3 \times 10^{-6}$ mol/dm³ BTMPPA in kerosene, the formation of monolayer is started and completed at $C_2 = 3 \times 10^{-2}$ mol/dm³. At a concentration of BTMPPA greater than 3×10^{-2} mol/dm³, the interlace is saturated with a monolayer and extractant

molecules start to form micelles through polymerization in the bulk organic phase.

The slope of the straight line at the inflexion of the plot in Fig. 23 represents $dy/d \log ([H_2A_2]_{(o)}, \text{mol/dm}^3)$. The slope of this line is -4.5 ; so that the number of adsorbed BTMPPA molecules, $\Gamma = 4.74 \times 10^{13} \text{ cm}^{-2}$ or, $4.74 \times 10^{17} \text{ m}^{-2}$. The value of the cross-sectional area of an adsorbed BTMPPA molecule at the interface (A) is $(10^{20} / 4.74 \times 10^{17}) = 211 \text{ \AA}^2$. This result is much higher than for D2EHPA ($113.6 \text{ \AA}^2$), though D2EHPA contains longer carbon chain [137].

Gatron and Horwitz [287] reported the shapes and sizes of various extractants including BTMPPA determined by the molecular modeling program '*Alchemy*'. According to the minimum energy shape of BTMPPA given by them, the distance between H of $>PO-OH$ group and a H of a terminal carbon atom of BTMPPA molecule is not more than $7 \text{ \AA}$ and so the maximum rotational area covered by an adsorbed BTMPPA molecule taking H of $>PO-OH$ group as center becomes $153 \text{ \AA}^2$ ($\pi 7^2 = 153$). It is therefore suggested that the phosphinic acid end of BTMPPA is at the interface and if BTMPPA molecules of the interface are in their preferred minimum energy shape there should be more molecules at the interface than is calculated using the data in Fig. 23 along with Eqs. (54) and $A = \frac{10^{20}}{\Gamma} \text{ \AA}^2$.

Experimentally determined cross sectional area of a BTMPPA molecule adsorbed at the interface ($211 \text{ \AA}^2$) is greater than the theoretically calculated cross sectional area of an adsorbed minimum energy shaped BTMPPA molecule ($153 \text{ \AA}^2$). It appears therefore that

considerable voids exist at the interface. Simple geometric drawings and calculations show that the areas of voids per BTMPPA molecule are 17, 42, 79, 102 and 130 Å², respectively, for voids created by 3, 4, 5, 6 and 7 BTMPPA molecules of area 153 Å². In the case of heptagonal arrangement of BTMPPA molecules, a BTMPPA molecule can occupy the void position. At 0.50 mol/dm³ H₂SO₄ (pH = 0.8) – kerosene interface, 57% and 43% of the voids are created, respectively, by 4 and 5 BTMPPA molecules; so that (153+0.57×42+0.43×79) Å² becomes equal to the experimentally determined cross-sectional area of BTMPPA (211 Å²). However if all the molecules are not in their preferred minimum energy shape, the distance between the H on the P-OH and the terminal H on the carbon chain could be greater than 7 Å and this shape of the molecule would then sweep larger area and result in a larger cross-sectional area. Some of the molecules at the interface may be in their minimum energy shape and the rests are not and so the experimental cross-sectional area is simply an average of all the molecules. The organic–aqueous interface in the BTMPPA kerosene / 0.50 mol/dm³ H₂SO₄ system appears to present the following picture:

- (i) The interface is saturated with adsorbed minimum energy shaped BTMPPA molecules leaving considerable voids of which 57% is created by square arrangement of four BTMPPA molecules (each having a circular area of 153 Å²) and the rest being created by regular pentagonal arrangement of five BTMPPA molecules. Otherwise, there are some BTMPPA molecules in their prepared minimum energy shape and some not at the interface.

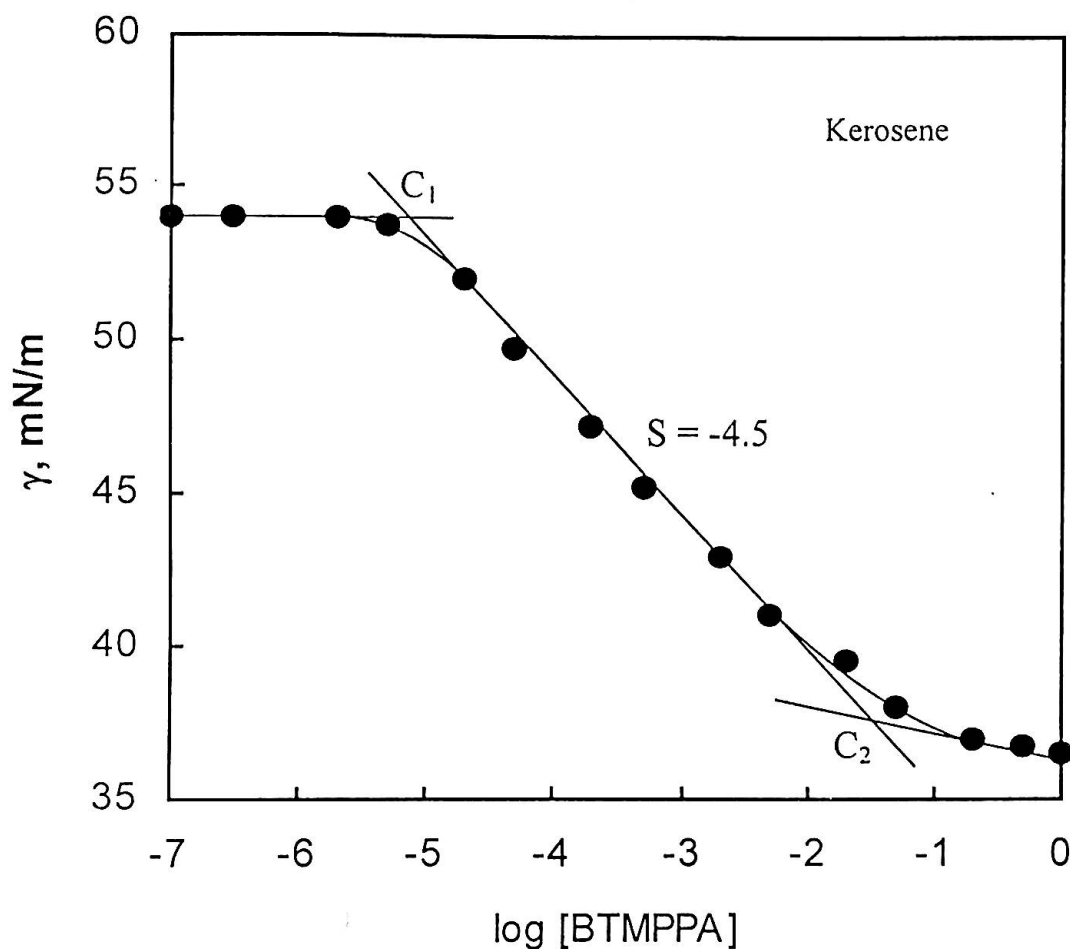


Figure 23. Variation of interfacial tension (γ) with BTMPPA concentration in kerosene - H_2SO_4 system. Aqueous phase : $0.50 \text{ mol/dm}^3 \cdot \text{H}_2\text{SO}$ ($\text{pH} = 0.8$); Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in kerosene Temperature : $(298 \pm 0.5) \text{ K}$, Phase equilibration time : 60 min and phase settling time = 24 h (Table X).

- (ii) The portion of a BTMPPA molecule adsorbed at the interface is oriented towards the aqueous phase (due to polarity of this end), where, it may be ionized at least partially. Hydrocarbon chains rest on the organic side of the interface.
- (iii) It appears that the free BTMPPA molecules are active at the aqueous / organic interface and obviously, during the extraction of a metal ion by BTMPPA, the metallic species attaches itself to BTMPPA anion / molecule at the interface, the resulting complex or ion-pair becomes less interface active (due to masking of polar group of BTMPPA) and moves into the organic phase. The vacancy at the interface is then taken by a free BTMPPA molecule.

The variation of interfacial tension (γ) with BTMPPA concentration in cyclohexane / n-hexane / benzene / toluene / chloroform / carbon tetrachloride / 1,2-dichloroethane / 1-heptanol / 1-hexanol - 0.50 mol/dm³ H₂SO₄ systems at (298±0.5) K are given in Tables XI - XIX, respectively. The corresponding γ , mN/m vs. log [BTMPPA], plots are displayed in Figs. 24 - 32. From the slope of the steep portion of each plot, A-values have been evaluated and are summarized in Table G. It also includes the values of C₁ and C₂. It is seen that the values of C₁, C₂ and A are changed with the variation of diluent used to prepare the organic phase. The effective cross-sectional area of a BTMPPA molecule (A) adsorbed at the interface varies with the diluents as shown: CCl₄ (157 Å²) < C₇H₁₂ (166 Å²) < ClCH₂-CH₂Cl (174 Å²) = n-C₆H₁₄ (176 Å²) < C₆H₅CH₃ (211 Å²) = kerosene (211 Å²) < C₆H₆ (262 Å²) < CHCl₃ (335 Å²) < n-1-C₇H₁₅OH (532 Å²) < n-1-C₆H₁₃OH (734 Å²). In the last three cases, the 'A'-values are abnormally high, which cannot be explained by the formation of voids by regular arrangement at BTMPPA molecules of the interface. However, it may be suggested that due to polarity of these

diluents, some sort of interactions between these diluents and BTMPPA molecules take place in the bulk organic phase which reduces the affinity of BTMPPA molecule to adsorb at the interface. This is likely the case since the hydrogen atom in each of these polar diluents is capable of hydrogen bonding to the phosphinic acid functionality. Moreover, aromatic diluents (benzene and toluene) through their π -electrons possibly interact with the polar group of BTMPPA ($>PO(OH)$) in the bulk organic phase, and thence the susceptibility of BTMPPA molecule to adsorb at the interface is decreased which apparently increases the effective cross sectional area. For other diluent (non-polar and non-aromatic) systems, adsorbed BTMPPA molecules have smaller cross sectional areas.

The BTMPPA concentration at which monolayer formation started at the interface (C_1) is found to be dependent on diluent as follows: $CHCl_3$ (9×10^{-7} mol/dm³) < n - l - $C_7H_{15}OH$ (2.5×10^{-6} mol/dm³) < kerosene (6.3×10^{-6} mol/dm³) < n - l - $C_6H_{13}OH$ (7.1×10^{-6} mol/dm³) < Cy - C_6H_{12} (1×10^{-5} mol/dm³) < CCl_4 (2×10^{-5} mol/dm³) < C_6H_6 (2.51×10^{-5} mol/dm³) < n - C_6H_{14} (2.82×10^{-5} mol/dm³) < $C_6H_5-CH_3$ (3.16×10^{-5} mol/dm³) < $ClCH_2CH_2Cl$ (5×10^{-5} mol/dm³). These values are 10–1000 times less than those reported for D2EHPA [137].

The C_2 -value indicates the minimum concentration of BTMPPA at which its dimerization / polymerization starts to form the micelles in the bulk organic phase. In the case of $CHCl_3$ (a polar diluent), the dimerization of BTMPPA occurs above its concentration of 0.158 mol/dm³; and for 1-heptanol and 1-hexanol that occurs above concentration of 0.10 mol/dm³. This is more likely due to the formation of hydrogen bond between each of these diluents with BTMPPA

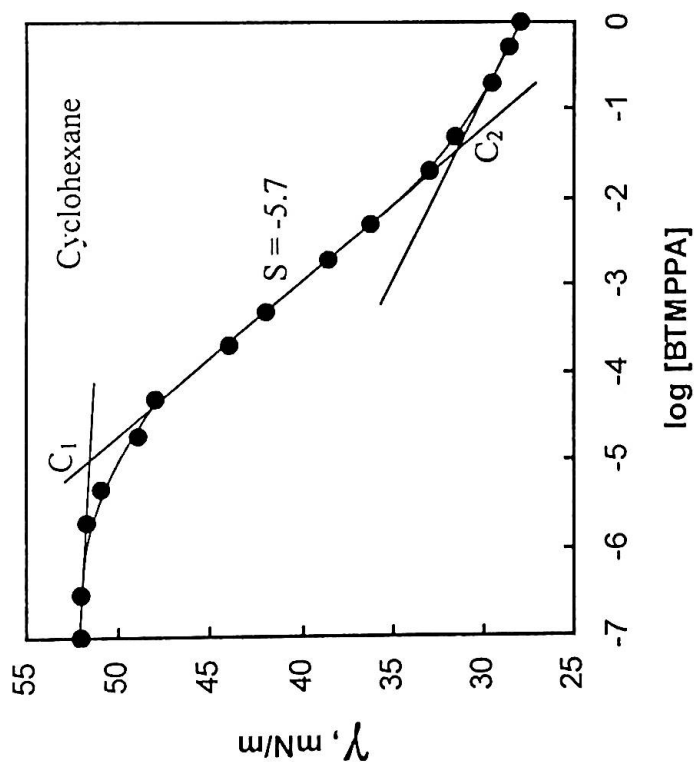


Figure 24. Variation of interfacial tension (γ) with BTMPPA concentration in cyclohexane - H_2SO_4 system. Aqueous phase : 0.50 mol/dm³ H_2SO_4 (pH = 0.8); Organic phase : 10^{-7} - 10^{-8} mol/dm³ BTMPPA in cyclohexane, Temperature : (298 ± 0.5) K, Phase equilibration time : 60 min, phase settling time = 24 h (Table XI)

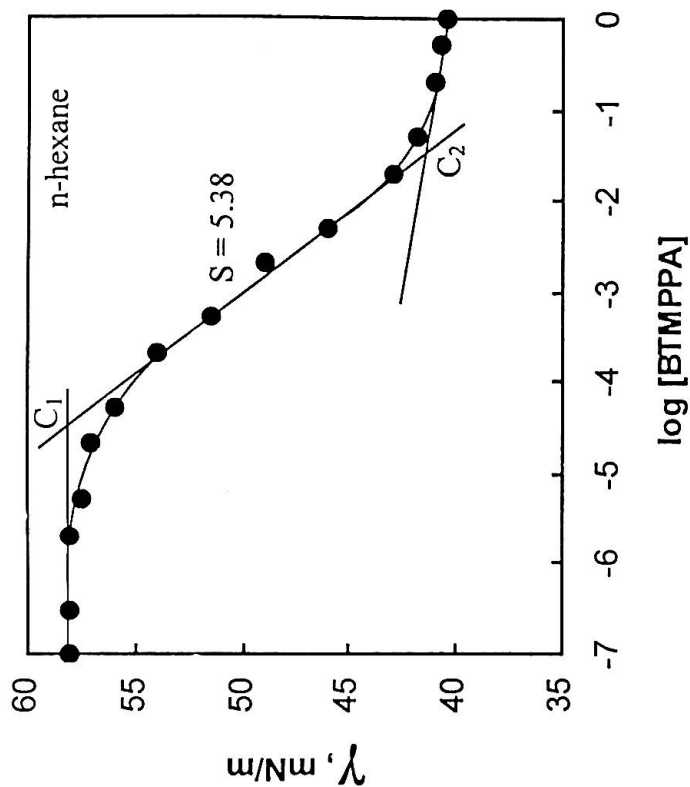


Figure 25. Variation of interfacial tension (γ) with BTMPPA concentration in n-hexane - H_2SO_4 system. Aqueous phase : 0.50 mol/dm³ H_2SO_4 (pH = 0.8); Organic phase : 10^{-7} - 10^{-8} mol/dm³ BTMPPA in n-hexane, Temperature : (298 ± 0.5) K, Phase equilibration time : 60 min, phase settling time : 24 h (Table XII).

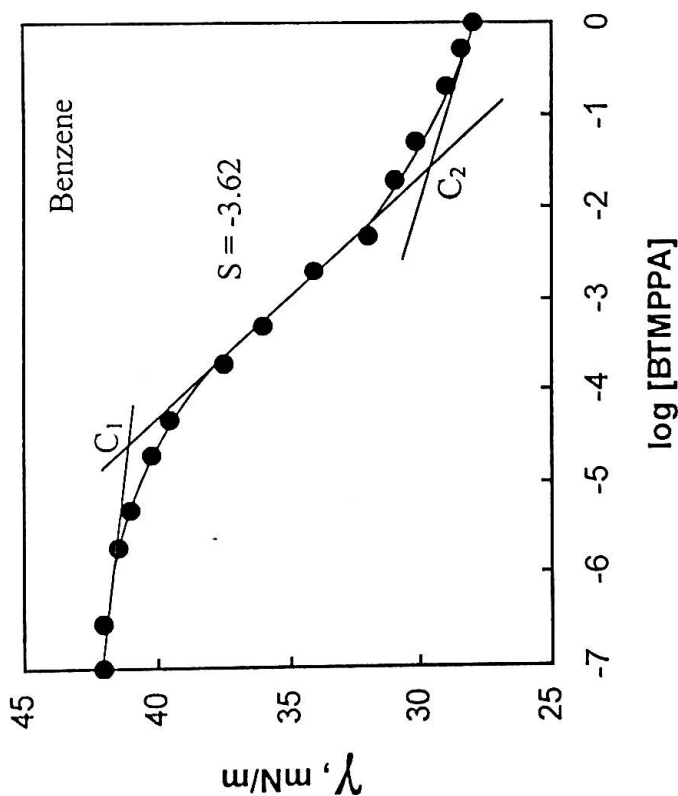


Figure 26. Variation of interfacial tension (γ) with BTMPPA concentration in benzene - H_2SO_4 system. Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ ($\text{pH} = 0.8$); Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in benzene Temperature : $(298 \pm 0.5) \text{ K}$, Phase equilibration time : 60 min, phase settling time : 24 h (Table XIII).

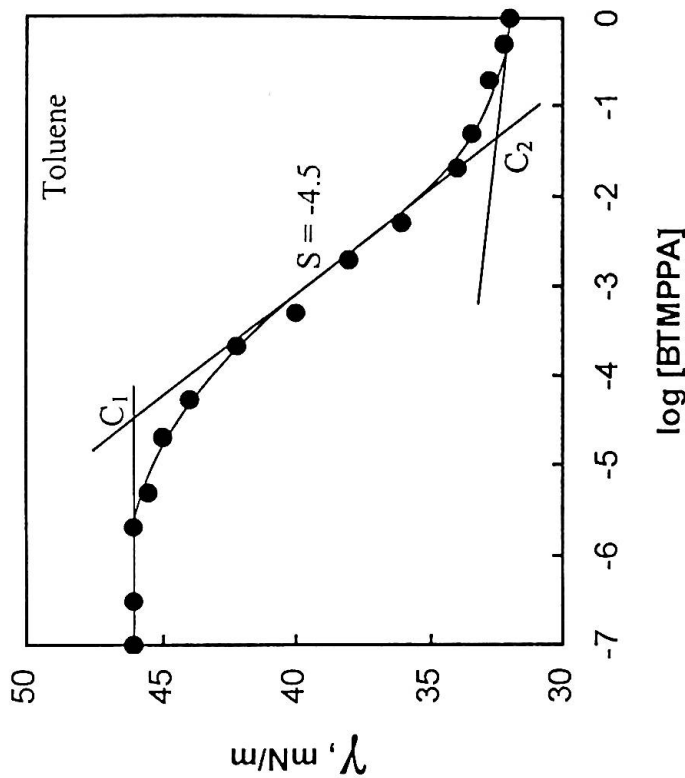


Figure 27. Variation of interfacial tension (γ) with BTMPPA concentration in toluene - H_2SO_4 system. Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ ($\text{pH} = 0.8$); Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in toluene Temperature : $(298 \pm 1) \text{ K}$, Phase equilibration time : 60 min, phase settling time : 24 h (Table XIV).

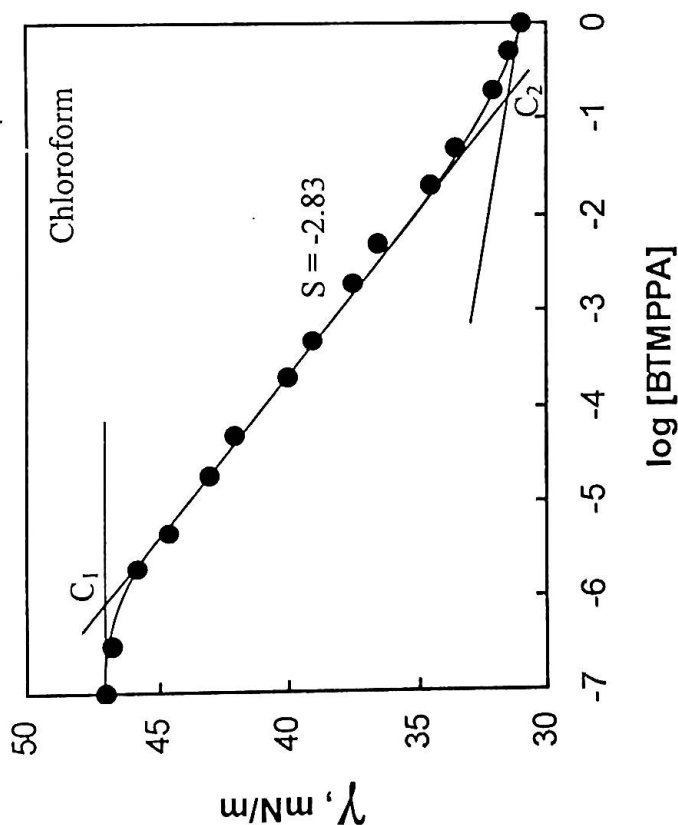


Figure 28. Variation of interfacial tension (γ) with BTMPPA concentration in chloroform - H_2SO_4 system. Aqueous phase : 0.50 mol/dm³ H_2SO_4 (pH = 0.8); Organic phase : 10^{-7} - 10^{-10} mol/dm³ BTMPPA in chloroform Temperature : (298 ± 0.5) K, Phase equilibration time : 60 min, phase settling time : 24 h (Table XV).

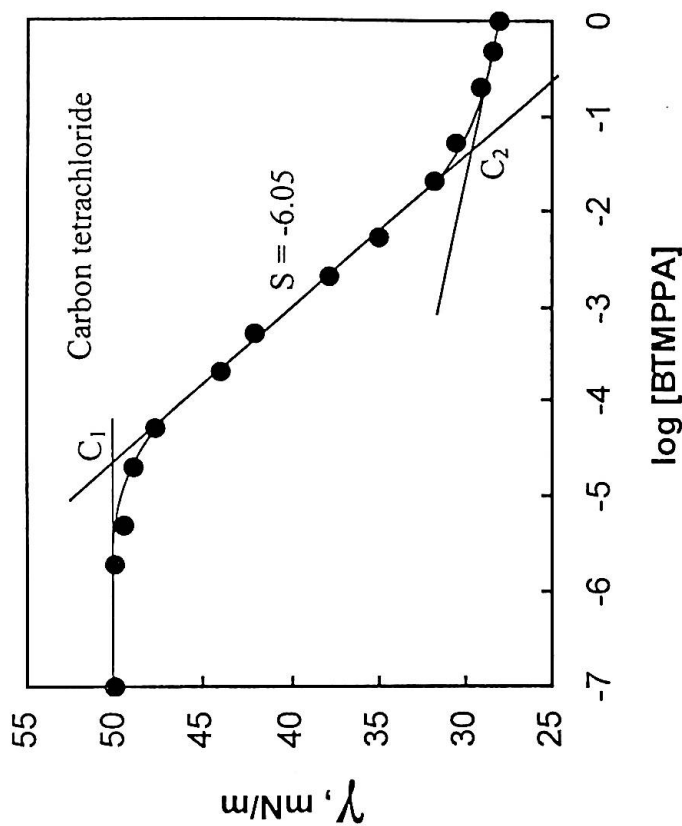


Figure 29. Variation of interfacial tension (γ) with BTMPPA concentration in carbon tetrachloride - H_2SO_4 system. Aqueous phase : 0.50 mol/dm³ H_2SO_4 (pH = 0.8); Organic phase : 10^{-7} - 10^{-10} mol/dm³ BTMPPA in carbon tetrachloride Temperature : (298 ± 0.5) K, Phase equilibration time : 60 min, phase settling time : 24 h (Table XVI).

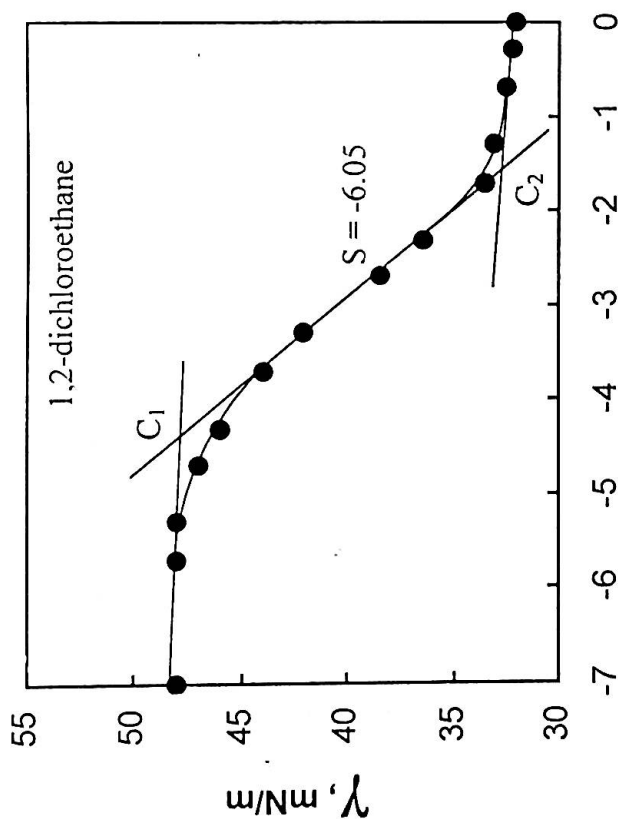


Figure 30. Variation of interfacial tension (γ) with BTMPPA concentration in 1,2-dichloroethane- H_2SO_4 system. Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ ($\text{pH} = 0.8$); Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in 1,2-dichloroethane. Temperature : $(298 \pm 0.5) \text{ K}$, Phase equilibration time : 60 min, phase settling time : 24 h (Table XVII).

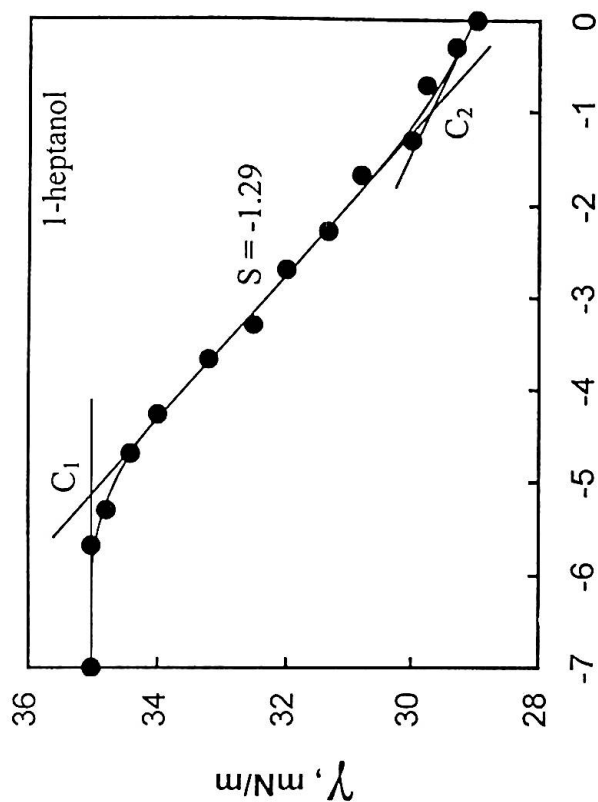


Figure 31. Variation of interfacial tension (γ) with BTMPPA concentration in 1-heptanol- H_2SO_4 system. Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ ($\text{pH} = 0.8$); Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in 1-heptanol Temperature : $(298 \pm 0.5) \text{ K}$, Phase equilibration time : 60 min, phase settling time : 24 h (Table XVIII).

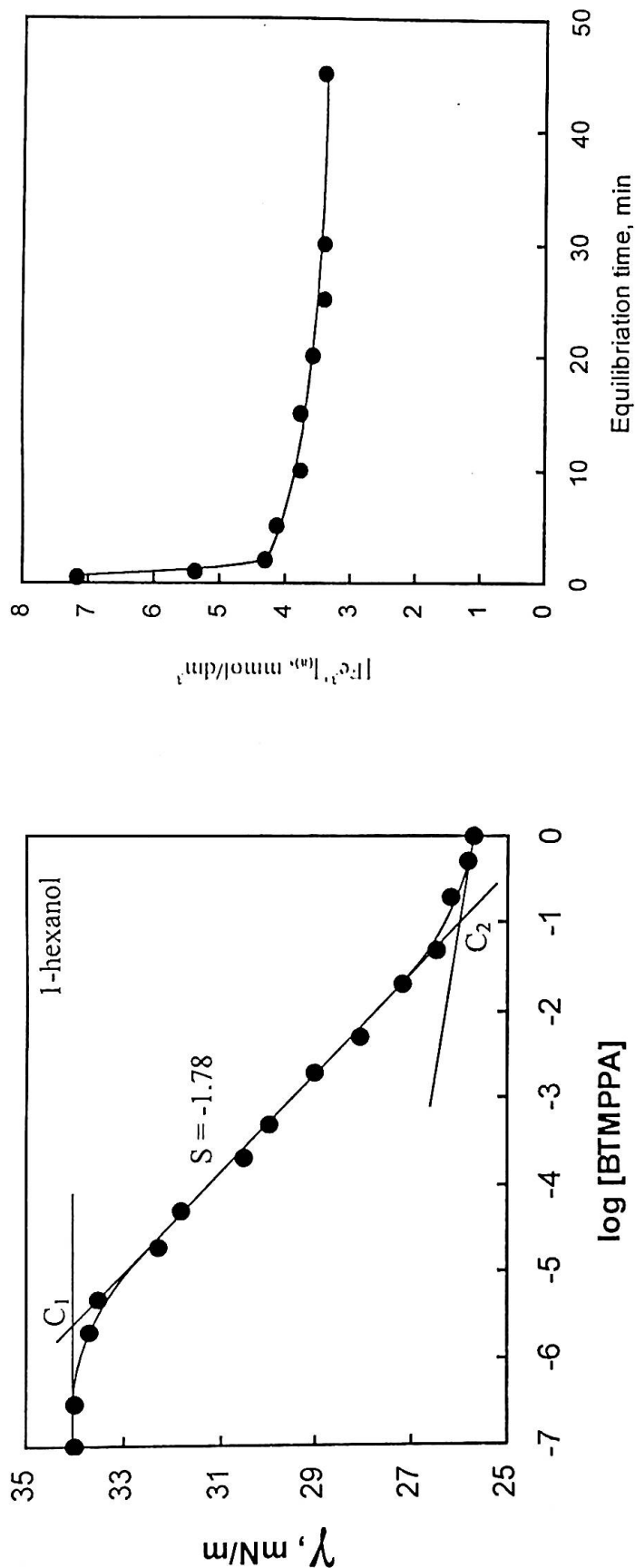


Figure 32. Variation of interfacial tension (γ) with BTMPPA concentration in 1-hexanol - H_2SO_4 system. Aqueous phase : 0.50 mol/dm³ H_2SO_4 (pH = 0.8); Organic phase : 10^{-7} - 10^0 mol/dm³ BTMPPA in hexanol-1 Temperature : (298 ± 0.5) K, Phase equilibration time : 60 min, phase settling time : 24 h (Table XIX).

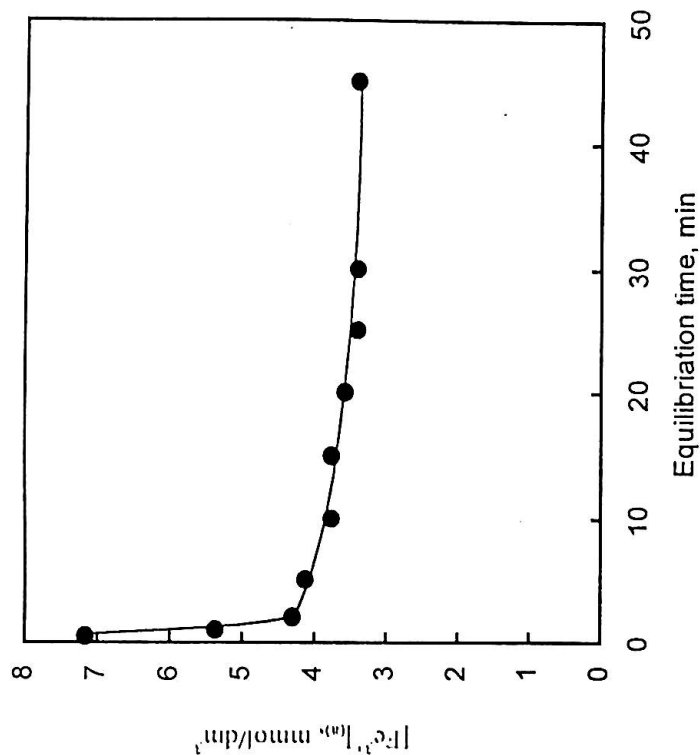


Figure 33. Rate of extraction of Fe^{3+} by purified Cyanex 272 (BTMPPA) in kerosene. $[\text{Fe}^{3+}]_{\text{a,ini}} = 13.43$ mmol/dm³, $[\text{SO}_4^{2-}] = 0.10$ mol/dm³, $\text{pH}_{\text{(ini)}} = 2$, $[\text{BTMPPA}]_{\text{(o,ini)}} = 0.025$ mol/dm³, Temp. = (298 ± 1) K (table XX).

Table G. Interfacial parameters of BTMPPA / 0.50 mol/dm³ H₂SO₄ (pH = 0.8) system in various diluents at 298 K

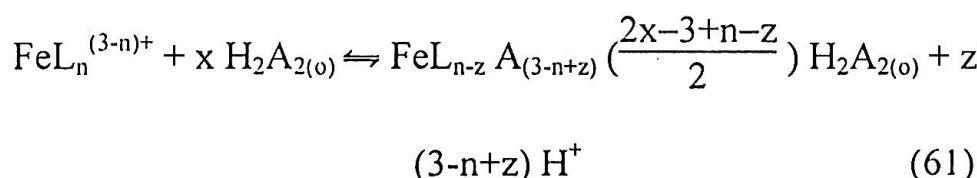
Diluent	$C_1 \times 10^5, \text{ mol/dm}^3$	$C_2 \times 10^2, \text{ mol/dm}^3$	$dy/d\log[H_2A_2]_{(o)}$	$\Gamma \times 10^{-17}, \text{ m}^{-2}$	$A, \text{ \AA}^2$	% of void created by				
						3 M ^a	4 M	5 M	6 M	7 M
CCl ₄	2.00	4.00	-6.05	6.389	157	100	-	-	-	-
Cy-C ₆ H ₁₂	1.00	3.20	-5.70	6.019	166	100	-	-	-	-
ClCH ₂ -CH ₂ Cl	5.00	2.50	-5.43	5.734	174	75	25	-	-	-
<i>n</i> -C ₆ H ₁₄	2.82	3.16	-5.38	5.681	176	68	32	-	-	-
C ₆ H ₅ CH ₃	3.16	5.00	-4.50	4.752	211	-	57	43	-	-
Kerosene	0.63	3.00	-4.50	4.752	211	-	57	43	-	-
C ₆ H ₆	2.51	2.50	-3.62	3.823	262	-	-	-	75	25
CHCl ₃	0.09	15.80	-2.83	2.988	335	-	-	-	-	-
<i>n</i> -I-C ₇ H ₁₅ OH	0.25	10.00	-1.78	1.880	532	-	-	-	-	-
<i>n</i> -I-C ₆ H ₁₃ OH	0.71	10.00	-1.29	1.362	734	-	-	-	-	-

M^a stands for molecules of BTMPPA.

molecules in the bulk organic phase hindering the intermolecular hydrogen bond formation between two BTMPPA molecules. In comparison to these, the concentrations of BTMPPA at which dimerization commences in different diluents are 0.025 mol/dm³ for C₆H₆ and ClCH₂-CH₂Cl, 0.03 mol/dm³ for kerosene, 0.0316 mol/dm³ for *n*-C₆H₁₄, 0.032 mol/dm³ for Cy-C₆H₁₂, 0.04 mol/dm³ for CCl₄ and 0.05 mol/dm³ for C₆H₅CH₃.

5.6. Extraction equilibria of Fe(III) by BTMPPA in Kerosene

BTMPPA is a dialkyl derivative of phosphinic acid. It acts as a mono-acidic chelating agent. If Fe³⁺ exists in the aqueous phase as FeL_n⁽³⁻ⁿ⁾⁺ (L being the coexisting anion of unit charge) and BTMPPA is considered as dimeric (H₂A₂) in non-polar solvents this works [144], then the extraction equilibrium reaction may be considered as follows:



where, the species with subscript (o) represent organic species and the species without any subscript represent aqueous species. The extraction equilibrium constant (K_{ex}) of the above reaction can be expressed as follows:

$$K_{\text{ex}} = \frac{[\text{FeL}_{n-z} \cdot \text{A}_{(3-n+z)} \cdot \left(\frac{2x-3+n-z}{2} \right) \text{H}_2\text{A}_2]_{(o)} [\text{H}^+]^{(3-n+z)} [\text{L}^-]^z}{[\text{FeL}_n^{(3-n)+}] [\text{H}_2\text{A}_2]_{(o)}^x} \quad (62)$$

Now, on defining the distribution ratio (D) as $[\text{FeL}_{n-z} \cdot \text{A}_{(3-n+z)} \cdot \left(\frac{2x-3+n-z}{2} \right) \text{H}_2\text{A}_2]_{(o)} / [\text{FeL}_n^{(3-n)+}]$, Eq. (62) can be expressed as:

$$K_{\text{ex}} = D \frac{[\text{H}^+]^{(3-n+z)} [\text{L}^-]^z}{[\text{H}_2\text{A}_2]_{(o)}^x} \quad (63)$$

On taking logarithm of both the sides of Eq. (63), one gets:

$$\log D = \log K_{\text{ex}} + (3-n+z) \text{pH} + x \log [\text{H}_2\text{A}_2]_{(o)} - z \log [\text{L}^-] \quad (64)$$

The temperature dependency of the distribution ratio (D) of Fe^{3+} by BTMPPA can be treated by the Vant' Hoff equation [288].

$$\log D = - \frac{\Delta H}{2.303 RT} \quad (65)$$

where, the symbols have usual significances. Eq. (65) states that the plot of $\log D$ against $(1/T) \text{ K}^{-1}$ will be a straight line with slope equaling to $-\Delta H/2.303 R$ from which the enthalpy change for the extraction reaction (ΔH) can be evaluated.

Preliminary experiments (data given in Table XX and Fig. 33) show that the equilibration time for the extraction of Fe^{3+} by BTMPPA is less than 25 min in comparison to 3 h by D2EHPA [86]. In subsequent experiments, the phase contact time of 30 min has been used.

The variation of the distribution ratio of Fe^{3+} with the variation of its initial concentration is given in Table XXI and shown graphically in Fig. 34. It seen that the $\log D$ vs. $\log (\text{Fe}^{3+})_{(\text{ini})}$, mol/dm^3 plot is a curve representing the manner in which the distribution ratio of Fe^{3+} is decreased with increasing its concentration in the aqueous phase. But in this case, the equilibrium pH and the equilibrium concentrations of BTMPPA and SO_4^{2-} are not constant for varying extents of extraction.

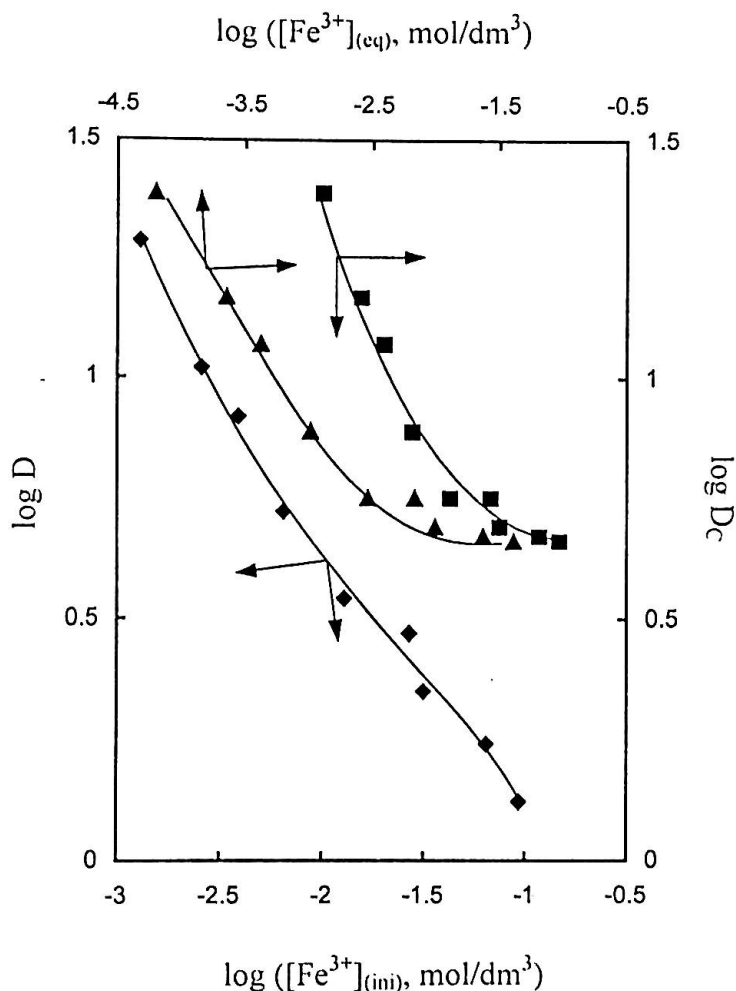


Figure 34. Dependence of distribution ratio (D) of Fe^{3+} on its concentration. (◆), $\log D$ vs. $\log ([Fe^{3+}]_{ini}, \text{mol/dm}^3)$ plot; (■), $\log D_c$ vs. $\log ([Fe^{3+}]_{ini}, \text{mol/dm}^3)$ plot; (▲), $\log D_c$ vs. $\log ([Fe^{3+}]_{eq}, \text{mol/dm}^3)$ plot. $pH_{(ini)} = 1.8$, $[BTMPPA]_{(o,ini)} = 0.20 \text{ mol/dm}^3$, $[SO_4^{2-}] = 0.20 \text{ mol/dm}^3$, equilibration time = 30 min, Temp. = $(298 \pm 1) \text{ K}$ (Table XXI).

Figure 34 also represents the $\log D_C$ vs. $\log([Fe^{3+}]_{(ini)}, \text{mol/dm}^3)$ and $\log D_C$ vs. $\log([Fe^{3+}]_{(eq)}, \text{mol/dm}^3)$ plots. D_C is the corrected distribution ratio at constant $pH_{(eq)} = 1.80$, $[BTMPPA]_{(eq)} = 0.10 \text{ mol/dm}^3$ and $[SO_4^{2-}]_{(eq)} = 0.20 \text{ mol/dm}^3$; and it is calculated using the following relationship after getting the pH, extractant and sulphate ion dependences:

$$\log D_C = \log D + y (pH_{(eq)}^{const} - pH_{(eq)}) + x (\log[BTMPPA]_{(o,eq)}^{const} - \log[BTMPPA]_{(o,eq)}) + z (\log[SO_4^{2-}]_{(eq)}^{const} - \log[SO_4^{2-}]_{(eq)}) \quad (66)$$

where, $y = \text{pH dependence} = 2$, $x = \text{extractant dependence} = 1$ and $z = \text{sulphate ion dependence} = -1$. The values of $[BTMPPA]_{(o,eq)}$ and $[SO_4^{2-}]_{(eq)}$ have been calculated from the relations:

$$[BTMPPA]_{(o,eq)} = [BTMPPA]_{(o,ini)} - x [Fe^{3+}]_{(o,eq)} \quad (67)$$

and,

$$[SO_4^{2-}]_{(eq)} = [SO_4^{2-}]_{(ini)} - x [Fe^{3+}]_{(o,eq)} \quad (68)$$

The $\log D_C$ vs. $\log [Fe^{3+}]_{(ini)}, \text{mol/dm}^3$ plot is a curve whose asymptotic slopes in lower and higher concentration regions approach to -0.7 and zero respectively. The $\log D_C$ vs. $\log ([Fe^{3+}]_{(eq)}, \text{mol/dm}^3)$ plot is also a curve whose asymptotic slopes approach to -0.43 and zero at lower and higher concentration regions of Fe^{3+} , respectively. This is possibly due to the formation of dimeric Fe^{3+} species in the aqueous phase; dimerization is enhanced with increasing Fe^{3+} concentration upto 13 m mol/dm^3 and beyond this concentration, Fe^{3+} is entirely present in the dimeric form.

The data on the variation of the distribution ratio (D) of $Fe(III)$ with variation of equilibrium pH for constant BTMPPA concentration of 0.05 mol/dm^3 and 0.025 mol/dm^3 are given in Table XXII. Figure 35

represents the $\log D_c$ vs. $pH_{(eq)}$ plots for constant equilibrium BTMPPA concentrations of 0.05 and 0.025 mol/dm³ and sulphate ion concentration of 0.10 mol/dm³. Here, $\log D_c$ values have been calculated from Eq. (66) after neglecting the second term of the right hand side. In both cases, straight lines with slope equaling to 2 in lower $pH_{(eq)}$ region are obtained. Slopes of the lines decrease with increasing $pH_{(eq)}$, approaching less than unity at $pH_{(eq)} = 2.25$. The lines with slope 2 have intercepts of -2.92 and -3.20 for $[BTMPPA]_{(o,eq)}^{const}$ of 0.05 and 0.025 mol/dm³, respectively. Therefore, the pH dependence is 2 and < 2 in lower and higher pH regions under investigation, respectively.

Table XXIII shows the D values at various BTMPPA concentrations but at constant equilibrium pH values of 1.75 and 2.20. The $\log D_c$ vs. $\log ([BTMPPA]_{(o,eq)}, \text{mol/dm}^3)$ plots at constant equilibrium pH values of 1.74 and 1.98 and sulphate ion concentration of 0.10 mol/dm³ are given in Fig. 36 (here the values of $\log D_c$ have been calculated from Eq. (66) after neglecting the third term of the right hand side). In both cases, straight lines with unity slopes are obtained. So the extractant dependency is 1. The intercept of the lines are 2.30 and 1.70 for $pH_{(eq)}^{const}$ values of 1.98 and 1.74, respectively.

Data on variation of D with variation of sulphate ion concentration are given in Table XXIV Fig. 37 represents the dependence of distribution ratio of iron(III) on sulphate ion concentration at constant equilibrium pH of 2.01 and BTMPPA concentration of 0.025 mol/dm³. The $\log D_c$ values have been calculated from Eq. (66) after omitting the last term of the right hand side. The plot is a straight line with slope equaling to -1 and has an intercept of -0.33. From the results in

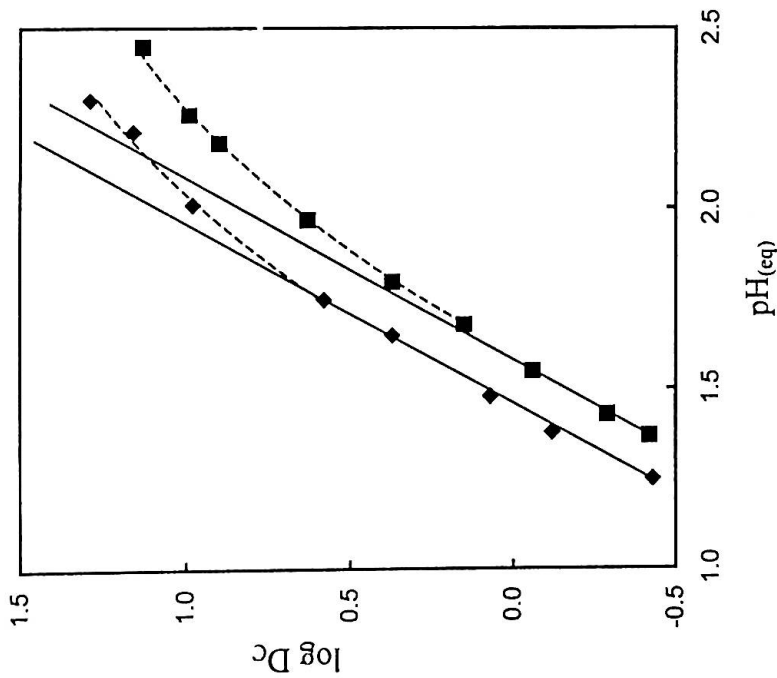


Figure 35. Dependence of corrected distribution ratio D_c on equilibrium pH. Equilibration time = 30 min, Temp. = (298 ± 1) K, $[\text{Fe}^{3+}]_{\text{ini}} = 0.75 \text{ g/L}$ (13.43 mmol/dm^3), $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$. (◆), $[\text{BTMPPA}]_{\text{a,ini}} = 0.05 \text{ mol/dm}^3$, $s = 2$ (at lower pH region), $I = -2.92$; (■), $[\text{BTMPPA}]_{\text{a,ini}} = 0.025 \text{ M}$, $s = 2$ (at lower pH region), $I = -3.20$, Table XXII).

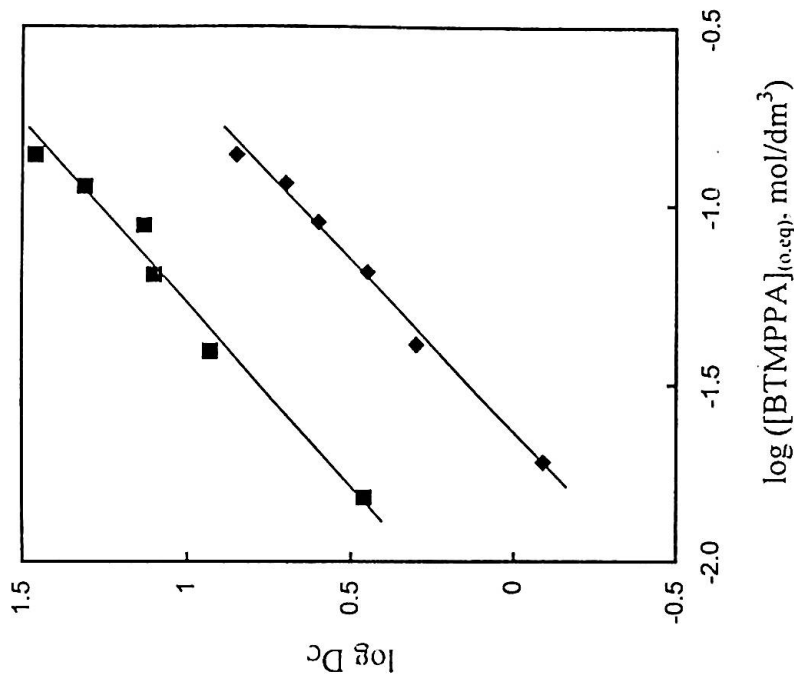


Figure 36. Dependence of D_c on equilibrium free extractant concentration. Equilibration time = 30 min, temperature = (298 ± 1) K, $[\text{Fe}^{3+}]_{\text{ini}} = 0.75 \text{ g/dm}^3$, $[\text{SO}_4^{2-}] = 0.1 \text{ mol/dm}^3$; (◆), $\text{pH}_{\text{ini}} = 1.75$, $\text{pH}_{\text{eq}}^{\text{ind}} = 1.74$, $s = 1$, $I = 1.70$; (■), $\text{pH}_{\text{ini}} = 2.20$, $\text{pH}_{\text{eq}}^{\text{ind}} = 1.98$, $s = 1$, $I = 2.3$, (Table XXIII).

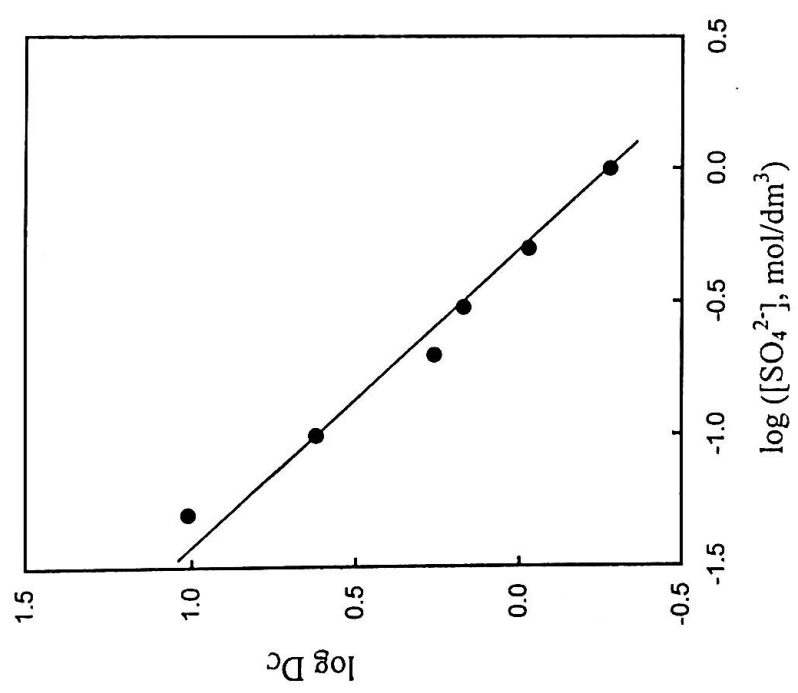


Figure 37. Dependence of D_c on sulphate ion concentration. Equilibration time = 30 min, Temp. = (298 ± 1) K, $[\text{Fe}^{3+}]_{(\text{ini})} = 0.75 \text{ g/dm}^3$, $\text{pH}_{(\text{ini})} = 2.35$, $[\text{BTMPPA}]_{(\text{o,ini})} = 0.025 \text{ mol/dm}^3$, $\text{pH}_{\text{res}} = 2.01$, $[\text{BTMPPA}]_{(\text{o,eq})}^{\text{const}} = 0.025 \text{ M}$, $s = -1$, $I = -0.34$ (Table XXIV).

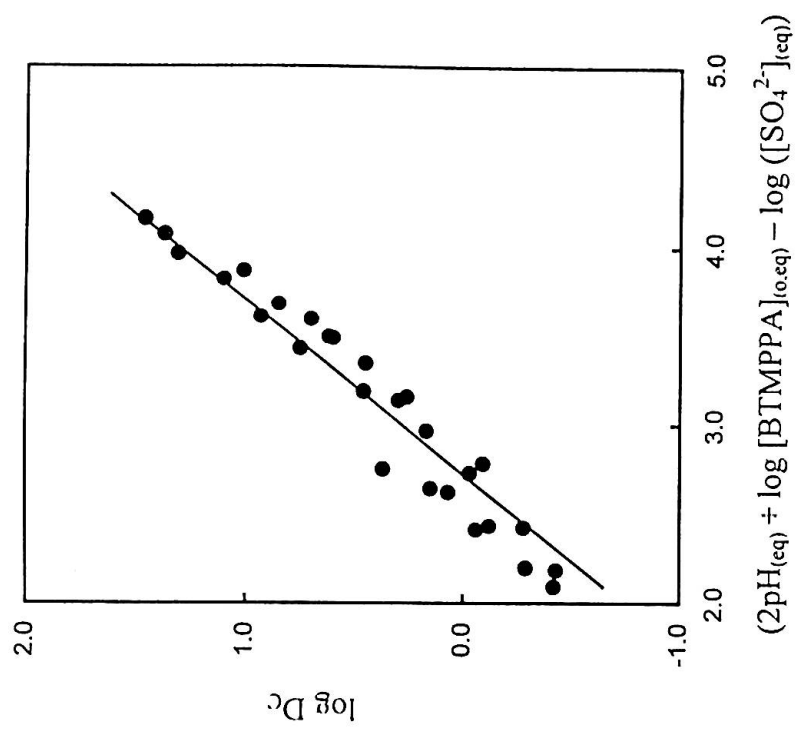


Figure 38. The $\log D_c$ vs. $(2\text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log [\text{SO}_4^{2-}]_{(\text{eq})})$ plot at 298 K. $I = \log K_{\text{ex}} = -2.3$, $s = 0.87$, Corr. Coeff. = 0.946 (Table XXV)

Figs. 35-37, the values of $(3-n+z)$, x and z of Eq. (61) are 2, 1 and 1, respectively. This gives the value of $n = 2$ and $(2x - 3 + n - z) / 2 = 0$. This means that the extracted complex is not solvated by an uncomplexed BTMPPA but it must be solvated by diluent if by nothing else and the bisulphate complex of the type $\text{Fe}(\text{HSO}_4)_2^+$ or its dimeric form existing in the aqueous phase take part in the extraction. The existence of $\text{Fe}(\text{HSO}_4)_2^+$ in sulphate medium of Fe^{3+} is supported by the ionization constant of HSO_4^- ($K_{a2(\text{H}_2\text{SO}_4)} = 10^{-2}$) and the stability constant of $\text{Fe}(\text{HSO}_4)_2^+$ ($[\text{Fe}(\text{HSO}_4)_2^+]/[\text{Fe}^{3+}][\text{HSO}_4^-]^2 = 10^2$) as given by Smith and Martel [289]. Therefore, Eq. (61) simplifies to



The extracted species is a non-solvated chelate: among six coordination positions of Fe^{3+} two are satisfied by a bisulphate group and other four positions by two anions of bidento-monomeric BTMPPA. Eq. (64) can be rewritten for Eq. (69) as:

$$\log D = \log K_{\text{ex}} + 2\text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{eq})} - \log [\text{HSO}_4^-]_{(\text{eq})} \quad (70)$$

Eq. (70) states that $\log D$ vs. $(2\text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{eq})} - \log [\text{HSO}_4^-]_{(\text{eq})})$ plot will be a straight line of unity slope and its intercept will be equal to $\log K_{\text{ex}}$. Such a plot at 298 K is shown in Fig. 38 (*cf.* Table XXV). The Least Squares slope and intercept of the line are 0.87 and -2.30 respectively with correlation coefficient of 0.946. Therefore, K_{ex} is equal to $10^{-2.30}$, compared to $10^{1.57}$ for Fe^{3+} by D2EHPA [82].

The variation of distribution ratio of Fe^{3+} on temperature is given in tabular form in Table XXVI and displayed in Fig. 39 at four different experimental parameters. In all cases under investigation, $\log D$ vs. $(1/T)$,

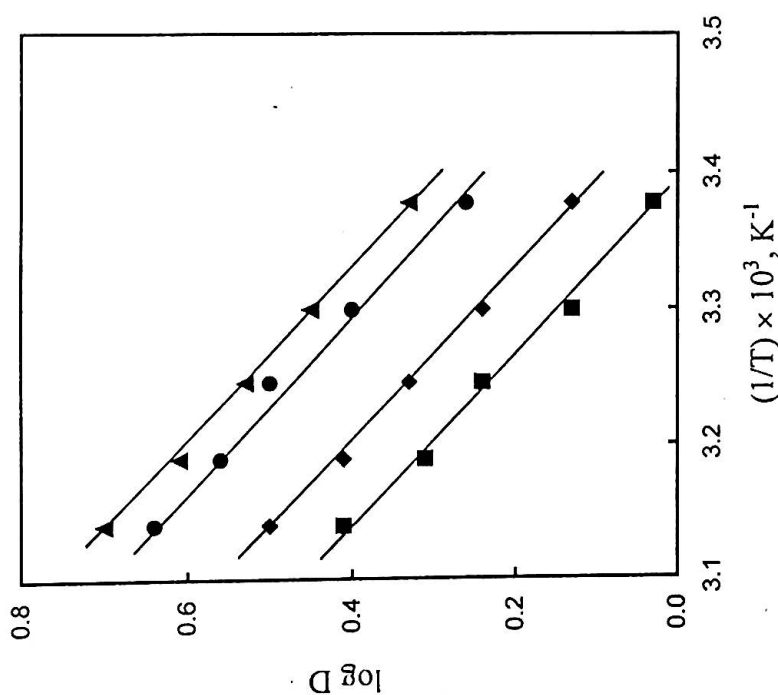


Figure 39. Dependence of D on temperature in the extraction of Fe^{3+} by BTMPPA. Equilibration time = 30 min, $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$, $[\text{Fe}^{3+}]_{\text{(ini)}} = 0.72 \text{ g/dm}^3$. ($\blacktriangle$), $\text{pH}_{\text{(ini)}} = 1.75$, $[\text{BTMPPA}]_{\text{(o,ini)}} = 0.025 \text{ mol/dm}^3$, $s = -1533$, $\Delta H = 29.37 \text{ kJ/mol}$; ($\bullet$), $\text{pH}_{\text{(ini)}} = 1.65$; $[\text{BTMPPA}]_{\text{(o,ini)}} = 0.025 \text{ mol/dm}^3$, $s = -1600$, $\Delta H = 30.66 \text{ kJ/mol}$; ($\blacklozenge$), $\text{pH}_{\text{(ini)}} = 1.75$, $[\text{BTMPPA}]_{\text{(o,ini)}} = 0.05 \text{ mol/dm}^3$, $s = -1538$, $\Delta H = 29.47 \text{ kJ/mol}$; ($\blacksquare$), $\text{pH}_{\text{(ini)}} = 1.65$, $[\text{BTMPPA}]_{\text{(o,ini)}} = 0.05 \text{ mol/dm}^3$, $s = -3025$, $\Delta H = 13.14 \text{ kJ/mol}$ (Table XXVI).

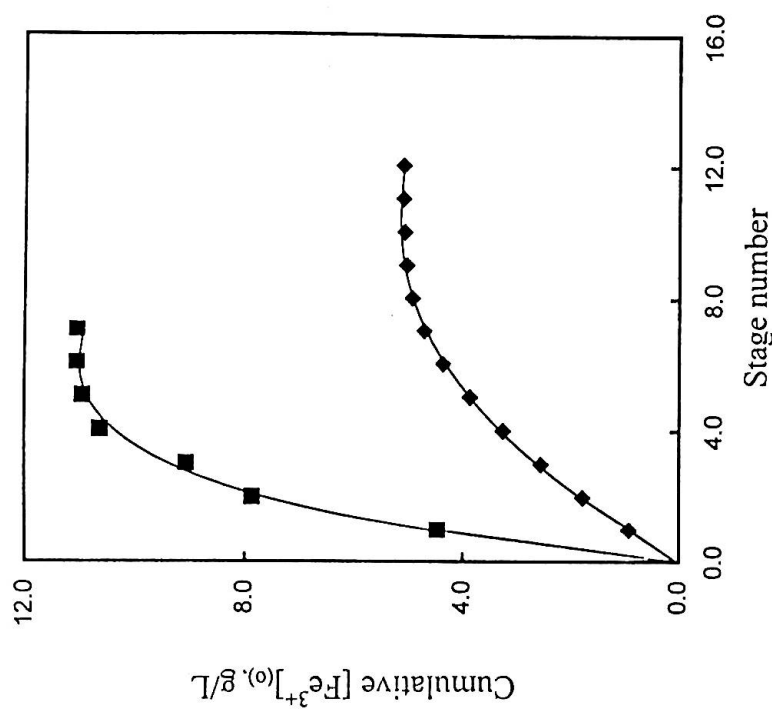


Figure 40. Loading of BTMPPA with Fe^{3+} : cumulative $[\text{Fe}^{3+}]_{\text{(o)}}$, g/dm^3 vs. phase contact time (aqueous phase renewed), $\text{pH}_{\text{(ini)}} = 2.40$, Equilibration time (each stage) = 30 min, Temp. = $(298 \pm 1) \text{ K}$. ($\bullet$), $[\text{Fe}^{3+}]_{\text{(ini)}} = 1 \text{ g/dm}^3$, $[\text{BTMPPA}] = 0.10 \text{ mol/dm}^3$; ($\blacksquare$), $[\text{Fe}^{3+}]_{\text{(ini)}} = 5 \text{ g/dm}^3$, $[\text{BTMPPA}]_{\text{(o, ini)}} = 0.20 \text{ mol/dm}^3$ (Table XXVII).

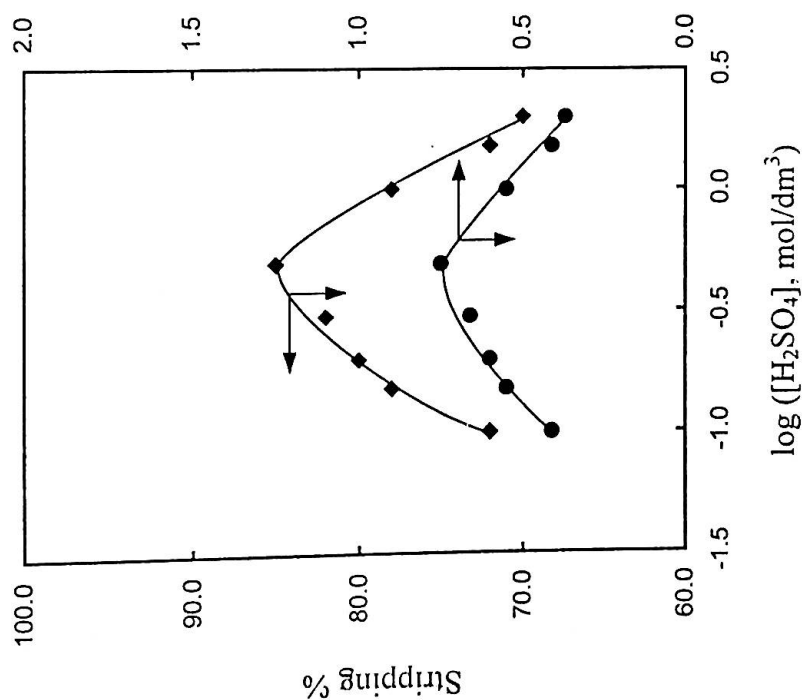


Figure 41. Stripping of Fe^{3+} - BTMPPA - HSO_4^- complex by aqueous sulphuric acid solution. Equilibration time = 30 min, $[\text{Fe}^{3+}]_{\text{(o.ini)}} = 2.21 \text{ g/dm}^3$, Temp. = $(298 \pm 1) \text{ K}$, $\text{O/A} = 1$, free $[\text{BTMPPA}]_{\text{(o.ini)}} = 0.025 \text{ mol/dm}^3$ (Table XXVIII).

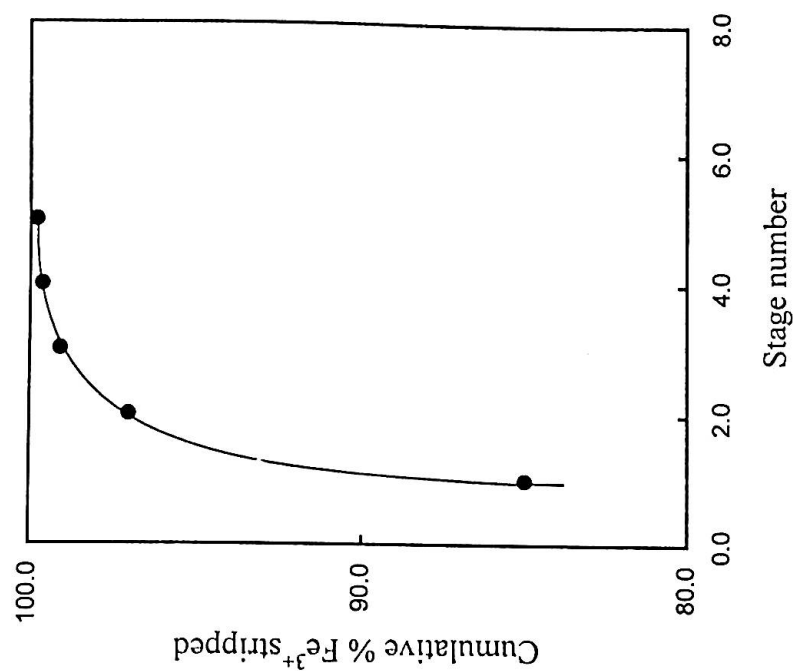


Figure 42. Stage-wise stripping by aqueous sulphuric acid solution. Equilibration time = 30 min, $[\text{Fe}^{3+}]_{\text{(o.ini)}} = 2.21 \text{ g/dm}^3$, Temp. = $(298 \pm 1) \text{ K}$, O/A (each stage) = 1, free $[\text{BTMPPA}]_{\text{(o.ini)}} = 0.025 \text{ mol/dm}^3$, $[\text{H}_2\text{SO}_4] = 0.50 \text{ mol/dm}^3$. Aqueous phase is renewed in each stage (Table XXIX).

K^{-1} plots are straight lines. With the help of Eq. (65), the ΔH values have been calculated from the slope of the lines. Average ΔH value is 30 kJ/mol with a variation of ± 0.70 . Positive ΔH value suggests that the extraction of Fe^{3+} from sulphate medium is endothermic in nature.

The loadings of Fe^{3+} in 0.10 and 0.20 mol/dm³ BTMPPA solution have been examined. The experimental data are given Table XXVII. The cumulative concentration of Fe^{3+} in the organic phase (in g/dm³) have been plotted against the number of stages in Fig. 40. It is seen from this figure that 0.10 mol/dm³ BTMPPA is saturated with 5.1 g/L Fe^{3+} ; whereas, 0.20 mol/dm³ BTMPPA is saturated with 11.05 g/dm³ Fe^{3+} . In the first case, 0.10 mol/dm³ BTMPPA is saturated with 0.0913 mol/dm³ Fe^{3+} instead of 0.10 mol/dm³ Fe^{3+} . The analytical error in calculating the cumulative concentration of ferric ion in the organic phase may explain the small discrepancy from a 1/1 ratio of ferric to BTMPPA. In the second case, 0.20 mol/dm³ BTMPPA is saturated with 0.198 mol/dm³ Fe^{3+} . Therefore, in both cases, Fe^{3+} to BTMPPA ratio at saturation is about 1:1; which is also obtained from the extractant dependence study. Thus the extraction mechanism near saturation remains unaltered. The loading capacity is calculated to be 9.6 g Fe^{3+} /100 g BTMPPA.

The stripping ability of H_2SO_4 solution for the extracted complex has been investigated. The stripping data is given in Table XXVIII. The result is given graphically in Fig. 41 as stripping percentage and log S vs. log ($[\text{H}_2\text{SO}_4]$, mol/dm³) plots. It is seen that the best stripping is obtained with 0.50 mol/dm³ H_2SO_4 solution when 85% of Fe^{3+} is stripped. The Table XXXIX and Fig. 42 shows the result of stage-wise stripping. In this figure, cumulative percentage of Fe^{3+} stripped has been plotted against the stage number. It is seen that three-stage stripping removes more than

99% Fe^{3+} from the organic phase; whereas, a five-stage stripping leaves only 0.2% Fe^{3+} in the organic phase. The stripping abilities of HCl and HNO_3 are also tested but shown not to be as effective as H_2SO_4 . For example, 1 mol/dm³ HCl and 1 mol/dm³ HNO_3 are able to strip respectively 35% and 38% Fe^{3+} from the organic phase in a single stage.

When Fe^{3+} (1 g/dm³) is extracted from 0.50 mol/dm³ sulphate medium at $\text{pH}_{(\text{ini})} = 2$ by 0.025 mol/dm³ BTMPPA dissolved in different diluents, then the value of distribution ratio (D) is found to decrease (Table XXX) in the following order : CCl_4 (0.92) > $\text{ClCH}_2\text{CH}_2\text{Cl}$ (0.87) > kerosene (0.81) > CHCl_3 (0.74) > $\text{C}_6\text{H}_5\text{CH}_3$ (0.70) $\approx$ $n\text{-C}_6\text{H}_{14}$ (0.70) > $\text{Cy-C}_6\text{H}_{12}$ (0.65) > $n\text{-I-C}_7\text{H}_{15}\text{OH}$ (0.60) > $n\text{-I-C}_6\text{H}_{13}\text{OH}$ (0.56) > C_6H_6 (0.47). This order is changed, when extraction is made from an aqueous solution of $\text{pH}_{(\text{ini})} = 0.80$ by 0.20 mol/dm³ BTMPPA (*cf.* Table XXX), as shown: CCl_4 (0.30) > $\text{ClCH}_2\text{CH}_2\text{Cl}$ (0.28) > $n\text{-C}_6\text{H}_{14}$ (0.25) = $\text{C}_6\text{H}_5\text{CH}_3$ (0.25) > $\text{Cy-C}_6\text{H}_{12}$ (0.24) > kerosene (0.22) > C_6H_6 (0.18) > CHCl_3 (0.16) > $n\text{-I-C}_7\text{H}_{15}\text{OH}$ (0.12) > $n\text{-I-C}_6\text{H}_{13}\text{OH}$ (0.11). These values of D in the logarithmic form have been plotted against the logarithm of the cross sectional area (A , Å²) of BTMPPA molecules adsorbed at the interface formed by different diluents in Fig. 43. In the first case, out of ten points, a six point fit correlation is obtained. A better result is obtained in the second case. The correlated lines have a slope of about -0.33 and -0.40 in the first and second cases, respectively. In the case of D2FHPA [137], a very sharp correlation was obtained between the distribution ratio (D) of TiO^{2+} and the cross-sectional area of D2EHPA (A). In that case, the slope of $\log D$ vs. $\log A$ plot was -4.0 . It is therefore concluded that in contrast to the extraction characteristics of D2EHPA reported earlier, the extraction

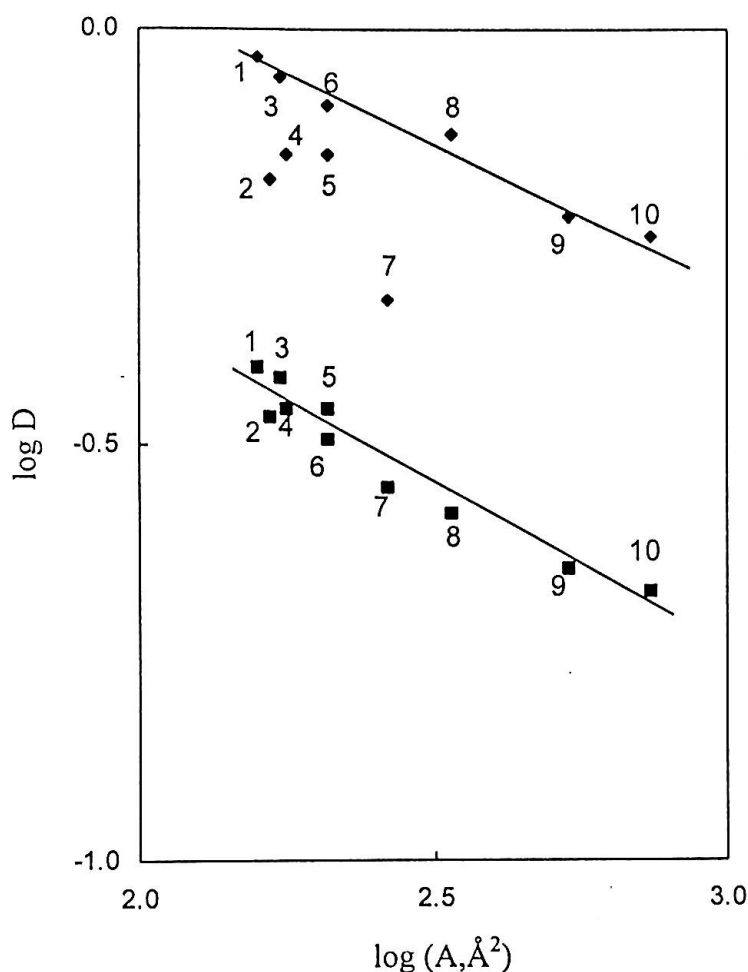
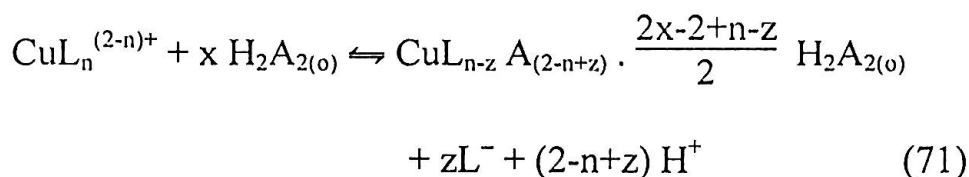


Figure 43. Correlation of cross sectional area of adsorbed BTMPPA molecule with the distribution ratio of Fe^{3+} in different diluents at 298 K. (◆), D is determined on extracting 1 g/dm^3 Fe^{3+} from 0.50 mol/dm^3 sulphate medium at $\text{pH}_{(\text{ini})} = 2$ by 0.025 mol/dm^3 BTMPPA; (■), D is determined on extracting 1 g/dm^3 Fe^{3+} from 0.50 mol/dm^3 sulphate medium at $\text{pH}_{(\text{ini})} = 0.8$ by 0.20 mol/dm^3 BTMPPA. 1. CCl_4 , 2. $\text{Cy-C}_6\text{H}_{12}$, 3. $\text{ClCH}_2\text{CH}_2\text{Cl}$, 4. $n\text{-C}_6\text{H}_{14}$, 5. $\text{C}_6\text{H}_5\text{CH}_3$, 6. kerosene, 7. C_6H_6 , 8. CHCl_3 , 9. $n\text{-I-C}_7\text{H}_{15}\text{OH}$, 10. $n\text{-I-C}_6\text{H}_{13}\text{OH}$ (Table XXX).

characteristics of BTMPPA is not so much dependent on the diluent used to constitute the organic phase.

5.7. Extraction equilibria of Cu(II) by BTMPPA in kerosene

BTMPPA being a dialkyl derivative of phosphinic acid, $H_2PO(OH)$ acts as a mono-acidic chelating agent. If Cu(II) exists in the aqueous phase as $CuL_n^{(2-n)+}$ (L being the co-existing anion of unit charge) and BTMPPA is considered as dimeric (H_2A_2) in non-polar solvents like kerosene [this work, 144], then the extraction equilibrium reaction may be depicted as:



where, subscript (o) represents organic species. The extraction equilibrium constant (K_{ex}) of the above reaction can be expressed as follows:

$$K_{ex} = \frac{[CuL_{n-z} A_{(2-n+z)} \cdot (\frac{2x-2+n-z}{2}) H_2A_2]_{(o)} [H^+]^{(2-n+z)} [L^-]^z}{[CuL_n^{(2-n)+}] [H_2A_2]_{(o)}^x} \quad (72)$$

Now, on defining the distribution ratio (D) as :

$$D = [CuL_{n-z} A_{(2-n+z)} \cdot (\frac{2x-2+n-z}{2}) H_2A_2]_{(o)} / [CuL_n^{(2-n)+}] \quad (73)$$

the Eq. (73) can be expressed as:

$$K_{ex} = D \frac{[H^+]^{(2-n+z)} [L^-]^z}{[H_2A_2]_{(o)}^x} \quad (74)$$

On taking logarithm of both the sides of Eq. (74), one gets the following relationship:

$$\log D = \log K_{ex} + (2-n+z) \text{pH} + x \log [H_2A_2]_{(o)} - z \log [L^-] \quad (75)$$

The temperature dependency of D can be treated by the Vant' Hoff Equation [288]:

$$\log D = - \frac{\Delta H}{2.303 RT} \quad (76)$$

Eq. (76) states that the plot of $\log D$ vs. $(1/T)$, K^{-1} will be a straight line with a slope equal to $-\Delta H / 2.303 R$, from which the enthalpy change for the extraction reaction (ΔH) can be evaluated.

The rate on the Cu(II) extraction by purified Cyanex 272 ie. BTMPPA is illustrated in Table XXXI and also in Fig. 44, as $[Cu^{2+}]$, mmol/dm³ vs. time, min plot for extraction of 14.37 mmol/dm³ initial copper in the aqueous phase containing 0.10 mol/dm³ $SO_4^{=}$ at $pH_{(ini)}$ of 4.75 by 0.065 mol/dm³ BTMPPA. It is found that equilibrium is reached within 12 min's shaking. In subsequent experiments, shaking time of 15 min has been used.

Table XXXII represents the experimental data on the variation of extraction / distribution ratio of Cu(II) with the variation of Cu(II) concentration in the aqueous phase at $pH_{(ini)} = 4.75$, $[SO_4^{=}] = 0.10$ mol/dm³ and $[BTMPPA]_{(o,ini)} = 0.10$ mol/dm³ Figure 45 shows the variation of D of Cu(II) with the variation of the initial concentration of Cu(II) in the aqueous phase in log-log scale. It is found that the $\log D$ values are decreased with increasing logarithm of initial concentration of Cu(II) in the aqueous phase particularly in the higher concentration region, where the asymptotic slope approach to -1.2 . It is expected from Eq. (75) that the distribution ratio (D) should be independent on initial

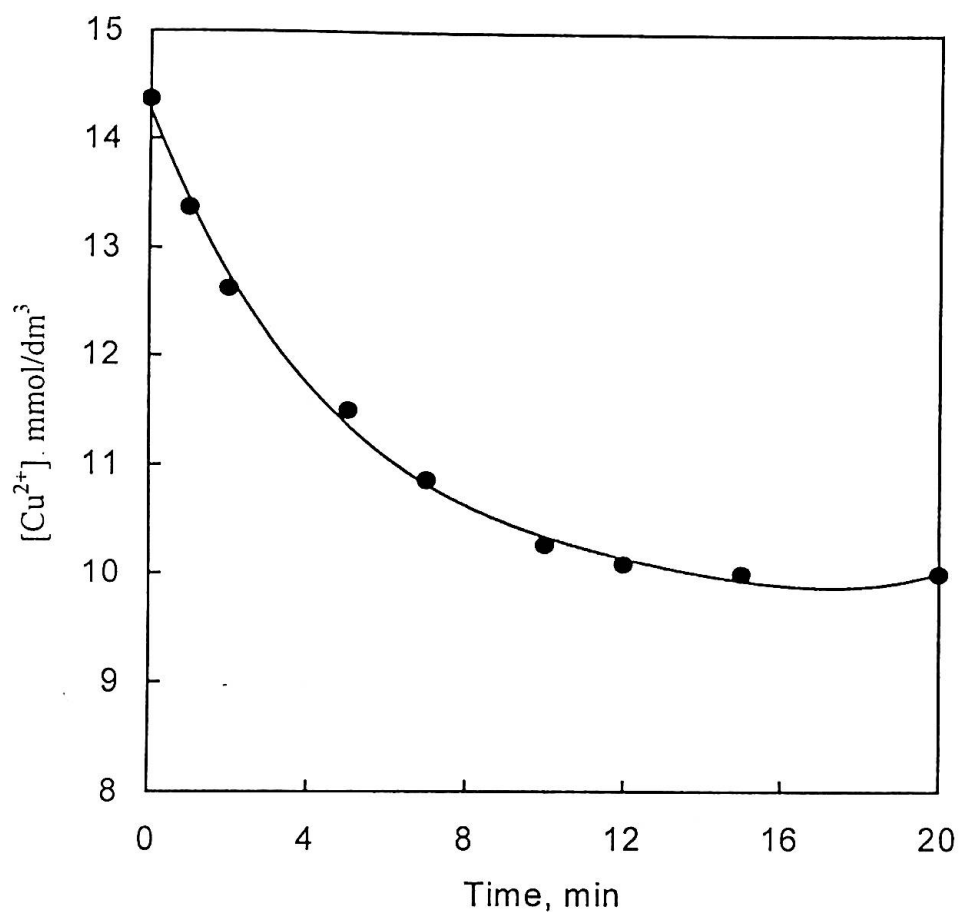


Figure 44. Dependence of extraction of Cu(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on time. $[\text{Cu}^{2+}]_{(\text{a},\text{ini})} = 0.9128 \text{ g/dm}^3 = 14.37 \text{ mmol/dm}^3$, $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$, $[\text{BTMPPA}]_{(\text{o},\text{ini})} = 0.065 \text{ mol/dm}^3$, $\text{Temp} = 298 \text{ K}$, $\text{pH}_{(\text{ini})} = 4.75$ (Table XXXI).

Cu(II) concentration at fixed equilibrium pH and concentrations of BTMPPA and co-existing anion. But in the above case, the equilibrium pH and the concentrations of BTMPPA and SO_4^{2-} are not constants for varying extents of extraction. Figure 45 also represents the $\log D_C$ vs. $\log [\text{Cu}^{2+}]_{(\text{ini})}$ and $\log D_C$ vs. $\log [\text{Cu}^{2+}]_{(\text{eq})}$ plots, where, D_C is the corrected distribution ratio at $\text{pH}_{(\text{eq})}^{\text{const}} = 3.86$, $\text{BTMPPA}_{(\text{o,eq})}^{\text{const}} = 0.10 \text{ mol/dm}^3$ and $[\text{SO}_4^{2-}]_{(\text{eq})}^{\text{const}} = 0.10 \text{ mol/dm}^3$; and it has been calculated using the following relationship after getting the pH, extractant and sulphate ion dependences:

$$\log D_C = \log D + y (\text{pH}_{(\text{eq})}^{\text{const}} - \text{pH}_{(\text{eq})}) + x(\log [\text{BTMPPA}_{(\text{o,eq})}^{\text{const}}] - \log [\text{BTMPPA}]_{(\text{o,eq})}) + z(\log [\text{SO}_4^{2-}]_{(\text{eq})}^{\text{const}} - \log [\text{SO}_4^{2-}]_{(\text{eq})}) \quad (77)$$

where, $y = \text{pH dependence} = 1$, $x = \text{extractant dependence} = 1.2$ and $z = \text{sulphate ion dependence} = -0.08$ (considered as zero). The values of $[\text{BTMPPA}]_{(\text{o,eq})}$ have been calculated from the relation:

$$[\text{BTMPPA}]_{(\text{o,eq})} = [\text{BTMPPA}]_{(\text{o,ini})} - x [\text{Cu}^{2+}]_{(\text{o,eq})} \quad (78)$$

The $\log D_C$ vs. $\log ([\text{Cu}^{2+}]_{(\text{ini})}, \text{mol/dm}^3)$ and the $\log D_C$ vs $\log ([\text{Cu}^{2+}]_{(\text{eq})}, \text{mol/dm}^3)$ plots are also curves as shown in Fig. 45. These curves have relatively lower asymptotic slopes (-0.60) in the higher concentration regions of Cu^{2+} in the aqueous phase. Upto about $30 \text{ mmol/dm}^3 \text{ Cu}^{2+}$, the D value remains almost unaltered in the last two cases as expected. At concentration above 30 mmol/dm^3 of Cu^{2+} , some sort of speciation change in one or either of phases might occur.

The variations of D_C of Cu(II) on equilibrium pH in the aqueous phase have been investigated at 0.05 and 0.10 mol/dm^3 BTMPPA concentrations. The results are presented in Table XXXIII and displayed

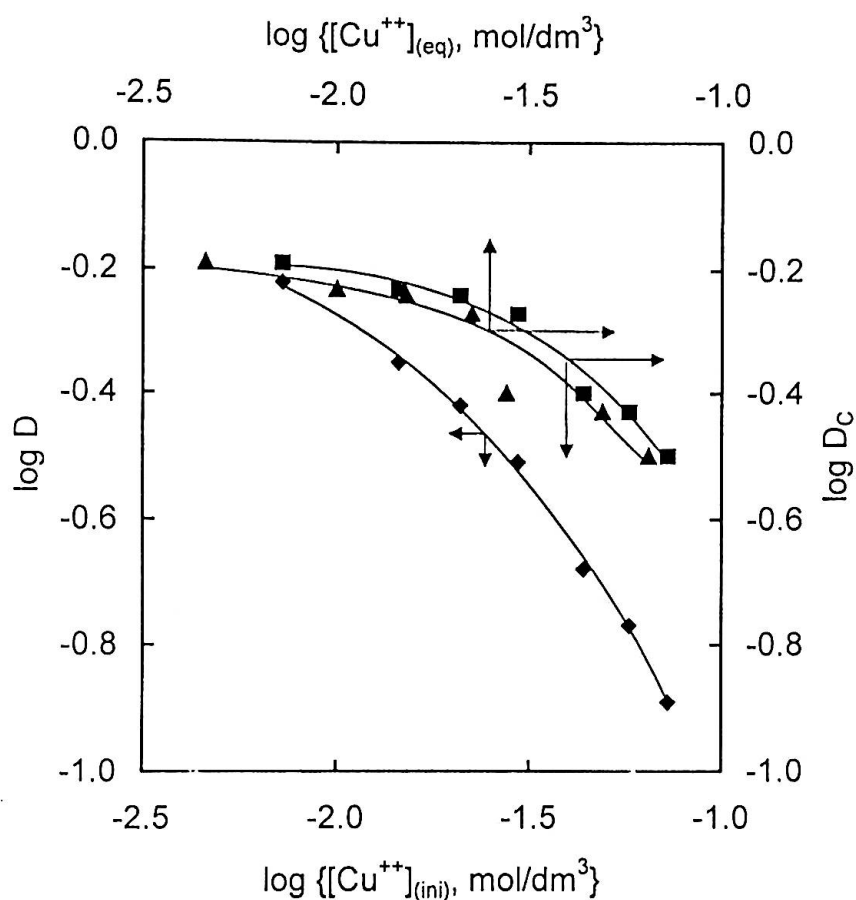


Figure 45. Dependence of extraction of Cu(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on Cu(II) concentration in the aqueous phase. $\log D$ vs. $\log \{[Cu^{2+}]_{(ini)}, \text{mol/dm}^3\}$ plot; $\log D_c$ vs. $\log \{[Cu^{2+}]_{(ini)}, \text{mol/dm}^3\}$ plot; $\log D_c$ vs. $\log \{[Cu^{2+}]_{(eq)}, \text{mol/dm}^3\}$ plot; $\text{pH}_{(ini)} = 4.75$, $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$, $[\text{BTMPPA}]_{(o,ini)} = 0.10 \text{ mol/dm}^3$, $\text{Temp} = 298 \text{ K}$, Equilibration time = 15 min. The $\log D_c$ values are at $\text{pH}_{(eq)}^{\text{const}} = 3.86$ and $[\text{BTMPPA}]_{(o,eq)}^{\text{const}} = 0.10 \text{ mol/dm}^3$. (Table XXXII).

in Fig. 46 at $[\text{BTMPPA}]_{(o,ini)} = (o,eq) = 0.05$ and 0.10 mol/dm^3 . In both cases, D_C (calculated by Eq. (77) after neglecting the second and fourth terms : fourth term automatically vanishes as $z = 0$) is found to increase with increasing equilibrium pH of the aqueous phase. The $\log D_C$ vs. $\text{pH}_{(eq)}$ plots have a slope of unity. It is therefore concluded that one gram ion of H^+ is liberated during the reaction of one gram ion of Cu^{2+} with the extractant, BTMPPA. The value $(2-n+z)$ in Eq.(75) is 1, so that the value of $(n-z)$ equals to 1.

The experimental data on the variation of Cu(II) - extraction / distribution ratio for the variation of BTMPPA concentration in the organic phase are provided in Table XXXIV. Figure 47 shows the $\log D$ vs. $\log [\text{BTMPPA}]_{(o,ini)}$ plots for two constant equilibrium pH values of 5.0 and 4.6. In both cases, straight lines are obtained with slope equaling to about 1.50 (1.47 and 1.58 for $\text{pH}_{(eq)}$ values of 4.6 and 5.0, respectively). The $\log D$ vs. $\log [\text{BTMPPA}]_{(o,eq)}$ plots at the same constant $\text{pH}_{(eq)}$ values given above are shown in Fig. 48. In this case, straight lines of lower slope values are obtained. The slopes are 1.16 and 1.25 at $\text{pH}_{(eq)}$ values of 4.6 and 5.0, respectively. It is therefore concluded that 60% of the extraction reactions occur via the Cu^{2+} to BTMPPA stoichiometric ratio of 1 and the rest 40% of the extraction reaction occurs via the Cu^{2+} to BTMPPA stoichiometric ratio of 2:3. The value of x in Eq.(75) becomes $(0.6 \times 1 + 0.4 \times 1.5 = 1.2)$.

Table XXXV represents the data on the dependence of Cu(II)-extraction by BTMPPA dissolved in kerosene on sulphate ion concentration in the aqueous phase at constant $\text{pH}_{(eq)} = 3.4$ and $[\text{BTMPPA}]_{(o,eq)} = 0.10 \text{ mol/dm}^3$. The $\log D_C$ vs. $\log [\text{SO}_4^{2-}]$ plot is displayed in Fig. 49 for $[\text{BTMPPA}]_{(o,eq)}^{\text{const}}$ and $\text{pH}_{(eq)}^{\text{const}}$ values of 0.10 mol/dm^3

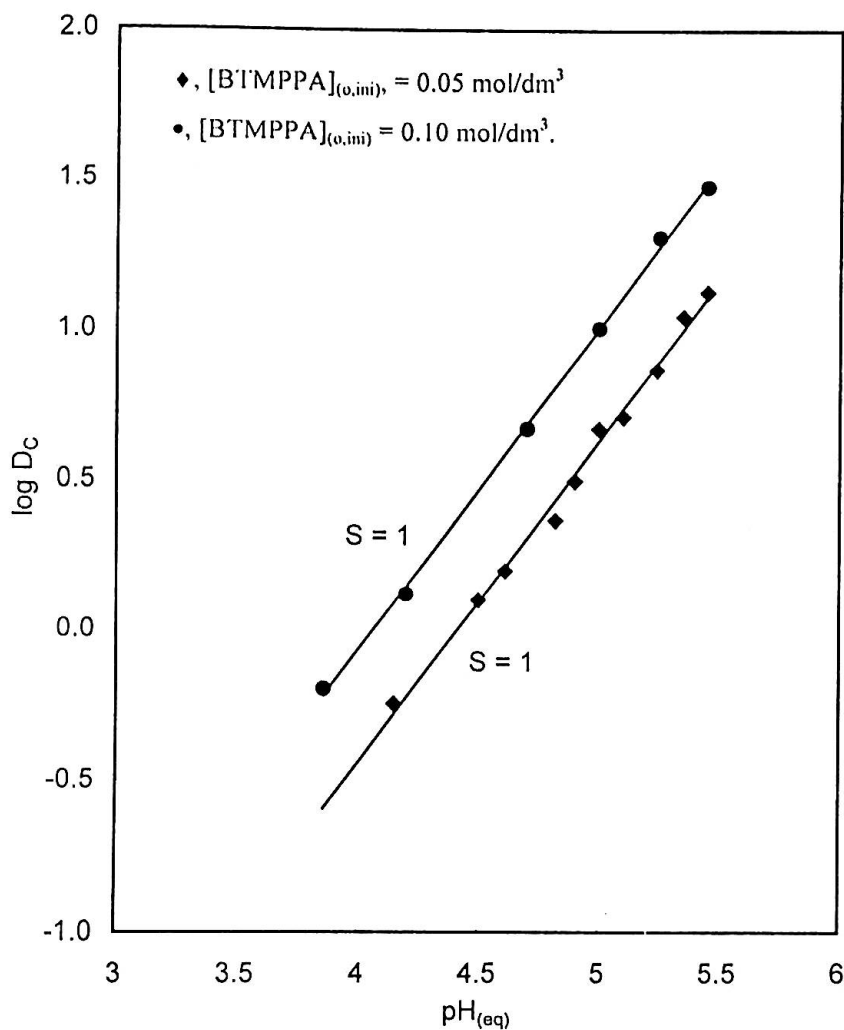


Figure 46. Dependence of extraction of Cu(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on equilibrium pH in the aqueous phase. $[\text{Cu}^{++}]_{(a,\text{ini})} = 0.8811 \text{ g/dm}^3 = 13.88 \text{ mmol/dm}^3$, Equilibration time = 15 min, Temp. = 298 K, $[\text{SO}_4^{=}] = 0.10 \text{ mol/dm}^3$. (♦), $[\text{BTMPPA}]_{(0,\text{ini})} = 0.05 \text{ mol/dm}^3$ and (•), $[\text{BTMPPA}]_{(0,\text{ini})} = 0.10 \text{ mol/dm}^3$ (Table XXXIII).

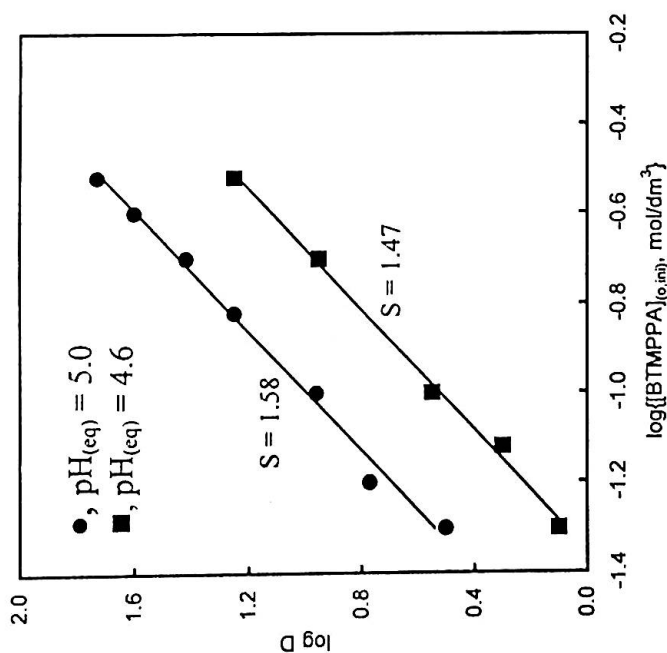


Figure 47. Dependence of extraction of Cu(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on initial extractant concentration in the organic phase: $\log D$ vs. $\log\{[BTMPPA]_{(o,ini)}, \text{mol/dm}^3\}$ plots (Table XXXIV).

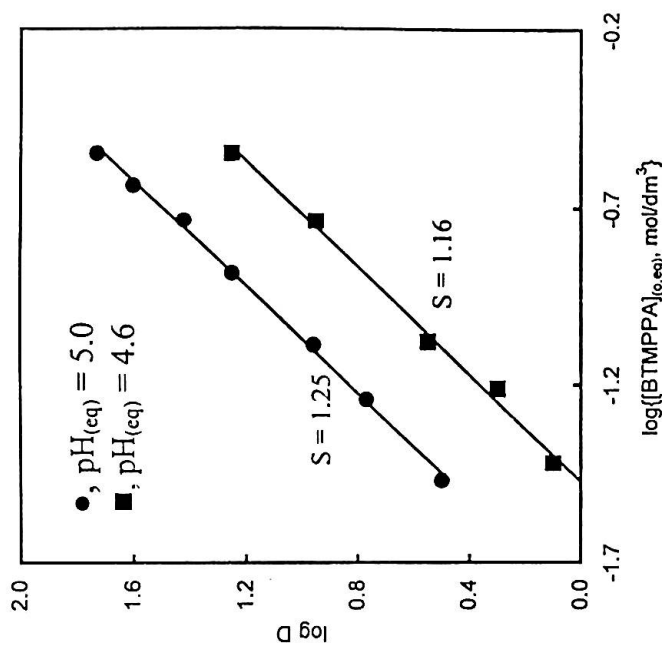


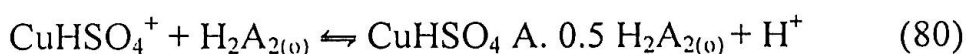
Figure 48. Dependence of extraction of Cu(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on equilibrium extractant concentration in the organic phase: $\log D$ vs. $\log\{[BTMPPA]_{(o,eq)}, \text{mol/dm}^3\}$ plots (Table XXXIV).

and 3.4, respectively. It is found that D is almost independent of sulphate ion concentration (the log-log plot has a slope of only -0.08). It is therefore concluded that sulphate or bisulphate ion is neither associated to or dissociated from the copper(II) species existing in the aqueous phase during extraction. The value of z in Eq. (75) is considered to be zero. It appears therefore that the value of n equals to 1. This means that CuSO_4 or CuHSO_4^+ species take part in the extraction reaction.

Since the stability constant [289] of $\text{Cu}(\text{OH})^+ (= \frac{[\text{CuOH}^+]}{[\text{Cu}^{++}][\text{OH}^-]})$, $\text{HSO}_4^- (= \frac{[\text{HSO}_4^-]}{[\text{SO}_4^{--}][\text{H}^+]})$ and $\text{CuHSO}_4^+ (= \frac{[\text{CuHSO}_4^+]}{[\text{Cu}^{++}][\text{HSO}_4^-]})$ are $10^{6.3}$, $10^{2.36}$ and $10^{6.3}$, respectively, it can be assumed that at around pH 5, the monohydroxylated Cu(II) concentration is almost zero and the CuHSO_4^+ species take part in the extraction reaction. As found earlier, $n = 1$, and this suggests the reaction of CuHSO_4^+ with BTMPPA (cf. Eq.(71)). On putting the values of n, x and z, Eq. (71) takes the form:



Eq. (79) is thought to be the combination of following two equations:



and,



among which 60% extraction occurs via Eq. (80) and the rest 40% extraction occurs via Eq. (81). Reacted copper(II) species in the organic phase produced by Eqs. (80) and (81) differ only in solvation number. Eq. (75) can be rewritten for Eq. (79) as:

$$\log D_c = \log K_{\text{ex}} + \text{pH}_{(\text{eq})} + 1.2 \log [\text{H}_2\text{A}_2]_{(\text{o}, \text{eq})} \quad (82)$$

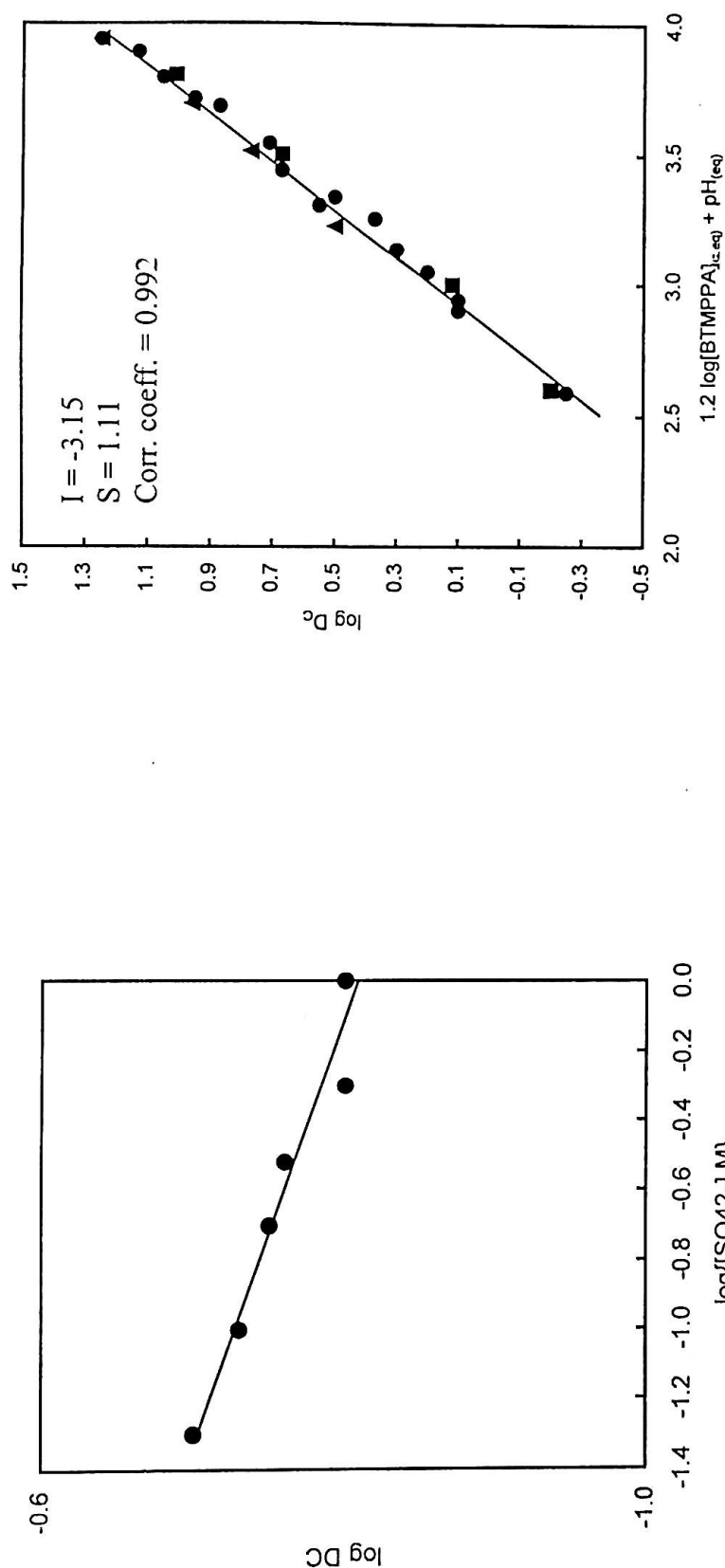


Figure 49. Dependence of extraction of Cu^{2+} by purified Cyanex 272 (BTMPPA) dissolved in kerosene on sulphate ion concentration in the aqueous phase. $[Cu^{2+}]_{(a,ini)} = 0.9234 \text{ g/dm}^3 = 14.14 \text{ mmol/dm}^3$; $[BTMPPA]_{(o,ini)} = 0.10 \text{ mol/dm}^3$; $[BTMPPA]_{(o,eq)}^{const} = 0.10 \text{ mol/dm}^3$, $pH_{(ini)} = 4.70$, $pH_{(eq)}^{const} = 3.40$. Equilibration time = 15 min, Temp = 298 K (Table XXXV).

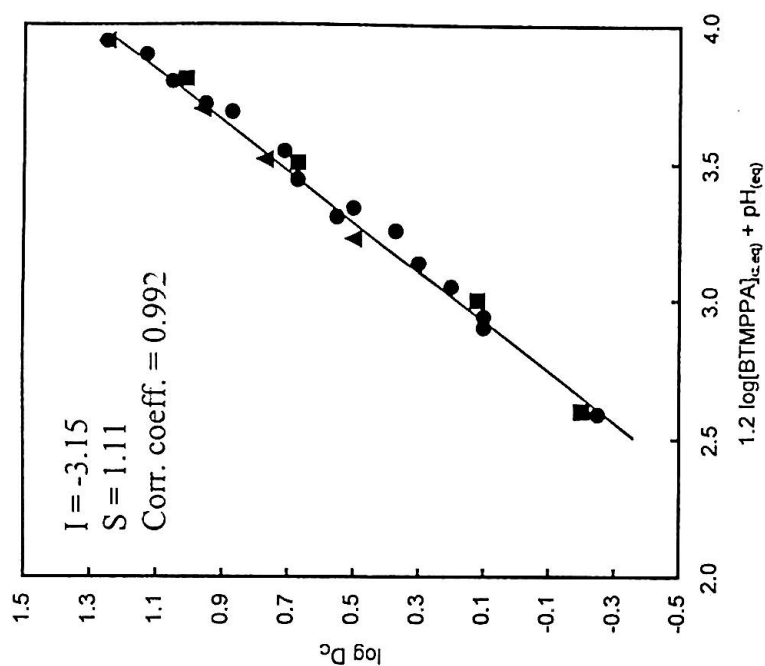


Figure 50. Evaluation of equilibrium constant of copper(II) extraction reaction by BTMPPA graphically at 298 K (Table XXXVI).

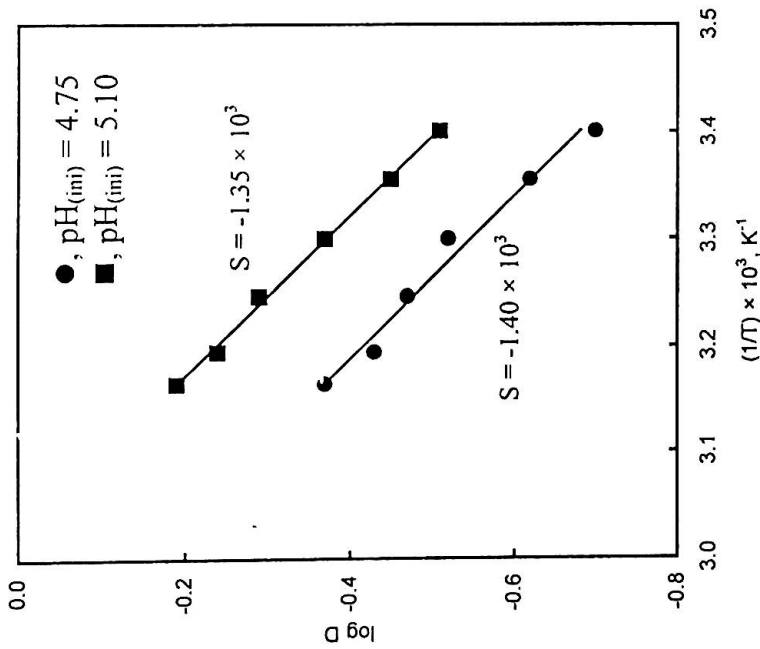


Figure 51. Dependence of extraction of copper(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on temperature. $[Cu^{2+}]_{(a,ini)} = 0.9234$ g/dm³ = 14.54 mmol/dm³, $[SO_4^{2-}] = 0.10$ mol/dm³, $[BTMPPA]_{(o,ini)} = 0.10$ mol/dm³, Equilibration time = 15 min (Table XXXVII).

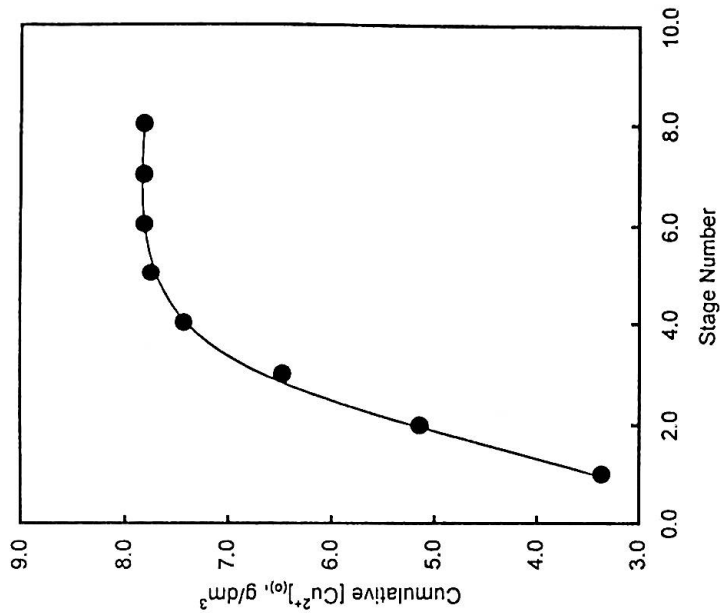


Figure 52. Loading of the organic phase containing BTMPPA in kerosene by Cu(II). $[Cu^{2+}]_{(ini)} = 5.715$ g/dm³ = 0.09 mol/dm³, Volume of each phase = 100 cm³, $[BTMPPA]_{(o,ini)} = 0.10$ mol/dm³, $pH_{(eq)} = 5.5$, Temp. = 298 K, Shaking time in each stage = 30 min. At every stage, aqueous phase is renewed, (Table XXXVIII).

Eq. (82) states that $\log D_C$ vs $(\text{pH}_{(\text{eq})} + 1.2 \log [\text{H}_2\text{A}_2]_{(\text{o,eq})})$ plot will be a straight line of unity slope and its intercept will be equal to $\log K_{\text{ex}}$. Such a plot is shown in Fig. 50 (Table XXXVI). The Least Squares slope and intercept of the line are 1.11 and -3.15 , respectively with correlation coefficient of 0.992. Therefore, the apparent extraction equilibrium constant at 298 K is equal to $10^{-3.15}$ compared to $10^{-2.30}$ for Fe^{3+} extraction from 0.10 mol/dm^3 sulphate medium by BTMPPA [This work] at 298 K.

The data on the variation of distribution ratio of Cu(II) on temperature are given in Table XXXVII for $\text{pH}_{(\text{eq})}$ values of 4.75 and 5.1 for $[\text{BTMPPA}]_{(\text{o,ini})} = 0.10 \text{ mol/dm}^3$. The variation of distribution ratio of Cu(II) on temperature is displayed in Fig. 51 at the said two different experimental parameters. In both cases under investigation, $\log D$ vs. $(1/T) \times 10^3, \text{ K}^{-1}$ plots are straight lines. With the help of Eq.(76), the apparent enthalpy change for the extraction reaction (ΔH – values) have been calculated from the slope of the lines. Average ΔH value is 27.3 kJ/mol with a variation of ± 0.5 . The positive ΔH value suggests that the extraction of Cu(II) from sulphate medium is endothermic in nature as in the case of Fe(III) extraction by BTMPPA [This work].

The loading of Cu(II) in 0.10 mol/dm^3 BTMPPA solution has been examined. The loading results are tabulated in Table XXXVIII for $[\text{BTMPPA}]_{(\text{o,ini})}$ of 0.10 mol/dm^3 . The cumulative concentration of copper(II) in the organic phase have been plotted against the number of stages in Fig. 52. It is seen that 0.10 mol/dm^3 BTMPPA is saturated with 7.812 g/dm^3 (0.123 mol/dm^3) Cu(II). Therefore, the molar ratio of Cu(II) to BTMPPA in the saturated complex is 1:0.81 and this value is lower than that obtained from the extractant dependence study (1:1.2). Thus the extraction mechanism near saturation is altered. It has been early reported

[127, 203, 290] that if $0.0001\text{--}0.001\text{ mol/dm}^3$ Cu(II) is extracted by about 0.10 mol/dm^3 BTMPPA, then the extracted species is $\text{CuA}_2\cdot\text{H}_2\text{A}_2$. In this study around 0.015 mol/dm^3 Cu(II) has been used in the extraction and in such a condition the extracted species is $\text{CuHSO}_4 \cdot 0.7\text{ H}_2\text{A}_2$ which is changed to a composition of $\text{CuHSO}_4 \cdot 0.31\text{ H}_2\text{A}_2$ at saturation with Cu(II). It is therefore concluded that the solvation number in the extracted complex depends largely on Cu(II) loadings in the organic phase and is decreased with increasing Cu(II) loading in the organic phase. The loading capacity of BTMPPA towards Cu(II) is $13.47\text{ g Cu(II)} / 100\text{ g BTMPPA}$.

The stripping abilities of H_2SO_4 , HNO_3 and HCl solutions for the extracted complex have been examined. The results are given in Table H. It is seen that 0.01 mol/dm^3 acid solutions are not so effective. Solutions of 0.10 mol/dm^3 H_2SO_4 , HCl and HNO_3 are almost equally effective; 77.9%, 81.8% and 81.8% Cu(II) are stripped, respectively, in a single stage. However, the effectiveness of stage-stripping is better for the sulphuric acid solution. 97.7%, 95% and 93.7% copper(II) are stripped by 0.10 mol/dm^3 H_2SO_4 , HCl and HNO_3 solutions, respectively, in three stages. Even better results are obtained with 1.0 mol/dm^3 acid solutions. 99.6%, 96.9% and 97% Cu(II) are stripped by 1.0 mol/dm^3 H_2SO_4 , HCl and HNO_3 solutions, respectively, in three stages. From these results, it is concluded that almost quantitative amount of Cu(II) extracted into the organic phase can be stripped off by 1.0 mol/dm^3 H_2SO_4 in three stages.

When Cu^{2+} (0.9 g/dm^3) is extracted from 0.50 mol/dm^3 sulphate medium of $\text{pH}_{(\text{ini})} = 4.0$ by 0.30 mol/dm^3 BTMPPA dissolved in different diluents, then the value of distribution ratio (D) is found to decrease in the

Table H. Stripping of Cu(II) loaded organic phase by different acid solutions. $[\text{Cu}^{++}]_{(\text{o},\text{ini})} = 1.5155 \text{ g/dm}^3$, $[\text{BTMPPA}]_{(\text{o},\text{ini})}^{\text{free}} = 0.025 \text{ mol/dm}^3$, equilibration time = 15 min, Temp. = 298 K, O/A = 1/1 (o = 25 cm³)

Stripping agent	Concentration mol/dm ³	Stripping stage number	Concentration of Cu(II) in aqueous phase, g/dm ³	% Stripped	Cumulative % Cu ²⁺ stripped
H ₂ SO ₄	1.00	1	1.21	79.8	79.8
		2	0.23	15.2	95.0
		3	0.07	4.6	99.6
	0.10	1	1.18	77.9	77.9
		2	0.25	16.5	94.4
		3	0.05	3.3	97.7
	0.01	1	0.83	54.8	-
	HCl	1.00	1	1.27	83.8
			2	0.16	10.5
			3	0.04	2.6
	0.10	1	1.24	81.8	81.8
		2	0.17	11.2	93.0
		3	0.03	2.0	95.0
	0.01	1	0.26	17.1	17.1
		2	0.22	14.5	31.6
		3	0.10	6.6	38.2
		4	0.06	4.0	42.2
HNO ₃	1.00	1	1.34	88.4	88.4
		2	0.10	6.6	95.0
		3	0.03	2.0	97.0
	0.10	1	1.24	81.8	81.8
		2	0.13	8.6	90.4
		3	0.05	3.3	93.7

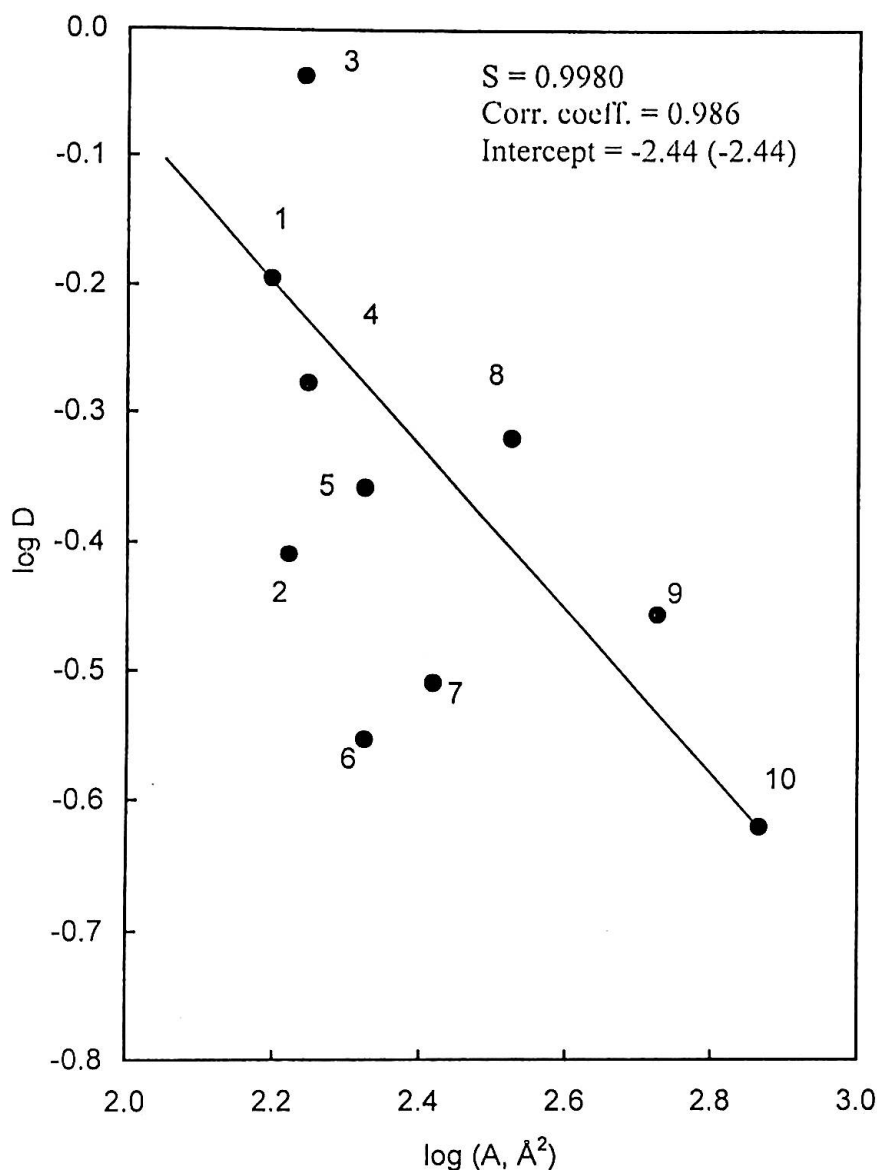


Figure 53. Correlation between distributions ratios of copper(II) in different diluents and the cross-sectional area of BTMPPA molecule at the interfaces. Extraction conditions: $[\text{Cu}^{2+}]_{(\text{a.ini})} = 0.8953 \text{ g/dm}^3$, $\text{pH}_{(\text{ini})} = 4$, $[\text{BTMPPA}]_{(\text{o})} = 0.30 \text{ mol/dm}^3$, $\text{Temp.} = 298 \text{ K}$, $\text{time} = 15 \text{ min}$, $[\text{SO}_4^{2-}] = 0.50 \text{ mol/dm}^3$. Cross-sectional area measurement condition: Aqueous phase = $0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ ($\text{pH} = 0.8$). 1. CCl_4 , 2. $\text{Cy-C}_6\text{H}_{12}$, 3. $\text{ClCH}_2\text{CH}_2\text{Cl}$, 4. $n\text{-C}_6\text{H}_{14}$, 5. $\text{C}_6\text{H}_5\text{CH}_3$, 6. kerosene, 7. C_6H_6 , 8. CHCl_3 , 9. $n\text{-I-C}_7\text{H}_{15}\text{OH}$, 10. $n\text{-I-C}_6\text{H}_{13}\text{OH}$ (Table XXXIX).

following order (cf. Table XXXIX) : 1,2-dichloroethane ($D = 0.92$) > carbon tetrachloride ($D = 0.64$) > n-hexane ($D = 0.53$) > chloroform ($D = 0.48$) > toluene ($D = 0.44$) > cyclohexane ($D = 0.39$) > 1-heptanol ($D = 0.35$) > benzene ($D = 0.31$) > kerosene ($D = 0.28$) > 1-hexanol ($D = 0.24$). These values of D in the logarithmic form have been plotted against the logarithm of the cross-sectional area (A , $\text{\AA}^2$) of BTMPPA molecules adsorbed at the interface of a diluent / $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ ($\text{pH} = 0.8$) [This work, interfacial tension investigation] in Fig. 53. Out of ten points, a very poor six point fit correlation is obtained. This failure to correlate D with A is attributed to the difference in the interfaces used in A measurements ($\text{pH} = 0.8$) and in D measurements ($\text{pH} = 4$). When interfacial conditions are kept constant, then it has been found [this work : iron (III) extraction] that a very good correlation is obtained between D and A . The correlated line has a slope of about 0.6. In the case of D2EHPA [137], a sharp correlation was obtained between the D of TiO^{2+} extraction and the cross-sectional area of D2EHPA. The extraction characteristics of BTMPPA is not so much dependent on the diluent used to constitute the organic phase.

CONCLUSIONS

The following conclusions have been drawn from this study:

1. 98.9% bis-2,4,4-trimethylpentylphosphinic acid (BTMPPA) can be obtained from as-received Cyanex 272 Extractant containing ~ 84% BTMPPA following a published procedure involving the formation of micro-emulsion phase. The product is colorless and has a density of 0.9152 g/cm^3 , refractive index of 1.4566, viscosity of 120 mN/m and water solubility of $4.65 \times 10^{-5} \text{ g mol/dm}^3$ (13.5 mg/dm^3) at 25°C .
2. BTMPPA can be oxidised to orthophosphate by heating with a large excess of concentrated HNO_3 (70%) – HClO_4 (70%) mixture of ratio 2:1 for 1 h. The orthophosphate so produced can be quantitatively estimated by the molybdenum blue colorimetric method at 830 nm. The method is very sensitive with the molar extinction coefficient of $\sim 2.6 \times 10^4 \text{ dm}^3/\text{mol cm}$. The reproducibility of the technique developed is quite good with a standard deviation of 1.89%. The method can be also applied in the estimations of purified Cyanex 302 and Cyanex 301 with good reproducibility.
3. The distribution of BTMPPA between kerosene and 0.10 mol/dm^3 (Na^+ , H^+) Cl^- medium gives the values of acid dissociation constant (K_a), distribution coefficient (K_d) and dimerization constant (K_2) of BTMPPA as 5.52×10^{-4} , 53 and 190, respectively.

4. Density and viscosity of each BTMPPA - diluent (n-hexane / cyclohexane / benzene / toluene / chloroform / carbon tetrachloride / 1,2-dichloroethane / 1-heptanol) mixture deviate from the ideal values (either positive or negative deviation is observed for a particular diluent system). This indicates that there exists interaction between BTMPPA and the diluent used to make up the extractant solution (organic phase). The excess molar volume (V_m^E) is positive for CCl_4 , CHCl_3 , DCE and 1-heptanol systems; whereas, it is negative for C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, n- C_6H_{14} and Cy- C_6H_{12} system over the almost entire mole fraction region of respective diluent. The excess viscosity (η^E) is negative; whereas, the excess Gibbs free energy change of activation of flow (ΔG^E) is positive over the entire mole fraction region of respective diluents used in the investigation. The Grunberg - Nissan interaction parameter (d) is positive for all diluent systems under investigation and the value is increased with increasing mole fraction of the diluent upto 0.80-0.95 and then falls to zero at $x_{\text{l.mol}}^{\text{di}} = 1$. The Cu^{2+} and Fe^{3+} - extraction data with BTMPPA cannot be correlated with the d values. Metal ion extraction characteristics of BTMPPA in different diluents cannot be explained by the interaction parameter or excess properties; other factors play roles.

5. The cross-sectional areas of BTMPPA molecule adsorbed at the 0.50 mol/dm³ H_2SO_4 (pH = 0.8) – diluent (CCl_4 / DCE / n- C_6H_4 / $\text{C}_6\text{H}_5\text{CH}_3$ / cy- C_6H_{12} / kerosene / C_6H_6 / CHCl_3 / 1- $\text{C}_7\text{H}_{15}\text{OH}$ / 1- $\text{C}_6\text{H}_{13}\text{OH}$) interface have been measured from the interfacial tension data and found to vary in the order; CCl_4 (157 Å²) < cy-

C_6H_{12} ($166 \text{ \AA}^2$) < 1,2-DCE ($174 \text{ \AA}^2$) < $n\text{-C}_6\text{H}_{14}$ ($176 \text{ \AA}^2$) < $\text{C}_6\text{H}_5\text{CH}_3$ ($211 \text{ \AA}^2$) = kerosene ($211 \text{ \AA}^2$) < C_6H_6 ($262 \text{ \AA}^2$) < CHCl_3 ($335 \text{ \AA}^2$) < $1\text{-C}_7\text{H}_{15}\text{OH}$ ($532 \text{ \AA}^2$) < $1\text{-C}_6\text{H}_{13}\text{OH}$ ($734 \text{ \AA}^2$). The cross-sectional areas obtained for different systems for interfaces formed by $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ ($\text{pH} = 0.8$) can be correlated with Fe^{3+} -extraction data with BTMPPA provided the extraction is carried out under similar condition ie, at $\text{pH} 0.80$.

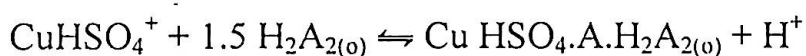
6. Iron(III) can be extracted by BTMPPA dissolved in kerosene over a wide range of conditions: $[\text{Fe}^{3+}] = 1.29 - 100 \text{ mmol/dm}^3$ or more, $\text{pH}_{(\text{ini})} = 1.25 - 2.25$ or more and $[\text{BTMPPA}] = 0.025 - 0.20 \text{ mol/dm}^3$ or higher. The equilibration time is 25 min. With increasing $[\text{Fe}^{3+}]$ and $[\text{SO}_4^{2-}]$ in the aqueous phase and a lowering of pH of the aqueous phase, $[\text{BTMPPA}]$ in the organic phase and temperature, the distribution ratio of Fe^{3+} decreases. The pH , $[\text{BTMPPA}]$ and $[\text{SO}_4^{2-}]$ dependences of distribution ratio (D), (2, 1 and -1 , respectively) suggest that the extraction occurs via the following reaction:



which has an equilibrium constant of $10^{-2.3}$ and ΔH value of $(30 \pm 0.7) \text{ kJ/mol}$. The loading of BTMPPA by Fe^{3+} shows that the extraction equilibrium reaction near saturation does not alter from that mentioned above. The loading capacity is $9.6 \text{ g Fe}^{3+} / 100 \text{ g BTMPPA}$. The extracted complex can be stripped by 0.50 mol/dm^3 sulphuric acid solution in 3-stages with cumulative stripping efficiency of 99%. A five-stage stripping removes 99.8% Fe^{3+} from

the organic phase. HCl and HNO₃ are not so effective as stripping agents.

7. Copper(II) can be extracted by BTMPPA dissolved in kerosene over a wide range of condition ; $[\text{Cu}^{2+}] = 7.3 - 73 \text{ mmol/dm}^3$, $\text{pH} = 3.86 - 5.45$ or more and $[\text{BTMPPA}] = 0.05 - 0.30 \text{ mol/dm}^3$ or more. The equilibration time is less than 15 min. With increasing $[\text{Cu}^{2+}]$ in the aqueous phase and lowering of pH, $[\text{BTMPPA}]$ and temperature, the distribution ratio (D) of Cu^{2+} decreases. The pH, $[\text{BTMPPA}]$ and $[\text{SO}_4^{2-}]$ dependences of D (1, 1.2 and 0.0, respectively) suggest that the reaction occurs via the following reactions:



among which 60% Cu^{2+} is extracted by the first reaction and the rest by the second reaction. The apparent extraction equilibrium constant is $10^{-3.15}$ and ΔH is $(27.3 \pm 0.5) \text{ kJ/mol}$. The solvation number of the extracted complex is decreased with increasing Cu^{2+} - loading in the organic phase. The loading capacity is $13.47 \text{ g Cu}^{2+} / 100 \text{ g BTMPPA}$. The extracted Cu^{2+} -complex can be stripped quantitatively by 1 mol/dm^3 sulphuric acid solution in three-stages. The distribution ratio (D) is found to be dependent on the diluent used. The D-values in different diluents are poorly correlated with the cross-sectional area (A) of BTMPPA molecules at interfaces.

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Table I. Data for the construction of calibration curve for the estimation phosphorous spectrophotometrically by the molybdenum blue method (Fig. 3)

Wave length, nm	Concentration of phosphorus, mg/dm ³	Absorbance
830	0.25	0.22
	0.50	0.42
	0.75	0.62
	1.00	0.84
	1.25	1.12
	1.50	1.26

Table II. Data for the construction of calibration curve for the estimation Fe³⁺ spectrophotometrically by the thiocyanate method (Fig. 4)

Wave length, nm	Conc. of Fe ³⁺ g/dm ³	Absorbance
480	0.001	0.15
	0.002	0.30
	0.003	0.45
	0.004	0.60
	0.005	0.75
	0.006	0.90

Table III. Data for drawing the potentiometric (pH-metric) titration curves of Cyanex 272 and BTMPPA. $[\text{NaOH}] = 0.20 \text{ mol/dm}^3$ in 75% 2-propanol in water, volume of Cyanex 272 solution in 75% 2-propanol taken for titration = 20 cm^3 (a), as-received Cyanex 272, composition of extractant = $2 \text{ g} / 20 \text{ cm}^3$ 75% 2-propanol; (b) purified Cyanex 272 or BTMPPA, composition of extractant = $2.63 \text{ g} / 20 \text{ cm}^3$ 25% 2-propanol. Cyanex 272 or BTMPPA was equilibrated with equal volume of $1 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ for 1 h at 303 K before use (Fig. 5)

As-received Cyanex 272		Purified Cyanex 272 or BTMPPA	
Vol. of NaOH added, ml cm^3	pH	Vol. of NaOH added, ml cm^3	pH
0.00	3.21	0.00	4.00
1.60	4.11	0.50	4.70
1.40	4.20	1.00	4.90
1.60	4.24	1.50	5.00
1.80	4.28	2.00	5.10
2.00	4.40	3.00	5.24
2.20	4.50	5.00	5.40
2.40	4.55	7.00	5.50
2.60	4.60	10.00	5.60
3.00	4.67	15.00	5.80
4.00	4.82	20.00	6.00
5.00	4.97	25.00	6.20
6.00	5.09	30.00	6.40
8.00	5.30	32.50	6.50
10.00	5.40	35.00	6.68
12.00	5.52	37.50	6.90
14.00	5.61	40.00	7.07
16.00	5.72	41.00	7.20
18.00	5.82	42.00	7.40
20.00	5.92	43.00	7.62
22.00	6.00	44.00	8.20
24.00	6.12	44.50	9.00
26.00	6.24	45.00	10.20
28.00	6.37	45.50	11.20
30.00	6.52	46.00	12.00
31.00	6.61	46.50	12.40
32.00	6.71	47.00	12.50
33.00	6.81	48.00	12.67
33.20	6.84	49.00	12.95
33.40	6.88	50.00	12.80
33.60	7.00		
33.80	7.17		
34.00	7.23		
34.20	7.27		
34.50	7.32		
35.00	7.37		
35.50	7.48		
35.70	7.55		
35.90	8.00		
36.10	8.80		
36.30	10.00		
36.50	11.10		
36.70	12.00		
36.90	12.30		
37.50	12.50		
40.00	12.98		

Table IV. Data for determination of solubility of BTMPPA in water at 298 K (Fig. 6).

Apparent concentration of BTMPPA $\times 10^5$ mol/dm ³	pH	Hydrogen ion activity $\times 10^6$
1	6.20	0.62
2	5.62	2.40
3	5.38	4.20
4	5.22	6.00
5	5.14	7.20
6	5.11	7.80
7	5.08	8.25
8	5.05	8.80
9	5.04	9.15
10	5.02	9.55

Table V. Data for the distribution of BTMPPA between aqueous NaCl solution and kerosene in relation to $[H^+]$. $\mu = 0.10 \text{ mol/dm}^3$ (Na^+ , H^+) Cl^- , Temp. = $(303 \pm 1) \text{ K}$ (Fig. 7)

[BTMPP A], mol/dm^3	$\log[H^+]$	$C_{HA} \times$ 10^4 , mol/dm^3	D	Experimental log D	$\log[H^+]$	Theoretical log D
0.05	-2.00	1.98	251	2.40	-2.0	2.38
	-2.35	2.22	224	2.35	-2.5	2.32
	-2.50	2.49	200	2.30	-3.0	2.19
	-2.80	2.49	200	2.30	-3.5	1.92
	-3.00	3.14	158	2.20	-4.0	1.53
	-3.20	3.94	126	2.10	-4.5	1.08
	-3.40	4.95	100	2.00	-5.0	0.59
	-3.50	6.22	79	1.90	-5.5	0.10
	-3.70	7.80	63	1.80		
	-3.87	12.25	40	1.60		
	-4.10	17.13	28	1.45		
0.10	-1.30	3.15	316	2.50	-2.0	2.48
	-1.70	3.15	316	2.50	-2.5	2.44
	-2.00	3.30	302	2.48	-3.0	2.32
	-2.37	3.54	282	2.45	-3.5	2.09
	-2.60	3.97	252	2.40	-4.0	1.72
	-2.80	4.45	224	2.35	-4.5	1.28
	-3.00	4.76	209	2.32	-5.0	0.80
	-3.23	6.27	158	2.20	-5.5	0.30
	-3.50	7.88	126	2.10		
	-3.70	10.36	79	1.90		
	-3.90	15.60	63	1.80		
	-4.15	24.50	40	1.60		
0.20	-1.40	4.47	447	2.65	-2.0	2.62
	-1.80	4.68	427	2.63	-2.5	2.57
	-2.05	4.90	407	2.61	-3.0	2.45
	-2.40	5.62	355	2.55	-3.5	2.21
	-2.70	6.30	316	2.50	-4.0	1.83
	-3.00	7.07	282	2.45	-4.5	1.38
	-3.28	9.97	200	2.30	-5.0	0.90
	-3.50	13.13	151	2.18	-5.5	0.41
	-3.80	19.80	100	2.00		
	-4.00	29.82	66	1.82		
	-4.25	49.00	40	1.60		

Table VI. Data for the distribution of BTMPPA between aqueous NaCl solution and kerosene in relation to its concentration in the aqueous phase. $\mu = 0.10 \text{ mol/dm}^3$ (Na^+, H^+) Cl^- , Temp. = $(303 \pm 1) \text{ K}$ (Fig. 8)

pH_{eq}	$C_{\text{HA}_{(\text{a.m})}}$, mol/dm^3	$C_{\text{HA}_{(\text{eq})}} \times 10^4$, mol/dm^3	$\log C_{\text{HA}}$	D	Experimental $\log D$	$\log C_{\text{HA}}$	Theoretical $\log D$
4	0.2500	31.62	-2.50	78	1.89	-2.0	2.40
	0.1250	22.89	-2.64	56	1.75	-2.5	1.93
	0.0625	13.80	-2.83	47	1.65	-3.0	1.51
	0.0315	10.00	-3.00	30	1.48	-3.5	1.20
	0.0158	6.650	-3.18	22	1.35	-4.0	1.02
	0.0079	4.081	-3.39	18	1.26	-4.5	0.94
	0.0040	2.650	-3.58	14	1.15	-5.0	0.91
	0.0020	1.608	-3.89	12	1.06		
	0.0012	1.000	-4.00	11	1.04		
	0.0006	0.562	-4.25	10	0.98		
	0.0003	0.316	-4.50	9	0.93		
3	0.45000	10.000	-3.00	447	2.65	-2.0	3.61
	0.25100	6.600	-3.18	339	2.53	-2.5	3.12
	0.11600	4.470	-3.35	245	2.39	-3.0	2.64
	0.05500	3.160	-3.50	174	2.24	-3.5	2.20
	0.02800	2.500	-3.63	120	2.08	-4.0	1.86
	0.01800	1.700	-3.77	105	2.02	-4.5	1.64
	0.00800	1.100	-3.96	71	1.85	-5.0	1.55
	0.00300	0.590	-4.23	50	1.70		
	0.00150	0.302	-4.52	49	1.69		
	0.00076	0.166	-4.79	41	1.61		
	0.00035	0.100	-5.00	34	1.53		

Table VII. Data for the density (ρ), viscosity (η), excess molar volume (V_m^E), excess viscosity (η^E), change of Gibbs free energy of activation of flow (ΔG^E) and the Grunberg-Nissan interaction parameter (d) for BTMPPA (2)+ various diluent (1) mixtures at 298.15 K and atmospheric pressure (Figs. 9-12 & 14-21)

X_1, vol	$X_1^{\text{di}}, \text{mol}$	$10^{-3} \times \rho, \text{g/dm}^3$	$\eta, \text{mPa.s}$	$\ln \eta$	$10^{-3} \times V_m^E, \text{dm}^3/\text{mol}$	$\eta^E, \text{mPa.s}$	$\Delta G^E, \text{kJ/mol}$	d
i. n-hexane (1) + BTMPPA (2)								
0.000	0.0000	0.9152	120.000	4.7875	0.00	00.0	000.0	0.00
0.022	0.0987	0.9100	89.320	4.4922	-0.38	-18.86	0.913	3.34
0.042	0.1765	0.9052	69.680	4.2439	-0.64	-29.19	1.581	3.55
0.073	0.2746	0.8985	47.910	3.8693	-1.25	-39.22	2.251	3.66
0.143	0.4476	0.8821	23.620	3.1621	-2.00	-42.80	3.257	4.45
0.270	0.6420	0.8542	9.432	2.2441	-3.48	-33.72	3.951	5.70
0.354	0.7262	0.8358	5.982	1.7887	-4.18	-27.09	4.031	6.84
0.360	0.7300	0.8348	5.931	1.7802	-4.20	-26.68	4.062	6.97
0.445	0.7960	0.8129	3.390	1.2208	-4.08	-21.32	3.588	7.45
0.517	0.8384	0.7945	2.461	0.9006	-3.82	-17.18	3.353	8.45
0.550	0.8555	0.7850	2.122	0.7523	-3.45	-15.47	3.210	8.89
0.676	0.9097	0.7494	1.221	0.1997	-2.45	-8.90	2.515	10.61
0.680	0.9111	0.7484	1.203	0.1848	-2.40	-9.74	2.496	10.68
0.841	0.9623	0.7008	0.504	-0.6852	-1.00	-4.31	0.930	8.34
0.921	0.9825	0.6785	0.368	-0.9997	-0.63	-2.02	0.374	6.35
0.927	0.9841	0.6764	0.360	-0.0217	-0.57	-1.84	0.337	6.19
0.960	0.9967	0.6605	0.305	-1.1874	-0.30	-0.38	0.054	2.07
1.0000	1.0000	0.6552	0.297	-1.2140	0.00	0.00	0.00	0.00
ii. Cyclohexane (1) + BTMPPA (2)								
0.0000	0	0.9152	120.000	4.7875	0.00	00.0	000	0.00
0.0221	0.1098	0.9121	97.920	4.5842	0.11	-9.00	1.067	3.42
0.0367	0.1822	0.9098	85.000	4.4426	0.12	-13.30	1.749	3.68
0.0785	0.3325	0.9044	59.340	4.0833	-0.16	-21.06	2.931	4.17
0.1486	0.5050	0.8953	32.700	3.4873	-0.47	-27.15	3.744	4.69
0.2419	0.6519	0.8826	16.560	2.8069	-0.75	-25.79	3.900	5.34
0.3473	0.7568	0.8695	8.757	2.1698	-0.95	-21.10	3.533	5.92
0.3533	0.7617	0.8687	8.623	2.1544	-0.95	-20.67	3.547	6.05
0.4941	0.8510	0.8489	4.302	1.4590	-0.80	-14.34	2.747	6.62
0.5224	0.8636	0.8452	3.779	1.3294	-0.76	-13.36	2.537	6.56
0.5790	0.8895	0.8365	3.032	1.1092	-0.65	-11.03	2.241	6.90
0.6711	0.9226	0.8233	2.188	0.7829	-0.54	-7.91	1.719	7.29
0.6799	0.9255	0.8220	2.102	0.7428	-0.54	-7.67	1.626	7.08
0.7930	0.9573	0.8056	1.489	0.3981	-0.42	-4.49	1.009	7.35
0.8486	0.9686	0.7985	1.301	0.2631	-0.34	-3.33	0.746	7.22
0.9187	0.9850	0.7870	1.052	0.0507	-0.25	-1.63	0.319	5.98
0.9206	0.9883	0.7840	0.998	-0.0020	-0.15	-1.29	0.209	4.46
0.9603	0.9930	0.7803	0.950	-0.0513	-0.13	-0.78	0.111	3.68
1.0000	1.0000	0.7738	0.895	-0.1109	0.00	0.00	0.000	0.00
iii. benzene (1) + BTMPPA (2)								
0.000	0.0000	0.9152	120.000	4.7875	0.00	00.00	0.000	0.00
0.019	0.1178	0.9145	93.820	4.5413	-0.04	-12.12	1.241	3.63

0.041	0.2304	0.9137	71.320	4.2671	-0.08	-21.17	2.306	3.94
0.078	0.3732	0.9122	46.062	3.8299	-0.11	-29.38	3.378	4.35
0.149	0.5517	0.9095	20.765	3.0332	-0.18	-33.36	3.976	4.71
0.246	0.6956	0.9059	8.438	2.1327	-0.23	-28.51	3.665	4.84
0.341	0.7840	0.9020	4.430	1.4883	-0.20	-21.96	3.138	5.01
0.358	0.7966	0.9012	4.061	1.4014	-0.17	-20.83	3.065	5.11
0.430	0.8411	0.8982	2.952	1.0824	-0.15	-16.62	2.754	5.58
0.513	0.8809	0.8947	2.165	0.7724	-0.13	-12.66	2.374	6.15
0.520	0.8838	0.8944	2.106	0.7447	-0.12	-12.37	2.333	6.17
0.666	0.9333	0.8882	1.332	0.3133	-0.09	-7.24	1.605	7.02
0.681	0.9375	0.8876	1.290	0.2546	-0.09	-6.78	1.555	7.29
0.800	0.9656	0.8824	0.940	-0.0618	-0.05	-3.77	0.948	7.81
0.841	0.9738	0.8807	0.830	-0.1485	-0.04	-2.90	0.682	6.99
0.921	0.9878	0.8773	0.678	-0.3382	-0.03	-1.38	0.270	4.16
0.931	0.9896	0.8768	0.661	-0.3652	-0.03	-1.19	0.186	3.40
0.960	0.9942	0.8754	0.631	-0.4079	-0.01	-0.67	0.088	2.12
1.0000	1.0000	0.8736	0.6045	-0.5025	0.00	0.00	0.000	0.00

iv. toluene (1) + BTMPPA (2)

0.000	0	0.9152	120.000	4.7875	0.00	00.00	000	0.00
0.021	0.1117	0.9141	88.230	4.4799	0.00	-18.43	0.971	2.95
0.041	0.2037	0.9130	66.680	4.1999	0.01	-29.00	1.675	3.12
0.073	0.3198	0.9114	43.900	3.7819	-0.03	-37.90	2.390	3.28
0.146	0.4972	0.9078	20.430	3.0170	-0.04	-40.18	3.079	3.60
0.241	0.6533	0.9026	9.197	2.2188	-0.03	-32.77	3.251	4.16
0.345	0.7579	0.8972	4.844	1.5777	-0.04	-24.63	3.005	4.70
0.357	0.7674	0.8966	4.562	1.5177	-0.04	-23.77	2.965	4.78
0.502	0.8571	0.8891	2.218	0.7966	-0.06	-15.41	2.159	5.01
0.519	0.8649	0.8883	2.075	0.7299	-0.08	-14.62	2.117	5.04
0.672	0.9241	0.8803	1.252	0.2247	-0.08	-8.37	1.429	5.73
0.681	0.9269	0.8797	1.219	0.1980	-0.06	-8.07	1.404	5.76
0.841	0.9692	0.8712	0.778	-0.2510	-0.04	-3.46	0.641	5.65
0.921	0.9857	0.8670	0.650	-0.4307	-0.04	-1.62	0.297	5.50
0.928	0.9871	0.8665	0.633	-0.4572	-0.02	-1.46	0.239	4.60
0.960	0.9931	0.8647	0.589	-0.5293	0.01	-0.79	0.099	2.74
1.000	1.0000	0.8626	0.557	-0.5852	0.00	0.0	00	0.00

v. chloroform (1) + BTMPPA (2)

0.0000	0.0000	0.9152	120.000	4.7875	0.00	00.00	000	0.00
0.018	0.1271	0.9249	90.020	4.5000	0.34	-14.80	1.342	3.60
0.033	0.2117	0.9328	75.090	4.3186	0.54	-19.62	2.238	4.05
0.076	0.3912	0.9553	50.440	3.9207	1.08	-22.83	4.038	5.24
0.136	0.5499	0.9850	30.020	3.4018	2.00	-24.29	5.106	6.41
0.233	0.7028	1.0313	11.910	2.4773	3.36	-24.13	4.930	7.13
0.310	0.7739	1.0640	6.921	1.9345	4.25	-20.63	4.486	7.60
0.340	0.8002	1.0760	5.613	1.7250	5.22	-18.80	4.288	7.90
0.353	0.8091	1.0853	5.202	1.6490	4.68	-18.14	4.195	8.00
0.400	0.8378	1.1128	3.942	1.3716	3.95	-15.98	3.814	8.18
0.498	0.8852	1.1730	2.458	0.8993	2.60	-11.79	3.103	8.83
0.517	0.8924	1.1856	2.301	0.8333	2.22	-11.09	2.995	9.05
0.666	0.9394	1.2733	1.350	0.3001	1.40	-6.43	2.033	10.37
0.679	0.9426	1.2825	1.280	0.2468	1.19	-6.12	1.919	10.25
0.840	0.9762	1.3779	0.818	-0.2008	0.68	-2.56	0.980	12.41
0.920	0.9890	1.4273	0.638	-0.4494	0.36	-1.22	0.402	10.03
0.931	0.9905	1.4356	0.615	-0.4861	0.20	-1.06	0.312	8.56
0.960	0.9947	1.4543	0.568	-0.5656	0.08	-0.60	0.122	4.50
1.000	1.0000	1.4784	0.539	-0.6180	0.00	0.0	00	0.00

vi. carbontetrachloride (1) + BTMPPA (2)

0.000	0.0000	0.9152	120.000	4.7875	0.00	0.0	00	0.00
0.020	0.1192	0.9299	98.300	4.5880	-0.70	-7.50	1.228	3.64
0.037	0.2010	0.9404	83.190	4.4211	-0.23	-12.87	1.983	3.83
0.066	0.3155	0.9577	66.360	4.1951	0.75	-18.06	2.958	4.25
0.135	0.5037	0.9977	36.060	3.5851	2.65	-23.95	4.074	5.03
0.234	0.6763	1.0581	19.270	2.9585	4.83	-20.19	4.706	6.73
0.338	0.7689	1.1049	12.880	2.5556	7.18	-15.55	4.790	8.57
0.354	0.7808	1.1153	11.730	2.4621	6.90	-15.28	4.685	8.69
0.395	0.8099	1.1425	9.498	2.2511	6.38	-14.05	4.464	9.21
0.502	0.8600	1.2049	5.932	1.7803	4.90	-11.65	3.771	9.90
0.516	0.8741	1.2261	4.951	1.5995	4.50	-10.95	3.448	9.82
0.666	0.9286	1.3290	2.263	0.8166	3.18	-6.92	1.936	8.50
0.680	0.9325	1.3412	2.124	0.7533	2.78	-6.82	1.800	8.25
0.841	0.9717	1.4605	1.255	0.2271	1.28	-3.02	0.710	6.70
0.905	0.9841	1.5071	1.076	0.0732	0.90	-1.73	0.380	5.80
0.921	0.9869	1.5222	1.040	0.0392	0.57	-1.43	0.300	5.50
0.960	0.9937	1.5518	0.961	-0.0398	0.36	-0.70	0.126	4.00
1.000	1.0000	1.5838	0.9088	-0.0956	0.00	0.0	00	0.00

vii. 1,2-dichloroethane (1) + BTMPPA (2)

0.000	0.0000	0.9152	120.000	4.7875	0.00	0.00	0.000	0.00
0.010	0.0747	0.9162	93.300	4.5380	1.50	-17.79	0.528	1.80
0.021	0.1457	0.9191	79.060	4.3702	1.81	-23.57	1.197	2.54
0.039	0.2376	0.9245	61.570	4.1201	1.69	-30.10	1.954	2.92
0.069	0.3715	0.9345	42.120	3.7405	1.59	-33.59	2.971	3.53
0.142	0.5680	0.9574	20.090	3.0002	1.50	-32.19	3.869	4.37
0.241	0.7166	0.9887	9.021	2.1995	1.42	-25.55	3.769	5.02
0.337	0.8017	1.0188	5.212	1.6509	1.38	-19.21	3.360	5.66
0.349	0.8105	1.0229	4.990	1.6075	1.36	-18.38	3.344	5.86
0.501	0.8887	1.0705	2.678	0.9850	1.30	-11.37	2.528	6.80
0.515	0.8942	1.0750	2.603	0.9566	1.29	-10.79	2.496	7.08
0.670	0.9417	1.1245	1.597	0.4681	1.17	-6.13	1.613	7.72
0.679	0.9439	1.1275	1.578	0.4561	1.15	-5.89	1.594	7.98
0.840	0.9767	1.1849	1.087	0.0834	0.60	-2.47	0.801	9.50
0.921	0.9893	1.2148	0.931	-0.0714	0.32	-1.13	0.430	11.43
0.929	0.9906	1.2190	0.891	-0.1154	0.23	-1.01	0.321	8.97
0.960	0.9948	1.2292	0.825	-0.1923	0.21	-0.58	0.139	5.58
1.000	1.0000	1.2456	0.7808	-0.2471	0.00	0.00	0.00	0.00

viii. 1-heptanol (1) + BTMPPA (2)

0.000	0.0000	0.9152	120.000	4.7875	0.00	0.00	0.000	0.00
0.020	0.0832	0.9130	103.000	4.6347	0.18	-7.50	0.387	1.30
0.038	0.1509	0.9107	92.760	4.5300	0.50	-10.01	0.743	1.56
0.080	0.2814	0.9055	72.970	4.2900	1.05	-14.90	1.310	1.75
0.146	0.4338	0.8971	51.940	3.9500	1.86	-18.52	1.773	1.93
0.249	0.5979	0.8848	33.450	3.5100	2.42	-18.27	2.000	2.22
0.337	0.6948	0.8790	24.290	3.1900	1.18	-16.37	1.912	2.39
0.361	0.7164	0.8772	22.650	3.1201	1.02	-15.54	1.887	2.47
0.503	0.8190	0.8657	14.880	2.7000	0.24	-11.60	1.503	2.65
0.522	0.8300	0.8640	13.870	2.6232	0.20	-10.96	1.462	2.72
0.664	0.8984	0.8516	10.180	2.3204	-0.13	-7.23	0.959	2.78
0.682	0.9056	0.8501	9.875	2.2900	-0.18	-6.71	0.951	2.86
0.841	0.9596	0.8356	7.316	1.9900	-0.33	-3.11	0.436	2.80
0.921	0.9811	0.8282	6.395	1.8657	-0.35	-1.57	0.279	2.10
0.930	0.9834	0.8271	6.297	1.8400	-0.32	-1.40	0.147	1.87
0.960	0.9909	0.8236	6.029	1.7965	-0.20	-0.82	0.064	1.08
1.000	1.0000	0.8191	5.8082	1.7590	0.00	0.00	0.000	0.00

Table VIII. Kendal-Monroe (theoretical) viscosities of BTMPPA + diluent mixtures at various mole fractions of different diluents used in the study (Fig. 13).

Mole fraction of diluent, $x_{l,mol}^{di}$	η , mN/m	$\ln \eta$	Mole fraction of diluent, $x_{l,mol}^{di}$	η , mN/m	$\ln \eta$
1. n-hexane			2. cyclohexane		
0.00	120.00	4.78	0.00	120.00	4.78
0.05	105.10	4.65	0.05	106.09	4.66
0.10	91.48	4.52	0.10	93.30	4.53
0.15	79.10	4.37	0.15	81.58	4.40
0.20	67.88	4.22	0.20	70.89	4.26
0.25	57.79	4.05	0.25	61.17	4.11
0.30	48.74	3.88	0.30	52.39	3.96
0.35	40.69	3.70	0.35	44.49	3.79
0.40	33.58	3.51	0.40	37.43	3.62
0.45	27.35	3.31	0.45	31.15	3.43
0.50	21.95	3.09	0.50	25.62	3.24
0.55	17.30	2.85	0.55	20.79	3.03
0.60	13.37	2.59	0.60	16.60	2.81
0.65	10.08	2.31	0.65	13.02	2.57
0.70	7.39	2.00	0.70	10.00	2.30
0.75	5.21	1.65	0.75	7.48	2.01
0.80	3.51	1.25	0.80	5.43	1.69
0.85	2.23	0.80	0.85	3.79	1.33
0.90	1.31	0.27	0.90	2.52	0.92
0.95	0.68	-0.38	0.95	1.57	0.45
1.00	0.30	-1.20	1.00	0.89	-0.12
3. benzene			4. toluene		
0.00	120.00	4.78	0.00	120.00	4.78
0.05	105.69	4.66	0.05	105.62	4.65
0.10	92.57	4.52	0.10	92.43	4.53
0.15	80.59	4.38	0.15	80.40	4.38
0.20	69.68	4.24	0.20	69.45	4.24
0.25	59.81	4.09	0.25	59.55	4.08
0.30	50.91	3.93	0.30	50.63	3.92
0.35	42.95	3.76	0.35	42.66	3.75

0.40	35.86	3.58
0.45	29.60	3.38
0.50	24.11	3.18
0.55	19.35	2.96
0.60	15.26	2.72
0.65	11.79	2.46
0.70	8.89	2.18
0.75	6.51	1.87
0.80	4.60	1.52
0.85	3.10	1.13
0.90	1.97	0.68
0.95	1.16	0.15
1.00	0.60	-0.51

0.40	35.56	3.57
0.45	29.31	3.37
0.50	23.83	3.17
0.55	19.08	2.95
0.60	15.01	2.70
0.65	11.56	2.45
0.70	8.69	2.16
0.75	6.33	1.84
0.80	4.45	1.49
0.85	2.98	1.09
0.90	1.88	0.63
0.95	1.09	0.08
1.00	0.56	-0.58

5. chloroform

0.00	120.00	4.78
0.05	105.59	4.65
0.10	92.38	4.53
0.15	80.32	4.38
0.20	69.36	4.24
0.25	59.45	4.08
0.30	50.52	3.92
0.35	42.54	3.75
0.40	35.45	3.57
0.45	29.19	3.37
0.50	23.72	3.16
0.55	18.97	2.94
0.60	14.91	2.70
0.65	11.47	2.44
0.70	8.61	2.15
0.75	6.26	1.83
0.80	4.39	1.48
0.85	2.93	1.07
0.90	1.80	0.59
0.95	1.06	0.06
1.00	0.54	-0.58

6. carbon tetrachloride

0.00	120.00	4.78
0.05	106.11	4.66
0.10	93.33	4.53
0.15	81.63	4.40
0.20	70.94	4.26
0.25	61.23	4.11
0.30	52.45	3.96
0.35	44.55	3.79
0.40	7.49	3.62
0.45	31.22	3.44
0.50	25.69	3.24
0.55	20.85	3.04
0.60	16.66	2.81
0.65	13.08	2.57
0.70	10.05	2.30
0.75	7.52	2.01
0.80	5.46	1.69
0.85	3.82	1.34
0.90	2.54	0.93
0.95	1.58	0.46
1.00	0.91	-0.09

7. 1,2-dichloroethane

0.00	120.00	4.78
0.05	105.96	4.66

8. 1-heptanol

0.00	120.00	4.78
0.05	108.92	4.69

0.10	92.04	4.53
0.15	81.22	4.39
0.20	70.45	4.25
0.25	60.68	4.11
0.30	51.85	3.95
0.35	43.93	3.78
0.40	36.85	3.60
0.45	30.58	3.42
0.50	25.07	3.22
0.55	20.26	3.00
0.60	16.11	2.78
0.65	12.57	2.53
0.70	9.59	2.26
0.75	7.12	1.96
0.80	5.12	1.63
0.85	3.53	1.26
0.90	2.31	0.84
0.95	1.41	0.34
1.00	0.98	-0.23

0.10	98.54	4.59
0.15	88.85	4.48
0.20	79.81	4.38
0.25	71.41	4.27
0.30	63.62	4.15
0.35	56.41	4.03
0.40	49.77	3.91
0.45	43.67	3.77
0.50	38.10	3.64
0.55	33.02	3.49
0.60	28.41	3.34
0.65	24.26	3.19
0.70	20.53	3.02
0.75	17.20	2.84
0.80	14.25	2.65
0.85	11.66	2.45
0.90	9.41	2.24
0.95	7.46	2.01
1.00	5.81	1.76

Table IX. The effect of sulphuric acid concentration on interfacial tension of H_2SO_4 -BTMPPA / kerosene interface. $[\text{BTMPPA}]_{(0)} = 0.06 \text{ mol/dm}^3$ in Kerosene, temperature = $(298 \pm 0.5) \text{ K}$; aqueous phase : $[\text{H}_2\text{SO}_4] = \text{variable}$, $[\text{SO}_4^{2-}] = 1.00 \text{ mol/dm}^3$, equilibration time = 1 h, settling time = 24 h (Fig. 22).

$[\text{H}_2\text{SO}_4], \text{ mol/dm}^3$	$-\log [\text{H}_2\text{SO}_4]$	Interfacial tension (γ) mN/m
1.00	0.00	38.5
0.50	0.30	38.0
0.30	0.52	35.0
0.20	0.70	32.0
0.10	1.00	29.0
0.05	1.30	27.0
0.03	1.52	26.5
0.02	1.70	26.0
0.01	2.00	25.2

Table X. Variation of interfacial tension (γ) with BTMPPA concentration in kerosene- H_2SO_4 system (Fig. 23)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; pH = 0.8

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in kerosene

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	+ log [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	54.0			
3×10^{-7}	-6.52	54.0			
2×10^{-6}	-5.70	54.0			
5×10^{-6}	-5.30	53.8			
2×10^{-5}	-4.70	52.0			
5×10^{-5}	-4.30	49.8			
2×10^{-4}	-3.70	47.2			
5×10^{-4}	-3.30	45.3	-4.5	6.3×10^{-6}	3×10^{-2}
2×10^{-3}	-2.70	43.0			
5×10^{-3}	-2.30	41.0			
2×10^{-2}	-1.70	39.5			
5×10^{-2}	-1.30	38.0			
2×10^{-1}	-0.70	37.0			
5×10^{-1}	-0.30	36.7			
1.0	-0.00	36.5			

Table XI. Variation of interfacial tension (γ) with BTMPPA concentration in cyclohexane- H_2SO_4 system (Fig. 24)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; $\text{pH} = 0.8$

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in cyclohexane

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	+ log [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	52.0			
3×10^{-7}	-6.52	52.0			
2×10^{-6}	-5.70	51.7			
5×10^{-6}	-5.30	51.0			
2×10^{-5}	-4.70	49.0			
5×10^{-5}	-4.30	48.0			
2×10^{-4}	-3.70	44.0			
5×10^{-4}	-3.30	42.0	-5.70	1×10^{-5}	3.2×10^{-2}
2×10^{-3}	-2.70	38.5			
5×10^{-3}	-2.30	36.2			
2×10^{-2}	-1.70	33.0			
5×10^{-2}	-1.30	31.5			
2×10^{-1}	-0.70	29.5			
5×10^{-1}	-0.30	28.5			
1.0	-0.00	28.0			

Table XII. Variation of interfacial tension (γ) with BTMPPA concentration in n-hexane- H_2SO_4 system (Fig. 25)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; $\text{pH} = 0.8$

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in n-hexane

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	+ log [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	58.0			
3×10^{-7}	-6.52	58.0			
2×10^{-6}	-5.70	58.0			
5×10^{-6}	-5.30	57.5			
2×10^{-5}	-4.70	57.0			
5×10^{-5}	-4.30	56.0			
2×10^{-4}	-3.70	54.0			
5×10^{-4}	-3.30	51.5	-5.38	2.82×10^{-5}	3.16×10^{-2}
2×10^{-3}	-2.70	49.0			
5×10^{-3}	-2.30	46.0			
2×10^{-2}	-1.70	43.0			
5×10^{-2}	-1.30	41.8			
2×10^{-1}	-0.70	41.0			
5×10^{-1}	-0.30	40.7			
1.0	-0.00	40.5			

Table XIII. Variation of interfacial tension (γ) with BTMPPA concentration in benzene- H_2SO_4 system (Fig. 26)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; pH = 0.8

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in benzene

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	+ log [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	42.0			
3×10^{-7}	-6.52	42.0			
2×10^{-6}	-5.70	41.5			
5×10^{-6}	-5.30	41.0			
2×10^{-5}	-4.70	40.2			
5×10^{-5}	-4.30	39.5			
2×10^{-4}	-3.70	37.5			
5×10^{-4}	-3.30	36.0	-3.62	2.51×10^{-5}	0.025
2×10^{-3}	-2.70	34.0			
5×10^{-3}	-2.30	32.0			
2×10^{-2}	-1.70	31.0			
5×10^{-2}	-1.30	30.2			
2×10^{-1}	-0.70	29.0			
5×10^{-1}	-0.30	28.4			
1.0	-0.00	28.0			

Table XIV. Variation of interfacial tension (γ) with BTMPPA concentration in toluene- H_2SO_4 system (Fig. 27)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; pH = 0.8

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in toluene

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	+ log [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	46.0			
3×10^{-7}	-6.52	46.0			
2×10^{-6}	-5.70	46.0			
5×10^{-6}	-5.30	45.5			
2×10^{-5}	-4.70	45.0			
5×10^{-5}	-4.30	44.0			
2×10^{-4}	-3.70	42.2			
5×10^{-4}	-3.30	40.0	-4.50	3.16×10^{-5}	5.0×10^{-2}
2×10^{-3}	-2.70	38.0			
5×10^{-3}	-2.30	36.0			
2×10^{-2}	-1.70	34.0			
5×10^{-2}	-1.30	33.4			
2×10^{-1}	-0.70	32.8			
5×10^{-1}	-0.30	32.2			
1.0	-0.00	32.0			

Table XV. Variation of interfacial tension (γ) with BTMPPA concentration in chloroform- H_2SO_4 system (Fig. 28)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; pH = 0.8

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in chloroform

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	+ log [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	47.0			
3×10^{-7}	-6.52	46.7			
2×10^{-6}	-5.70	45.8			
5×10^{-6}	-5.30	44.6			
2×10^{-5}	-4.70	43.0			
5×10^{-5}	-4.30	42.0			
2×10^{-4}	-3.70	40.0			
5×10^{-4}	-3.30	39.0	-2.83	9×10^{-7}	0.158
2×10^{-3}	-2.70	37.5			
5×10^{-3}	-2.30	36.5			
2×10^{-2}	-1.70	34.5			
5×10^{-2}	-1.30	33.5			
2×10^{-1}	-0.70	32.0			
5×10^{-1}	-0.30	31.5			
1.0	-0.00	31.0			

Table XVI. Variation of interfacial tension (γ) with BTMPPA concentration in carbon tetrachloride- H_2SO_4 system (Fig. 29)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; pH = 0.8

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in carbon tetrachloride

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	+ log [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	50.0			
2×10^{-6}	-5.70	50.0			
5×10^{-6}	-5.30	49.5			
2×10^{-5}	-4.70	49.0			
5×10^{-5}	-4.30	47.8			
2×10^{-4}	-3.70	44.0			
5×10^{-4}	-3.30	42.0			
2×10^{-3}	-2.70	37.8	-6.05	2×10^{-5}	0.04
5×10^{-3}	-2.30	35.0			
2×10^{-2}	-1.70	31.8			
5×10^{-2}	-1.30	30.5			
2×10^{-1}	-0.70	29.0			
5×10^{-1}	-0.30	28.4			
1.0	-0.00	28.0			

Table XVII. Variation of interfacial tension (γ) with BTMPPA concentration in 1,2-dichloroethane - H_2SO_4 system (Fig. 30)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; $\text{pH} = 0.8$

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in 1,2-dichloroethane

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	$+\log$ [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	48.0			
2×10^{-6}	-5.70	48.0			
5×10^{-6}	-5.30	48.0			
2×10^{-5}	-4.70	47.0			
5×10^{-5}	-4.30	46.0			
2×10^{-4}	-3.70	44.0			
5×10^{-4}	-3.30	42.0			
2×10^{-3}	-2.70	38.5	-5.43	5×10^{-5}	0.025
5×10^{-3}	-2.30	36.4			
2×10^{-2}	-1.70	33.5			
5×10^{-2}	-1.30	33.0			
2×10^{-1}	-0.70	32.5			
5×10^{-1}	-0.30	32.2			
1.0	-0.00	32.0			

Table XVIII. Variation of interfacial tension (γ) with BTMPPA concentration in 1-heptanol - H_2SO_4 system (Fig. 31)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; pH = 0.8

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in 1-heptanol

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	+ log [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	35.0			
2×10^{-6}	-5.70	35.0			
5×10^{-6}	-5.30	34.8			
2×10^{-5}	-4.70	34.4			
5×10^{-5}	-4.30	34.0			
2×10^{-4}	-3.70	33.2			
5×10^{-4}	-3.30	32.5			
2×10^{-3}	-2.70	32.0	-1.29	7.1×10^{-6}	0.10
5×10^{-3}	-2.30	31.3			
2×10^{-2}	-1.70	30.8			
5×10^{-2}	-1.30	30.0			
2×10^{-1}	-0.70	29.8			
5×10^{-1}	-0.30	29.3			
1.0	0.00	29.0			

Table XIX. Variation of interfacial tension (γ) with BTMPPA concentration in 1-hexanol - H_2SO_4 system (Fig. 32)

Aqueous phase : $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; $\text{pH} = 0.8$

Organic phase : 10^{-7} - 10^0 mol/dm^3 BTMPPA in 1-hexanol

Temperature : $(298 \pm 0.5) \text{ K}$

Phase equilibration time : 60 min

Phase settling time : 24 h

[BTMPPA], mol/dm^3	+ log [BTMPPA]	γ , mN/m	Slope	C_1 , mol/dm^3	C_2 , mol/dm^3
1×10^{-7}	-7.00	34.0			
3×10^{-7}	-6.52	34.0			
2×10^{-6}	-5.70	33.7			
5×10^{-6}	-5.30	33.5			
2×10^{-5}	-4.70	32.3			
5×10^{-5}	-4.30	31.8			
2×10^{-1}	-3.70	30.5			
5×10^{-4}	-3.30	30.0	-1.78	2.51×10^{-6}	0.10
2×10^{-3}	-2.70	29.0			
5×10^{-3}	-2.30	28.1			
2×10^{-2}	-1.70	27.2			
5×10^{-2}	-1.30	26.5			
2×10^{-1}	-0.70	26.2			
5×10^{-1}	-0.30	25.8			
1.0	-0.00	25.7			

Table XX. Rate of extraction of Fe^{3+} by purified Cyanex 272 (BTMPPA) in kerosene. $[\text{Fe}^{3+}]_{(\text{a},\text{ini})} = 13.43 \text{ mmol/dm}^3$, $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$, $\text{pH}_{(\text{ini})} = 2$, $[\text{BTMPPA}]_{(\text{o},\text{ini})} = 0.025 \text{ mol/dm}^3$, $\text{Temp.} = (298 \pm 1) \text{ K}$ (Fig. 33).

Equilibration time, min	$[\text{Fe}^{3+}]_{(\text{a})}, \text{g/dm}^3$	$[\text{Fe}^{3+}]_{(\text{a})}, \text{mmol/dm}^3$
0.50	0.40	7.16
1.00	0.30	5.37
2.00	0.24	4.30
5.00	0.23	4.12
10.00	0.21	3.76
15.00	0.21	3.76
20.00	0.20	3.58
25.00	0.19	3.40
30.00	0.19	3.40
45.00	0.19	3.40

Table XXI. Dependence of extraction of Fe^{3+} by purified Cyanex 272 (BTMPPA) in kerosene on Fe^{3+} concentration. $[\text{BTMPPA}]_{(\text{o},\text{ini})} = 0.20 \text{ mol/dm}^3$, $[\text{SO}_4^{2-}] = 0.20 \text{ mol/dm}^3$, time = 30 min, Temp. = $(298 \pm 1) \text{ K}$, $\text{pH}_{(\text{ini})} = 1.8$ (Fig. 34).

$[\text{Fe}^{3+}]_{(\text{ini})}$, mmol/dm ³	$\log\{[\text{Fe}^{3+}]_{(\text{ini})}$, mol/dm ³ \}	$\text{pH}_{(\text{eq})}$	$[\text{Fe}^{3+}]_{(\text{eq})}$, g/dm ³	$\log\{[\text{Fe}^{3+}]_{(\text{eq})}$, mol/dm ³ \}	$[\text{Fe}^{3+}]_{(\text{o},\text{eq})}$, g/dm ³	D	log D	* log D _C
1.29	-2.89	1.75	0.0035	-4.20	0.0685	19.50	1.29	1.39
2.58	-2.59	1.73	0.0126	-3.65	0.1315	10.47	1.02	1.17
3.87	-2.41	1.73	0.0232	-3.38	0.1930	8.32	0.92	1.07
6.44	-2.19	1.72	0.0575	-2.99	0.3022	5.25	0.72	0.89
12.89	-1.89	1.71	0.1600	-2.54	0.5600	3.63	0.54	0.75
26.85	-1.57	1.69	0.3800	-2.17	1.1200	2.95	0.47	0.75
31.33	-1.50	1.66	0.5400	-2.01	1.2100	2.24	0.35	0.69
64.45	-1.19	1.65	1.3160	-1.63	2.2840	1.73	0.24	0.67
93.98	-1.03	1.63	2.2497	-1.39	2.9813	1.32	0.12	0.66

* The value is given at $\text{pH}_{(\text{eq})}^{\text{const}} = 1.8$, $[\text{BTMPPA}]_{(\text{o},\text{eq})}^{\text{const}} = 0.1 \text{ mol/dm}^3$ and $[\text{SO}_4^{2-}]_{(\text{eq})}^{\text{const}} = 0.20 \text{ mol/dm}^3$: log D_C is calculated using the following relation: $\log D_C = \log D + y (\text{pH}_{(\text{eq})}^{\text{const}} - \text{pH}_{(\text{eq})}) + x (\log[\text{BTMPPA}]_{(\text{o},\text{eq})}^{\text{const}} - \log[\text{BTMPPA}]_{(\text{o},\text{eq})}) + z (\log[\text{SO}_4^{2-}]_{(\text{eq})}^{\text{const}} - \log[\text{SO}_4^{2-}]_{(\text{eq})})$; where, y is the slope of log D_C vs $\text{pH}_{(\text{eq})}$ plot, x is the slope of log D_C vs log [BTMPPA]_(o,eq) plot and z is the slope of log D_C vs log [SO₄²⁻] plot. Here x = 1, y = 2 and z = -1.

Table XXII. Dependence of extraction ratio of Fe^{3+} (extracted) by purified Cyanex 272 or BTMPPA on equilibrium pH. Equilibration time = 30 min, Temp. = 298 K, $[\text{Fe}^{3+}]_{(\text{ini})} = 0.75 \text{ g/dm}^3$ (13.43 mmol/dm³), $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$ (Fig. 35).

$[\text{BTMPPA}]_{(\text{o,ini})}$ mol/dm ³	pH _(ini)	pH _(eq)	$[\text{Fe}^{3+}]_{(\text{eq})}$, g/dm ³	$[\text{Fe}^{3+}]_{(\text{o,eq})}$, g/dm ³	D	log D	$[\text{BTMPPA}]_{(\text{o,eq})}$, mol/dm ³	*log D _C at $[\text{BTMPPA}]_{(\text{o,eq})}$ = $[\text{BTMPPA}]_{(\text{o,ini})}$
0.050	2.76	2.30	0.0425	0.7075	16.60	1.22	0.0373	1.29
	2.65	2.21	0.0550	0.6950	12.59	1.10	0.0376	1.16
	2.50	2.01	0.0800	0.6700	8.31	0.92	0.0380	0.98
	2.00	1.75	0.1750	0.5750	3.31	0.52	0.0397	0.58
	1.75	1.65	0.2400	0.5100	2.13	0.33	0.0409	0.37
	1.52	1.48	0.3600	0.3900	1.07	0.03	0.0430	0.07
	1.40	1.38	0.4400	0.3100	0.71	-0.15	0.0445	-0.12
	1.25	1.25	0.5500	0.2000	0.36	-0.44	0.0464	-0.43
0.025	2.76	2.45	0.0835	0.6665	7.94	0.90	0.0131	1.13
	2.60	2.26	0.1074	0.6426	5.89	0.77	0.0135	0.99
	2.50	2.18	0.1500	0.6000	4.00	0.60	0.0143	0.90
	2.25	1.97	0.1963	0.5537	2.82	0.45	0.0151	0.63
	2.00	1.80	0.2799	0.4701	1.66	0.22	0.0166	0.37
	1.80	1.68	0.3538	0.3962	1.12	0.05	0.0179	0.15
	1.65	1.55	0.4360	0.3140	0.72	-0.14	0.0194	-0.06
	1.52	1.43	0.5172	0.2327	0.45	-0.35	0.0209	-0.29
	1.45	1.37	0.5569	0.1931	0.35	-0.46	0.0215	-0.42

$$*\log D_C = \log D + x [\log [\text{BTMPPA}]_{(\text{o,ini})} - \log [\text{BTMPPA}]_{(\text{o,eq})}]$$

where, x is the slope of log D vs. log [BTMPPA] plot and in this case it is 1.

Table XXIII. Dependence of extraction of Fe^{3+} by purified Cyanex 272 (BTMPPA) in kerosene on extractant concentration. Equilibration time = 30 min, Temp. = 298 K, $[\text{Fe}^{3+}]_{(\text{a},\text{ini})} = 0.75 \text{ g/dm}^3$ (13.43 mmol/dm³), $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$ (Fig. 36).

$\text{pH}_{(\text{ini})}$	$[\text{BTMPPA}]_{(\text{o})}$ mol/dm ³		log $\{[\text{BTMPPA}]_{(\text{o},\text{eq})}$ mol/dm ³ $\}$	$\text{pH}_{(\text{eq})}$	$[\text{Fe}^{3+}]_{(\text{a},\text{eq})}$ g/dm ³	$[\text{Fe}^{3+}]_{(\text{o},\text{eq})}$ g/dm ³	D	log D	$\text{pH}_{(\text{eq})}^{\text{const}}$	log D_{C}
	ini	eq								
1.75	0.150	0.139	-0.86	1.65	0.1200	0.6300	5.25	0.72	1.74	0.85
	0.125	0.114	-0.94	1.68	0.1423	0.6077	4.27	0.63		0.70
	0.100	0.089	-1.05	1.70	0.1589	0.5911	3.71	0.57		0.60
	0.075	0.065	-1.19	1.72	0.1933	0.5567	2.88	0.46		0.45
	0.050	0.041	-1.39	1.73	0.2427	0.5073	2.09	0.32		0.30
	0.025	0.019	-1.72	1.74	0.4011	0.3489	0.87	-0.06		-0.09
2.20	0.150	0.138	-0.86	1.77	0.0600	0.6900	11.48	1.06	1.98	1.46
	0.125	0.113	-0.95	1.79	0.0725	0.6775	9.33	0.97		1.37
	0.100	0.088	-1.06	1.80	0.0738	0.6762	9.12	0.96		1.31
	0.075	0.063	-1.20	1.84	0.0938	0.6562	6.92	0.84		1.10
	0.050	0.039	-1.41	1.87	0.1246	0.6254	5.01	0.70		0.93
	0.025	0.015	-1.82	1.98	0.1803	0.5697	3.16	0.50		0.46

Table XXIV. Dependence of extraction of Fe^{3+} by purified Cyanex 272 in kerosene on sulphate ion concentration. $[\text{Fe}^{3+}]_{(\text{a},\text{ini})} = 0.72 \text{ g/dm}^3$ (12.89 mmol/dm³), $\text{pH}_{(\text{ini})} = 2.35$, equilibration time = 30 min, Temp. = 298 K, $[\text{BTMPPA}]_{(\text{o},\text{ini})} = 0.025 \text{ mol/dm}^3$ (Fig. 37).

$[\text{SO}_4^{2-}]$, mol/dm ³	$\log\{[\text{SO}_4^{2-}]\}$, mol/dm ³	$\text{pH}_{(\text{eq})}$	$[\text{Fe}^{3+}]_{(\text{a},\text{eq})}$, g/dm ³	$[\text{Fe}^{3+}]_{(\text{o},\text{eq})}$, g/dm ³	$[\text{BTMPPA}]_{(\text{o},\text{eq})}$, mol/dm ³	D	log D	*log D _C
0.05	-1.30	2.01	0.1075	0.6125	0.014	5.75	0.76	1.01
0.10	-1.00	2.06	0.1740	0.54600	0.015	3.16	0.50	0.62
0.20	-0.70	2.16	0.2140	0.5060	0.016	2.34	0.37	0.26
0.30	-0.52	2.19	0.2275	0.4925	0.016	2.19	0.34	0.17
0.50	-0.30	2.27	0.2400	0.4800	0.016	2.00	0.30	-0.03
1.00	0.00	2.36	0.2600	0.4600	0.017	1.78	0.25	-0.28

* log D_C is the log D value at constant equilibrium pH of 2.01 and BTMPPA concentration of 0.025 M and is calculated by following relationship:

$$\log D_C = \log D + 2(2.01 - \text{pH}_{(\text{eq})}) + (\log 0.025 - \log [\text{BTMPPA}]_{(\text{o},\text{eq})})$$

Table XXV. Data for estimation of extraction equilibrium constant of Fe^{3+} by BTMPPA : for $\log D_c$ vs. $(2 \text{ pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log [\text{SO}_4^{2-}])$ plot at 298 K (Fig. 38).

$(2 \text{ pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(\text{o,eq})} - \log [\text{SO}_4^{2-}])$	$\log D_c$
3.35	0.47
3.00	0.37
2.66	0.07
2.46	-0.12
2.20	-0.43
2.76	0.15
2.50	-0.06
2.26	-0.29
2.14	-0.42
3.62	1.00
3.54	0.85
3.43	0.75
3.29	0.60
3.09	0.44
2.76	0.04
4.10	1.52
4.01	1.37
3.90	1.36
3.76	1.15
3.55	0.98
3.14	0.50
3.72	1.01
3.42	0.62
3.12	0.26
2.94	0.17
2.72	-0.03
2.42	-0.28

Table XXVI. Dependence of extraction of Fe^{3+} by purified Cyanex 272 in kerosene on temperature. $[\text{Fe}^{3+}]_{(a,ini)} = 0.72 \text{ g/dm}^3$, $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$, equilibration time = 30 min (Fig. 39).

$[\text{BTMPPA}]_{(o,eq)}$, mol/dm^3	$\text{pH}_{(ini)}$	Temp., K	$[\text{Fe}^{3+}]_{(a,eq)}$, g/dm^3	$[\text{Fe}^{3+}]_{(o,eq)}$, g/dm^3	log D	$(1/T) \times 10^3$, K^{-1}	Slope	ΔH , kJ/mol
0.025	1.75	296	0.3080	0.4120	0.13	3.378	-1533	29.37
		303	0.2540	0.4660	0.26	3.300		
		308	0.2280	0.4920	0.33	3.247		
		313	0.2000	0.5200	0.41	3.190		
		318	0.1740	0.5460	0.50	3.140		
0.025	1.65	296	0.3480	0.3720	0.03	3.378	-1600	30.66
		303	0.3070	0.4130	0.13	3.300		
		308	0.2630	0.4570	0.24	3.247		
		313	0.2367	0.4833	0.31	3.190		
		318	0.2000	0.5200	0.41	3.140		
0.05	1.75	296	0.2295	0.4905	0.38	3.378	-1538	29.47
		303	0.1886	0.5314	0.45	3.300		
		308	0.1650	0.5550	0.53	3.247		
		313	0.1419	0.5781	0.61	3.190		
		318	0.1200	0.6000	0.70	3.140		
0.05	1.65	296	0.2554	0.4646	0.26	3.378	-1579	30.25
		303	0.2050	0.5150	0.40	3.300		
		308	0.1740	0.5460	0.50	3.247		
		313	0.1550	0.5650	0.56	3.190		
		318	0.1350	0.5850	0.64	3.140		

Table XXVII. Loading of BTMPPA with Fe^{3+} . $\text{pH}_{(\text{ini})} = 2.4$, equilibration time = 30 min, Temp. = 298 K (Fig. 40).

$[\text{Fe}^{3+}]_{(\text{a,ini})}$, g/dm^3	$[\text{BTMPPA}]_{(\text{o,ini})}$, mol/dm^3	No. of stage	$[\text{Fe}^{3+}]_{(\text{n,eq})}$, g/dm^3	$[\text{Fe}^{3+}]_{(\text{o,eq})}$, g/dm^3	Cumulative $[\text{Fe}^{3+}]_{(\text{o})}$, g/dm^3
1.00	0.10	1	0.07	0.93	0.93
		2	0.15	0.85	1.78
		3	0.22	0.78	2.56
		4	0.30	0.70	3.26
		5	0.39	0.61	3.87
		6	0.50	0.50	4.37
		7	0.65	0.35	4.72
		8	0.78	0.22	4.94
		9	0.90	0.10	5.04
		10	0.96	0.04	5.08
		11	0.98	0.02	5.10
		12	1.00	0.00	5.10
5.00	0.20	1	0.53	4.47	4.47
		2	1.60	3.40	7.87
		3	2.80	2.20	9.07
		4	3.44	1.56	10.63
		5	4.68	0.32	10.95
		6	4.90	0.10	11.05
		7	5.00	0.00	11.05

Table XXVIII. Stripping of Fe^{3+} -BTMPPA complex by aqueous sulphuric acid solution. Equilibration time = 30 min, $[\text{Fe}^{3+}]_{(\text{o.ini})} = 2.21 \text{ g/dm}^3$ (39.56 mmol/dm³), Temp. = 298 K, O/A = 1, free [BTMPPA]_(o,ini) = 0.025 mol/dm³ (Fig. 41).

$[\text{H}_2\text{SO}_4]$, mol/dm ³	$\log\{[\text{H}_2\text{SO}_4]\}$, mol/dm ³	$[\text{Fe}^{3+}]_{(\text{a.eq})}$, g/dm ³	$[\text{Fe}^{3+}]_{(\text{o.eq})}$, g/dm ³	S	log S	Stripping %
2.00	0.30	1.547	0.663	2.33	0.37	70.00
1.50	0.18	1.591	0.619	2.57	0.41	72.00
1.00	0.00	1.724	0.483	3.57	0.55	78.00
0.50	-0.30	1.879	0.331	5.68	0.75	85.00
0.30	-0.52	1.812	0.398	4.55	0.66	82.00
0.20	-0.70	1.768	0.442	4.00	0.60	80.00
0.15	-0.82	1.724	0.486	3.55	0.55	78.00
0.10	-1.00	1.591	0.619	2.57	0.41	72.00

Table XXIX. Stage-wise stripping of Fe^{3+} -BTMPPA complex. Equilibration time = 30 min, $[\text{Fe}^{3+}]_{(\text{o},\text{ini})} = 2.21 \text{ g/dm}^3$, Temp. = 298 K, O/A = 1, free $[\text{BTMPPA}]_{(\text{o},\text{ini})} = 0.025 \text{ mol/dm}^3$, $[\text{H}_2\text{SO}_4] = 0.50 \text{ mol/dm}^3$, aqueous phase being renewed in each stage (Fig. 42).

Stage No.	$[\text{Fe}^{3+}]_{(\text{a},\text{eq})}, \text{ g/dm}^3$	% stripped*	Cumulative % of Fe^{3+} stripped
1	1.879	85.00	85.00
2	0.265	12.00	97.00
3	0.046	2.08	99.08
4	0.012	0.54	99.62
5	0.004	0.18	99.80

* Based on initial amount of Fe^{3+} present in the organic phase.

Table XXX. Data for the correlation between extraction ratio (D) of Fe^{3+} in different diluents of BTMPPA solution and cross-sectional area of BTMPPA molecules at interface at 298 K (Fig. 43).

[BTMPPA], mol/dm ³	pH _(int)	[SO ₄ ²⁻], mol/dm ³	Diluent	A, Å ²	log (A, Å ²)	D	log D
0.025	2.00	0.50	Carbon tetrachloride	157	2.20	0.923	-0.035
			Cyclohexane	166	2.22	0.648	-0.182
			1,2-dichloroethan	174	2.24	0.875	-0.058
			n-hexane	176	2.25	0.705	-0.152
			toluene	211	2.32	0.705	-0.152
			kerosene	211	2.32	0.807	-0.093
			benzene	262	2.42	0.470	-0.327
			chloroform	335	2.53	0.744	-0.128
			n-1-heptanol	532	2.73	0.562	-0.225
			n-1-hexanol	734	2.87	0.596	-0.250
0.200	0.80	0.50	Carbon tetrachloride	157	2.20	0.39	-0.409
			Cyclohexane	166	2.22	0.34	-0.468
			1,2-dichloroethan	174	2.24	0.38	-0.420
			n-hexane	176	2.25	0.35	-0.456
			toluene	211	2.32	0.35	-0.456
			kerosene	211	2.32	0.32	-0.495
			benzene	262	2.42	0.28	-0.552
			chloroform	335	2.53	0.26	-0.585
			n-1-heptanol	532	2.73	0.22	-0.650
			n-1-hexanol	732	2.87	0.21	-0.678

Table XXXI. Dependence of extraction of Cu(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on time. $[\text{Cu}^{2+}]_{(\text{ini})} = 0.9128 \text{ g/dm}^3 = 14.37 \text{ mmol/dm}^3$, $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$, $[\text{BTMPPA}]_{(\text{o,ini})} = 0.065 \text{ mol/dm}^3$, Temp = 298 K, $\text{pH}_{(\text{ini})} = 4.75$ (Fig. 44).

Time, min	Concentration of Cu^{2+} left in the aqueous phase in	
	g/dm^3	mmol/dm^3
0	0.9128	14.37
1	0.8490	13.37
2	0.8020	12.63
5	0.7300	11.50
7	0.6905	10.87
10	0.6522	10.27
12	0.6405	10.09
15	0.6350	10.00
20	0.6350	10.00

Table XXXII. Dependence of extraction of Cu(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on Cu(II) concentration in the aqueous phase. $\text{pH}_{(\text{ini})} = 4.75$, $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$, $[\text{BTMPPA}]_{(\text{o,ini})} = 0.10 \text{ mol/dm}^3$, Temp = 298 K, Equilibration time = 15 min (Fig. 45).

$[\text{Cu}^{++}]_{(\text{ini})}$, mmol/dm ³	$\log\{[\text{Cu}^{++}]_{(\text{ini})}\}$, mol/dm ³	$\text{pH}_{(\text{eq})}$	$[\text{Cu}^{++}]_{(\text{eq})}$		$\log\{[\text{Cu}^{++}]_{(\text{eq})}\}$, mol/dm ³	$[\text{Cu}^{++}]_{(\text{o,eq})}$, g/dm ³	D	log D	*log D _C
			g/dm ³	mmol/dm ³					
7.29	-2.14	3.86	0.2890	4.55	-2.34	0.1746	0.60	-0.22	-0.19
14.60	-1.84	3.78	0.6428	10.01	-2.00	0.2843	0.45	-0.35	-0.23
20.89	-1.68	3.74	0.9612	15.14	-1.82	0.3655	0.38	-0.42	-0.24
29.20	-1.53	3.70	1.4154	22.29	-1.65	0.4388	0.31	-0.51	-0.27
43.80	-1.36	3.66	2.3013	36.24	-1.56	0.4800	0.21	-0.68	-0.40
57.14	-1.24	3.60	3.1047	48.89	-1.31	0.5238	0.17	-0.77	-0.43
73.00	-1.14	3.55	4.0905	64.41	-1.19	0.5450	0.13	-0.89	-0.50

* at $\text{pH}_{(\text{eq})}^{\text{const}} = 3.86$ and $[\text{BTMPPA}]_{(\text{o,eq})}^{\text{const}} = 0.10 \text{ mol/dm}^3$; log D_C is calculated using the following relation :

$$\log D_C = \log D + y(3.86 - \text{pH}_{(\text{eq})}) + x(\log 0.1 - \log [\text{BTMPPA}]_{(\text{o,eq})})$$

where, y and x are pH and extractant dependences which are 1 and 1.2, respectively. $[\text{BTMPPA}]_{(\text{o,eq})}$ can be calculated by the following relation:

$$[\text{BTMPPA}]_{(\text{o,eq})} = [\text{BTMPPA}]_{(\text{o,ini})} - 1.2[\text{Cu}^{++}]_{(\text{o,eq})} \text{ mol/dm}^3$$

Table XXXIII. Dependence of extraction of Cu(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on equilibrium pH in the aqueous phase. $[\text{Cu}^{++}]_{(\text{ini})} = 0.8811 \text{ g/dm}^3 = 13.88 \text{ mmol/dm}^3$, Equilibration time = 15 min, Temp. = 298 K, $[\text{SO}_4] = 0.10 \text{ mol/dm}^3$ (Fig. 46).

$[\text{BTMPPA}]_{(\text{o}, \text{ini})}$, mol/dm ³	pH _(eq)	$[\text{Cu}^{++}]_{(\text{eq})}$, g/dm ³	$[\text{Cu}^{++}]_{(\text{o}, \text{eq})}$, g/dm ³	D	log D	*log D _c
0.05	5.45	0.0801	0.8010	10.00	1.00	1.13
	5.35	0.0965	0.7846	8.13	0.92	1.05
	5.24	0.1330	0.7480	5.62	0.75	0.87
	5.10	0.1769	0.7042	3.98	0.60	0.71
	5.00	0.1905	0.6906	3.62	0.56	0.67
	4.90	0.2510	0.6301	2.51	0.40	0.50
	4.82	0.3016	0.5795	1.92	0.28	0.37
	4.61	0.3749	0.5062	1.35	0.13	0.20
	4.50	0.4257	0.4554	107	0.03	0.10
	4.15	0.5835	0.2976	0.51	-0.29	-0.25
	5.45	0.0394	0.8417	21.36	1.33	1.48
	5.25	0.0558	0.8253	14.79	1.17	1.31
	5.00	0.1029	0.7782	7.56	0.88	1.01
	4.70	0.1936	0.6875	3.55	0.55	0.67
	4.20	0.4156	0.4655	1.12	0.05	0.12
	3.86	0.5678	0.3163	0.56	-0.25	-0.20

* at $[\text{BTMPPA}]_{(\text{o}, \text{eq})} = 0.10 \text{ mol/dm}^3$ and log D_c is calculated by the following formula: $\log D_c = \log D + 1.2 (\log 0.10 - \log$

$\{ [\text{BTMPPA}]_{(\text{o}, \text{eq})}^{\text{const}} \text{ mol/dm}^3 - 1.2 [\text{Cu}^{++}]_{(\text{o}, \text{eq})} \text{ mol/dm}^3 \}$.

Table XXXIV. Dependence of extraction of Cu(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on extractant concentration in the organic phase. $[\text{Cu}^{2+}]_{(\text{ini})} = 0.8811 \text{ g/dm}^3 = 13.88 \text{ mmol/dm}^3$, Equilibration time = 15 min, Temp = 298 K, $[\text{SO}_4] = 0.10 \text{ mol/dm}^3$ (Fig. 47 & 48).

$\text{pH}_{(\text{eq})}$	$[\text{BTMPPA}]_{(\text{o,ini})}$ mol/dm^3	$\log \{[\text{BTMPPA}]_{(\text{o,ini})}\}$ mol/dm^3	$[\text{Cu}^{++}]_{(\text{eq})}$ g/dm^3	D	$[\text{Cu}^{++}]_{(\text{o,eq})}$ g/dm^3	$\log D$	$*[\text{BTMPPA}]_{(\text{o,eq})}$ mol/dm^3	$\log \{[\text{BTMPPA}]_{(\text{o,eq})}\}$ mol/dm^3
5.00	0.050	-1.30	0.2118	3.16	0.6693	0.50	0.0337	-1.47
	0.075	-1.20	0.1279	5.83	0.7532	0.77	0.0572	-1.24
	0.100	-1.00	0.0871	9.12	0.7940	0.96	0.0812	-1.09
	0.150	-0.82	0.0469	17.78	0.8342	1.25	0.1303	-0.89
	0.200	-0.70	0.0323	26.30	0.8488	1.42	0.1799	-0.74
	0.250	-0.60	0.0216	39.81	0.8595	1.60	0.2297	-0.64
	0.300	-0.52	0.0161	53.70	0.8650	1.73	0.2796	-0.55
4.60	0.050	-1.30	0.3899	1.26	0.4912	0.10	0.0384	-1.42
	0.075	-1.12	0.2937	2.00	0.5874	0.30	0.0611	-1.21
	0.100	-1.00	0.1936	3.55	0.6875	0.55	0.0838	-1.08
	0.200	-0.70	0.0889	8.91	0.7922	0.95	0.1813	-0.74
	0.300	-0.52	0.0469	17.78	0.8342	1.25	0.2803	-0.55

* $[\text{BTMPPA}]_{(\text{o,eq})}$, $\text{mol/dm}^3 = [\text{BTMPPA}]_{(\text{o,ini})}$, $\text{mol/dm}^3 - 1.2[\text{Cu}^{++}]_{(\text{o,eq})}$, mol/dm^3

Table XXXV. Dependence of extraction of Cu^{2+} by purified Cyanex 272 (BTMPPA) dissolved in kerosene on sulphate ion concentration in the aqueous phase. $[\text{Cu}^{2+}]_{(\text{ini})} = 0.9234 \text{ g/dm}^3 = 14.14 \text{ mmol/dm}^3$, $[\text{BTMPPA}]_{(\text{o.ini})} = 0.10 \text{ mol/dm}^3$, $\text{pH}_{(\text{ini})} = 4.70$, Equilibration time = 15 min, Temp = 298 K (Fig. 49).

$[\text{SO}_4^{2-}]$, mol/dm^3	$\log\{[\text{SO}_4^{2-}]\}$, mol/dm^3	$\text{pH}_{(\text{eq})}$	$[\text{Cu}^{2+}]_{(\text{eq})}$, g/dm^3	$[\text{Cu}^{2+}]_{(\text{o.eq})}$, g/dm^3	D	log D	*log D _C
0.05	-1.30	3.40	0.7695	0.1539	0.20	-0.70	-0.70
0.10	-1.00	3.62	0.6970	0.2264	0.32	-0.49	-0.73
0.20	-0.70	3.71	0.6643	0.2591	0.39	-0.41	-0.75
0.30	-0.52	3.78	0.6295	0.2909	0.46	-0.34	-0.76
0.50	-0.30	3.84	0.6197	0.3037	0.49	-0.31	-0.80
1.00	0.00	3.94	0.5700	0.3534	0.62	-0.21	-0.80

* at $\text{pH}_{(\text{eq})}^{\text{const}} = 3.4$ and $[\text{BTMPPA}]_{(\text{o.eq})}^{\text{const}} = 0.10 \text{ mol/dm}^3$; log D_C is calculated using the relation :

$$\log D_C = \log D + (3.40 - \text{pH}_{(\text{eq})}) + 1.2 [\log 0.1 - \log [\text{BTMPPA}]_{(\text{o.eq})}]$$

where, $[\text{BTMPPA}]_{(\text{o.eq})}$, mol/dm³ = $[\text{BTMPPA}]_{(\text{o.ini})}$, mol/dm³ - 1.2 $[\text{Cu}^{2+}]_{(\text{o.eq})}$, mol/dm³

Table XXXVI. Data for the evaluation of equilibration constant of copper(II) extraction reaction graphically at 298 K (Fig. 50).

$[\text{BTMPPA}]_{(\text{o,eq})}$, M	$\text{pH}_{(\text{eq})}$	$1.2 \log [\text{BTMPPA}]_{(\text{o,eq})} + \text{pH}_{(\text{eq})}$	$\log D_{\text{Cu}}$
0.0500	5.45	3.89	1.13
	5.35	3.79	1.05
	5.24	3.68	0.87
	5.10	3.54	0.71
	5.00	3.44	0.67
	4.90	3.34	0.50
	4.82	3.26	0.37
	4.61	3.05	0.20
	4.50	2.94	0.10
	4.15	2.59	-0.25
0.1000	5.45	4.25	1.48
	5.25	4.05	1.31
	5.00	3.80	1.01
	4.70	3.50	0.67
	4.20	3.00	0.12
	3.80	2.60	-0.20
0.0337	5.00	3.23	0.50
0.0572		3.51	0.77
0.0812		3.69	0.96
0.1303		3.94	1.25
0.1799		4.11	1.42
0.2297		4.23	1.60
0.2796		4.34	1.73
0.0384	4.60	2.90	0.10
0.0611		3.14	0.30
0.0838		3.31	0.55
0.1813		3.71	0.95
0.2803		3.94	1.25

Table XXXVII. Dependence of extraction of copper(II) by purified Cyanex 272 (BTMPPA) dissolved in kerosene on temperature. $[\text{Cu}^{2+}]_{(\text{ini})} = 0.9234 \text{ g/dm}^3 = 14.54 \text{ mmol/dm}^3$, $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$, $[\text{BTMPPA}]_{(\text{0,ini})} = 0.10 \text{ mol/dm}^3$, Equilibration time = 15 min (Fig. 51).

$\text{pH}_{(\text{ini})}$	Temp, °C	Temp, K	$(1/T) \times 10^3, \text{K}^{-1}$	$[\text{Cu}^{++}]_{(\text{eq})}, \text{g/dm}^3$	$[\text{Cu}^{++}]_{(\text{0,eq})}, \text{g/dm}^3$	D	log D
4.75	21	294	3.401	0.7695	0.1539	0.20	-0.70
	25	298	3.356	0.7447	0.1787	0.24	-0.62
	30	303	3.300	0.7103	0.2131	0.30	-0.52
	35	308	3.247	0.6891	0.2343	0.34	-0.47
	40	313	3.195	0.6740	0.2494	0.37	-0.43
	43	316	3.165	0.6457	0.2777	0.47	-0.37
5.10	21	294	3.401	0.7049	0.2185	0.31	-0.51
	25	298	3.356	0.6840	0.2394	0.35	-0.45
	30	303	3.300	0.6457	0.2777	0.43	-0.37
	35	308	3.247	0.6115	0.3119	0.51	-0.29
	40	313	3.195	0.5881	0.3352	0.57	-0.24
	43	316	3.165	0.5596	0.3638	0.65	-0.19

Table XXXVIII. Loading of the organic phase containing BTMPPA in kerosene by Cu(II), $[\text{Cu}^{++}]_{(\text{ini})} = 5.715 \text{ g/dm}^3 = 0.09 \text{ mol/dm}^3$, Volume of each phase = 100 cm^3 , $\text{pH}_{(\text{eq})} = 5.5$, $[\text{BTMPPA}]_{(\text{o,ini})} = 0.10 \text{ mol/dm}^3$, temp = 298 K, Shaking time in each stage = 30 min. At every stage, aqueous phase is renewed (Fig. 52).

Stage number	$[\text{Cu}^{++}]_{(\text{eq})}, \text{g/dm}^3$	$[\text{Cu}^{++}]_{(\text{o,eq})}, \text{g/dm}^3$	Cumulative $[\text{Cu}^{++}]_{(\text{o,eq})}, \text{g/dm}^3$
1	2.3495	3.3655	3.3655
2	3.9370	1.7780	5.1435
3	4.3815	1.3335	6.4770
4	4.7625	0.9525	7.4295
5	5.3915	0.3175	7.7470
6	5.6515	0.0635	7.8105
7	5.7000	0.0015	7.8120
8	5.7150	0.0000	7.8120

Table XXXIX. Data for showing correlation between distributions ratios of copper(II) in different diluents and the cross-sectional area of BTMPPA molecule at the interface. Extraction conditions: $[\text{Cu}^{2+}]_{(\text{ini})} = 0.8953 \text{ g/dm}^3$, $\text{pH}_{(\text{ini})} = 4$, $[\text{BTMPPA}]_{(\text{o})} = 0.30 \text{ mol/dm}^3$, Temp. = 298 K, time = 15 min, $[\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3$. Cross-sectional area measurement condition: Aqueous phase = 0.5 mol/dm³ H₂SO₄ (pH = 0.8) (Fig. 53).

Diluent	Cross-sectional area, A in Å ²	log (A, Å ²)	$[\text{Cu}^{2+}]_{(\text{eq})}$, g/dm ³	$[\text{Cu}^{2+}]_{(\text{o,eq})}$, g/dm ³	D	log D
CCl ₄	157	2.196	0.5459	0.3494	0.64	-0.194
Cy-C ₆ H ₁₂	166	2.220	0.6441	0.2512	0.39	-0.409
1,2-DCE	174	2.241	0.4663	0.4290	0.92	-0.036
n-C ₆ H ₁₄	176	2.246	0.5852	0.3101	0.53	-0.276
C ₆ H ₅ CH ₃	211	2.324	0.6217	0.2736	0.44	-0.357
Kerosene	211	2.324	0.6995	0.1958	0.28	-0.553
C ₆ H ₆	262	2.418	0.6834	0.2119	0.31	-0.509
CHCl ₃	335	2.525	0.6049	0.2904	0.48	-0.319
n-1-C ₇ H ₁₅ OH	532	2.726	0.6632	0.2321	0.35	-0.456
n-1-C ₆ H ₁₃ OH	734	2.866	0.7220	0.1733	0.24	-0.620

APPENDIX

LIST OF PUBLICATIONS

1. R.K. Biswas, M.A. Habib and H.P. Singha, Colorimetric estimation and some physicochemical properties of purified Cyanex 272. Hydrometallurgy (ELSEVIER), 76 (2005) 97-104.
2. R.K. Biswas and H.P. Singha, Purified Cyanex 272: its interfacial adsorption and extraction characteristics towards iron (III), Hydrometallurgy (ELSEVIER), in press.
3. R.K. Biswas, H.P. Singha, Densities, viscosities and excess properties of bis-3,4,4-trimethylpentylphosphinic acid (Cyanex 272) + diluent binary mixtures. J. Mol. Liq. (ELSEVIER) (communicated).
4. R K Biswas, H P Singha, Solvent extraction of Cu(II) by purified Cyanex 272. Ind. J. Chem. Tech. (Communicated).

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Colorimetric estimation and some physicochemical properties of purified Cyanex 272

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Abstract

A technique for the colorimetric estimation of purified Cyanex 272 has been developed. The technique consists of the digestion of pure sample or its aqueous solution with concentrated nitric acid (70%)–perchloric acid (70%) mixture for 1 h. The oxidizing mixed acid quantitatively converts Cyanex 272 to a clear solution of orthophosphate that can be easily estimated by the molybdenum-blue colorimetric method at 830 nm. The method is sensitive with a molar extinction coefficient of $\sim 2.6 \times 10^4$ and reproducible within $\pm 2\%$. Applying this technique of analysis, the dimerization constant (K_2), distribution or partition coefficient (K_d) and ionization constant (K_a) of the purified Cyanex 272 (bis-2,4,4-trimethylpentylphosphinic acid, BTMPPA) have been estimated to be 190, 53 and 5.52×10^{-4} , respectively.

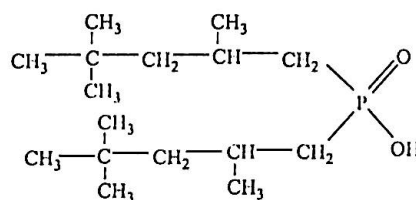
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Keywords: Cyanex 272; Acid digestion; Colorimetric estimation; Ionization constant; Dimerization constant; Partition coefficient

1. Introduction

The extractant, Cyanex 272, is a proprietary but technical grade item of Cytec Canada Inc. (CCI). Its active component is bis-2,4,4-trimethylpentylphos-

phinic acid, which may be abbreviated as BTMPPA. The structure of BTMPPA is as follows:



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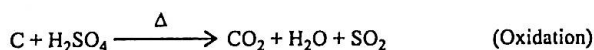
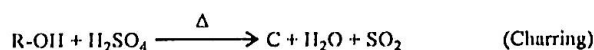
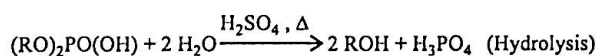
This technical grade extractant has been used since 1983 and found to be very effective for the extractive separation of Co(II) from Ni(II) (Preston, 1983; Danesi

et al., 1984; Xun and Golding, 1987; Cho and Dai, 1994; Chou and Beckstead, 1990; etc.). Some reports (Sole and Hiskey, 1991; Cao et al., 1992; Wang and Li, 1994; Zou et al., 1994; etc) are also available for possible separations of other cation pairs.

For better understanding of the extraction processes involving Cyanex 272, it is necessary to know about its basic physicochemical constants. To know about these constants, it is necessary to purify Cyanex 272, at least up to 98% BTMPPA. Moreover, it is important to develop a convenient colorimetric method for its estimation to study its distribution in aqueous and organic phases.

Organo-phosphoric acids such as di-2-ethylhexyl-phosphoric acid (D2EHPA), di-octyl-phosphoric acid (DOPA), etc., and tri-esters of phosphoric acid like tributyl phosphate (TBP) can be easily estimated by a nonsophisticated colorimetric method after digestion with concentrated sulphuric acid (Islam and Biswas, 1981; Ulyanov and Sviridova, 1963). On digestion, orthophosphate is formed, which can be estimated by the molybdenum-blue method at 830 nm (Vogel, 1961). This sort of handy analytical technique permits the determination of dimerization, partition and ionization constants of organo-phosphoric acids (Biswas et al., 2000; Biswas et al., 2003).

But it is found by preliminary experiments that organo-phosphinic acid cannot be quantitatively converted to orthophosphate even on digestion for 6 h with concentrated sulphuric acid. It appears, therefore, that concentrated sulphuric acid can easily eliminate alkyl group of organo-phosphoric acid in which it is bonded to oxygen atom and consequently orthophosphate is formed by hydrolysis. During the latter period of digestion, the alkyl group is charred and oxidized by concentrated sulphuric acid to form a clear solution. The probable reactions occurring during the digestion of a dialkyl phosphoric acid with concentrated sulphuric acid are as follows:



In the case of organo-phosphinic acid, hydrolysis cannot take place because of the fact that alkyl radical is directly bonded to P in this type of compounds. In other words, there are only two oxygen atoms in phosphinic acid and so to convert it to orthophosphate, a strong oxidizing environment is needed. Previously, no work has been done on this line.

Martinez et al. (1993) estimated the $\text{p}K_{\text{a}}$ value of BTMPPA by potentiometric titration method and the data was analyzed both graphically and numerically using the LETAGROP-ZETA program. The reported $\text{p}K_{\text{a}}$ value is 5.42 for 75% ethanol–25% H_2O system. Using Hammett equation, they obtained the $\text{p}K_{\text{a}}$ value of 3.38 for water system. On the other hand, Kean et al. (1995) used the technique of inductively coupled plasma (ICP)–atomic emission spectroscopy for estimation of phosphinic acid and determined the distribution ratio (K_{d}), dimerization constant (K_2) and dissociation constant K_{a} of BTMPPA as 43.8 ± 1.8 , 184.3 ± 16.1 and $(6.6 \pm 0.7) \times 10^{-4}$ ($\text{p}K_{\text{a}} = 3.15$), respectively, for chloroform–water system. Values of these constants will obviously depend on the nature of the diluent in the organic phase and the composition of aqueous phase (ionic strength and anion present) as found in the case of D2EHPA (Huang and Juang, 1986).

This paper reports a technique for easy colorimetric estimation of BTMPPA and some physicochemical constants such as K_2 , K_{d} and K_{a} for BTMPPA in kerosene/0.1 M (H^+ , Na^+) Cl^- system.

2. Experimental technique

2.1. Reagents

Cyanex 272 was provided by Cytec Canada Inc. (CCI). It was purified by the method of microemulsion formation of Zhengshui et al. (1995). Local kerosene was distilled to collect the fraction distilling over 200–260 °C. The collected fraction was mostly aliphatic. Ammonium molybdate (BDH, 99%), hydrazine sulphate (BDH, 99%), hydrochloric acid (BDH, 35.4%), perchloric acid (Merck-India, >70%), nitric acid (Merck, >70%), *n*-hexane (Merck, 95%), sodium hydroxide (Fluka, 97%), sodium sulphate (BDH,

99%), sodium carbonate (Merck, 99.5%), etc. were used without further purifications.

2.2. Analytical

Purities of Cyanex 272 and its purified form were justified by the pH-metric titration in propanol–water system. The density was determined by a Density-meter (model DMA-5000 Anton Paar, Austria). The refractive index was determined by an ABBE refractometer (ATAGO Type-3, No-21402, Japan). For pH-metric titration, a Mettler Toledo 320 pH-meter was used. For viscosity measurement an Ostwald viscometer and a thermostatic water bath were used. The orthophosphate was estimated by the ammonium molybdate–hydrazine sulphate (molybdenum blue) colorimetric method at 830 nm (Vogel, 1961).

2.3. Titration procedure

Titration of as-received and purified Cyanex 272 were carried out as suggested in the technical brochure of Cyanex 272 extractant (Cytec Canada Inc.). Stirring during titration was done by a magnetic stirrer. Extractants were first equilibrated with 1 M H_2SO_4 for 1 h at 303 K.

2.4. Purification of Cyanex 272

Purification of Cyanex 272 was carried out by the middle phase microemulsion method of Zhengshui et al. (1995). Twenty-percent Cyanex 272 solution in *n*-hexane was mixed with an equal volume of aqueous solution containing 0.22 mol/L Na_2SO_4 and NaOH to react with all the acid present in Cyanex 272. This was agitated for 3 h in a separating funnel and stood overnight for phase separation. In such a condition, a three-phase system resulted. The middle phase was isolated and stripped with 6 M HCl to return the extractant in the acidic form to the organic phase. The organic phase was washed with distilled water until no chloride ion could be detected in water. The organic phase was then dehydrated by anhydrous sodium sulphate, decanted and the diluent from the decanted solution was distilled out gently for *n*-hexane recovery and the trace amount of *n*-hexane was removed under vacuum at 80 °C for 8 h to get the purified extractant.

2.5. Distribution procedure

Several aqueous solutions (50 mL), each containing variable amounts of NaCl and HCl, were prepared so that they contained 0.10 M (Na^+ , H^+) Cl^- . The organic phase was 0.05 and 0.10 M purified Cyanex 272 (BTMPPA) in kerosene. Kerosene was saturated with water prior to equilibration to avoid change in volumes of the aqueous and organic phases due to saturation of organic phase by water during equilibration. Equal volumes (20 mL) of the organic and aqueous phases were taken into a 125 mL separating funnel and agitated for at least 12 h at ambient temperature of (30 ± 1) °C. After equilibration, the separatory funnels were left for at least 72 h for complete phase separation by allowing the small organic droplets in the aqueous phase to enter the organic phase. The phases were then disengaged very carefully. The equilibrium hydrogen ion concentration in the aqueous phase was measured. The concentration of BTMPPA in the aqueous phase was determined by estimating colorimetrically the amount of orthophosphate produced by applying a developed technique.

To determine the distribution ratio at constant equilibrium pH of 4.0 and 3.0, organic solutions containing different amount of BTMPPA (0.0003–0.25 M) were prepared. Two sets of 250 mL aqueous phase containing 0.1 M (Na^+ , H^+) Cl^- were prepared and their pH values adjusted to pH 4 and 3 by anhydrous Na_2CO_3 . Aliquots of 20 mL of each phase were taken and agitated as above. The pH of the aqueous phase during equilibration was checked and adjusted from time to time.

2.6. Procedure for solubility measurement

Solubility of purified Cyanex 272 was determined by the method reported by Xun et al. (1990) following the pH measurement technique.

3. Results and discussion

Fig. 1(a) shows the pH-metric titration curve of Cyanex 272 as received from CCI. The curve shows three inflexions. The first inflexion in lower pH region is for H_2SO_4 neutralization, the second is for neutralization of Cyanex 272 (BTMPPA) and the first proton

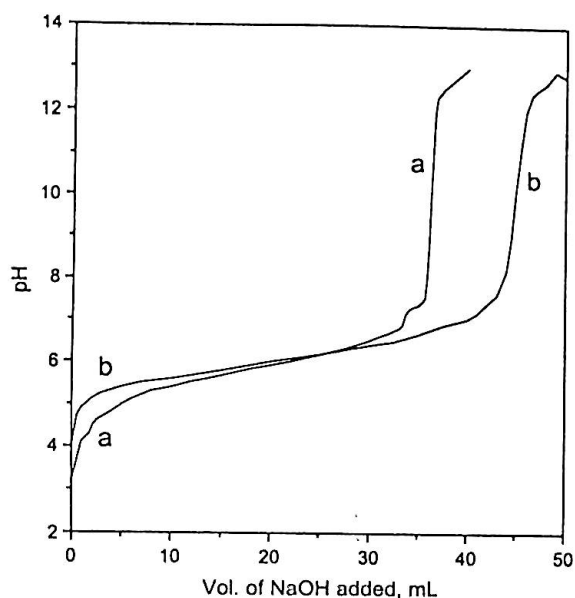


Fig. 1. Potentiometric (pH-metric) titration curves of Cyanex 272 in 75% propanol. $[\text{NaOH}] = 0.20 \text{ M}$, Cyanex solution = 20 mL; (a), as-received Cyanex (2 g); (b), purified Cyanex (2.63 g).

of organo-phosphorous acid ($\text{R-PO}(\text{OH})_2$) and the third one is for the neutralization of the second proton of $\text{RPO}(\text{OH})_2$. The volume of NaOH solution at the equivalence points was determined by the second derivative method. From these volumes of NaOH, as-received Cyanex 272 was found to contain 84.4% BTMPPA and 4.6% $\text{RPO}(\text{OH})_2$. So the sample contains 11% non-acidic impurities.

The titration curve of purified Cyanex 272 (BTMPPA) under similar condition is shown in Fig. 1(b). The curve shows only one inflexion and from the volume of NaOH solution at the mid-point of inflexion (determined by the second derivative method), the purity of Cyanex 272 is calculated to be 98.9% based on mono-acid content. Some physical

characteristics of as-received and purified Cyanex 272 are compared in Table 1.

In order to determine K_2 , K_d and K_a values of BTMPPA, a technique has been developed for the conversion of organo-derivatives of phosphinic acid into ortho-phosphate followed by its easy colorimetric estimation using the well-known molybdenum-blue method. To develop this technique, a known amount of purified Cyanex 272 is heated in a beaker covered with a watch glass on a sand bath for a definite period with H_2SO_4 , HCl , HNO_3 , HClO_4 or HNO_3 – HClO_4 mixture, and the heated mass is used for phosphate estimation. Results are given in Table 2. It is found that the concentrated H_2SO_4 and HCl are ineffective (<4% conversion). On the other hand, the concentrated HNO_3 and HClO_4 are better than H_2SO_4 and HCl . It is found that the mixture of concentrated (70%) HNO_3 and (70%) HClO_4 can convert phosphinic acid to ortho-phosphoric acid. To get quantitative conversion, a ratio of HNO_3 to HClO_4 equal to 2 was needed. This mixture of HNO_3 and HClO_4 converts not only Cyanex 272 (BTMPPA) but also Cyanex 301 (2,4,4-tri-methylpentyl-dithio-phosphinic acid) and Cyanex 302 (2,4,4-tri-methylpentyl-thio-phosphinic acid) to ortho-phosphate.

To determine the reproducibility of the developed technique, the error analysis in estimation has been done for purified Cyanex 272, Cyanex 301 and Cyanex 302. Results are shown in Table 3. It is found that the percentage error is within $\pm 2.5\%$; and for six estimations the standard deviations are 1.89%, 1.78% and 1.72% for Cyanex 272, Cyanex 301 and Cyanex 302, respectively. Therefore, it is concluded that the technique developed can be used successfully for the estimation of organo-derivatives of phosphinic acid.

Cyanex 272 containing more than 98% BTMPPA is subjected to estimate the physicochemical constants (K_2 , K_d and K_a) of BTMPPA (HA). HA may be dimerized through hydrogen bonding in the organic

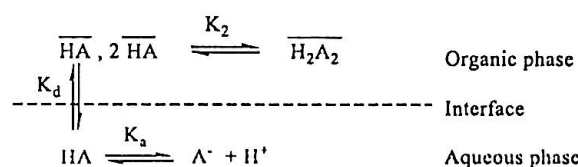
Table 1
Physical characteristics of as-received and purified Cyanex 272

Property	As-received Cyanex 272		Purified Cyanex 272		
	This work	Brochure of CCI	This work	Zhengshui et al. (1995)	Xun et al. (1990)
Colour	Amber	Amber/colourless	Colourless	Colourless	–
Density ²⁵ (g/mL)	0.9215	0.92	0.9152	0.9199	–
Refractive index	1.4575	–	1.4566	1.4568	–
Viscosity ²⁵ (cp)	140.02	142.00	120.02	–	–
Solubility H_2O ²⁵ (mol/L)	5.48×10^{-5}	5.52×10^{-5}	4.65×10^{-5}	–	4.58×10^{-5}

Table 2
Digestion of BTMPPA with various acids and mixtures of HNO₃ and HClO₄

Acid	Amt. of acid, (mL)	Ratio, (v/v)	Wt. of BTMPPA taken, (g)	Digestion, time (h)	% Ortho-phosphate conversion
H ₂ SO ₄	5	–	0.0325	1	2.5
			0.0317	2	2.9
			0.0328	4	3.1
			0.0330	6	3.2
HCl	5	–	0.0324	1	1.0
			0.0328	2	1.2
HNO ₃	5	–	0.0322	1	10.5
			0.0326	2	12.4
			0.0320	6	15.2
HClO ₄	5	–	0.0333	1	7.5
			0.0322	2	9.6
			0.0326	4	10.5
			0.0325	6	11.3
HNO ₃ /HClO ₄	9	1/8	0.0326	1	97.0
		2/7	0.0320	1	97.5
		3/6	0.0325	1	98.0
		4/5	0.0328	1	98.0
		5/4	0.0330	1	99.5
		6/3	0.0328	1	100.2
		7/2	0.0334	1	96.8
		8/1	0.0329	1	90.0

phase. The dimer cannot enter the aqueous phase, but it can be ionized at the interface (interfacial adsorption). The monomer can be distributed to the aqueous phase and ionized as depicted below:



where the species with bars represent organic species and

$$\text{dimerization constant, } K_2 = \frac{[\overline{\text{H}_2\text{A}_2}]}{[\overline{\text{HA}}]^2} \quad (1)$$

$$\text{distribution constant, } K_d = \frac{[\overline{\text{HA}}]}{[\text{HA}]} \quad (2)$$

$$\text{and, ionization constant, } K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (3)$$

Now, the net distribution ratio of HA can be defined as

$$D = \frac{\overline{C}_{\text{HA}}}{C_{\text{HA}}} = \frac{[\overline{\text{HA}}] + 2[\overline{\text{H}_2\text{A}_2}]}{[\text{HA}] + [\text{A}^-]} \quad (4)$$

When $[\overline{\text{H}_2\text{A}_2}] \gg [\overline{\text{HA}}]$ and $\overline{\text{H}_2\text{A}_2}$ is not distributed, then the above four equations on neglecting the

$[\overline{\text{HA}}]$ term in Eq. (4) generate the following equation (Biswas et al., 2000, 2003; Ulyanov and Sviridova, 1963):

$$\log D = \log(1.41)\sqrt{K_2K_d}\sqrt{C_{\text{HA}}} - \log\left(1 + \frac{K_a}{[\text{H}^+]}\right) \quad (5)$$

Eq. (5) indicates that the log–log plot of D vs. $[\text{H}^+]$ has two asymptotes:

$$\begin{aligned} \text{when } [\text{H}^+] \rightarrow \infty, \text{ then } \log D \\ = \log(1.41\sqrt{K_2K_d}\sqrt{C_{\text{HA}}}) \end{aligned} \quad (6)$$

and,

$$\begin{aligned} \text{when } [\text{H}^+] \rightarrow 0, \text{ then } \log D \\ = \log(1.41\sqrt{K_2K_d}\sqrt{C_{\text{HA}}}) - \log K_a + \log[\text{H}^+] \end{aligned} \quad (7)$$

Table 3
Error analysis in estimation by the developed technique

Purified reagent	No. of expt.	Wt. of sample taken, (g)	Amount of P (mg)		% Error	Stand. dev.
			Theoretical	Estimated		
Cyanex 272	1	0.0205	2.19	2.23	2.0	1.89%
	2	0.0395	4.22	4.16	–1.4	
	3	0.0577	6.17	6.01	–2.5	
	4	0.0790	8.44	8.46	0.1	
	5	0.1072	11.46	11.72	2.3	
	6	0.1373	14.68	14.58	–0.7	
Cyanex 301	1	0.0222	2.14	2.19	2.3	1.78%
	2	0.0233	2.24	2.19	–2.5	
	3	0.0430	4.14	4.06	–1.2	
	4	0.0442	4.26	4.26	0.1	
	5	0.0658	6.34	6.33	–0.2	
	6	0.0662	6.37	3.34	–0.5	
Cyanex 302	1	0.0176	1.72	1.76	2.6	1.72%
	2	0.0253	2.47	2.50	1.1	
	3	0.0460	4.50	4.39	–2.3	
	4	0.0472	4.61	4.54	–1.4	
	5	0.0720	7.03	7.09	0.8	
	6	0.0728	7.11	7.13	0.3	

Digestion time=1 h; digestion acid=70% HNO₃ (6 mL)+70% HClO₄ (3 mL).

At the point of intersection of two asymptotes, the following relationship holds:

$$-\log K_a + \log[H^+] = 0 \quad (8)$$

Therefore, the value of K_a can be easily obtained from the abscissa of the point of intersection of two asymptotes.

The $\log D$ vs. $\log [H^+]$ plots for 0.05, 0.10 and 0.20 M BTMPA are shown in Fig. 2. In all cases, the experimental points form a curve. According to Eq. (6), the asymptotic $\log D$ values at higher $[H^+]$ region equals $\log(1.41\sqrt{K_2K_d}\sqrt{C_{IIA}})$ and these values are 2.40, 2.50 and 2.65 for 0.05, 0.10 and 0.20 M extractant systems, respectively, and are shown by dashed lines. The dashed with dotted lines represent asymptotes at lower $[H^+]$ region. At the point of intersection of respective two asymptotes, abscissae are -3.20 , -3.30 and -3.28 , which give K_a value (cf. Eq. (8)) as 6.31×10^{-4} , 5.01×10^{-4} and 5.25×10^{-4} for 0.05, 0.10 and 0.20 M BTMPA systems, respectively. So, the average value of K_a for BTMPA can be taken as 5.52×10^{-4} . This value of K_a for BTMPA is comparable to those reported earlier (Kean et al., 1995; Martinez et al., 1993; Xun et al., 1990).

Again, on defining φ as $\{1+(K_a/[H^+])\}$ and without neglecting the $[IIA]$ term in Eq. (4), the

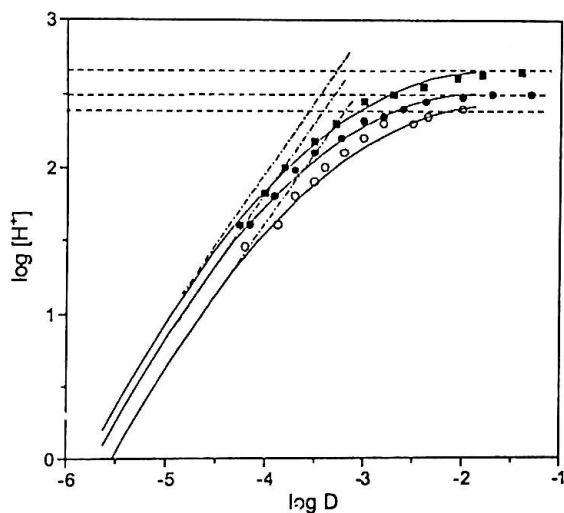


Fig. 2. Distribution of BTMPA between aqueous NaCl solution and kerosene in relation to $[H^+]$. $\mu=0.10$ M $(Na^+, H^+)Cl^-$, Temp. $=(303 \pm 1)$ K. $[BTMPA]=0.05$ M (○), 0.10 M (●) and 0.20 M (■). Points are experimental and curves are theoretical.

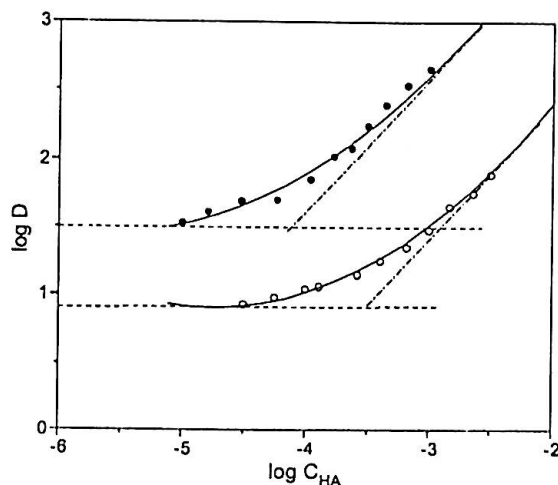


Fig. 3. Distribution of BTMPA between aqueous NaCl solution and kerosene in relation to its concentration in the aqueous phase $\mu=0.10$ M $(Na^+, H^+)Cl^-$, Temp. $=(303 \pm 1)$ K. $pH_{eq}=4$ (○) and 3 (●). Points are experimental and curves are theoretical.

following relationship can be deduced (Biswas et al., 2000):

$$\log D = \log(K_d/\varphi) + \log\{(2K_2K_dC_{IIA}/\varphi) + 1\} \quad (9)$$

The above equation indicates that the $\log D$ vs. $\log C_{IIA}$ plot will have the following two asymptotes:

$$\text{when } C_{IIA} \rightarrow 0, \text{ then } \log D = \log(K_d/\varphi) \quad (10)$$

and, when $C_{IIA} \rightarrow \infty$, then $\log D$

$$= \log(K_d/\varphi) + \log(2K_2K_d/\varphi) + \log C_{IIA} \quad (11)$$

Therefore, at the point of intersection of Eqs. (10) and (11), the following relationship holds:

$$\log(2K_2K_d/\varphi) + \log C_{IIA} = 0 \quad (12)$$

The $\log D$ vs. $\log C_{IIA}$ plots for constant equilibrium pH values of 3 and 4 are shown in Fig. 3. Experimental points in each case form a curve. In the lower concentration region of the aqueous phase, the curve has an asymptotic $\log D$ value of 1.55 and 0.90 at pH 3 and 4, respectively. These values equal

$\log(K_d/\varphi)$. The value of φ at pH 3 and 4 are 6.52 and 1.55, respectively. Consequently, Eq. (10) gives K_d values of 55.0 and 51.5 for pH 3 and 4 systems, respectively. Therefore, the estimated distribution ratio of BTMPPA for kerosene–0.1 M (Na^+ , H^+) Cl^- system is ~ 53 in comparison to 44 for chloroform–water system (Kean et al., 1995).

The abscissa of the point of intersection of two asymptotes, represented by Eqs. (10) and (11), is -4.1 and -3.5 for pH 3 and 4 systems, respectively. So, Eq. (12) yields the respective K_2 value of 186 and 195. Hence, the average K_2 value is 190, which is comparable to 184 ± 16 as reported by Kean et al. (1995).

Using the values of $K_2=190$ and $K_d=53$, the value of $\log(1.41\sqrt{K_2K_d}\sqrt{C_{\text{HA}}})$ is found to be 2.36, 2.51 and 2.66 for 0.05, 0.10 and 0.20 M BTMPPA systems, respectively, which are almost identical to the corresponding asymptotic $\log D$ values at lower concentration region of H^+ in Fig. 2. This coincidence proves that the experimental results are correct and the values of $K_2=15848$ and $K_d=933$ reported by Xun et al. (1990) using the conductivity measurements are not true.

4. Conclusions

The following conclusions have been drawn:

- (1) 98.9% BTMPPA can be obtained from Cyanex 272 ($\sim 84\%$ BTMPPA) following a published procedure involving the formation of a micro-emulsion phase.
- (2) BTMPPA can be oxidised to ortho-phosphate by heating with concentrated HNO_3 (70%)– HClO_4 (70%) mixture (6 mL/3 mL) for 1 h and quantitatively estimated by the molybdenum–blue method.
- (3) Reproducibility of the technique developed is quite good with a standard deviation of 1.89%.
- (4) The method can also be applied in the estimation of purified Cyanex 301 and Cyanex 302 with good reproducibility.
- (5) The values of K_a , K_d and K_2 for BTMPPA in kerosene–0.10 M (Na^+ , H^+) Cl^- medium are 5.52×10^{-4} , 53 and 190, respectively.

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Purified Cyanex 272: Its interfacial adsorption and extraction characteristics towards iron(III)

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Abstract

The interfacial adsorption property of purified Cyanex 272 and its extraction characteristics towards Fe^{3+} from sulphate medium have been investigated. Using the interfacial tension data, the cross-sectional area (A) of purified Cyanex 272 (bis-2,4,4-trimethylpentylphosphinic acid, BTMPPA, H_2A_2) molecules adsorbed at the interface has been measured for the 0.50 M H_2SO_4 - H_2A_2 in different diluent systems and was found to vary in the following order: $\text{CCl}_4 < \text{C}_6\text{H}_6 < \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} < n\text{-C}_6\text{H}_{14} < \text{C}_6\text{H}_5-\text{CH}_3 = \text{kerosene} < \text{C}_6\text{H}_6 < \text{CHCl}_3 < n\text{-C}_7\text{H}_{15}\text{OH} < n\text{-C}_6\text{H}_{13}\text{OH}$. This order has been correlated with the Fe^{3+} -extraction data.

The equilibration time for extraction of Fe^{3+} by purified Cyanex 272 dissolved in kerosene is less than 25 min. The Fe^{3+} dependence curve at a constant equilibrium pH and concentrations of extractant and sulphate ion has a slope of -0.5 and zero at lower and higher concentration regions of Fe^{3+} . The pH dependence at lower pH region is 2; whereas, the extractant and sulphate ion dependences are 1 and -1 , respectively. The pH dependence is decreased at higher pH regions. The temperature dependence of the distribution ratio (D) indicates that the extraction process is exothermic with an average ΔH value of 13 kJ/mol. The extraction equilibrium reaction is suggested to be: $\text{Fe}(\text{HSO}_4)_2 + \text{H}_2\text{A}_{2(\text{aq})} \rightleftharpoons \text{FeHSO}_4\cdot\text{A}_{2(\text{org})} + \text{HSO}_4^- + 2\text{H}^+$ at the lower pH region of investigation. At the higher pH region, the hydrolytic species of Fe^{3+} is involved. The extraction equilibrium constant (K_{ex}) has been evaluated to be $10^{2.3}$. The loading capacity of BTMPPA is 9.6 g Fe^{3+} /100 g BTMPPA. The extracted complex can be stripped by 0.50 M H_2SO_4 solution; but a three-stage stripping ($O/A=1$ in each stage) is needed for 99% Fe^{3+} removal from the organic phase.

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Keywords: Cyanex 272; Bis-2,4,4-trimethylpentylphosphinic acid; BTMPPA; Interfacial tension; Cross-sectional area; Extraction; Stripping; Iron(III)

1. Introduction

Cyanex 272, a proprietary technical grade extractant produced by Cytec Canada Inc (active component being bis-2,4,4-trimethylpentylphosphinic acid-abbreviated as

BTMPPA) has been used since 1983 and found wide commercial use for the extraction of cobalt from nickel (Sole et al., 2005; Soldenhoff et al., 1998; Cheng, 2001; Cheng and Urbani, 2003; Darvishi et al., 2005 etc.). Moreover, it has been proposed for the extraction of a number of other metal ions (Reddy et al., 2004; Saleh et al., 2002; Sole et al., 1994; Inoue et al., 1994 etc.).

Iron(III) co-exists as an impurity in the sulphuric acid leach solutions of metallic sources, such as the primary and secondary sources of Cu–Co–Ni (Miralles et al.,

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1992) and roasted sphalerite in an integrated hydrometallurgical zinc plant (Gupta et al., 1989). Iron(III) has to be recovered/removed from the leach solution prior to the recovery of a desirable metal. The selective precipitation of Fe^{3+} from the leach solution followed by solid–liquid separation presents some problems, such as the adsorption of valuable metal in the precipitate or handling of the precipitate. So the removal of iron(III) by solvent extraction is widely studied as an alternative to solid–liquid separation. In a commercial plant using Cyanex 272 to extract cobalt from nickel, it is noticed that Fe^{3+} is removed from the sulphate leach liquor prior to cobalt extraction.

The extractants used for the extraction of Fe^{3+} prior to 1976 have been referenced by Sekine and Hasegawa (1977). After that, the following extractants have been suggested for the extraction of Fe^{3+} : N,N' -tetra-substituted malonamides (Paiva and Costa, 2005; Costa et al., 2004, 2003), 3-phenyl-4-acyl-5-isoxazolones (Remya et al., 2004), Cyanex 302 using hollow fibre membrane modules (Luo et al., 2004), octylphenyl acid phosphate (Principe and Demopoulos, 2004), 1-hydroxy-1-phosphono-hexadecyl (and -1-phosphono-dodecyl) phosphinic acid (Didi et al., 2002), a commercial trialkyl amine ADOGEN 364 (Rodríguez de San Miguel et al., 2000), Cyanex 923 (Saji et al., 1998), a commercial aldoxime MOC-55 TD (Ocana and Alguacil, 1998), LIX 984 (Rodríguez de San Miguel et al., 1997), TBP-MIBK mixture (Reddy and Sarma, 1996), a commercial salicyl aldoxime LIX 860 (Simpson et al., 1996), 1-phenyl-3-methyl-4-(*p*-nitrobenzoyl)-5-pyrazolone (Ogwuegbu and Oforka, 1994), a primary amine Primene 81 *R* sulphate (Alguacil and Amer, 1986), a synergistic mixture of Kelex 100 and D2EHPA (Demopoulos and Gefvert, 1984) etc. Moreover, Miralles et al. (1992) have reported the extraction of Fe^{3+} from nitrate medium by BTMPPA, the active component of Cyanex 272 dissolved in Isopar-H (a commercial hydrocarbon) and shown that the extraction ratio is decreased appreciably with the change of the anion existing in the aqueous phase, particularly at lower pH regions. Demopoulos et al. (1993) have found the synergistic effect of Cyanex 272 on the extraction of Fe^{3+} from sulphate medium by Kelex 100. There appears no report on the thorough investigation on the extraction of Fe^{3+} from sulphate medium by BTMPPA dissolved in kerosene or other diluents.

In a previous paper, Biswas et al. (2005) have reported a method for the colorimetric estimation of purified Cyanex 272 and also the values of dimerization constant (K_2), distribution coefficient (K_d) and ionization constant (K_a) of BTMPPA. In another paper,

Biswas and Singha (2006) have reported the densities, viscosities and excess properties of BTMPPA + diluent binary mixtures at 298.15 K and atmospheric pressure. This paper reports the interfacial adsorption properties of BTMPPA at various aqueous/diluent interfaces and the extraction characteristics of Fe^{3+} from sulphate medium by BTMPPA dissolved in kerosene. An attempt has also been taken to correlate interfacial adsorption properties with Fe^{3+} -extraction characteristics.

2. Experimental technique

2.1. Reagents

Cyanex 272 was donated by Cytec Canada Inc. It was purified by the method of micro-emulsion formation of Zhengshui et al. (1995). Titration of purified Cyanex 272 showed that purified Cyanex 272 contained 98.9% BTMPPA. Kerosene from the local market was distilled to collect the fraction distilling over at 200–260 °C. The collected fraction was colorless and mostly aliphatic in nature. Other diluents were bought from E. Merck-BDH and distilled before use. Other chemicals were of reagent grade and used without further purifications.

2.2. Analytical

The iron(III) content of the aqueous phase was determined by the HNO_3 – NH_4SCN colorimetric method at 480 nm using a WPA S104 spectrophotometer. The pH values of aqueous solutions were determined by a Mettler Toledo 320 pH-meter. For pH adjustment of aqueous solutions, either anhydrous sodium carbonate or dil H_2SO_4 was used.

2.3. Interfacial tension measurement

Interfacial tensions were measured with a Du Nouy Tensiometer (Itoh Seisakusho, precision 0.10 mN/m) at (298 ± 0.5) K using a platinum ring. Before measuring the interfacial tension, the aqueous and organic phases were equilibrated for 1 h and settled for 24 h. Evaporating discs of 6 cm i.d. were used for the tension measurements. Proper care was given to clean the ring and the pot. The accuracy of interfacial tension measurement was ± 0.05 mN/m.

2.4. Procedure for distribution of Fe^{3+}

In the case of extraction, an aliquot of the aqueous phase (25 mL) containing specific concentrations of

Fe³⁺ and SO₄²⁻ at a definite pH was agitated with an equal aliquot of the organic phase consisting of BTMPPA and kerosene in a 125 mL separating funnel for a predetermined time (30 min at 298 ± 1) K. The phase agitation was performed by a Stuart Flask Shaker, controlled at 300 strokes/min, and the temperature was controlled by putting the agitating flasks in a thermostatic water bath. After equilibration, phases were allowed to settle within the water bath and then disengaged. Separated aqueous solutions were subjected to equilibrium pH-measurements and Fe³⁺-concentration determinations. The concentration of Fe³⁺ in the organic phases at equilibrium was calculated by difference and the distribution ratio (*D*) was calculated.

In the cases of the loading of the organic phase by Fe³⁺ and the stage-wise stripping, a definite amount of the organic phase was repeatedly contacted with equal volumes of fresh aqueous solutions. In the case of stripping, 25 mL of an organic phase containing Fe³⁺ and free BTMPPA in kerosene was equilibrated for 30 min at 298 K with an equal volume of a sulphuric acid solution and the stripping ratio (*S*) was calculated.

2.5. Treatment of interfacial tension data

The Gibbs adsorption isotherm provides a means for calculating the number of adsorbed molecules per unit area (*Γ*) or, the interfacial molecular area (*A*) from the interfacial tension (*γ*, mN/m) vs. concentration (*C*) data. For a given temperature, the general form of Gibbs equation (Glasstone, 1968) is:

$$\Gamma = \frac{1}{A} = -\frac{1}{kT} \frac{d\gamma}{d \ln C} = -\frac{1}{2.303 kT} \frac{d\gamma}{d \log C} \quad (1)$$

where, *k* is the Boltzman constant (1.38 × 10⁻¹⁶ erg/K) and *T* is the absolute temperature (K). When the slope of *γ* vs. log *C* is negative, then the right hand side of Eq. (1) becomes positive and adsorption occurs. On the other hand, when the slope is positive, then desorption occurs.

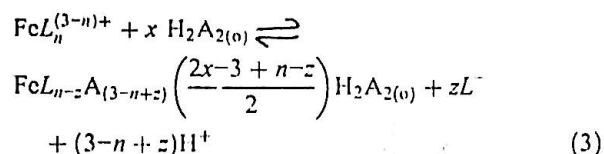
On knowing the value of *Γ* (number of adsorbed molecules per square metre), the cross-sectional area (*A*) of adsorbed molecule in Å² can be obtained from the following relation (since 1 m² = 10²⁰ Å²):

$$A = \frac{10^{20}}{\Gamma} \text{ Å}^2 \quad (2)$$

2.6. Treatment of Fe³⁺-extraction equilibrium data

BTMPPA is a di-alkyl derivative of phosphinic acid. It acts as a mono-acidic chelating agent. If Fe³⁺ exists in the aqueous phase as FeL_{*n*}^{(3-*n*)⁺} (*L* being the co-existing

anion of unit charge) and BTMPPA is considered as dimeric (H₂A₂) in non-polar solvents (Biswas and Singha, 2005; Ke-an et al., 1985), then the extraction equilibrium reaction may be considered as follows:



where subscript (*o*) represent organic species. The extraction equilibrium constant (*K_{ex}*) of the above reaction can be expressed as follows:

$$K_{\text{ex}} = \frac{[\text{FeL}_{n-z}\text{A}_{(3-n+z)} \left(\frac{2x-3+n-z}{2} \right) \text{H}_2\text{A}_{2(o)}] [\text{H}^+]^{(3-n+z)} [\text{L}^-]^z}{[\text{FeL}_n^{(3-n)+}] [\text{H}_2\text{A}_{2(o)}]^x} \quad (4)$$

Now, on defining the distribution ratio (*D*) as

$$D = \frac{[\text{FeL}_{n-z}\text{A}_{(3-n+z)} \left(\frac{2x-3+n-z}{2} \right) \text{H}_2\text{A}_{2(o)}]}{[\text{FeL}_n^{(3-n)+}]}$$

Eq. (4) can be expressed as:

$$K_{\text{ex}} = D \frac{[\text{H}^+]^{(3-n+z)} [\text{L}^-]^z}{[\text{H}_2\text{A}_{2(o)}]^x} \quad (5)$$

On taking logarithm of both the sides of Eq. (5):

$$\log D = \log K_{\text{ex}} + (3-n+z) \text{pH} + x \log [\text{H}_2\text{A}_{2(o)}] - z \log [\text{L}^-] \quad (6)$$

The temperature dependency of the distribution ratio (*D*) of Fe³⁺ by BTMPPA can be treated by the Van't Hoff equation (Islam et al., 1979):

$$\log D = -\frac{\Delta H}{2.303 RT} \quad (7)$$

where the symbols have their usual significance.

Eq. (7) states that the plot of log *D* against (1/*T*) K⁻¹ will be a straight line with a slope equal to -Δ*H*/2.303 *R* from which the enthalpy change for the extraction reaction (Δ*H*) can be evaluated.

3. Results and discussion

3.1. Cross-sectional areas of adsorbed BTMPPA molecules at the interface from interfacial tension

Interfacial tensions for 0.01–1.00 M H₂SO₄ ([SO₄²⁻] = 1.00 M)–0.06 M BTMPPA in kerosene have been

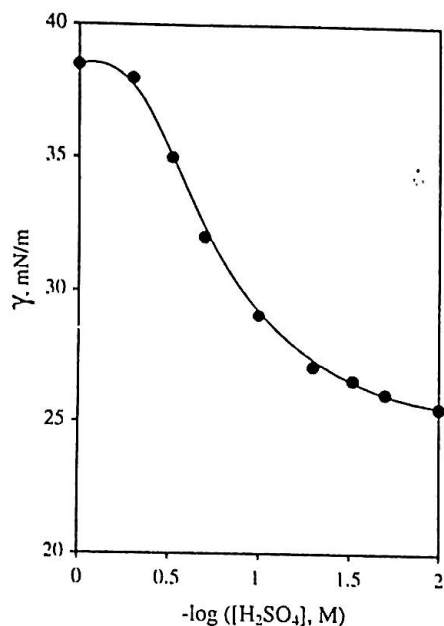


Fig. 1. Effect of H_2SO_4 concentration on interfacial tension. $[BTMPA]_{(o)} = 0.06$ M in kerosene; $T = 298 \pm 0.5$ K; $[H_2SO_4]$ = variable, $[SO_4^{2-}] = 1.00$ M; equilibration time 1 h; settling time 24 h.

increasing pH because of the inability of ionized BTMPA to desorb. Consequently, the number of population (ionized and non-ionised BTMPA) at the interface at any moment is increased with increasing pH — which results in lowering of interfacial tension.

Fig. 2 shows the γ (mN/m) vs. $\log([BTMPA], M)$ plot for 0.50 M H_2SO_4 ($pH = 0.8$)–kerosene system at (298 ± 0.5) K. Tensions have been measured after equilibration for 1 h and settling for 24 h. It is found that the γ -value decreases gradually with increasing BTMPA concentration after 2.0×10^{-6} M in the organic phase. At $C_1 = 6.3 \times 10^{-6}$ M BTMPA in kerosene, the formation of a monolayer is started and completed at $C_2 = 3 \times 10^{-2}$ M. At a concentration of BTMPA greater than 3×10^{-2} M, the interface is saturated with a monolayer and extractant molecules start to form micelles through polymerization in the bulk organic phase.

The slope of the straight line at the inflection of the plot in Fig. 2 represents $d\gamma/d \log([H_2A_2]_{(o)}, M)$. The slope of this line is -4.5 ; so that the number of adsorbed BTMPA molecules, $1/4.74 \times 10^{13} \text{ cm}^{-2}$ or $4.74 \times 10^{17} \text{ m}^{-2}$. The value of the cross-sectional area of an adsorbed BTMPA molecule at the interface (A) is $(10^{20}/4.74 \times 10^{17}) = 211 \text{ \AA}^2$. This result is much higher than for D2EHPA ($113.6 \text{ \AA}^2$), even though

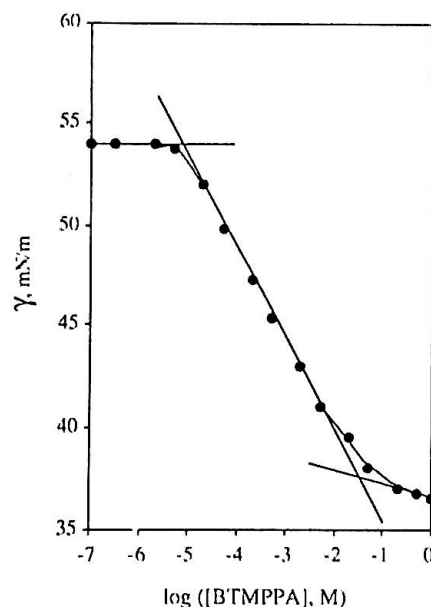


Fig. 2. Variation of interfacial tension with extractant concentration. $[H_2SO_4] = 0.50$ M ($pH = 0.80$), 10^{-8} – 10^{-2} M BTMPA in kerosene, $T = 298 \pm 0.5$ K, equilibration time 1 h, settling time 24 h.

measured at (298 ± 0.5) K for equilibrated conditions. The interfacial tension, γ (mN/m) vs. $-\log([H_2SO_4], M)$ plot is shown in Fig. 1. It is seen that the interfacial tension decreases with decreasing H_2SO_4 concentration. A similar trend has been reported by Flett et al. (1975a, b), Al-Diwan et al. (1977) and Biswas et al. (2003) for D2EHPA. It can be explained by the following ways:

- At higher acid concentrations in the aqueous phase, the adsorbed extractant molecules cannot be ionized and so they do not exist in close packed condition. On the other hand, at lower acid concentrations in the aqueous phase, the extractant molecules can exist in a more regular packed way to yield lower interfacial tension.
- It is apparent that more molecules of BTMPA at the interface results in a lower interfacial tension. But when the same number BTMPA molecules exist at the interface, then it is expected that the interfacial tension would decrease as the number of ionized molecules of BTMPA at the interface increases with increasing pH. This is due to the fact that the ionized BTMPA is more polar than when it is not ionized.
- From the dynamic nature of adsorption–desorption at the interface, it is expected that the desorption rate (per unit area) decreases with

D2EHPA contains a longer carbon chain (Biswas et al., 2003).

Gatton and Horwitz (1988) reported the shapes and sizes of various extractants including BTMPPA determined by the molecular modeling program 'Alchemy'. According to the minimum energy shape of BTMPPA given by them, the distance between H of >PO–OH group and a H of a terminal carbon atom of BTMPPA molecule is not more than 7 Å and so the maximum rotational area covered by an adsorbed BTMPPA molecule taking H of >PO–OH group as the center becomes 153 Å^2 ($\pi r^2 = 153$). It is therefore suggested that the phosphinic acid end of BTMPPA is at the interface and if BTMPPA molecules of the interface are in their preferred minimum energy shape there should be more molecules at the interface than is calculated using the data in Fig. 2 along with Eqs. (1) and (2).

Experimentally determined cross-sectional area of a BTMPPA molecule adsorbed at the interface (211 Å^2) is greater than the theoretically calculated cross-sectional area of an adsorbed minimum energy shaped BTMPPA molecule (153 Å^2). It appears therefore that considerable voids exist at the interface. Simple geometric drawings and calculations show that the areas of voids per BTMPPA molecule are 17, 42, 79, 102 and 130 Å^2 , respectively, for voids created by 3, 4, 5, 6 and 7 BTMPPA molecules of area 153 Å^2 . In the case of heptagonal arrangement of BTMPPA molecules, a BTMPPA molecule can occupy the void position. At 0.50 M H_2SO_4 (pH=0.8)–kerosene interface, 57% and 43% of the voids are created, respectively, by 4 and 5 BTMPPA molecules; so that $(153 + 0.57 \times 42 + 0.43 \times 79) \text{ Å}^2$ becomes equal to the experimentally determined cross-sectional area of BTMPPA (211 Å^2). However, if all the molecules are not in their preferred minimum energy shape, the distance between the H on the P–OH and the terminal

H on the carbon chain could be greater than 7 Å and this shape of the molecule would then sweep a larger area and result in a larger cross-sectional area. Some of the molecules at the interface may be in their minimum energy shape and the rest not, so the experimental cross-sectional area is simply an average of all the molecules. The organic–aqueous interface in the BTMPPA kerosene/0.50 M H_2SO_4 system appears to present the following picture:

- (i) The interface is saturated with adsorbed minimum energy shaped BTMPPA molecules leaving considerable voids of which 57% is created by square arrangement of four BTMPPA molecules (each having a circular area of 153 Å^2) and the rest being created by regular pentagonal arrangement of five BTMPPA molecules. Otherwise, there are some BTMPPA molecules in their preferred minimum energy shape and some not at the interface.
- (ii) The polar $>\text{P}=\text{O}$ portion of a BTMPPA molecule adsorbed at the interface is oriented towards the aqueous phase where it may be ionized at least partially. Hydrocarbon chains rest on the organic side of the interface.
- (iii) It appears that the free BTMPPA molecules are active at the aqueous/organic interface and obviously, during the extraction of a metal ion, the resulting complex or ion-pair becomes less interfacially active and moves into the organic phase. The vacancy at the interface is then taken by a free BTMPPA molecule.

Using various diluents, similar studies on the interfacial tension of BTMPPA — 0.50 M H_2SO_4 (pH=0.8) have been carried out and results are given in Table 1. It is seen that the values of C_1 , C_2 and A are

Table 1
Interfacial parameters of BTMPPA/0.50 M H_2SO_4 (pH=0.8) system in various diluents at 298 K

Diluent	$C_1 \times 10^5$, M	$C_2 \times 10^2$, M	$d\gamma/d \log$ [H_2A_2] _(a)	$I \times 10^{-17}$, m^{-2}	A , Å^2	% void created by				
						3 M ^a	4 M	5 M	6 M	7 M
CCl_4	2.00	4.00	−6.05	6.389	157	100	—	—	—	—
C_7H_{12}	1.00	3.20	−5.70	6.019	166	100	—	—	—	—
$\text{ClCH}_2\text{—CH}_2\text{Cl}$	5.00	2.50	−5.43	5.734	174	75	25	—	—	—
$n\text{-C}_6\text{H}_{14}$	2.82	3.16	−5.38	5.681	176	68	32	—	—	—
$\text{C}_6\text{H}_5\text{CH}_3$	3.16	5.00	−4.50	4.752	211	—	57	43	—	—
Kerosene	0.63	3.00	−4.50	4.752	211	—	57	43	—	—
C_6H_6	2.51	2.50	−3.62	3.823	262	—	—	—	75	25
CHCl_3	0.09	15.80	−2.83	2.988	335	—	—	—	—	—
$n\text{-I-C}_7\text{H}_{13}\text{OH}$	0.25	10.00	−1.78	1.880	532	—	—	—	—	—
$n\text{-I-C}_6\text{H}_{13}\text{OH}$	0.71	10.00	−1.29	1.362	734	—	—	—	—	—

^a M stands for molecules of BTMPPA.

changed with the variation of diluent used to prepare the organic phase. The effective cross-sectional area of a BTMPPA molecule (A) adsorbed at the interface varies with the diluents as shown: CCl_4 ($157 \text{ \AA}^2$) $<$ $\text{C}_7\text{H}_{15}\text{OH}$ ($166 \text{ \AA}^2$) $<$ C_6H_6 ($174 \text{ \AA}^2$) $=$ $n\text{-C}_6\text{H}_{14}$ ($176 \text{ \AA}^2$) $<$ $\text{C}_6\text{H}_5\text{CH}_3$ ($211 \text{ \AA}^2$) $\sim$ kerosene ($211 \text{ \AA}^2$) $<$ C_6H_6 ($262 \text{ \AA}^2$) $<$ CHCl_3 ($335 \text{ \AA}^2$) $<$ $n\text{-C}_7\text{H}_{15}\text{OH}$ ($532 \text{ \AA}^2$) $<$ $n\text{-C}_6\text{H}_{13}\text{OH}$ ($734 \text{ \AA}^2$). In the last three cases, the 'A'-values are abnormally high, which cannot be explained by the formation of voids by regular arrangement at BTMPPA molecules of the interface. However, it may be suggested that due to polarity of these diluents, some sort of interactions between these diluents and BTMPPA molecules take place in the bulk organic phase, which reduces the affinity of BTMPPA molecule to adsorb at the interface. This is likely the case since the hydrogen atom in each of these polar diluents is capable of hydrogen bonding to the phosphinic acid functionality. Moreover, aromatic diluents (benzene and toluene) through their π -electrons may interact with the polar group of BTMPPA ($>\text{PO}(\text{OH})$) in the bulk organic phase, and hence the susceptibility of BTMPPA molecule to adsorb at the interface is decreased which apparently increases the effective cross-sectional area. For other diluent systems (non-polar and non-aromatic), adsorbed BTMPPA molecules have smaller cross-sectional areas.

The BTMPPA concentration at which monolayer formation started at the interface (C_1) is found to be dependent on diluent as follows: CHCl_3 ($9 \times 10^{-7} \text{ M}$) $<$ $n\text{-C}_7\text{H}_{15}\text{OH}$ ($2.5 \times 10^{-6} \text{ M}$) $<$ kerosene ($6.3 \times 10^{-6} \text{ M}$) $<$ $n\text{-C}_6\text{H}_{13}\text{OH}$ ($7.1 \times 10^{-6} \text{ M}$) $<$ $\text{C}_7\text{H}_{15}\text{OH}$ ($1 \times 10^{-5} \text{ M}$) $<$ CCl_4 ($2 \times 10^{-5} \text{ M}$) $<$ C_6H_6 ($2.51 \times 10^{-5} \text{ M}$) $<$ $n\text{-C}_6\text{H}_{14}$ ($2.82 \times 10^{-5} \text{ M}$) $<$ $\text{C}_6\text{H}_5\text{CH}_3$ ($3.16 \times 10^{-5} \text{ M}$) $<$ $\text{CICH}_2\text{CH}_2\text{Cl}$ ($5 \times 10^{-5} \text{ M}$). These values are 10–1000 times less than those reported for D2EHPA (Biswas et al., 2003).

The C_2 -value indicates the minimum concentration of BTMPPA at which its dimerization/polymerization starts to form the micelles in the bulk organic phase. In the case of CHCl_3 (a polar diluent), the dimerization of BTMPPA occurs above 0.158 M; and for heptanol and hexanol that occurs above 0.10 M. This is more likely due to the formation of hydrogen bond between each of these diluents with BTMPPA molecules in the bulk organic phase hindering the intermolecular hydrogen bond formation between two BTMPPA molecules. In comparison to these, the concentrations of BTMPPA at which dimerization commences in different diluents are 0.025 M for C_6H_6 and $\text{CICH}_2\text{CH}_2\text{Cl}$, 0.03 M for kerosene, 0.0316 M for $n\text{-C}_6\text{H}_{14}$, 0.032 M for $\text{C}_7\text{H}_{15}\text{OH}$, 0.04 M for CCl_4 and 0.05 M for $\text{C}_6\text{H}_5\text{CH}_3$.

3.2. Extraction of Fe^{3+} by BTMPPA

Preliminary experiments show that the equilibration time for the extraction of Fe^{3+} by BTMPPA is less than 25 min in comparison to 3 h by D2EHPA (Islam and Biswas, 1981). In subsequent experiments, the phase contact time of 30 min has been used.

The variation of the distribution ratio of Fe^{3+} with the variation of its initial concentration is shown in Fig. 3. It is seen that $\log D$ vs. $\log [\text{Fe}^{3+}]_{(\text{ini})}$ plot is a curve. But in this case, the equilibrium pH and the equilibrium concentrations of BTMPPA and SO_4^{2-} are not constant for varying extents of extraction. Fig. 3 also represents the $\log D_c$ vs. $\log [\text{Fe}^{3+}]_{(\text{ini})}$ and $\log D_c$ vs. $\log [\text{Fe}^{3+}]_{(\text{eq})}$ plots where D_c is the corrected distribution ratio at constant $\text{pH}_{(\text{eq})} = 1.80$, and calculated using the following relationship after getting the pH, extractant and sulphate ion dependences.

$$\log D_c = \log D + y(\text{pH}_{(\text{eq})}^{\text{const}} - \text{pH}_{(\text{eq})}) + x(\log [\text{BTMPPA}]_{(\text{o,eq})}^{\text{const}} - \log [\text{BTMPPA}]_{(\text{o,eq})}) + z(\log [\text{SO}_4^{2-}]_{(\text{eq})}^{\text{const}} - \log [\text{SO}_4^{2-}]_{(\text{eq})}) \quad (8)$$

where, $y = \text{pH dependency} = 2$, $x = \text{extractant dependency} = 1$ and $z = \text{sulphate ion dependency} = -1$. The values of $[\text{BTMPPA}]_{(\text{o,eq})}$ and $[\text{SO}_4^{2-}]_{(\text{eq})}$ have been calculated from the relations:

$$[\text{BTMPPA}]_{(\text{o,eq})} = [\text{BTMPPA}]_{(\text{o,ini})} - x[\text{Fe}^{3+}]_{(\text{o,eq})} \quad (9)$$

and,

$$[\text{SO}_4^{2-}]_{(\text{eq})} = [\text{SO}_4^{2-}]_{(\text{ini})} - x[\text{Fe}^{3+}]_{(\text{o,eq})} \quad (10)$$

The $\log D_c$ vs. $\log [\text{Fe}^{3+}]_{(\text{ini})}$ plot is a curve whose asymptotic slopes in lower and higher concentration regions approach to -0.7 and zero respectively. The $\log D_c$ vs. $\log [\text{Fe}^{3+}]_{(\text{eq})}$ plot is also a curve whose asymptotic slopes approach to -0.43 and zero at lower and higher concentration regions of Fe^{3+} , respectively. This is believed to be due to the formation of dimeric Fe^{3+} species in the aqueous phase; dimerization is enhanced with increasing Fe^{3+} concentration up to 13 mM and beyond this concentration, Fe^{3+} is entirely present in the dimeric form.

Fig. 4 represents the $\log D_c$ vs. $\text{pH}_{(\text{eq})}$ plots for constant equilibrium BTMPPA concentrations of 0.05 and 0.025 M and sulphate ion concentration of 0.10 M. Here, $\log D_c$ values have been calculated from Eq. (8) after neglecting the second term of the right hand side. In both cases, straight lines with a slope equal to 2 in lower $\text{pH}_{(\text{eq})}$ region are obtained. Slopes of the lines decrease with increasing $\text{pH}_{(\text{eq})}$, approaching less than

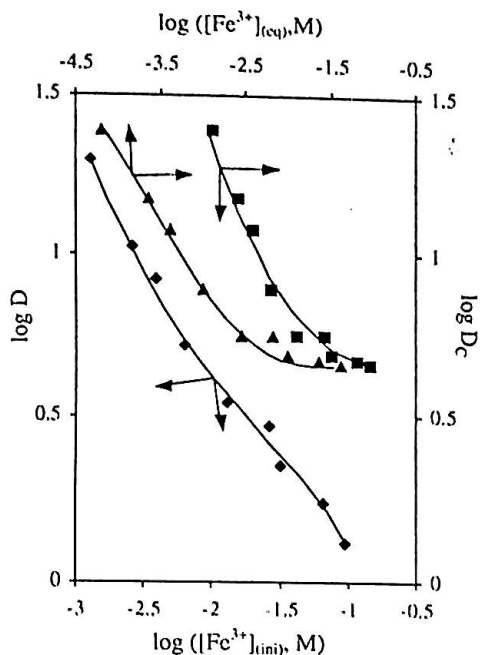


Fig. 3. Dependence of distribution ratio (D) of Fe^{3+} on its concentration. $\text{pH}_{\text{ini}}=1.8$, $[\text{BTMPPA}]_{\text{ini}}=0.20$ M, $[\text{SO}_4^{2-}]=0.20$ M.

unity at $\text{pH}_{\text{eq}}=2.25$. The lines with slope 2 have intercepts of -2.92 and -3.20 for $[\text{BTMPPA}]_{\text{eq}}^{\text{const}}$ of 0.05 and 0.025 M, respectively. Therefore, the pH dependence is 2 and <2 in lower and higher pH regions under investigation, respectively.

The $\log D_c$ vs. $\log ([\text{BTMPPA}]_{\text{eq}}, \text{M})$ plots at constant equilibrium pH values of 1.74 and 1.98 and sulphate ion concentration of 0.10 M are given in Fig. 5. Here the values of $\log D_c$ have been calculated from Eq. (8) after neglecting the third term of the right hand side. In both cases, straight lines with unity slopes are obtained. So the extractant dependency is 1. The intercept of the lines are 2.30 and 1.70 for $\text{pH}_{\text{eq}}^{\text{const}}$ values of 1.98 and 1.74 , respectively. Fig. 6 represents the dependence of the distribution ratio of iron on sulphate ion concentration at constant equilibrium pH of 2.01 and BTMPPA dimeric concentration of 0.025 M. The $\log D_c$ values have been calculated from Eq. (8) after omitting the last term of the right hand side. The plot is a straight line with slope equaling to -1 and has an intercept of -0.33 . From the results in Figs. 4–6, the values of $(3-n+z)$, x and z of Eq. (3) are 2 , 1 and 1 , respectively. This gives the value of $n=2$ and $(2x-3+n-z)/2=0$. This means that the extracted complex is not solvated by uncomplexed BTMPPA but it must be solvated by diluent and the bisulphate complex of the type $\text{Fe}(\text{HSO}_4)_2^+$, or

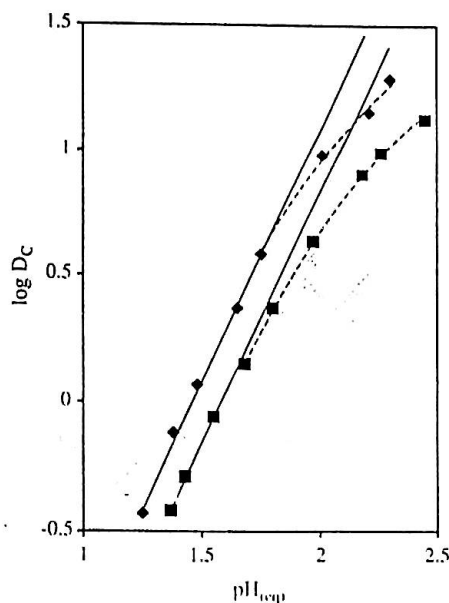


Fig. 4. Dependence of D_c on equilibrium pH. $[\text{Fe}^{3+}]_{\text{ini}}=0.75$ g/L (13.43 mM), $[\text{SO}_4^{2-}]=0.10$ M; ($\circ$), $[\text{BTMPPA}]_{\text{ini}}=0.05$ M, slope = 2, $I = -2.92$; ($\blacksquare$), $[\text{BTMPPA}]_{\text{ini}}=0.025$ M, slope = 2, $I = -3.20$.

its dimeric form existing in the aqueous phase, take part in the extraction. The existence of $\text{Fe}(\text{HSO}_4)_2^+$ is supported by the ionization constant of HSO_4 (K_{a2})

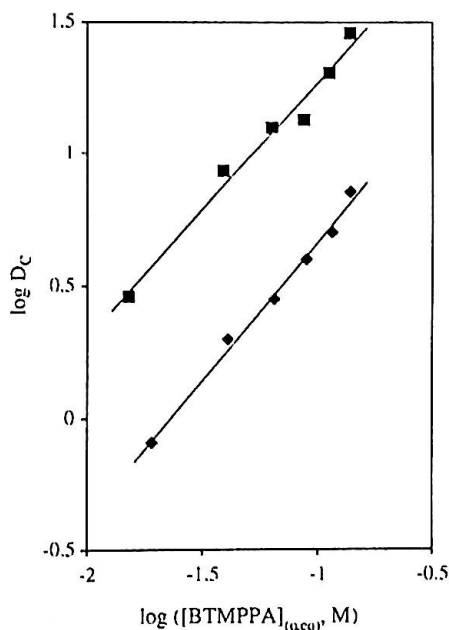


Fig. 5. Dependence of D_c on equilibrium free extractant concentration. $[\text{Fe}^{3+}]_{\text{ini}}=0.75$ g/L, $[\text{SO}_4^{2-}]=0.1$ M; ($\circ$), $\text{pH}_{\text{ini}}=1.75$, $\text{pH}_{\text{eq}}^{\text{const}}=1.74$, slope = 1, $I = 1.70$; ($\blacksquare$), $\text{pH}_{\text{ini}}=2.20$, $\text{pH}_{\text{eq}}^{\text{const}}=1.98$, slope = 1, $I = 2.30$.

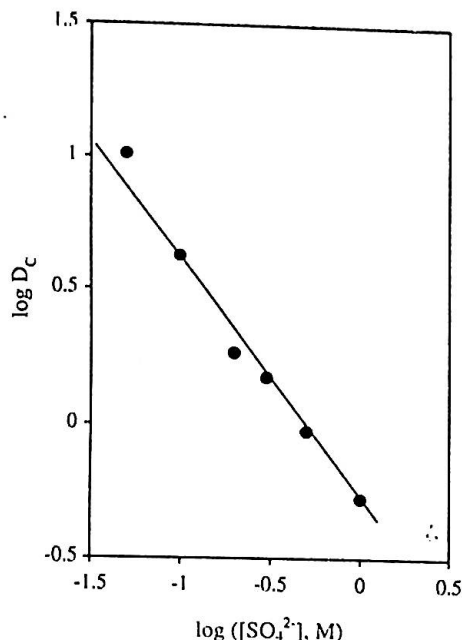


Fig. 6. Dependence of D_c on sulphate ion concentration. $[\text{Fe}^{3+}]_{\text{ini}} = 0.75 \text{ g/L}$, $\text{pH}_{\text{ini}} = 2.35$, $[\text{BTMPPA}]_{\text{ini}} = 0.025 \text{ M}$, $\text{pH}_{\text{eq}}^{\text{const}} = 2.01$, $[\text{BTMPPA}]_{\text{eq}}^{\text{const}} = 0.025 \text{ M}$, slope = -1 , $r = -0.34$.

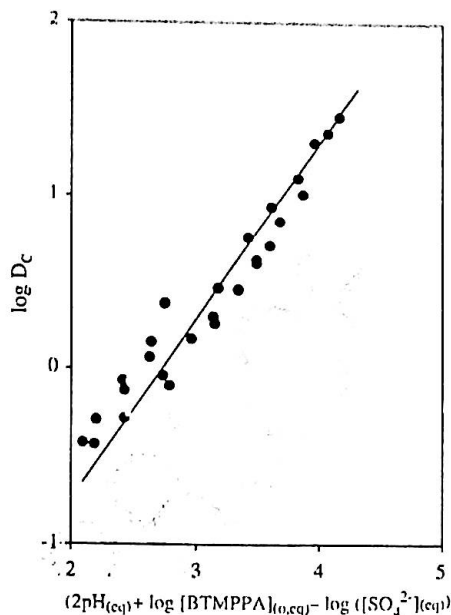
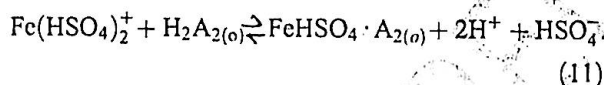


Fig. 7. Plot of Eq. (12). $-\log K_{\text{ex}} = -2.3$, slope = -0.87 , corr. coeff. = 0.946 .

469 $(\text{H}_2\text{SO}_4) = 10^{-2})$ and the stability constant of $\text{Fe}(\text{HSO}_4)_2^+$
 470 $([\text{Fe}(\text{HSO}_4)_2^+]/[\text{Fe}^{3+}][\text{HSO}_4^-]^2 = 10^2)$ as given by Smith
 471 and Martell (1981). Therefore, Eq. (3) simplifies to



474 The extracted species is a non-solvated chelate:
 475 among six co-ordination positions of Fe^{3+} , two are
 476 satisfied by a bisulphate group and other four positions
 477 by two anions of bidentate-monomeric BTMPPA.

478 Eq. (6) can be rewritten for Eq. (11) as:

$$\log D = \log K_{\text{ex}} + 2\text{pH}_{\text{eq}} + \log [\text{H}_2\text{A}_2]_{\text{eq}} - \log [\text{HSO}_4^-]_{\text{eq}} \quad (12)$$

489 Eq. (12) states that $\log D$ vs. $(2\text{pH}_{\text{eq}} + \log [\text{H}_2\text{A}_2]_{\text{eq}} - \log [\text{HSO}_4^-]_{\text{eq}})$ plot will be a straight line of unity slope
 482 and its intercept will be equal to $\log K_{\text{ex}}$. Such a plot is
 483 shown in Fig. 7. The least squares slope and intercept of
 484 the line are 0.87 and -2.30 respectively with correlation
 485 coefficient of 0.946 . Therefore, K_{ex} is equal to $10^{-2.30}$,
 487 compared to $10^{1.57}$ for Fe^{3+} by D2EHPA (Islam and
 488 Biswas, 1981).

489 The variation of distribution ratio of Fe^{3+} on
 490 temperature is displayed in Fig. 8 at four different
 491 experimental parameters. In all cases under investiga-

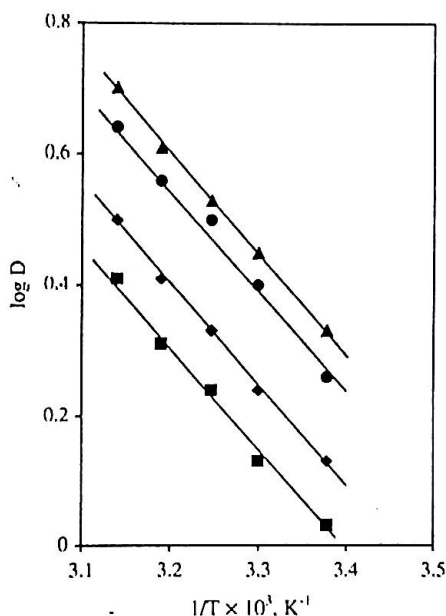


Fig. 8. Dependence of D on temperature. $[\text{SO}_4^{2-}] = 0.10 \text{ M}$, $[\text{Fe}^{3+}]_{\text{ini}} = 0.72 \text{ g/L}$, $\text{pH}_{\text{ini}} = 1.75$, $[\text{BTMPPA}]_{\text{ini}} = 0.025 \text{ M}$, slope = -15.33 , $\Delta H = 12.75 \text{ kJ/mol}$; (■), $\text{pH}_{\text{ini}} = 1.65$, $[\text{BTMPPA}]_{\text{ini}} = 0.025 \text{ M}$; slope = -16.00 , $\Delta H = 13.31 \text{ kJ/mol}$; (▲), $\text{pH}_{\text{ini}} = 1.75$, $[\text{BTMPPA}]_{\text{ini}} = 0.05 \text{ M}$, slope = -15.38 , $\Delta H = 12.80 \text{ kJ/mol}$; (●), $\text{pH}_{\text{ini}} = 1.65$, $[\text{BTMPPA}]_{\text{ini}} = 0.05 \text{ M}$, slope = -15.79 , $\Delta H = 13.14 \text{ kJ/mol}$.

tion, $\log D$ vs. $(1/T)$, K^{-1} plots are straight lines. With the help of Eq. (7), the ΔH values have been calculated from the slope of the lines. Average ΔH value is 13 kJ/mol with a variation of ± 0.30 . Positive ΔH value suggests that the extraction of Fe^{3+} from sulphate medium is endothermic in nature.

The loadings of Fe^{3+} in 0.10 and 0.20 M BTMPPA solution have been examined. The cumulative concentration of Fe^{3+} in the organic phase have been plotted in Fig. 9 against the number of stages. It is seen that 0.10 M BTMPPA is saturated with 5.1 g/L Fe^{3+} ; whereas, 0.20 M BTMPPA is saturated with 11.05 g/L Fe^{3+} . In the first case, 0.10 M BTMPPA is saturated with 0.0913 M Fe^{3+} . In the second case, 0.20 M BTMPPA is saturated with 0.198 M Fe^{3+} . Therefore, in both cases, Fe^{3+} to BTMPPA ratio at saturation is about 1:1; which is also obtained from the extractant dependence study. Thus the extraction mechanism near saturation remains unaltered. The loading capacity is calculated to be 9.6 g Fe^{3+} /100 g BTMPPA.

3.3. Stripping of Fe^{3+} –BTMPPA– HSO_4^- complex

The stripping ability of H_2SO_4 solution for the extracted complex has also been investigated. The result in Fig. 10 given as stripping % and $\log S$ vs. $\log ([H_2SO_4], M)$ plots shows that the best stripping is

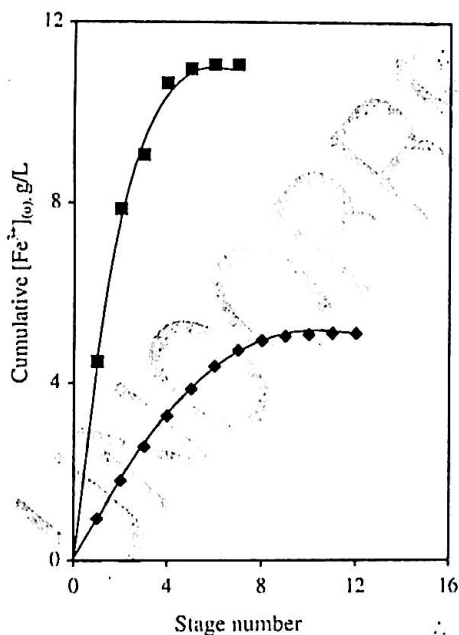


Fig. 9. Loading of BTMPPA with Fe^{3+} ; Cumulative $[Fe^{3+}]_{org}$ vs. phase contact time (aqueous renewed). $pH_{(ini)} = 2.40$, Equilibration time (each stage) = 30 min, (●), $[Fe^{3+}]_{(ini)} = 1$ g/L, $[BTMPPA] = 0.10$ M; (■), $[Fe^{3+}]_{(ini)} = 5$ g/L, $[BTMPPA]_{(org, ini)} = 0.20$ M.

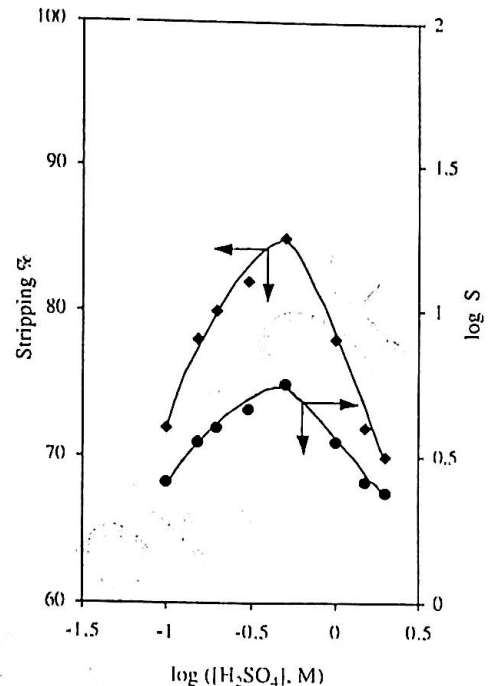


Fig. 10. Stripping of Fe^{3+} –BTMPPA– HSO_4^- complex by aqueous sulphuric acid solution. $(Fe^{3+})_{(org, ini)} = 2.21$ g/L, O/A = 1, free $[BTMPPA]_{(org, ini)} = 0.025$ M.

obtained with 0.50 M H_2SO_4 solution when 85% of Fe^{3+} is stripped. Fig. 11 shows the result of stage-wise stripping where the cumulative % Fe^{3+} stripped has been plotted against the stage number. It is seen that three-stage stripping removes more than 99% Fe^{3+} from the organic phase; whereas, a five-stage stripping leaves only 0.2% Fe^{3+} in the organic phase. The stripping abilities of HCl and HNO_3 are also tested but shown to be not as effective as H_2SO_4 . For example, 1 M HCl and 1 M HNO_3 are able to strip respectively 35% and 38% Fe^{3+} from the organic phase in a single stage.

3.4. Correlation of Fe^{3+} –BTMPPA extraction data with interfacial tension data

When Fe^{3+} (1 g/L) is extracted from 0.50 M sulphate medium at $pH_{(ini)} = 2$ by 0.025 M BTMPPA dissolved in different diluents, then the value of distribution ratio (D) is found to decrease in the following order: CCl_4 (0.92) > $ClCH_2CH_2Cl$ (0.87) > kerosene (0.81) > $CHCl_3$ (0.74) > $C_6H_5CH_3$ (0.70) $\approx$ n - C_6H_{14} (0.70) > $C_7H_{15}OH$ (0.65) > n -1- $C_7H_{15}OH$ (0.60) > n -1- $C_6H_{13}OH$ (0.56) > C_6H_6 (0.47). This order is changed, when extraction is made from an aqueous solution of $pH_{(ini)} = 0.80$ by 0.20 M BTMPPA, as shown: CCl_4 (0.30) > $ClCH_2CH_2Cl$ (0.28)

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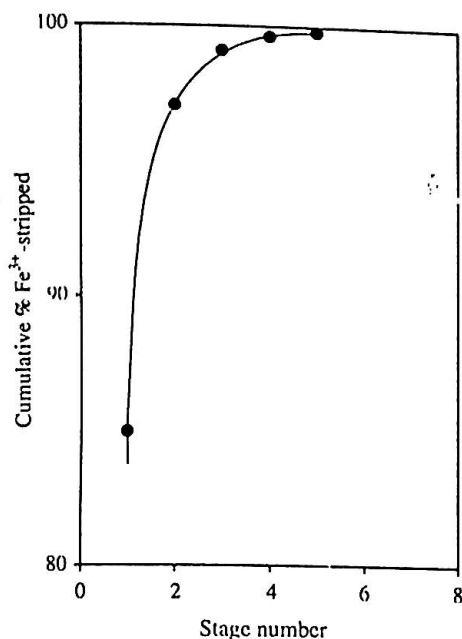
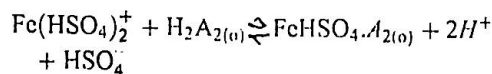


Fig. 11. Stage-wise stripping by aqueous sulphuric acid solution. $[\text{Fe}^{3+}]_{(0,\text{ini})} = 2.21 \text{ g/L}$, O/A (each stage) = 1, free [BTMPPA] $_{(0,\text{ini})} = 0.025 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.50 \text{ M}$. Aqueous phase renewed in each stage.

cial tension data and found to vary in the order: CCl_4 ($157 \text{ \AA}^2$) < $\text{C}_7\text{-C}_6\text{H}_{12}$ ($166 \text{ \AA}^2$) < $\text{C}_6\text{H}_5\text{CH}_3$ ($211 \text{ \AA}^2$) < CH_2Cl ($174 \text{ \AA}^2$) < $n\text{-C}_6\text{H}_{14}$ ($176 \text{ \AA}^2$) < $\text{C}_6\text{H}_5\text{CH}_3$ ($211 \text{ \AA}^2$) = kerosene ($211 \text{ \AA}^2$) < C_6H_6 ($262 \text{ \AA}^2$) < CHCl_3 ($335 \text{ \AA}^2$) < $n\text{-1-C}_7\text{H}_{15}\text{OH}$ ($532 \text{ \AA}^2$) < $n\text{-1-C}_6\text{H}_{13}\text{OH}$ ($734 \text{ \AA}^2$). The cross-sectional area can be correlated with Fe^{3+} -extraction data.

- (ii) Fe^{3+} may be extracted by BTMPPA over a wide range of conditions: $[\text{Fe}^{3+}] = 1.29 \text{ } 100 \text{ mM}$ or more, $\text{pH}_{(\text{ini})} = 1.25 - 2.25$ or more and $[\text{BTMPPA}] = 0.025 - 0.20 \text{ M}$ or higher. With increasing $[\text{Fe}^{3+}]$ and $[\text{SO}_4^{2-}]$ in the aqueous phase and a lowering of pH, [BTMPPA] and temperature, the distribution ratio of Fe^{3+} decreases.
- (iii) The pH, [BTMPPA] and $[\text{SO}_4^{2-}]$ dependences of distribution ratio suggest that the extraction occurs via the following reaction:



which has an equilibrium constant of $10^{-2.3}$ and ΔH value of $(13 \pm 0.3) \text{ kJ/mol}$.

- (iv) The loading capacity is $9.6 \text{ g Fe}^{3+}/100 \text{ g BTMPPA}$.

$> n\text{-C}_6\text{H}_{14}$ (0.25) = $\text{C}_6\text{H}_5\text{CH}_3$ (0.25) > $\text{C}_7\text{-C}_6\text{H}_{12}$ (0.24) > kerosene (0.22) > C_6H_6 (0.18) > CHCl_3 (0.16) > $n\text{-1-C}_7\text{H}_{15}\text{OH}$ (0.12) > $n\text{-1-C}_6\text{H}_{13}\text{OH}$ (0.11). These values of D in the logarithmic form have been plotted against the logarithm of the cross-sectional area (A , $\text{\AA}^2$) of BTMPPA molecules adsorbed at the interface formed by different diluents in Fig. 12. In the first case, out of ten points, a six point fit correlation is obtained. A better result is obtained in the second case. The correlated lines have a slope of about -0.33 and -0.40 in the first and second cases, respectively. In the case of D2FHPA (Biswas et al., 2003), a very sharp correlation was obtained between the distribution ratio (D) of TiO^{2+} and the cross-sectional area of D2EHPA (A). In that case, the slope of $\log D$ vs. $\log A$ plot was -4.0 . It is therefore concluded that in contrast to the extraction characteristics of D2EHPA reported earlier, the extraction characteristics of BTMPPA is not so much dependent on the diluent used to constitute the organic phase.

4. Conclusions

The following conclusions have been drawn:

- (i) The cross-sectional areas of a BTMPPA molecule adsorbed at the $0.50 \text{ M H}_2\text{SO}_4$ /diluent interface have been measured from the interfa-

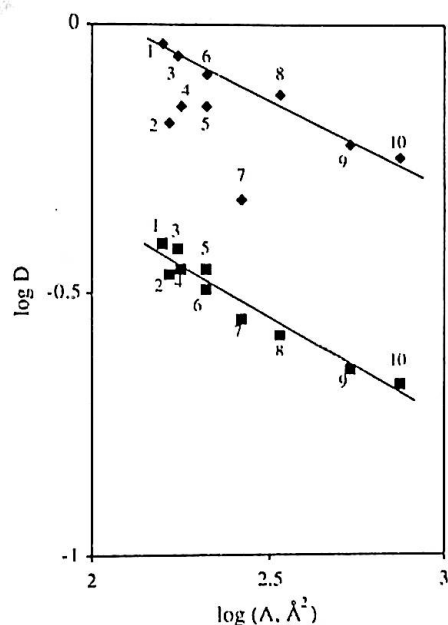


Fig. 12. Correlation of cross-sectional area of adsorbed BTMPPA molecule with the distribution ratio of Fe^{3+} in different diluents. D is determined on extracting 1 g/L Fe^{3+} from 0.50 M sulphate medium. (●), at $\text{pH}_{(\text{ini})} = 2$ by 0.025 M BTMPPA ; (■), at $\text{pH}_{(\text{ini})} = 0.8$ by 0.20 M BTMPPA . 1. CCl_4 , 2. $\text{C}_7\text{-C}_6\text{H}_{12}$, 3. $\text{C}_6\text{H}_5\text{CH}_3$, 4. $n\text{-C}_6\text{H}_{14}$, 5. $\text{C}_6\text{H}_5\text{CH}_3$, 6. kerosene, 7. C_6H_6 , 8. CHCl_3 , 9. $n\text{-1-C}_7\text{H}_{15}\text{OH}$, 10. $n\text{-1-C}_6\text{H}_{13}\text{OH}$.

(v) The extracted Fe^{3+} -complex with BTMPPA can be stripped by 0.5 M sulphuric acid in 2–3 stages. HCl and HNO_3 are not so effective as stripping agents.

Notations and abbreviations

A = Cross-sectional area, Å^2
 BTMPPA = Active compound of Cyanex 272, bis-2,4,4-trimethylpentylphosphinic acid
 C_1 = Concentration of BTMPPA at which monolayer formation starts
 C_2 = Concentration of BTMPPA at which micelles formation starts
 D = Distribution ratio, $[\text{Fe}^{3+}]_{(\text{o},\text{eq})} / [\text{Fe}^{3+}]_{(\text{eq})}$
 D_c = Corrected distribution ratio at a fixed equilibrium pH and concentrations of extractant and sulphate
 H_2A_2 = Dimeric BTMPPA
 ΔH = Enthalpy change
 I = Intercept
 S = Stripping ratio, $[\text{Fe}^{3+}]_{(\text{eq})} / [\text{Fe}^{3+}]_{(\text{o},\text{eq})}$
 s = Slope
 γ = Interfacial tension, mN/m
 Γ = Number of molecules adsorbed per unit area, m^{-2}

Subscripts

(eq) = equilibrium
 (o) = organic phase
 (ini) = initial

Superscripts

const = constant

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