

THE ADSORPTION OF STEARIC ACID AND PYRIDINE AND DETERMINATION OF SPECIFIC SURFACE AREA OF POWDERED SOLIDS



A thesis submitted to the University of Rajshahi
for the Degree of Master of Philosophy

Submitted by
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3/4/2022

DECLARATION

Abstract

CHAPTER 1 Introduction

CHAPTER 2 Literature Survey

2.1 Adsorption of fatty acids and deter-

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solids

The author declares the work presented for the degree of Master of Philosophy at the University of Rajshahi is the result of his own investigation. He further certifies that this work has not been submitted previously for any degree.

The determination of specific surface area of ferric oxide and alumina by adsorption of stearic acid carried out by the author for the partial fulfilment of his M.Sc degree has been quoted in places to help draw general conclusions from the present results.

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ABSTRACT

The BET gas adsorption, flow micro-calorimetric and adsorption from solution methods for the determination of surface areas of cupric oxide, ferric oxide and alumina powders have been compared with a view to examine the validity of the method of adsorption from solution as a standard. Nitrogen gas has been chosen for the BET method whereas stearic acid, a commonly employed solute, has been used for the flow micro-calorimetric and adsorption from solution measurements. It has been found that adsorption of nitrogen gas on all the adsorbents is physical in nature but stearic acid employed in the flow micro-calorimetric and adsorption from solution methods gives mostly chemisorption of the molecules on the adsorbent powders. Surface areas determined by the flow micro-calorimetric and adsorption from solutions have been found to be identical for the respective powders. Despite the difference in mechanism of adsorption of nitrogen and stearic acid molecules the flow micro-calorimetric and adsorption from solution surface areas agree fairly well with the BET nitrogen gas adsorption surface areas of the adsorbents if it is assumed that the area occupied per molecule of stearic acid to be of the order of $60-70 \text{ \AA}^2$. The orientation of stearic acid molecules on the solid/liquid interface, therefore, take place so that acid molecules lie neither completely perpendicular nor completely parallel to

(ii)

neither completely perpendicular nor completely parallel to the surface. Possible orientations of the stearic acid chain on the surface are envisaged.

Correspondence of the surface areas of the adsorbents using nitrogen gas and stearic acid solution reveal that the total sites of the adsorbents are independent of the nature of the solute molecules.

To study this hypothesis further pyridine, an organic base, has been chosen as solute and its adsorption on the same adsorbents have been studied. The surface areas obtained by adsorption of pyridine from solution have been found to be identical to the respective areas obtained by BET method and stearic acid adsorption if it is considered that the area occupied by one molecule of pyridine to be around $24.7 \text{ \AA}^2$, the molecular area of pyridine.

Adsorption of stearic acid on magnesium oxide and silica gel powders gave surface areas to be 90 and $370 \text{ m}^2/\text{g}$ respectively considering area occupied per molecule of stearic acid to be 63.3 and $67.5 \text{ \AA}^2$. These value agree fairly well with the values quoted in literature. Surface areas of these two powders determined by adsorption of pyridine agree fairly well with the above mentioned value if it is considered that one molecule of pyridine occupies $24.8 \text{ \AA}^2$.

(iii)

It may, therefore, be concluded that with the appropriate values of areas occupied per molecule of solute method adsorption of stearic acid and pyridine may be taken as standard for the determination of surface area of the adsorbents considered.

The author is aware of the fact that the work is not perfect, and that it contains many errors, but he trusts that it will be found to contain many valuable suggestions and facts, and that it will be of some service to the public. The author is also aware of the fact that the work is not perfect, and that it contains many errors, but he trusts that it will be found to contain many valuable suggestions and facts, and that it will be of some service to the public.

CHAPTER - I

INTRODUCTION

The purpose of this book is to present a clear and concise statement of the principles of the science of the mind, and to show how these principles can be applied to the study of the human mind. The book is divided into two parts, the first of which is devoted to a general statement of the principles of the science of the mind, and the second of which is devoted to a more detailed statement of the principles of the science of the mind.

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1. Introduction

The determination of surface area of powdered solids is of immense industrial importance. And, therefore, a wide range of methods is available⁽¹⁾ which may broadly be classified as (i) those based on gaseous adsorption, and (ii) those based on adsorption of a surface active solute from solutions. Direct determination of the amount of solute adsorbed at equilibrium adsorption by analytical means, measurement of heat of immersion by static calorimeters and measurement of preferential heat of adsorption by flow micro-calorimeters fall under category (ii). In all these methods surface area of powdered solids are evaluated either from the knowledge of maximum amount of solute adsorbed or from the knowledge of the maximum amount of the heat evolved. Both these approaches demand some assumptions to be valid of which formation of close-packed monolayer of the solute molecules on the adsorption surface is common. These assumptions have been found to be fairly valid for a wide range of interfaces, although formation of multilayers indicated by the departure from the Langmuir type of isotherm limits the scope of all the methods.

The evaluation of surface area from the amount of solute adsorbed further requires the area occupied by one molecule of the solute to be known. This could theoretically be obtained for the two ideal cases, (i) when all the solute molecules lie perpendicular to the surface and (ii) when all the

solute molecules lie parallel to the surface, to form close-packed monolayers. In between these two extremes the area occupied per molecule of solute should be determined experimentally against some standards. If the BET nitrogen gas adsorption method is employed for this purpose area occupied per molecule of solute is given by

$$A_m = \frac{S}{Nx_m} \quad (1)$$

where, A_m = area occupied by one molecule of solute, S = surface area of adsorbent determined by BET method, m^2/g , x_m = the amount of solute adsorbed at monolayer coverage, mol/g, and N = the Avogadro's number.

The amount of solute adsorbed at monolayer coverage (x_m) may be determined from the Langmuir plot assuming Langmuir form of equation⁽²⁾ for monolayer coverage,

$$\frac{C}{x} = \frac{1}{kx_m} + \frac{C}{x_m} \quad (2)$$

the corresponding BET equation for multilayer coverage being,

$$\frac{C}{x(1-C)} = \frac{1}{kx_m} + \frac{C}{x_m} \quad (3)$$

where, C = concentration of solute solution, mol/lit.,

x = amount of solute adsorbed (mol/g) from solution of concentration (C) and k is a constant.

On the other hand the determination of surface area, S , which may be assumed to be directly proportional to the integral heat of adsorption per gram of adsorbent at monolayer coverage (q_0) requires the value of K , the proportionality constant in equation (4) to be known.

$$S = Kq_0 \quad (4)$$

The value of K should be evaluated experimentally against some adsorbents having standard surface area.

Literature⁽²⁻⁸⁾ shows the application of both the approaches, namely, the determination of surface area of adsorbent from the knowledge of (i) the amount of solute adsorbed, and (ii) the amount of integral heat of adsorption. To evaluate the area occupied per molecule (A_m) of solute on adsorbent surfaces in equation (1) and proportionality constant (K) in equation (4) BET nitrogen gas adsorption surface area is customarily equated to the area occupied by the solute molecules at equilibrium adsorption to form monolayer coverage.

Both the BET nitrogen gas adsorption method and the static calorimetric method are well established but tedious. Moreover, both the methods require skilled operators and also drastic conditions for degassing the adsorbent powders. Recently, flow micro-calorimeter has proved itself to be a

useful tool for the determination of surface area of powdered solids. However the flow micro-calorimeter is an expensive equipment and needs skilled operators. In addition, the reliability of flow micro-calorimetric results have recently received criticism. On the other hand, the method based on direct measurement of the amount of solute adsorbed on adsorbent surfaces from solution by analytical means is simple and does not involve much instrumentations. Using stearic acid as solute in benzene solution this method has been found to give results as good as that of BET nitrogen gas adsorption method for ferric oxide and alumina powders. The present work is intended to examine the applicability of this method for cupric oxide, magnesium oxide and silica gel powders. Recently, pyridine and its derivatives have been found to exhibit anti-wear properties in boundary lubricity. Pyridine and its derivatives are organic bases which differ in terms of chemical nature from that of long chain fatty acid like stearic acid. The purpose of the present work has also been to study the adsorption of pyridine on cupric oxide, ferric oxide, magnesium oxide, alumina and silica gel powders with a view to examine the possibility of determining the surface area of these powdered solids.

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CHAPTER - II

LITERATURE SURVEY

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2.1. Adsorption of fatty acids and determination of surface area of powdered solids.

Literature shows a large volume of work involving adsorption of long chain fatty acids from solution on different adsorbents. In the method of adsorption from solution adsorbent powder is immersed in a solution containing long chain fatty acids and the suspension is shaken until the equilibrium is attained. The powder is allowed to settle and a sample of the supernatant liquid is drawn off to estimate the amount of fatty acid left after adsorption. The previous works involving adsorption of long chain fatty acids from solution is critically reviewed here.

Harkins and Gans⁽⁹⁾ determined the area of titanic oxide and silicon dioxide powders using oleic acid in benzene solution. Assuming the adsorption to be of unimolecular layer specific surface areas of TiO_2 -I and TiO_2 -II powders were found to be 22.9 and 14.4 m^2 per c.c of titanic oxide (3.89 g) respectively. The area occupied per molecule of oleic acid was taken to be 20 $\text{\AA}^2$.

Ewing⁽¹⁰⁾ investigated the adsorption method for determining the surface area of pigments of small particle size. Zinc oxide was chosen as the pigment. Adsorption was carried out from benzene solution of various aliphatic long chain compounds like methyl stearate, glycol dipalmitate and glycerol tristearate which strongly adsorb on zinc oxide. Using the

horizontal pull method described by Harkins and Anderson⁽¹¹⁾, the cross-sectional area of methyl stearate and glycol dipalmitate were evaluated to be 26.6×10^{-16} and 48×10^{-16} cm² respectively. On the basis of these assumptions the specific surface area of the pigments were calculated. These areas compared favourably with those obtained by photomicrographic measurements.

Smith and Fusek⁽¹²⁾ determined the surface area of raney nickel by adsorption of capric, lauric, palmitic, nonadecylic and behenic acids from solution of methanol, acetone, heptane, benzene, and cyclohexane. According to Adam⁽¹³⁾, the cross-sectional area of fatty acid molecule was taken $20.5 \text{ \AA}^2$ units. The authors concluded that although the fatty acid adsorption method for the determination of specific surfaces was not as generally applicable as the nitrogen isotherm method, it was experimentally much simpler. In addition, the assumption of the cross-sectional area occupied by a fatty acid chain was probably better than the assumptions made concerning the cross-sectional area of the nitrogen molecule.

Russel and Cochran⁽¹⁴⁾ measured the surface areas of non-porous hydrated aluminas by stearic acid sorption from solution. These values agreed with those by nitrogen gas adsorption, assuming that the area occupied by one molecule of stearic acid to be $17 \text{ \AA}^2$.

Hirst and Lancaster⁽¹⁵⁾ estimated the surface areas of powders from the temperature dependence of adsorption from solution of stearic acid in benzene. Measurements of powders, titanium dioxide, silicon dioxide, TiC and SiC by both methods, namely, temperature variation and concentration variation, gave good agreement. It was claimed that the temperature-dependence method involved less manipulation and smaller experimental error.

Glueckauf⁽¹⁶⁾, and MaxNestlar and Cassidy⁽¹⁷⁾ in separate study measured the surface area of charcoal by adsorption of fatty acids. Ito and Fukao⁽¹⁸⁾ studied the adsorption of valeric, caproic and heptylic acid from aqueous solutions by active charcoal. Kinnouske⁽¹⁹⁾ also studied the adsorption of fatty acids including valeric, caproic, heptanoic and butyric acid from aqueous solution by active charcoal.

Smith and Hurley⁽²⁰⁾ calculated the surface area of carbon black by calculating the particle size of the fatty acids (acetic, behenic, capric, lauric, palmitic and stearic acid) after adsorption from various solvents. Surface areas calculated by this method gave good agreement with the areas calculated by other methods. Morrison and Miller⁽²¹⁾ also measured the maximum adsorption of the monocarboxylic acids - acetic, propionic, butyric, valeric, caproic, of the dicarboxylic acids - oxalic, malonic, glutamic, etc. on coconut-shell charcoal.

Suito et al⁽²²⁾ reported the estimation of the specific surface area of calcium carbonate by adsorption of stearic acid. The specific surface area was established by the application of the BET measurements. The results were in agreement with those obtained by other methods using Gibbs adsorption formula. The authors also reported the influence of adsorbates and solvents. The results obtained with stearic acid, palmitic acid, oleic acid, benzoic acid and methyl ester and glycol ester of stearic acid agreed with one another. They argued that benzene should be used as solvent rather than toluene or carbon tetrachloride.

Loomis⁽²³⁾ determined the surface area of clays and sedimentary rock by a liquid phase adsorption method. A unimolecular layer of stearic acid was assumed to be adsorbed on the surface. The amount of adsorption was determined by the change in concentration of the original solution added to the clay or rock samples. Measurements were made gravimetrically and volumetrically.

Tamaki⁽²⁴⁾ compared the gas adsorption method and the liquid-phase adsorption method for the determination of the surface area of powders. For the purpose of establishing the surface area of active alumina and carbon black, the adsorption of various substances on alumina and carbon black were studied, viz (i) nitrogen at -195°C , (ii) stearic acid from C_6H_6 solution, (iii) iodine from hexane solution, (iv) iodine

from an aqueous solution of potassium iodide. In alumina the surface area established by method (i) was greater than by methods (ii), (iii) and (iv). In carbon black the value obtained by methods (i), (iii) and (iv) almost agreed between themselves.

Medvedeva⁽²⁵⁾ determined the specific surface area of finely dispersed alumina by adsorption of stearic acid from liquid phase on the method developed by Russel and Cochran⁽¹⁴⁾. Values of specific surface area determined in this way ranged from 32.1 to 34.2 m²/g, assuming the area occupied by one molecule of stearic acid to be 17.2 Å². In the cases where the grinding was performed without the presence of surface agents, results were slightly lower. These values were from 10 to 15 times greater than those determined by the permeability method of Tovarov⁽²⁶⁾. Tovarov's method, however, was considered unreliable by Ries et al⁽²⁷⁾.

Kordecki and Gandy⁽²⁸⁾ investigated the sorption of stearic-1-C¹⁴ acid from benzene solution for the measurement of surface area of non-porous powders. Specific surface areas obtained by this method compared favourably with nitrogen adsorption values (BET method). The results in square meter per gram were 21.1 for clay, 4.7 and 6.3 for two zinc oxides, 3.6 for alumina, 21.4 for calcium sulphate, 22.3 for nickel, 0.6 for glass beads, 6.5 for titanium oxide, 4.0 and 10.2 for two ferric oxide, 5.5 for zinc carbonate, 50.1 for manganese oxide, 6.0 for

zinc chloride and values of 4.0, 3.9 and 3.4 for different grade of zinc sulphide.

Kravchenko et al⁽²⁹⁾ evaluated the method of determination of specific surface area based on Knudson equation for titration through media by comparing with that of adsorption from solution using dyes and fatty acids. Finally, the results were compared with that of nitrogen gas adsorption method.

Jankovics⁽³⁰⁾ proposed a method for the determination of surface area of solids, based on the adsorption of stearic acid. Upon completion of adsorption, the amount of stearic acid left in the solution was determined by titration with dilute solution of sodium hydroxide by using either alcohol or methyl alcohol as solvent. The surface area of calcium phosphate determined by this method was found to be $30.4 \text{ m}^2/\text{g}$ and this value agreed with that of BET nitrogen gas adsorption method.

Korenev and Lunina⁽³¹⁾ compared the surface areas of nickel, iron, aluminium powders measured from adsorption of stearic acid, lauric acid, and aluminium soaps (stearate and naphthenate) from toluene solvent. The adsorption of the acids on nickel was greater than on iron and aluminium. The surface areas of the three metal powders were found different from one another.

In adsorption from solutions in cyclohexane, Kipling and Wright⁽³²⁾ showed that stearic acid was adsorbed with the major axis of the molecule parallel to the surface of silica, but perpendicular to the surfaces of alumina and titania. The limiting value of adsorption were compared with calculated monolayer values based on the two orientations for stearic acid, with molecular areas (expressed in terms of the monomeric molecules) of $114 \text{ \AA}^2$ for the parallel orientation⁽³³⁾, and $20.5 \text{ \AA}^2$ for the perpendicular orientation. The results, with these orientations, slightly differed with the calculated values.

Recently, Groszek^(6,7) has determined the surface areas of a number of solid powders flow calorimetrically using stearic acid solution and compared these values with those of nitrogen gas adsorption methods. An examination of Groszek's results shows that for ferric oxide powder the area occupied by one molecule of stearic acid is $66 \text{ \AA}^2$ so that total nitrogen gas adsorption area is occupied by stearic acid molecules. Allen and Patel^(2,3) found the area occupied by one molecule of stearic acid to be 60 to $70 \text{ \AA}^2$ assuming that the total nitrogen gas adsorption surface area of ferric oxide powder was occupied by stearic acid molecules. Recently, Rahman⁽⁸⁾ has confirmed that an agreement between nitrogen gas adsorption surface area and surface area determined by flow calorimeter using stearic acid is obtained if the area occupied by one molecule of stearic acid is taken to be $70 \text{ \AA}^2$.

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From the account of the previous works given in this chapter it is seen that in the early works of determination of specific surface area of powdered solids using the method of adsorption from solution area occupied by one molecule of fatty acid have been assumed to be $17 - 20 \text{ \AA}^2$ which is approximately equal to the cross-sectional area of the fatty acid molecules. In these studies the implicit assumption involved was that the fatty acid molecules were oriented perpendicularly on the surface. A critical examination of the published results shows that specific surface area calculated under the above assumption agrees with the BET nitrogen gas adsorption area only for some limited cases, for example, for the determination of specific surface area of hydrated alumina⁽¹⁴⁾ and calcium phosphate⁽³⁰⁾. On the other hand the specific surface areas of alumina and titania^(32,33) measured from adsorption of stearic acid from cyclohexane agree approximately considering the parallel orientation of stearic acid molecules with the molecular area $114 \text{ \AA}^2$. Also an examination of Medvedeva's⁽²⁵⁾ findings shows that the specific surface area of alumina determined by the method of adsorption of stearic acid from solution agrees with the BET nitrogen gas adsorption area if it is considered that the area occupied by one molecule of stearic acid to be about $60 \text{ \AA}^2$. With the advent of the technique of flow micro-calorimetry adsorption of stearic acid on ferric oxide powder has been studied by a number of workers⁽²⁻⁸⁾. In

all these works agreement between the specific surface area of ferric oxide powder determined flow calorimetrically using stearic acid solution in n-heptane and that determined by BET nitrogen gas adsorption method was found if area occupied by one molecule of stearic acid is considered to be $60 - 70 \text{ \AA}^2$.

It has also been found that of the fatty acids stearic acid appears to be a most common solute in the measurement of adsorption from solution. Literature involving study of mechanism of adsorption of stearic acid on powdered solids are, therefore, summarized in the following section.

2.2. Mechanism of adsorption of stearic acid on powdered solids.

From flow micro-calorimetric study Groszek⁽⁷⁾ concluded that stearic acid molecules do not form close-packed monolayer on ferric oxide powder in the sense that the molecules lie perpendicular to the surface with the carboxylic groups resting on it. From the study of adsorption of fatty acids of different chain length on ferric oxide, titanium oxide and barium sulphate. Allen and Patel⁽⁴⁾ argued that $-\text{COOH}$ polar head rested at the adsorbed layer and the first six $-\text{CH}_2$ groups form a loop above the surface and extending into the liquid. They also argued that while the seventh $-\text{CH}_2$ group rested on the interface the eighth and subsequent groups lie above the surface. Kipling and Wright^(32,33) assumed that stearic acid molecules were physically adsorbed on the surface

as dimers. This is in contrast to the perpendicular orientation of stearic acid molecules in close-packed monolayer. Recent infra-red and thermogravimetric analysis of Hasegawa et al⁽³⁴⁾ and Tyler et al⁽³⁵⁾ revealed that the model of adsorbed layer of stearic acid on alumina and silica gel powder differ from that of Kipling and Wright^(32,33). It has been evidenced that on alumina and silica gel powders the adsorption layer consisted predominantly of monolayers at low surface coverage, and weak and reversible dimers at high concentration of solution.

2.3. Adsorption of pyridine and determination of surface area of powdered solids.

Like fatty acids which are weak organic acids literature shows a number of studies involving adsorption of weak organic bases, pyridines, on powdered solids.

Bertoluzza et al⁽³⁶⁾ and Lorenzeli et al⁽³⁷⁾ carried out infra-red spectroscopic studies separately on the adsorption of pyridine on aluminium chloride, silica gel and alumina-silica surfaces. They argued that the mechanism of the adsorption on aluminium chloride and silica-alumina were similar and involved both aprotic (Lewis) and protonic (Bronsted) centres on the catalyst surfaces.

The orientation of pyridine sorbed on Na-montmorillonite was studied with infra-red spectroscopy by Serratosa⁽³⁸⁾ who argued that pyridine molecules were disposed with their

planes perpendicular to the silicate layers and with the principal axis parallel to the layers. The above results agreed with those from x-ray spacing measurements and dimensional synthesis.

The adsorption of aromatic compounds including pyridine from cyclohexane solution on a carbon black (specific surface area obtained by the BET method $76.1 \text{ m}^2/\text{g}$) and on a graphite with a specific surface area of $9.2 \text{ m}^2/\text{g}$ was studied by Sugimura et al⁽³⁹⁾. The adsorption isotherm obtained were of the Langmuir type. The results showed a higher amount of adsorption and higher heat of adsorption. This result agreed well with that of Matsen⁽⁴⁰⁾ who assumed that the adsorption was caused by the charge-transfer type intermolecular force.

Waksmundzki⁽⁴¹⁾ studied the specific surface, adsorbing capacity, number of sorption layer, surface layer volume per gram of adsorbent and pore radius of silica gel with some aromatic compounds including pyridine and 2-picoline (2-methyl pyridine). In their study the specific surface area of the gel depended on the number of CH_2 groups of sorbate substance, and pyridine gave greatest adsorption on silica. The activation on all silica gels prepared was of the multilayer type, the number of monomolecular adsorption layers being the greatest on the gels activated with pyridine.

The infra-red spectra taken by Low et al⁽⁴²⁾ at the time of pyridine sorbed on highly dehydroxylated, deuterated silica gels. The results showed that the pyridine was sorbed on the silica gels in a multilayer type.

and flourinated porous glass, as well as on pure silica and boria-impregnated silica showed that the H-atoms of sorbed pyridine exchange with surface OD groups. They argued that physical adsorption occurred by hydrogen bonding of pyridine to SiOH and B-OH groups via the pyridine nitrogen atom, there was some interaction of the system with OH group and surface B-pyridine complexes formed by co-ordination of pyridine to B, the B-pyridine surface complex could be hydrogen bonded to B-OH groups.

The spectroscopic studies of adsorption of H_2O and pyridine on silica gel were made by Chukin et al⁽⁴³⁾. The experiment with the adsorption of H_2O showed that H_2O took place not on the OH groups but on Si-atoms with open co-ordination sites; the H_2O was bound to the silica gel surface in the molecular state and remained there upto $450^{\circ}C$. The experiments with pyridine showed that on the silica gel, protonic and aprotonic centres were not present and the adsorption of pyridine took place by means of the hydrogen bonds of the OH groups. They argued that the proton centres were formed after addition of small amounts of H_2O , in the case of insufficient pyridine on the sample, pyridine passed from OH group to the proton centres.

Bandiera⁽⁴⁴⁾ measured gravimetrically the amounts of NH_3 and pyridine fixed on γ -alumina and silica-alumina. Their experiments revealed the presence of several types of adsorption sites. The author explained that pyridine which is a

weaker base apparently was fixed only on acid centres, but it could combine by charge-transfer to electron-acceptor $-O-Al^+-O$ sites which have an oxidation character.

During the adsorption of pyridine on oxide catalysts of iron(III), molybdate(VI) and molybdenum(VI) the infra-red spectroscopy revealed that the vacancies in the co-ordination shell of cations of the catalyst activated at $410^{\circ}C$ most likely acted as adsorption centres for pyridine as well as H_2O . These studies were carried out by Kubelkova et al⁽⁴⁵⁾ who argued that the H_2O adsorption caused the formation of Brønsted acid centres on the surface which interacted with pyridine giving rise to $(PyH)^+$ species. The pyridine adsorption probably took place also on the OH groups which remained the surface after H^+ abstraction from adsorbed H_2O .

The surface chemistry of titanium dioxide was studied infra-red spectrophotometrically by Chukin et al⁽⁴⁶⁾. They found that both the H-bond and the co-ordinated H_2O on the surface of TiO_2 were escaped on heating. The co-ordinated H_2O was thought to be responsible for the surface acidity. When TiO_2 , having surface bound H_2O , was exposed to pyridine(Py), $(PyH)^+$ was formed on its surface. The anhydrous titanium dioxide surface formed co-ordinated bonds with anhydrous pyridine.

The adsorption of polar (formic, acetic, propionic and pyridine) and non-polar molecules (hexane, cyclohexane

and benzene) from gas phase by allophane at room temperature (30 - 40°C) and at 150 - 180°C was measured by Nishimura⁽⁴⁷⁾. He found that non-polar molecules were adsorbed solely physically, but polar molecules were adsorbed chemically with little dependence on micropore structure of the adsorbent. Adsorbed amounts of the non-polar molecules were small, but those of the polar molecules were large and adsorbed amount of formic acid, for example, on allophane (specific surface area 280 cm²/g) at room temperature was almost the same as that on carbon (specific surface area 1500 cm²/g).

Hirokawa et al⁽⁴⁸⁾ studied the vibrational spectra of , and -picoline (methyl derivatives of pyridine) adsorbed on aerosil SiO₂. At high coverage, 2 kinds of surface species were found, which were assignable to the liquid-like species and the H-bonded species persisting at low coverage.

Hiromitsu et al⁽⁴⁹⁾ determined the amounts of physisorbed and chemisorbed pyridine on silica-alumina in the hexane solution at 30°C which were 1.25 and 0.25 mols/100 Å² respectively. The number of strong acid sites determined by Benesis method were in good agreement with the chemisorbed molecules which indicated that the ratio of the number of chemisorbed pyridine molecules to that of the strong acid sites on the surface of silica-alumina were equal. The adsorption calorimetry was carried out on the same system by means of a flow

calorimeter. The results showed that the heats of physisorption of pyridine were 11.3 ± 0.3 and 22 ± 4 kcal/mole respectively.

A comparative adsorption of methyl substituted pyridine on aluminium oxide was studied by Kozlov et al⁽⁵⁰⁾. They argued that both basicity and steric factors were important in the adsorption of pyridine, picolines, lutidine, and 2,4,6-trimethyl pyridine on alumina at 300°C and the plane of these molecules was oriented perpendicular to the alumina surface.

The effect of ionization on adsorption from solution was studied by Rendall⁽⁵¹⁾. The adsorption of picoline at the silica-H₂O interface was reported as a function of pH. A model was developed which allowed for the adsorption of the cationic and neutral molecules. For the zero coverage limit, expressions were derived which gave simultaneous fit of adsorption and electrokinetic measurements and the model is extended to consider the complete adsorption isotherm. The magnitudes and initial slopes of the isotherms, and the occurrence and position of the maximum in the adsorption - pH curve were explained. The adsorption of the methyl picolinium ion was examined for comparison with the adsorption behavior of the picolinium ion. The two forms of the picoline molecules were found to have adsorption potentials of 4 KT, the neutral molecules being adsorbed more strongly by 0.3 KT.

Organic polar and heterocyclic compounds in hydrocarbon oil have been found to exhibit antiwear properties in steel-on-steel sliding system. The effect of pyridine, several alkyl pyridines and related aromatic compounds on the boundary lubricity properties was studied⁽⁵²⁻⁵⁶⁾. The extent of the antiwear action exerted by the alkyl derivatives has been found to depend on the position of the substituent on the ring. From this structure - activity relationship it has been argued that perpendicular approach of the molecule toward the metal surface and bonding via the nitrogen atom are considerable importance in the overall antiwear performance of pyridine.

Unlike those of fatty acids studies involving adsorption of pyridine on powdered solids are mostly mechanistic. There has been hardly any attempt to evaluate surface area of the powdered solids using the results of adsorption of pyridines on powdered solids.

2.4. Purpose of the present work.

An examination of the published results involving adsorption of stearic acid on powdered solids leads us to the conclusion that solid adsorbents may broadly be classified as (i) those on which stearic acid forms close-packed monolayers in the sense that stearic acid molecules lie perpendicularly on the solid surface so that area occupied by one molecule of stearic acid on the adsorbent surface is of the order of

17 - 20 $\text{\AA}^2$, which is approximately equal to the cross-sectional area of the fatty acid molecules, and (ii) those on which stearic acid molecules lie neither completely perpendicular nor completely parallel to the surface so that area occupied by one molecule of stearic acid is of the order of 60 - 70 $\text{\AA}^2$. It is interesting to note that powdered solids on which one molecule of stearic acid occupies an area of 17 - 20 $\text{\AA}^2$, for example, hydrated alumina and calcium phosphate are non-porous; on the other hand powdered solids on which one molecule of stearic acid occupies an area of 60 - 70 $\text{\AA}^2$ are porous. Therefore, a hypothesis may be put forward that the area occupied by one molecule of stearic acid on non-porous powders is different from that on porous powders giving values of area occupied by one molecule of stearic acid to be 17 - 20 $\text{\AA}^2$ and 60 - 70 $\text{\AA}^2$ respectively. To substantiate this hypothesis study of adsorption of stearic acid on a number of porous and non-porous powders is needed. The present study is, however, limited to the determination of specific surface area of five porous powders, namely, ferric oxide, cupric oxide, magnesium oxide, alumina and silica gel so that the orientation of stearic acid molecules on these surfaces be determined. The aim has primarily been to examine the possibility that stearic acid can be taken as a standard solute in the determination of surface area of porous solids by the adsorption from solution method. For this purpose adsorption of stearic acid from solution on different

porous solids have been studied both by flow micro-calorimetric method and adsorption from solution method, and specific surface areas of the powdered solids determined by these methods are compared with those obtained from BET nitrogen gas adsorption method.

It has already been pointed out that pyridine has recently been proved to be a surface active agent to exhibit antiwear property in boundary lubricity. Because of the simplicity of the pyridine molecule this compound has warrant our attention so that possibility of determining surface area of solids using pyridine as a solute be examined. Adsorption of pyridine on all the aforesaid porous solids has, therefore, been studied.

CHAPTER - III

EXPERIMENTALS

The first experiment was carried out to determine the effect of the concentration of the reactants on the rate of the reaction. The reaction was carried out in a closed system at a constant temperature of 25°C. The rate of the reaction was determined by measuring the volume of gas evolved at regular intervals of time. The results of the experiment are shown in the following table:

Concentration of Reactants	Rate of Reaction (ml/min)
0.1M	1.2
0.2M	2.4
0.3M	3.6
0.4M	4.8
0.5M	6.0

From the above table, it is evident that the rate of the reaction increases linearly with the concentration of the reactants. This indicates that the reaction is first order with respect to the concentration of the reactants.

3.1. Materials used.

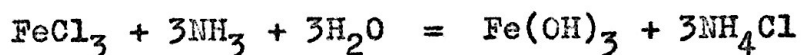
- | | |
|-----------------|---|
| Ferric oxide | - Prepared in the laboratory, purity 99.5 %, BET nitrogen gas adsorption surface area 9.5 m ² /g. |
| Cupric oxide | - Matheson Coleman & Bell (U.S.A), Purity 99 %, BET nitrogen gas adsorption surface area 9.7 m ² /g. |
| Magnesium oxide | - Matheson Coleman & Bell (U.S.A), Purity 97 %. |
| Alumina | - M.Woelm Eschwage (Germany), Extra pure, BET nitrogen gas adsorption surface area 123.8 m ² /g. |
| Silica gel | - BDH Laboratories (London), Extra pure. |
| Benzene | - BDH Laboratories (London), Purity 99.9 %, further purified by percolating through a silica gel and alumina column, kept in contact of sodium wire for at least 24 hours before use. |
| n-heptane | - BDH Laboratories (London), Purity 99 %, further purified by percolating through a silica gel and alumina column, distilled in contact of sodium wire, fraction boiling between 98-98.5°C was collected and the stock in contact of sodium wire. |

- Stearic acid - BDH Laboratories (London), Purity 99 %, m.p 67 - 70°C, neutralisation value 196 - 198.
- Pyridine - BDH Laboratories (London), Purity 99.5 %, boiling range 114-116°C, d = 0.9815 g/c.c, refractive index n_D^{20} 1.509 - 1.510.

3.2.1. Preparation of ferric oxide⁽⁵⁷⁾.

Ferric oxide is a red powder and used as a paints under the name of red oxide, 'rouge' and also 'venetian'. It may be obtained by heating hydroxides, nitrates or oxalates. Ferric oxide used in this work was prepared in the laboratory by the following method.

The ferric hydroxide prepared from the solution containing the ferric salt treated with a slight excess of aqueous ammonia solution.



10 g of anhydrous AnalaR ferric chloride was dissolved in 400 ml of water containing 4 ml of commercial hydrochloric acid to make it weakly acidic, and was filtered, and then was slightly heated, and ammonium hydroxide was added slightly in excess, as was shown by the odour of the steam above the liquid. The liquid was boiled gently for 1 minute and the precipitate was allowed to settle. The precipitate first formed a

3.2.2. Estimation of iron in a sample of Fe_2O_3 .

To obtain an idea about the purity of ferric oxide prepared the amount of iron present in a sample of iron oxide was determined and compared with the theoretical amount. Two methods were employed for this purpose - (a) complexometric titration using salicylic acid, and (b) spectrophotometric estimation.

(a) Complexometric titration of iron(III) using salicylic acid- The test solution was prepared by dissolving 0.143 g of ferric oxide in hydrochloric acid and was diluted with water to 200 ml. Since 1.43 g of ferric oxide is equivalent to 1 g of iron, the test solution contained 50 mg of iron per 100 ml of the solution. pH of the solution was then adjusted to about 4 by adding excess glycine (0.2 - 0.5 g per 100 ml found sufficient), and about 0.2 g of salicylic acid was added. The solution was warmed to about 40°C and was titrated with standard (0.05M) EDTA solution. The amount of iron present and its percentage in the sample was calculated (99.5 %).

(b) Spectrophotometric estimation of iron(III) - The iron content of the prepared ferric oxide was also determined by the spectrophotometric method with the help of Bauch and Lomb spectrophotometer (spectronic - 20) using thiocyanate.

2M KSCN solution was prepared by dissolving 20 g of AnalaR potassium thiocyanate in 100 ml of water. A given amount

of the iron oxide was dissolved in hydrochloric acid and evaporated to dryness to expell the excess acid. It was then diluted to slight extent and taken into a volumetric flask. For each 50 ml of the resultant solution 5 ml of thiocyanate and 2.4 ml of 4N nitric acid was added. This gave the test solution. The same amount of reagents were added to 50 ml distilled water and using this solution the apparatus was adjusted at wavelength 480 mμ. The absorbance of the test solution was then measured at the same wavelength. Using the value of this absorbance the concentration of iron was determined from the calibration curve. The calibration curve was determined as follows :

0.864 g of AnalaR ferric ammonium sulphate was accurately weighed and dissolved in 10 ml concentrated hydrochloric acid contained in a 1 litre flask and made upto the mark. Then 1 ml of the solution is equivalent to 0.1 mg of iron. 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml of this solution was taken in six different 100 ml flask. To each flask 10 ml of thiocyanate solution and 4-6 ml of hydrochloric acid was added and up with water upto the mark. Absorbances of these solutions were measured at 480 mμ. These results are tabulated in Table-IV and the calibration curve is shown in the Figure-1.

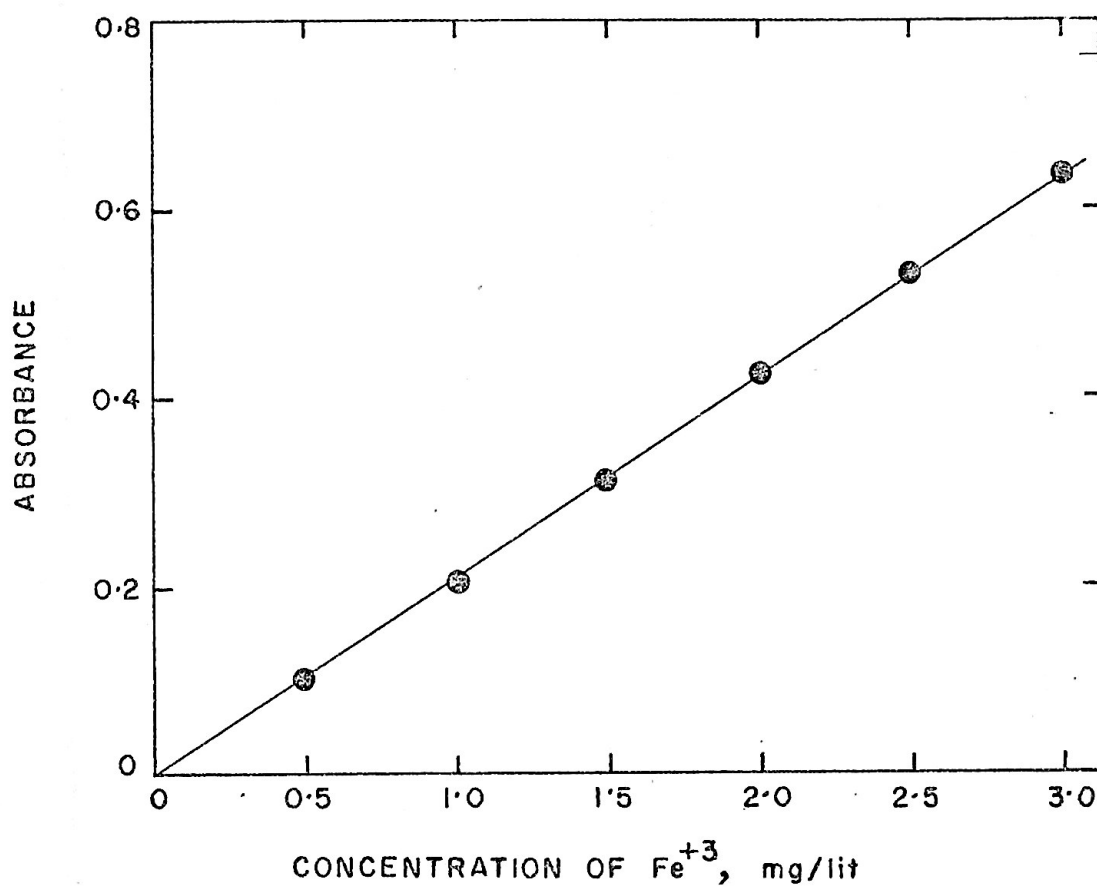


Fig.1. Calibration curve for the estimation of iron (III).

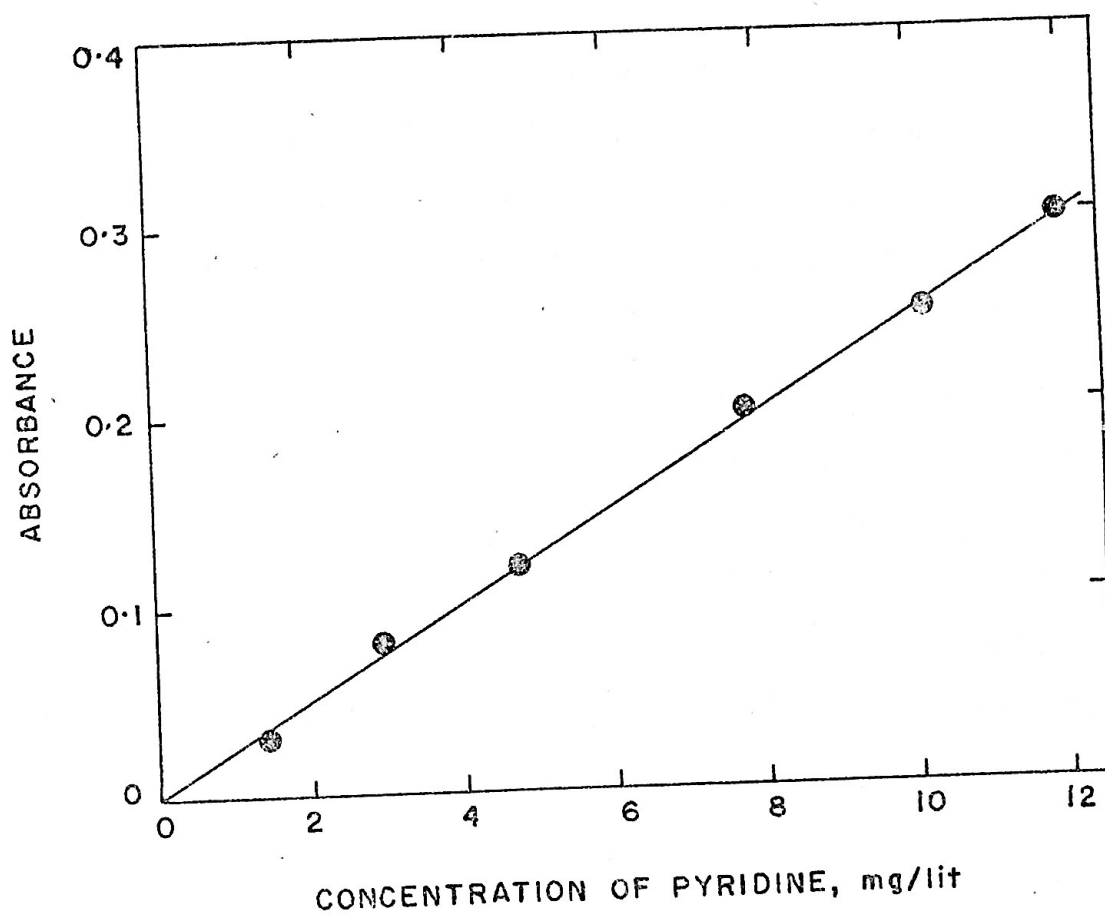


Fig.2. Calibration curve for the estimation of pyridine.

3.2.3. Determination of BET nitrogen gas adsorption*.

The sample tube containing a known weight (w) of adsorbent was fitted to the BET apparatus. The sample was then degassed slowly by using first a rotary pump and finally a water jacketed mercury diffusion pump to give vacuum of 10^{-5} mm Hg. The sample tube was then covered by a thermostatically controlled heater. Power input to the heater was adjusted by a 'Variac' set at a predetermined point. Degassing was continued for 3-4 hours at the preset temperature. After the degassing was over the sample tube was slowly cooled first by switching off the heater, then as the temperature fell down to about 150°C the heater was removed and the sample was allowed to air cool. Volume (V_w) of nitrogen gas adsorbed at liquid nitrogen temperature (-196°C) was then determined at an equilibrium pressure (P) so that P/P_0 lies between 0.30 and 0.35 where P_0 is the vapour pressure of the gas at that temperature, value of P_0 being 76 cm Hg at -196°C .

3.2.4. Determination of heat evolved and amount of stearic acid adsorbed by flow micro-calorimeter.

Flow micro-calorimetry is a fairly new technique. This technique is summarized in the following sections and details are given in Appendix-B.

*BET nitrogen gas adsorption results of the adsorbents were obtained from the Sakurai Laboratories, TIT, Tokyo, Japan.

(a) Description of apparatus.

A flow micro-calorimeter (Mark II, Microscal Ltd., London) has been used for the determination of heat of adsorption and the amount of stearic acid adsorbed. The apparatus shown schematically in Fig.3 consists of a metal block (1) surrounding a cylindrical cavity in which the Teflon calorimeter cell (2) is situated. The cell is connected to a carrier liquid inlet (3) and outlet (4) tube. The outlet is fitted with a 500 mesh stainless steel gauze on which the adsorbent (5) are placed.

The temperature-sensing elements comprise of four thermistors, two for reference (T_1 , T_2) and two for measurement (T_3 , T_4), the latter being embedded in the powdered adsorbent.

(b) Experimental procedure.

To carry out experiment with the flow micro-calorimeter the outlet tube is fitted to the apparatus. Adsorbent powder was then introduced into the calorimeter cell from a measuring tube by a long stem glass funnel. Before introducing the powder the calorimeter cell was filled with the carrier liquid (solvent) and it was ensured that the tip of the stem of the funnel remained just above the surface of the liquid. The carrier liquid was then drained off and experiments were carried out under continuous flow of solvent at

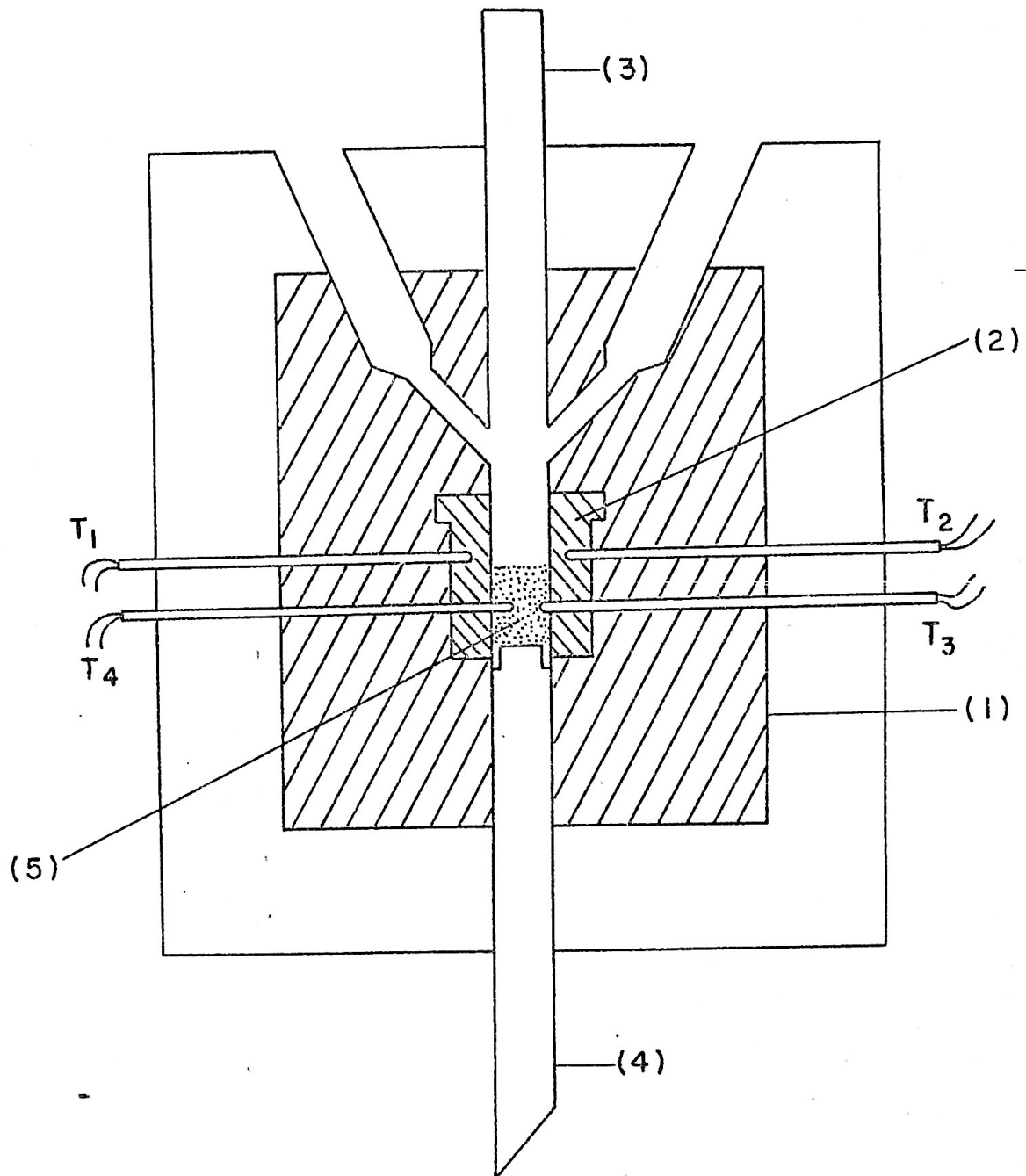


Fig.3. Schematic diagram of the flow micro-calorimeter.

(1) Metal block, (2) Teflon calorimeter cell, (3) inlet tube for carrier liquid, (4) outlet tube, (5) adsorbent bed. T_1 , T_2 - reference thermistors; T_3 , T_4 - measuring thermistors.

a rate of 0.1 ml/minute through the powder bed. The solvent from a reservoir funnel was introduced with a stainless steel tube extending upto the powder bed. Heat generated in the powder bed due to addition of a surface active agent in the solvent was recorded as a peak by a potentiometric recorder (Leeds & Northup Speedomax-H Recorder).

(c) Calibration of the flow micro-calorimeter.

To determine the amount of heat associated with a given peak in the recorder chart the apparatus was calibrated. For this experiment a calibration tube instead of the outlet tube was fitted to the calorimeter. A powder bed in the calorimeter cell was then prepared as in the preceding section. Solvent stream was allowed to flow through the powder bed at a rate same as that of adsorption experiment and when a steady base line was achieved a known quantity of heat was introduced into the powder bed by switching on the calibration circuit. This gave a peak in the recorder chart. Area of the peak was calculated in square centimeters. The amount of heat supplied to the powder bed was determined from the expression,

$$H = \frac{V^2 r t}{(R+r)^2} \times \frac{1000}{4.2} \text{ millicalories}$$

where, R = circuit resistance in ohm, r = resistance of the calibration coil in ohm, V = calibration battery voltage, and t = time in second.

Calibrations were carried out at recorder amplifications of FSD = 5000 μ V using value of $R = 150$ and 200 ohms, and FSD = 1000 μ V using value of $R = 300$ and 400 ohms. Calibration curve at these recorder full scale deflections (FSD) are shown in Fig.4.

(d) Determination of Integral heat of adsorption by Saturation method.

The integral heats of adsorption at different concentrations of solute were determined by the saturation method as follows. The solvent (benzene) was percolated at a rate of 0.1 ml/minute through the bed of the adsorbent in the calorimeter cell and sufficient time was allowed to obtain a steady base-line in the recorder chart. The whole of the solvent stream was then replaced by a stream of equal flow-rate of a solution of stearic acid in benzene. The solution stream was allowed to run until the concentration of solute on the powder bed came into equilibrium with that in the solution. This resulted in the evolution of heat and produced a peak in the recorder chart. By replacing the stream step-wise with solutions of increasing concentrations it was possible to saturate the adsorbent. The cumulative heat in this process is known as integral heat of adsorption.

(e) Determination of the amount of solute adsorbed by Pre-column method.

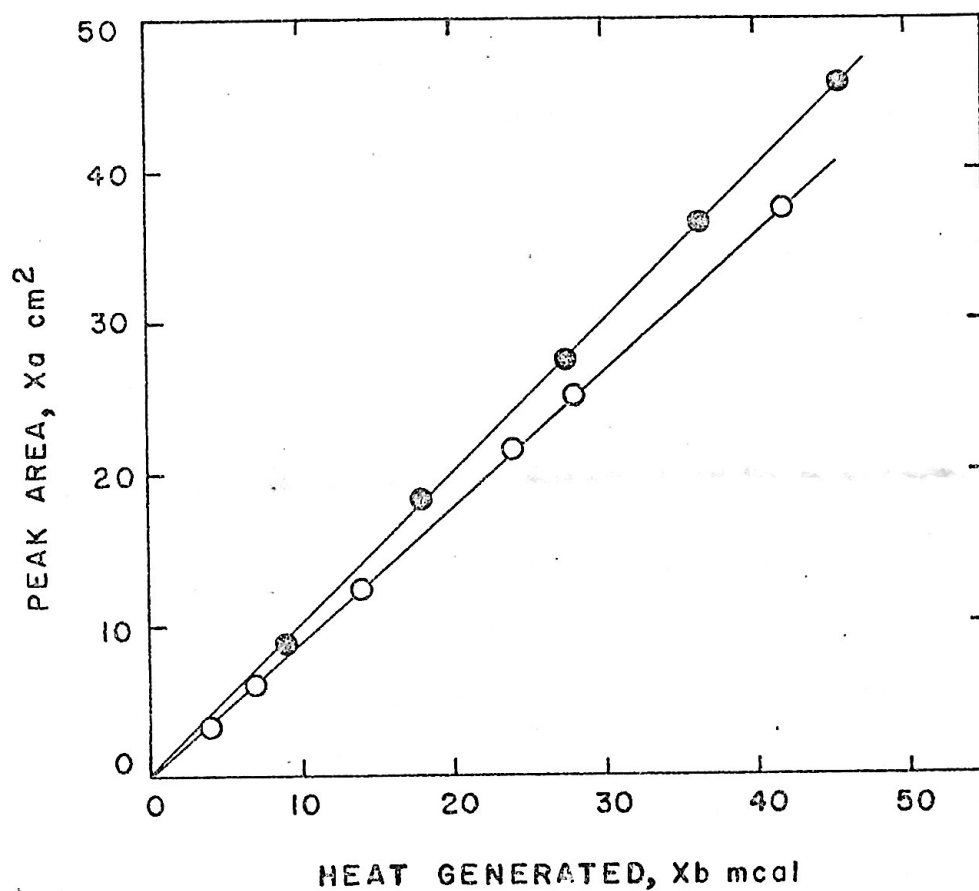


Fig.4. Calibration curve for the estimation of integral heat by flow micro-calorimeter. ● FSD = 1000 μ V (a = 4, b = 2), ○ FSD = 5000 μ V (a = 10, b = 10).

Groszek⁽⁷⁾ used a flow micro-calorimeter to determine the amount of solute adsorbed and this method has been adopted for the present work.

The adsorbent was placed in a precolumn constructed from a glass tube with the same internal diameter as the Teflon cell in the calorimeter. The carrier liquid was then percolated through the adsorbent in the precolumn before it entered the adsorbent in the calorimeter. To determine the amount of solute adsorbed from a given solution, the flow of carrier liquid was stopped at time (t_1) as shown in Fig.5 and at the same time the flow of solution was started. If the precolumn contained an inert solid, the solution would emerge at time (t_0) and would then contact the adsorbent in the calorimeter, but when the precolumn contains an adsorbent, the solute is retained, so that solvent only at time (t_0), the solution emerging at a later time (t_2). The difference between t_2 and t_1 is a measure of the amount of solute adsorbed.

In the above method the critical steps are accurate determination of the time at which the solution emerges from the precolumn and an accurate knowledge of the constant flow-rate of solution through the precolumn. It is also necessary to ensure, for all adsorbent, that the flow-rates used are sufficiently low to enable full saturation of the adsorbate in the precolumn. If the flow-rate of solution is too high, solution may emerge from the precolumn before the adsor-

3.2.5. Determination of the amount of stearic acid adsorbed on adsorbents by Adsorption from solution method.

Dried adsorbent powder (1 or 5 g) was weighed accurately and was placed in a clean-dry 250 ml or 1 litre glass-stoppered flask. 100 or 500 ml of different standard stearic acid solution in benzene were added and the flask was held in a constant temperature bath for 1 hour with intermittent shaking; the solution was allowed to settle for 2 hours. That adsorption time of 1 hour was sufficient for equilibrium to reach both at low and high concentrations of stearic acid solution has been established experimentally, Table-IX. 10 ml of the supernatant solution were pipetted carefully into a small beaker. The solution was then evaporated at room temperature and the amount of stearic acid remaining in the beaker was estimated either by potentiometric⁽⁵⁹⁾ or by pH-metric⁽⁶⁰⁾ titration with standardized sodium methoxide or potassium hydroxide. The amount of stearic acid adsorbed was found from the amount of stearic acid present before and after the adsorption.

3.2.6. Determination of the amount of pyridine adsorbed on adsorbent by Adsorption from solution method.

The adsorption of pyridine from n-heptane solution on adsorbent powders was carried out by a method similar to that of stearic acid. Dried adsorbent powder (5 g) was weigh-

ed accurately and was placed in a clean-dry 1 litre glass-stoppered flask. 500 ml solution of pyridine in n-heptane was added and the flask was held in a constant water bath at 30°C for 24 hours with intermittent shaking; the solution was then allowed to settle for 2 hours. The time allowed for adsorption was same as that used by Kipling and Peakall⁽⁶¹⁾. The supernatant solution from the adsorption flask was pipetted carefully into a flask and was diluted with n-heptane. The absorbance of the solution was measured spectrophotometrically at 251 mμ using a Double Beam Beckman Spectrophotometer. The concentration of the solution was measured from a plot of absorbance versus concentration of pyridine (Figure-2) using the calibration data given in Table-IV along with the calibration data for estimation of iron in Appendix-A.

CHAPTER - IV

RESULTS

The first part of the work was devoted to the study of the effect of the concentration of the solution on the rate of reaction. It was found that the rate of reaction increased with the concentration of the solution. The second part of the work was devoted to the study of the effect of the temperature on the rate of reaction. It was found that the rate of reaction increased with the temperature. The third part of the work was devoted to the study of the effect of the catalyst on the rate of reaction. It was found that the rate of reaction increased with the concentration of the catalyst.

The fourth part of the work was devoted to the study of the effect of the solvent on the rate of reaction. It was found that the rate of reaction increased with the concentration of the solvent.

4.1. BET nitrogen gas adsorption measurements.

The BET gas adsorption method has been carried out for the determination of surface areas of cupric oxide, ferric oxide and alumina powders. Surface areas of the powders have been determined by 'one point' method using adsorption of nitrogen gas on the degassed samples at P/P_0 between 0.30 to 0.35. Replicate measurements have been carried out for each powders. These results are shown in Table-V in Appendix-A. Repeated evacuation and adsorption of nitrogen at liquid nitrogen temperature, -196°C , of a given sample were performed for all the powders. The results of first and second stage of operations are also incorporated in Table-V. The limiting value of the volume in cm^3 of nitrogen gas adsorbed per gram of adsorbent, V_m , was determined by the 'one point' method using the expression,

$$V_m = V(1 - P/P_0) \quad (6)$$

where, V is the volume of nitrogen gas adsorbed per gram of adsorbent, being equal to V_w/w . The values of limiting volume, V_m , obtained by this method are 2.14, 2.10 and 27.41 cm^3 respectively per gram of cupric oxide, ferric oxide and alumina powders. These values are converted to mol per gram of adsorbent and summarized in Table-I.

BET surface area of the adsorbent was obtained from the expression,

Table-I. Amount of solute adsorbed on different adsorbents.

Adsorbent	Amount of solute adsorbed at limiting value (x_m), molX10 ⁻⁵ /g		
	Nitrogen gas	* Stearic acid	Pyridine
CuO	9.6	2.2	6.3
Fe ₂ O ₃	9.4	2.4	6.4
MgO ^a	-	23.6	60.3
Al ₂ O ₃	122.4	32.0	86.0
Silica gel ^a	-	91.0	247.8

* Flow micro-calorimetric and adsorption from solution results.

^a Amount determined from adsorption from solution measurements only.

Table-I(a). Area occupied by one molecule of solute.

Adsorbent	Surface area, m ² /g	*Area occupied by one molecule, Å ²	
		Stearic acid	Pyridine
CuO	9.3	70.2	24.5
Fe ₂ O ₃	9.1	62.9	23.7
MgO	90.0	63.3	24.8
Al ₂ O ₃	119.4	62.0	23.0
Silica gel	370.0	67.5	24.8

*Assuming the adsorbate molecules cover the whole surface of adsorbent.

$$S_w = NA_m w V_m / V_o \quad (7)$$

where, N = Avogadro's number, A_m = area occupied by one molecule of nitrogen, and $V_o = 22400 \text{ cm}^3$, molar volume of gas at NTP.

Specific surface area of the adsorbent is given by,

$$S = \frac{S_w}{w} \quad (8)$$

Assuming area occupied per molecule (A_m) of nitrogen to be 16.2, 16.8 and 20.2 $\text{\AA}^2$ specific surface area of cupric oxide, ferric oxide and alumina powders have been computed. These results are summarized in Table-III.

4.2. Flow micro-calorimetric measurements.

Both integral heat of adsorption (q) and amount of stearic acid adsorbed (x) on the adsorbents, cupric oxide, ferric oxide and alumina, have been measured by the flow micro-calorimetric method.

(a) Determination of integral heat of adsorption (q).

Using cupric oxide, ferric oxide and alumina powders as adsorbents integral heats of adsorption have been measured by the saturation method with increasingly higher concentration of stearic acid solution in benzene. These results are tabulated in Tables VI - VIII given in Appendix-A. Plots of

concentration (C) of stearic acid versus amount of cumulative heat evolved are shown in Figure-6. The heat of adsorption at monolayer coverage (q_0) may be obtained from the plateau of these plots and more accurately using the expression⁽²⁾,

$$\frac{C}{q} = \frac{1}{kq_0} + \frac{C}{q_0} \quad (9)$$

assuming monolayer coverage, Langmuir type of adsorption. The corresponding BET equation for multilayer coverage being,

$$\frac{C}{q(1-C)} = \frac{1}{kq_0} + \frac{C}{q_0} \quad (10)$$

where, C = concentration, q = integral heat evolved for the solute adsorbed from solution of concentration (C) and k is a constant.

Values of C/q have been computed and tabulated in Tables VI - VIII in Appendix-A. Plots of C/q versus C are shown in Figure-7. In all the cases straight line relationship are noticed. From the slopes and intercepts of these straight lines heats evolved at monolayer coverage (q_0) have been evaluated for all the cases. These values are summarized in Table-II.

It is possible to measure heat of desorption by the flow micro-calorimeter by exchanging the flow of a solution with a solvent. After the adsorbent surfaces have been satu-

Table-II. Amount of heat evolved at monolayer coverage measured by Flow Micro-calorimeter.

Adsorbent	Heat evolved at monolayer coverage			
	Cumulative heat of adsorption (q_o) mcal/g	Desorption heat (q_d) mcal/g	Integral energy of adsorption Kcal/mole	Integral heat (q_o/S) mcal/m ²
CuO	439	154	17.9	47.2
Fe ₂ O ₃	485	146	21.3	55.3
Al ₂ O ₃	6184	1784	19.6	51.8

Table-III. Surface area of adsorbents measured by Nitrogen gas adsorption, Stearic acid adsorption and Pyridine adsorption.

Adsorbent	Surface area (S), m ² /g							
	Nitrogen gas adsorption			*Stearic acid adsorption			Pyridine adsorption	
	Area per molecule of N ₂ Å ²			Area per molecule of acid Å ²			Area per molecule of pyridine, Å ²	
	16.2	16.8	20.2	18	60	70	100	24.7
CuO	9.3	9.7	11.6	2.6	8.7	10.1	14.5	9.4
Fe ₂ O ₃	9.1	9.5	11.4	2.4	8.0	9.3	13.3	9.5
MgO ^a	-	-	-	25.6	85.3	99.5	142.1	87.1
Al ₂ O ₃	119.4	123.8	148.9	34.7	115.6	134.9	192.7	127.9
Silica gel ^a	-	-	-	98.7	328.8	383.7	548.1	320.6

*Flow micro-calorimetric and adsorption from solution results.

^aSurface area measured from adsorption from solution measurements only.

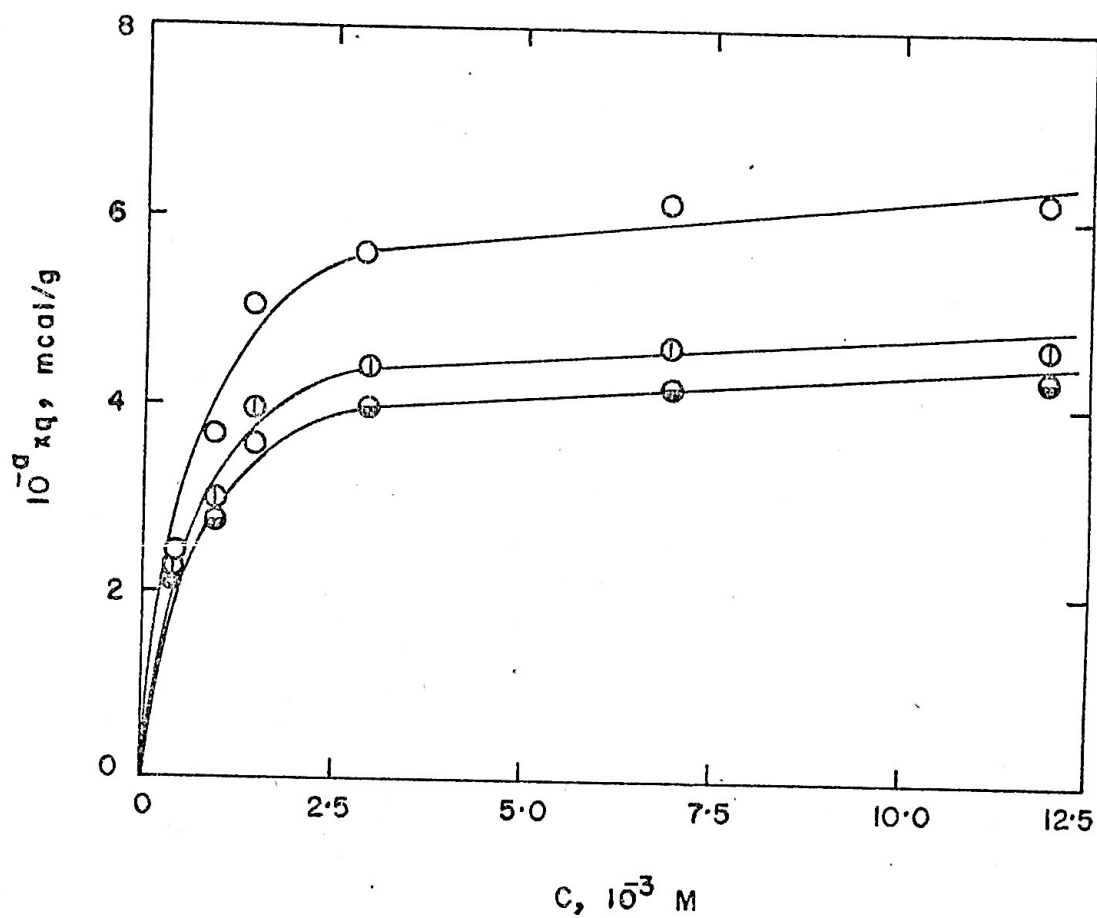


Fig.6. Variation of the amount of integral heat evolved (q) with the concentration (C) for calorimetric measurements. ● CuO ($a = 2$), ⊙ Fe₂O₃ ($a = 2$), ○ Al₂O₃ ($a = 3$).

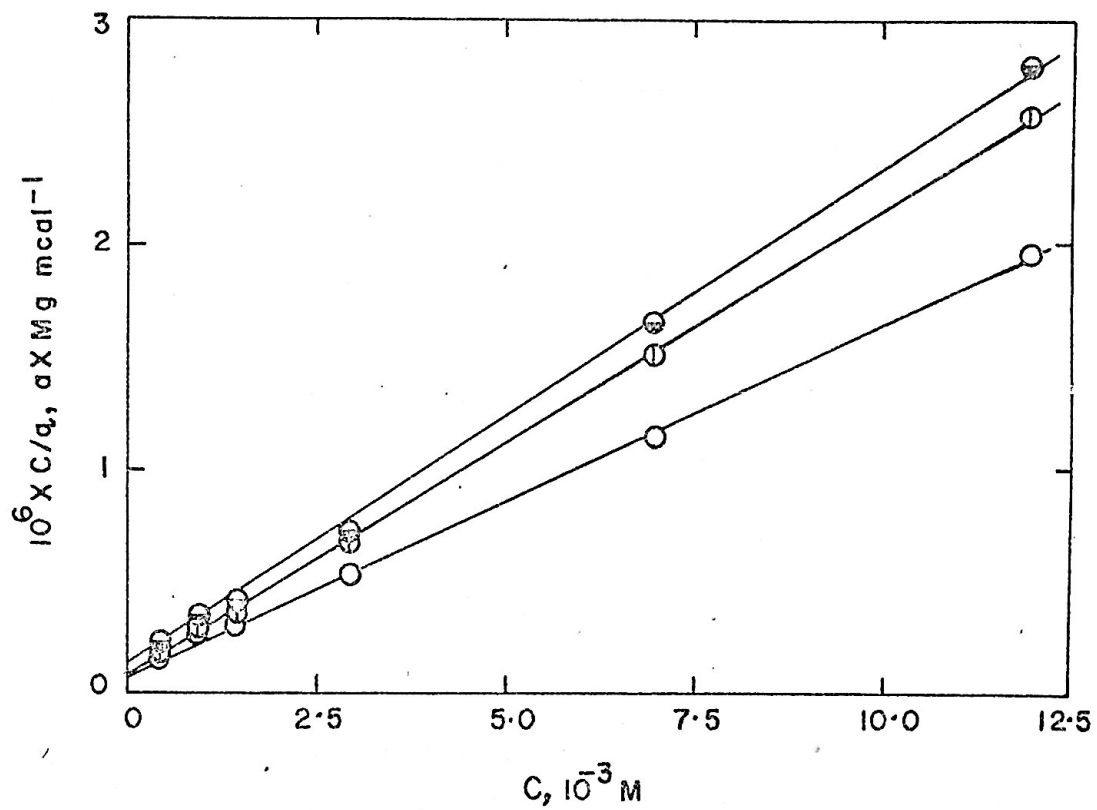


Fig.7. Langmuir plots (C/q versus C) for calorimetric measurements. ● CuO ($a = 10$), ⊙ Fe₂O₃ ($a = 10$), ○ Al₂O₃ ($a = 1$).

rated to form monolayer coverage the flow of solutions were replaced by solvent; these produced peaks in the recorder chart indicating negative heat effects. These negative value of heat that is desorption heats are summarized. These results are also incorporated in Table-II.

(b) Determination of amount of stearic acid adsorbed (x) by precolumn method.

The amount of stearic acid adsorbed on cupric oxide, ferric oxide and alumina powders from benzene solution was determined by flow micro-calorimeter using precolumn method. The amount of solute adsorbed by the powder bed in the precolumn was computed using the equation,

$$x = tCf/w$$

where, x = amount of solute adsorbed (mg/g), t = retention time (minute), C = concentration of solute (mg/ml), f = flow-rate of solution (0.1 ml/minute), and w = weight of adsorbent in the precolumn (g). The results are tabulated in Tables VI-VIII in Appendix-A.

Variation of amount of stearic acid adsorbed with concentration are shown in Figure-8. Amount of stearic acid adsorbed at monolayer coverage (x_m) may be determined from the plateau of the curves in Figure-8. The values of x_m may also be determined more accurately from the following equa-

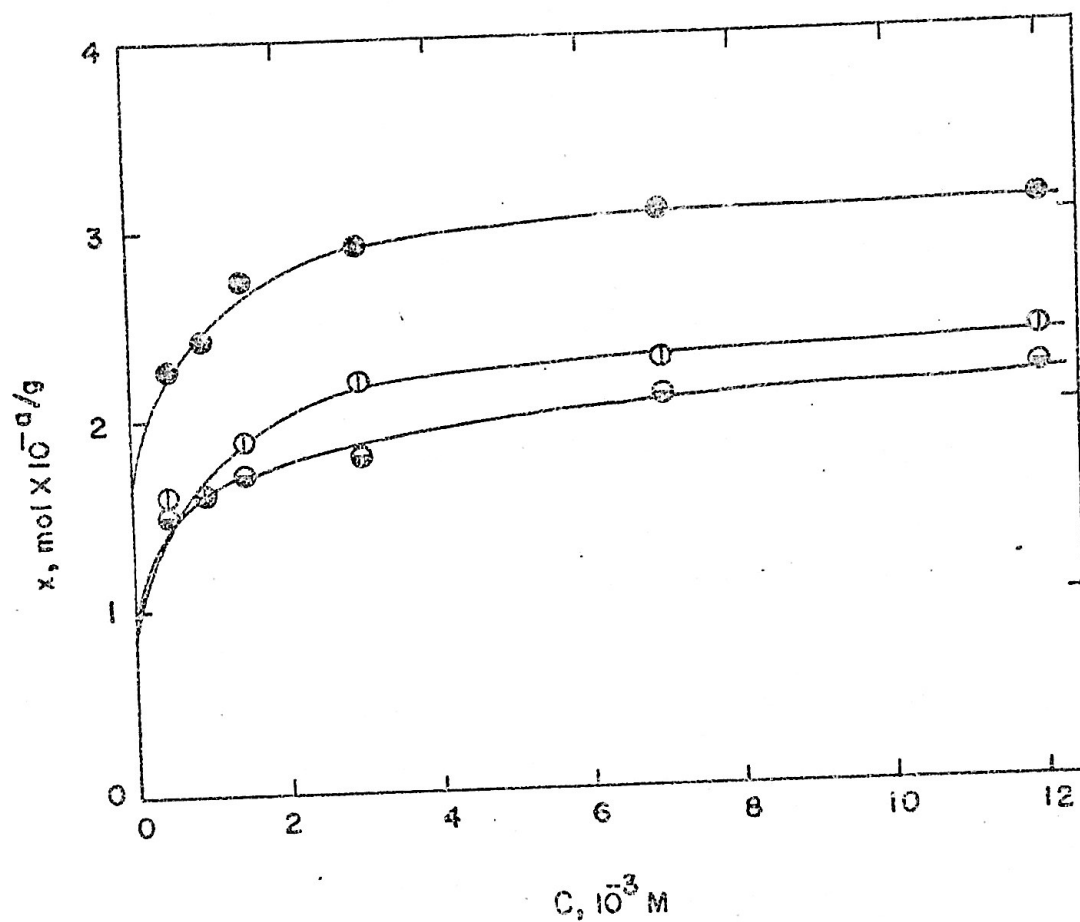


Fig.8. Variation of the amount of stearic acid adsorbed (x) with concentration of stearic acid solution (C) for calorimetric measurements. $\odot$ CuO ($a = 5$), $\bullet$ Fe₂O₃ ($a = 5$), $\circ$ Al₂O₃ ($a = 4$).

tion which is similar to equation (8),

$$\frac{C}{x} = \frac{1}{kx_m} + \frac{C}{x_m}$$

where, x is the amount of solute adsorbed at the concentration (C), x_m is the monolayer capacity and k is a constant. From the slopes and intercepts of straight line relationship, assuming Langmuir type adsorption, of plots of C/x against C shown in Figure-9 the values of x_m were determined and these values are incorporated in Table-I.

4.3. Adsorption from solution measurements.

4.3.1. Adsorption of stearic acid.

Adsorption of stearic acid from benzene solution has been carried out on cupric oxide, ferric oxide, magnesium oxide, alumina and silica gel powders at 30°C. The amounts of stearic acid adsorbed at different concentrations of solution of stearic acid in benzene have been determined from the concentration of solutions before and after adsorption. These results are summarized in Tables I - III. Variation of amount of stearic acid adsorbed (x) with concentration (C) are shown in Figures 10 and 11. To saturate the adsorbent surfaces increasingly higher concentrations of stearic acid solution are found to be required in the order $\text{CuO} < \text{Fe}_2\text{O}_3 < \text{MgO} <$

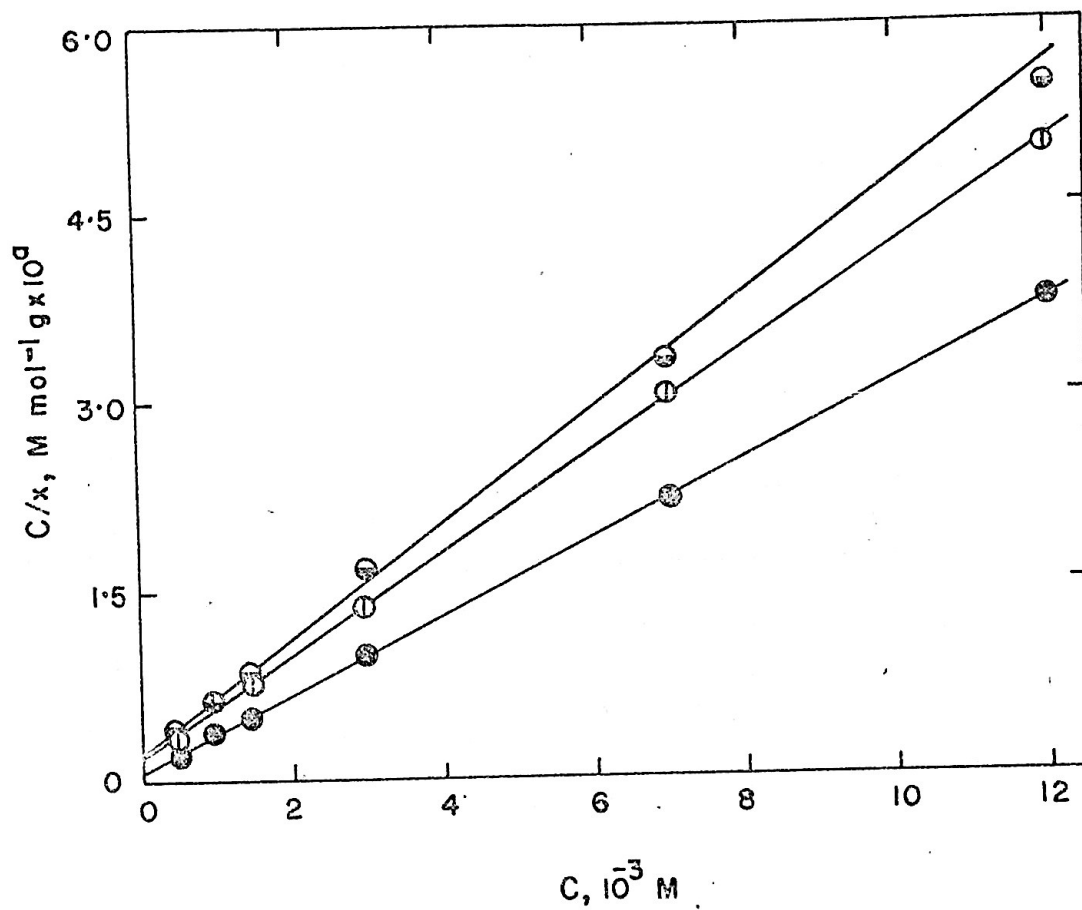


Fig.9. Langmuir plots (C/x versus C) for calorimetric measurements. $\circ$ CuO ($a = 2$), $\bullet$ Fe₂O₃ ($a = 2$), $\bullet$ Al₂O₃ ($a = 1$).

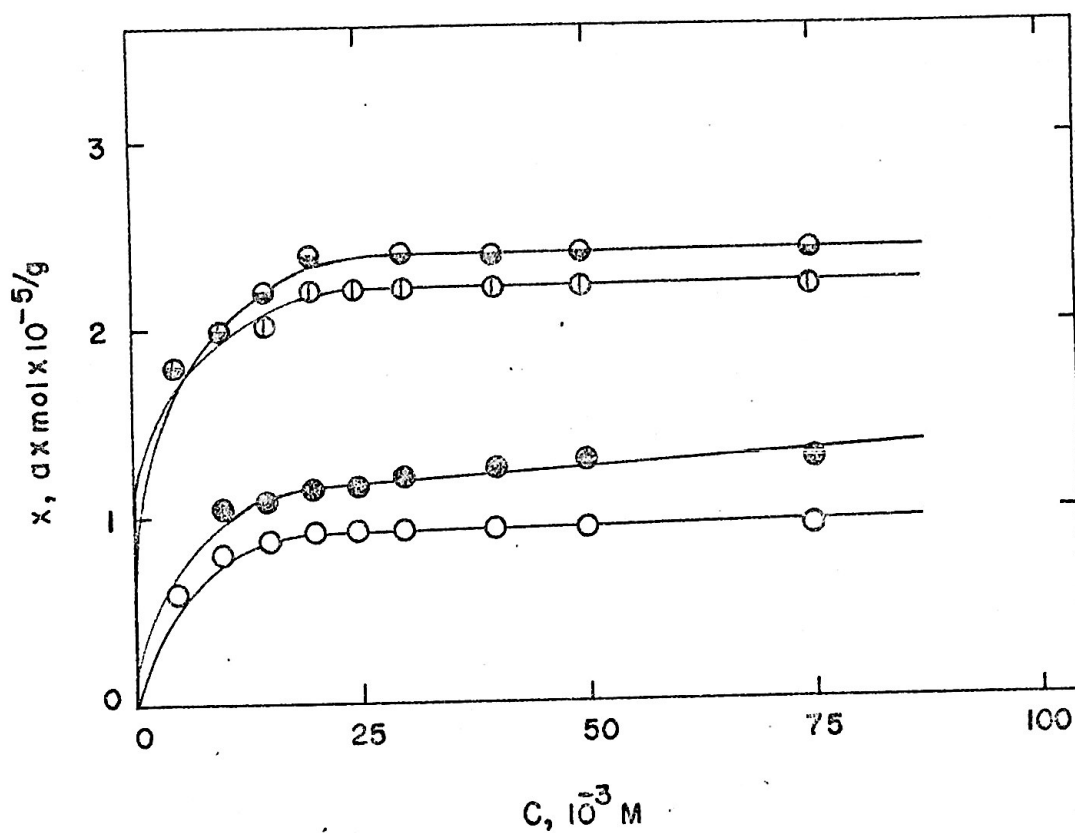


Fig.10. Variation of the amount of stearic acid adsorbed (x) on powders with concentration of stearic acid solution (C) for adsorption from solution method.

● CuO ($a = 1$), ○ Fe₂O₃ ($a = 1$), ○ MgO ($a = 25$), and
● Al₂O₃ ($a = 25$).

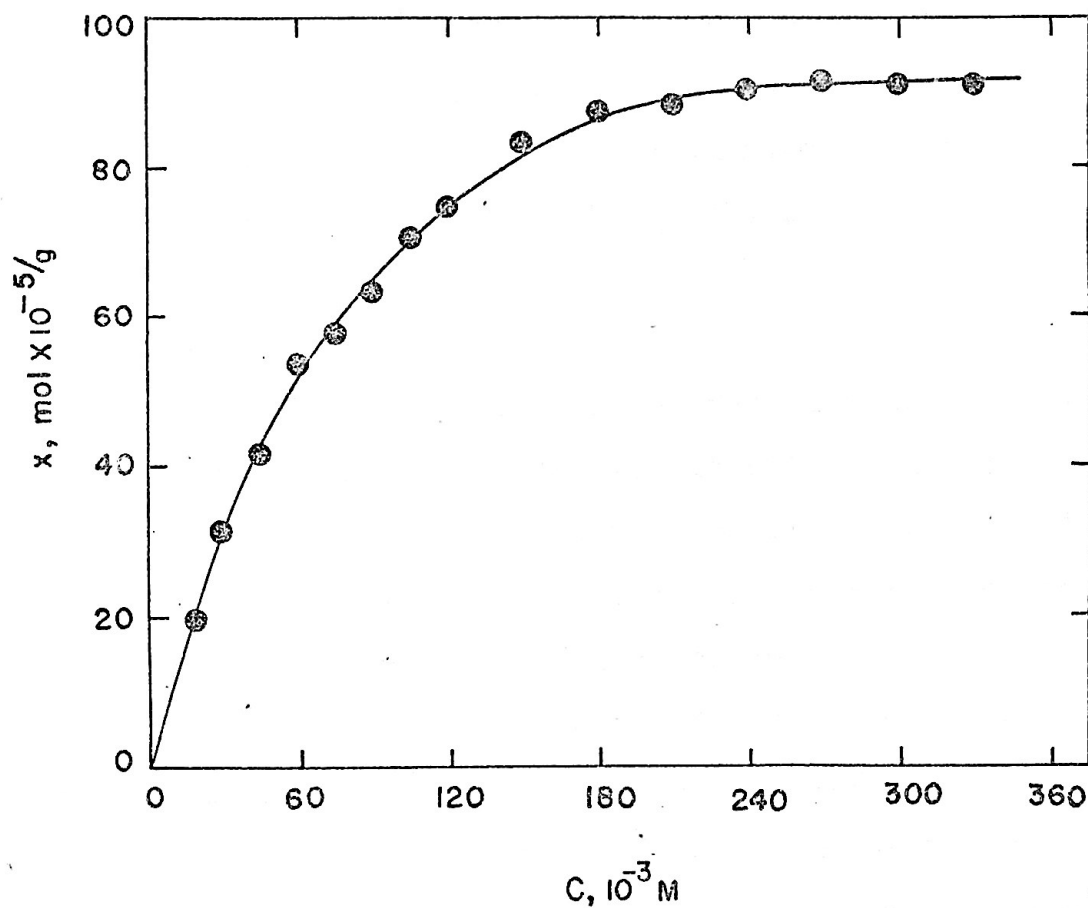


Fig.11. Variation of the amount of stearic acid adsorbed (x) on Silica gel powder with concentration of stearic acid solution (C) for adsorption from solution method.

Al_2O_3 < Silica gel. Langmuir plots similar to that obtained in the flow calorimetric measurements are shown in Figures 12 and 13. Amount of stearic acid adsorbed at monolayer coverage by the adsorbents are determined from the plateau of the curves in Figures 10 and 11 or more accurately from the slopes and intercepts of the straight lines in Figures 12 and 13 assuming Langmuir type of adsorption given by the expression (2) shown in the introduction.

4.3.2. Adsorption of pyridine.

The adsorption of pyridine from n-heptane solution on metal oxides, cupric oxide, ferric oxide, magnesium oxide, alumina and silica gel powders were carried out at 30°C . For adsorption from solution of a given concentration duplicate experiments were carried out, and for each experiment concentrations of pyridine both before and after adsorption were determined. For duplicate adsorption the difference in the concentration of pyridine after adsorption was observed to be in the range of $\pm 1\%$. The adsorption isotherms are shown in the Figures 14 and 15. From each of the isotherms it is possible to obtain a limiting value of adsorption from the plateau. Plots of C/x against C shown in Figures 16 and 17 give straight lines, showing Langmuir type adsorption in general, although the results for alumina tend to depart from Langmuir

type of adsorption indicated by the curvature of the plots shown in dashed line for alumina in Figure-16. From the slopes and intercepts of the straight lines in Figures 16 and 17 the appropriate amounts of pyridine adsorbed at the monolayer coverage have been determined. These results are summarized in the Table-I.



TABLE I
Monolayer coverage of pyridine on alumina
at 25°C. and 1 atm. pressure
for various relative humidities
of the gas phase

Relative humidity, %	Monolayer coverage, $\mu\text{mole/g.}$
100	1.2
90	1.1
80	1.0
70	0.9
60	0.8
50	0.7
40	0.6
30	0.5
20	0.4
10	0.3

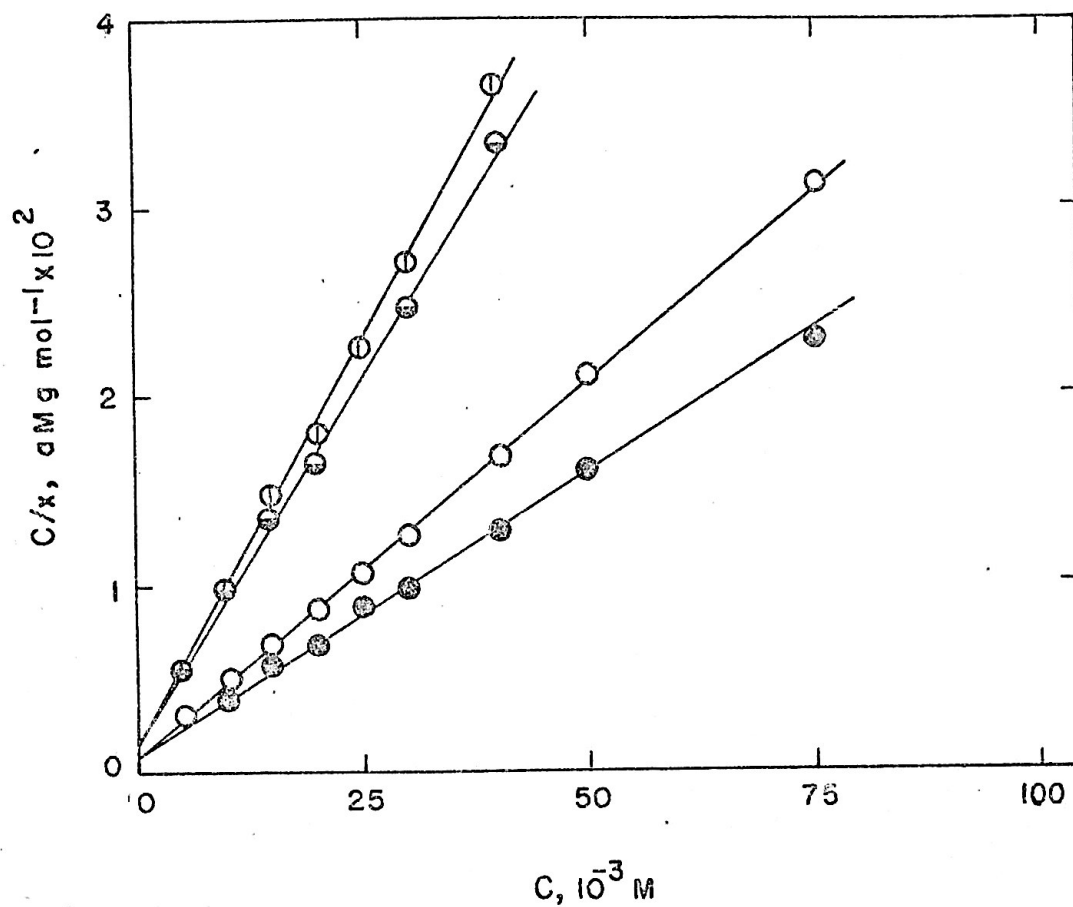


Fig.12. Langmuir plots (C/x versus C) for adsorption of stearic acid for adsorption from solution method.

● CuO ($a = 5$), ○ Fe_2O_3 ($a = 5$), ○ MgO ($a = 1$),
● Al_2O_3 ($a = 1$).

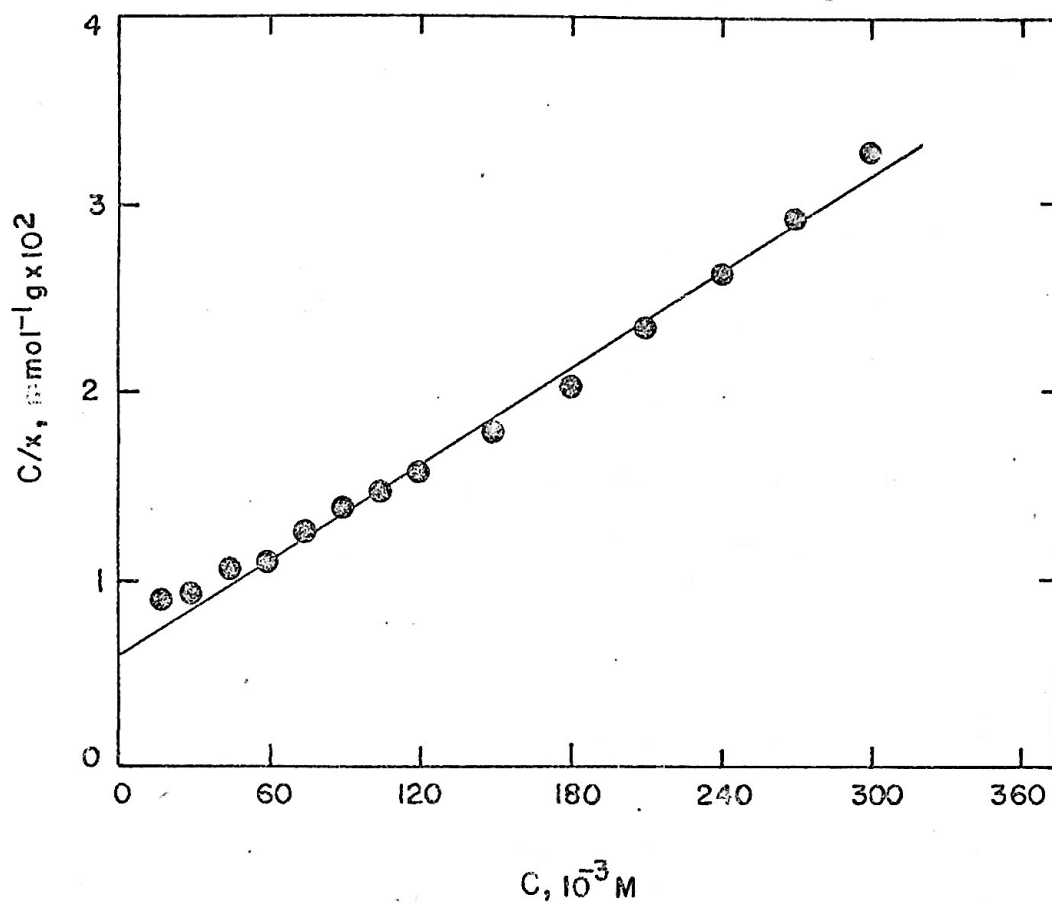


Fig.13. Langmuir plots (C/x versus C) for adsorption of stearic acid on Silica gel powder for adsorption from solution method.

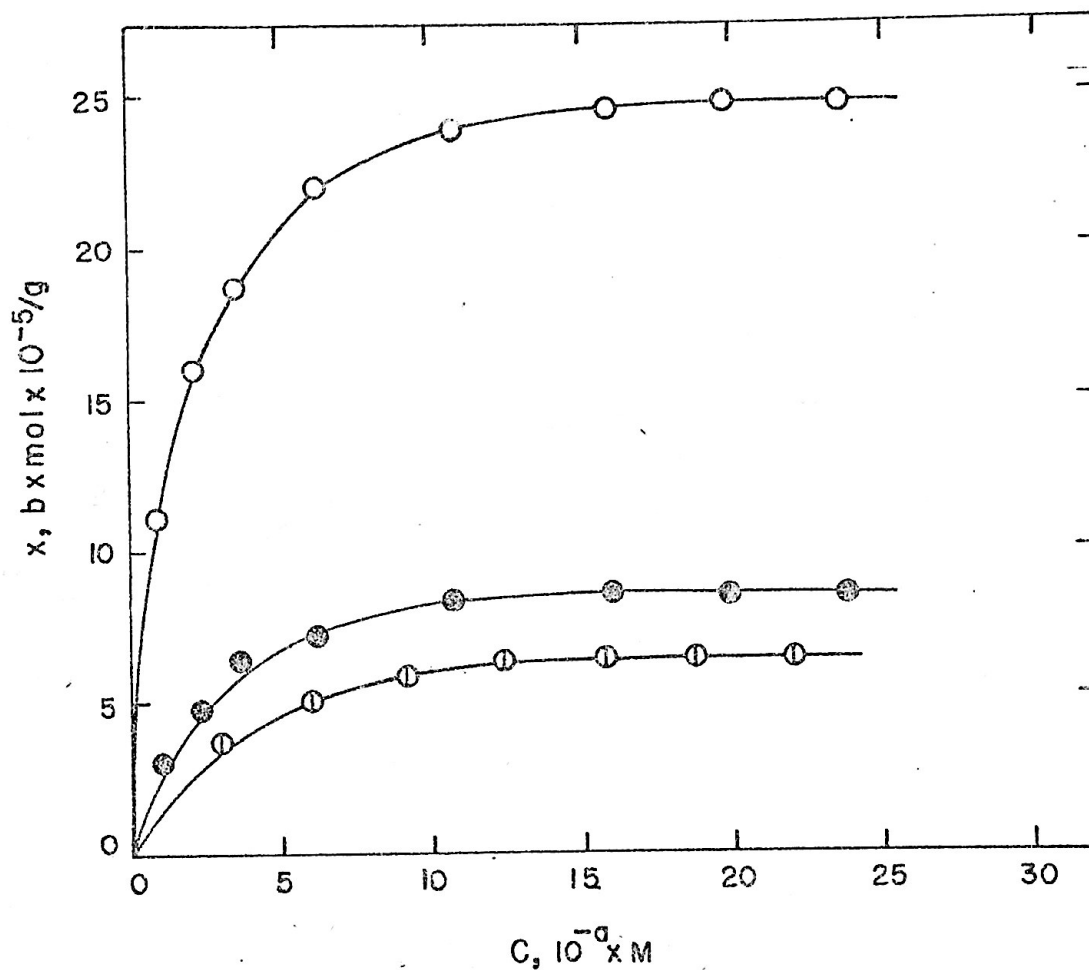


Fig.14. Variation of the amount of pyridine adsorbed (x) on powders with concentration of pyridine solution (C). $\odot$ Fe_2O_3 ($a = 3$, $b = 1$), $\bullet$ Al_2O_3 ($a = 2$, $b = 10$), $\circ$ Silica gel ($a = 2$, $b = 10$).

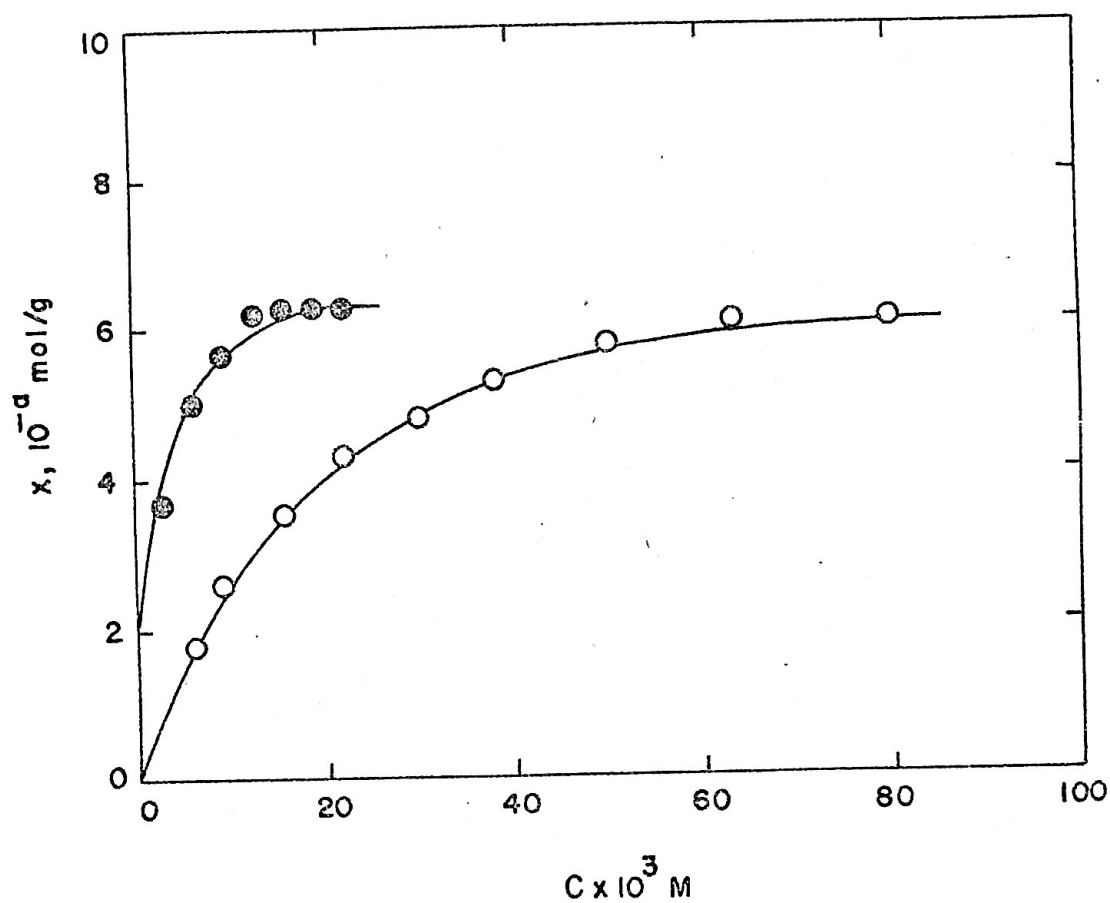


Fig.15. Variation of the amount of pyridine adsorbed (x) with concentration of pyridine solution (C).

● CuO ($a = 5$), ○ MgO ($a = 4$).

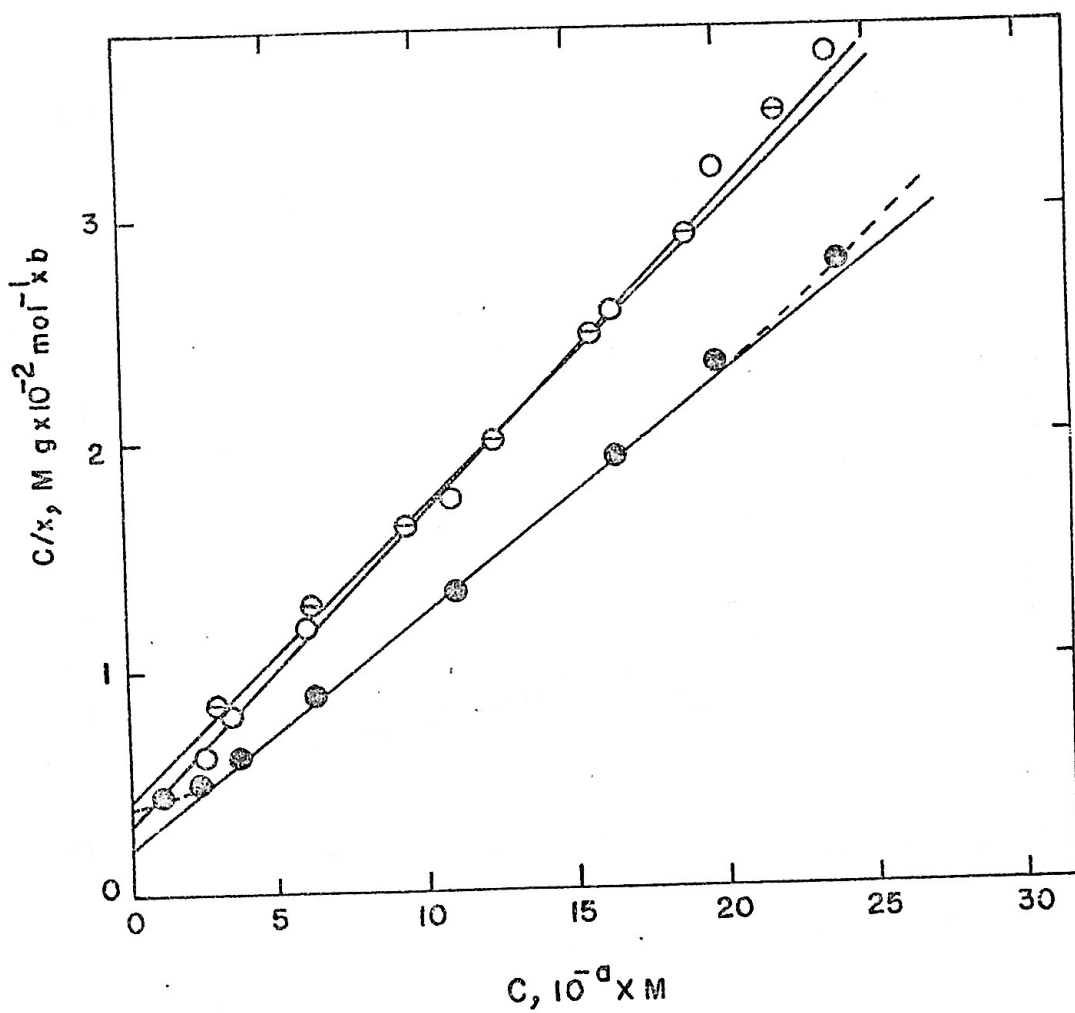


Fig.16. Langmuir plots (C/x versus C) for pyridine adsorption. $\ominus$ Fe_2O_3 ($a = 3$, $b = 1$), $\bullet$ Al_2O_3 ($a = 2$, $b = 1$), $\circ$ Silica gel ($a = 2$, $b = 0.25$).

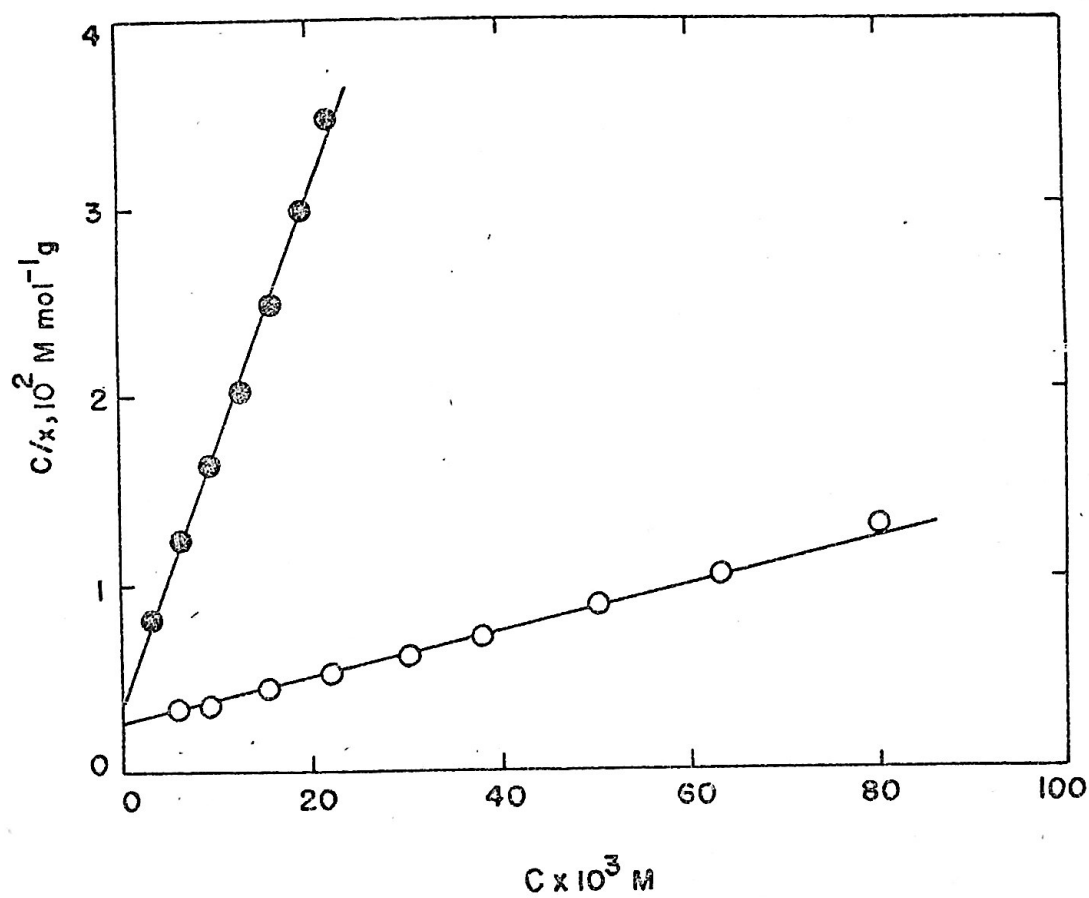


Fig.17. Langmuir plots (C/x versus C) for pyridine adsorption.

● CuO, ○ MgO.

CHAPTER - V

DISCUSSIONS

5.1. Surface area of the adsorbents from BET nitrogen gas adsorption measurements.

The specific surface areas of cupric oxide, ferric oxide and alumina powders have been determined using the results of nitrogen gas adsorption at liquid nitrogen temperature, -196°C . The limiting volume of nitrogen adsorbed, V_m , on the surfaces are 2.14, 2.10 and 27.41 cm^3 per gram of adsorbent powder respectively for cupric oxide, ferric oxide and alumina. It is seen that these values are close to one another for cupric oxide and ferric oxide powders but this value is about 13 times greater in the case of alumina powder. It is also seen from the Table-V that the volume of nitrogen gas adsorbed by a given sample on repeated evacuation and adsorption gave the volumes of nitrogen gas adsorbed within the range of experimental error. This shows that the adsorption of nitrogen gas on the adsorbents are reversible. This indicates that the adsorption of nitrogen is physical in nature in all the cases studied. To compute surface area from the expression (7) the commonly used values of area per molecule of nitrogen (A_m) are 16.2 and $16.8\text{ \AA}^2$, the molecular area of nitrogen based on solid and liquid nitrogen densities. Values as high as $20.2\text{ \AA}^2$ have been used for adsorption on Sterling MTG powder⁽⁶²⁾. Using these values of A_m surface areas of the adsorbents have been evaluated. Surface areas of

the adsorbents particularly of alumina have been found to be too high compared with the values reported in the literature⁽¹⁴⁾. Area occupied by one molecule of nitrogen has therefore been assumed to be $16.2 \text{ \AA}^2$ for all the cases.

5.2. Surface area of the adsorbents from flow calorimetric measurements.

The oxide powders same as that used in the BET nitrogen gas adsorption were used in the flow micro-calorimetric measurements. Figure-6 shows the isotherm obtained by plotting q vs C . Straight line relationship of the plots of C/q vs C shown in Figure-7 indicates that the adsorption is of Langmuir type in all the cases. It is possible to measure heat of desorption by the flow micro-calorimeter by exchanging the flow of a solution with a solvent. The desorption heats were found to be 35, 30 and 28 percent respectively of the adsorption heat due to cupric oxide, ferric oxide and alumina powders. The fact that the adsorption of stearic acid on cupric oxide, ferric oxide and alumina powders are only partially reversible indicates that unlike nitrogen molecules stearic acid molecules are mostly chemisorbed on these adsorbents. Integral heats evolved per unit surface of adsorbents for a given adsorbate and integral energies per mole of adsorbate are characteristics of the adsorbent surfaces. Using the flow

micro-calorimetric results these values have been evaluated for cupric oxide, ferric oxide and alumina powders. Comparison of these results summarized in Table-II shows that despite wide variation of the integral heat evolved per gram of the adsorbents both integral heat per unit adsorbent surface and integral energy of adsorption per mole of adsorbate are very close to one another. These results lead to the conclusion that the surfaces of cupric oxide, ferric oxide and alumina powders are identical in nature. Reciprocals of the values of integral heat evolved per unit surface are equal to constant K in equation (4) for the respective powders. The value of K depends upon the nature of the adsorbent surface and adsorbate molecules. Therefore, for practical purposes the use of equation (4) to compute surface area is limited. However an average value of K based on the data obtained for cupric oxide, ferric oxide and alumina give good estimate of specific surface areas of these adsorbents. These have been found to be 8.6, 9.5 and 121.7 m^2/g compared with the corresponding BET nitrogen gas adsorption 9.3, 9.1 and 119.4 m^2/g respectively for cupric oxide, ferric oxide and alumina powders. Taking any one of these adsorbents as standard (i.e., using value of K of any one of these adsorbents) if surface area of the other two powders are evaluated it would be revealed that the results would not differ over $\pm 13 \%$ compared with the BET nitrogen gas adsorption surface area of

the adsorbents. Therefore, any one of the adsorbents may be chosen as standard to give reasonable estimate of surface area using equation (4).

Flow calorimetric measurements using precolumn method gave amounts of adsorbate at monolayer coverage. From these results summarized in the Tables VI - VIII surface area of the adsorbents have been computed using equation (7). In doing so area occupied by one molecule of stearic acid has to be assumed. In early works^(14,25,32,33) area occupied by one molecule of stearic acid (A_m) were taken to be around $18 \text{ \AA}^2$ assuming that the molecules rested on the adsorbent surfaces perpendicularly. Examinations of Medvedeva's⁽²⁵⁾ results gave the value of A_m to be $58 \text{ \AA}^2$ if the results are equated to the BET nitrogen gas adsorption surface area for alumina as adsorbent. Similar examination of Groszek's⁽⁶⁾ results gave area occupied per molecule of stearic acid to be $60 \text{ \AA}^2$. Recent flow micro-calorimetric studies⁽²⁻⁸⁾ gave the value of A_m to be $60-70 \text{ \AA}^2$. Whereas according to Courtauld model of paraffin the value of A_m would be approximately $100 \text{ \AA}^2$ if the stearic acid molecules are to lie parallel to the adsorbent surface with the whole chain resting on it. Using the values of A_m to be 18, 60, 70 and $100 \text{ \AA}^2$ the surface area of the adsorbents were calculated from the equation (7). They are summarized in Table-III. The results in Table-III would reveal that flow

micro-calorimetric surface area of the adsorbents agree very closely with the BET nitrogen gas adsorption surface area if area occupied per molecule of stearic acid is assumed to be $65 \text{ \AA}^2$.

5.3. Surface area from adsorption from solution measurements using stearic acid as solute.

Although limiting adsorptions are reached at correspondingly higher concentrations the amounts of stearic acid adsorbed in the method of adsorption from solution are found respectively to be the same as that of flow micro-calorimetric method. Amounts of stearic acid adsorbed per unit surface of cupric oxide, ferric oxide and alumina monolayer coverage summarized in Table-I are found to be close to one another. This finding supports the conclusion drawn from the flow calorimetric results mentioned in the preceding section that these adsorbent surfaces are identical in nature. In this case also if area occupied by one molecule of stearic acid is assumed to be $65 \text{ \AA}^2$ the evaluated surface areas agree fairly well with the BET nitrogen gas adsorption areas.

5.4. Comparison of surface areas evaluated from BET nitrogen gas adsorption, flow micro-calorimetric and adsorption from solution measurements.

Surface areas of cupric oxide, ferric oxide and alumina

powders evaluated from the results obtained by BET nitrogen gas adsorption, flow micro-calorimetric and adsorption from solution methods are summarized in Table-III. It is seen from Table-III that while BET nitrogen gas adsorption surface area of alumina powder appears to agree with the literature value if area occupied per molecule of nitrogen is assumed to be $16.2 \text{ \AA}^2$ an agreement between this surface area and flow micro-calorimetric and adsorption from solution surface areas using stearic acid as solute is found if area occupied per molecule of stearic acid is assumed to be $65 \text{ \AA}^2$. Assuming area occupied by one molecule nitrogen to be the same i.e., $16.2 \text{ \AA}^2$. BET nitrogen gas adsorption surface areas of cupric oxide and ferric oxide powders are found respectively to be 9.3 and $9.1 \text{ m}^2/\text{g}$. In these cases also BET nitrogen gas adsorption areas agree fairly well with the corresponding flow micro-calorimetric and adsorption from solution surface areas of the powders provided the same assumption that area occupied per molecule of stearic acid to be $65 \text{ \AA}^2$ is made.

5.5. Determination of surface area of magnesium oxide and silica gel powders by adsorption from solution method using stearic acid as a solute.

From the results obtained by adsorption from solution method using stearic acid in benzene surface area of

magnesium oxide and silica gel powders have been evaluated assuming area occupied per molecule of stearic acid to be the same as that for cupric oxide, ferric oxide and alumina powders i.e., $65 \text{ \AA}^2$. They come out to be 89 and $370 \text{ m}^2/\text{g}$ respectively for magnesium oxide and silica gel powders. These values agree fairly well with the corresponding BET nitrogen gas adsorption surface area of these powders reported in literature. Amount of stearic acid occupied per unit surface of these adsorbents at monolayer coverage are summarized in Table-I. They are found to be close to one another and agree fairly well with that of cupric oxide, ferric oxide and alumina powders. These findings indicate that stearic acid may be considered to be a standard solute in the adsorption from solution method for the successful determination of surface area of all the adsorbents studied. Further all the adsorbent surfaces studied may be considered to be standards for evaluating the parameters involved in all the expressions (1,7,8) required for the determination of surface area of powdered solids by BET nitrogen gas adsorption and flow micro-calorimetric methods.

5.6. Mechanism of adsorption of stearic acid on the adsorbents.

With the help of the flow micro-calorimeter heats of adsorption of stearic acid on adsorbent surfaces which have

been previously saturated by stearic acid was measured by replacing the solution with the solvent. It is seen from the Table-II that the desorption heats of stearic acid are 35, 30 and 28 percent respectively of the adsorption heat due to the cupric oxide, ferric oxide and alumina at limiting adsorption of stearic acid. This finding indicates that the adsorption of stearic acid on the adsorbents is only partially reversible and unlike nitrogen molecules stearic acid molecules are mostly chemisorbed on these adsorbents. This is supported by the high values of integral energies of adsorption of stearic acid on the adsorbents quoted in Table-II. Integral heats evolved per unit surface of the adsorbents quoted in Table-II are close to one another and so also the amount of stearic acid per unit surface of the adsorbent quoted in Table-I. Also despite wide variation of surface areas the area occupied per molecule of stearic acid at the limiting adsorption on the adsorbents are close to one another. These facts lead to the conclusion that the surfaces of cupric oxide, ferric oxide, magnesium oxide, alumina and silica gel powders are similar in nature to give adsorbed layers of stearic acid molecules on them where the molecules lie neither completely parallel nor completely perpendicular on the surfaces. These findings are in keeping with the recent infra-red and thermogravimetric studies^(34,35) which reveal

that the model of adsorbed layer of stearic acid on alumina and silica gel powders differs from that of Kipling and Wright⁽³²⁾ who assumed long chain fatty acids to be physically adsorbed on the surfaces as dimers parallel to the plane of the surfaces. It has been evidenced^(34,35) that on alumina and silica powders the adsorption layers consisted predominantly of monomers at low degrees of coverage, and weak and reversible dimers at high concentration of solution. It has further been evidenced that on alumina mostly stearate are formed but in case of silica gel in addition to the stearate some monomers are hydrogen bonded to silanols and others to siloxane groups. Similar results have been observed for magnesia using adsorption of decanoic acid so that magnesium distearate may be assumed to form on the magnesium oxide surface. There appears to be no mechanistic studies on adsorption of stearic acid on cupric oxide and ferric oxide. In view of the similarity of the type of surfaces evidenced by the present results formation of stearate molecules may also be assumed on cupric oxide and ferric oxide powders.

5.7. Determination of surface area of powdered solids using adsorption of pyridine from n-heptane solution.

Pyridine and its derivatives have recently been found to exhibit boundary lubricity. They are weak organic bases, and

are different from fatty acids as a class of organic compounds. In view of the mechanism of adsorption envisaged by Miller pyridine is expected to be a standard solute for the determination of surface area of powdered solids. From the limiting values of the amount of pyridine adsorbed the surface areas of cupric oxide, ferric oxide, magnesium oxide, alumina and silica gel powders have been evaluated. To do so area occupied per molecule of pyridine on the adsorbent surface is required to be known. In the case of cupric oxide, ferric oxide and alumina powders BET nitrogen gas adsorption area has been equated to surface area obtainable by adsorption of pyridine from n-heptane solution. It has been found that the pyridine adsorption surface area agree with the corresponding BET nitrogen gas adsorption surface area if areas occupied per molecule of pyridine are assumed to be 24.8, 23.7 and 23.0 Å² respectively for cupric oxide, ferric oxide and alumina powders. With these values of area occupied per molecule of pyridine these surface areas also agree with the corresponding surface areas using stearic acid as solute. Agreements between pyridine adsorption surface areas and stearic acid adsorption surface areas are also obtained in the cases of magnesium oxide and silica gel if areas occupied per molecule of pyridine are taken to be 24.8 and 24.6 Å² respectively. From the data of Pauling and Schomaker⁽⁶³⁾,

Kipling and Peakall⁽⁶¹⁾ found the molecular area of pyridine to be $24.7 \text{ \AA}^2$. The latter authors used this value to determine the maximum amount of chemisorption possible on boehmite. The present results would reveal that the specific surface areas of cupric oxide, ferric oxide, magnesium oxide, alumina and silica gel powders evaluated on the assumption of close-packed monolayers so that the area occupied per molecule of pyridine equals to its molecular area, $24.7 \text{ \AA}^2$, gives an over-estimate of not exceeding 6.6 % in any of the cases studied compared with the BET nitrogen gas adsorption and adsorption of stearic acid from benzene solution surface areas. It may, therefore, be concluded that the method of adsorption of pyridine from n-heptane solution be employed for successful estimation of specific surface area of the adsorbents.

5.8. Mechanism of adsorption of pyridine on the adsorbents.

It has already been pointed out that to equate pyridine adsorption surface areas of the adsorbents to the corresponding BET nitrogen gas adsorption surface area the area occupied per molecule of pyridine slightly differ from adsorbent to adsorbent. These values are summarized in Table-I(a). Similar situation occurred in the case of adsorption of stearic acid. Therefore, corresponding value of area occupied

per molecule of stearic acid on the adsorbent surfaces are also incorporated in the same Table. It is seen from the Table that the areas occupied per molecule of pyridine on cupric oxide, ferric oxide and alumina powders are less than the molecular area of pyridine. This is improbable and therefore, these results indicate the possibility of formation of some multilayers on these adsorbent surfaces. This seems to be more pronounced in the case of alumina as has been indicated by the curvature of the Langmuir plot for alumina in Figure-16. The phenomenon that a molecule of pyridine occupies an area less than its molecular area may also be partly due to the formation of bipyridine molecules on the adsorbent surfaces.

Waksmundzki et al⁽⁴¹⁾ claimed that silica gel activated with pyridine gave adsorption mainly of monolayer type but they did not rule out the possibility of some multilayer. Miller⁽⁵²⁾ has indicated the presence of bipyridine molecules in the adsorbed layers during his study of wear on steel-on-steel system using pyridine as an anti-wear agent. Although on the basis of infra-red study⁽³⁶⁾ it has been claimed that the mechanism of adsorption pyridine involves both protonic (Bronsted) centres and aprotonic (Lewis) centres, far infra-red studies^(37,64) revealed in silica gel there was mainly co-ordination with the Lewis acid centres,

and certain surface hydroxyl groups bound pyridine by hydrogen bond. Similar mechanism have also been envisaged in the case of alumina^(44,65). The formation of multilayers may be attributed to the bonding of pyridine with the surface hydroxy groups of the adsorbents.

Adsorption experiments using neutral pyridine on sodium montmorillonite have revealed that the pyridine molecules were disposed with their planes perpendicular to the silicate layers⁽³⁸⁾. The fact that the area occupied per molecule of pyridine on ferric oxide, cupric oxide and alumina is of the same order suggests the orientation of pyridine molecules in all the cases studied to be the same; so that adsorption of pyridine molecules takes place through nitrogen atom probably via perpendicular approach of the molecules. This mechanism has also been envisaged by Miller⁽⁵²⁾ during his study of wear in steel-on-steel system using pyridine as an anti-wear agent.

BIBLIOGRAPHY

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1. Orr, C., and Valle, J.M.D., 'Fine particle measurement', The McMillan Co., New York, 1959.
2. Allen, T., and Patel, R.M., Powder Technol., 2, 111, (1968/69).
3. Allen, T., and Patel, R.M., J.appl.Chem., 20, 165, (1970).
4. Allen, T., and Patel, R.M., J.Colloid and Interface Sc., 35, 647, (1971).
5. Allen, T., and Patel, R.M., Paper presented to the particle size analysis conference, held at Bradford, 1970.
6. Groszek, A.J., Chem.Ind., (1965), 2003; Ibid., (1966), 1765.
7. Groszek, A.J., Soc.Chem.Ind.Monograph No 28, 174, (1968).
8. Rahman, M.A., Bang.J.Sc.Ind.Res., 12, 151, (1977).
9. Harkins, W.D., and Gans, D.M., J.Am.Chem.Soc., 53, 2804, (1931).
10. Ewing, W.W., Ibid., 61, 1317, (1939).
11. Harkins, W.D., and Anderson, T.F., Ibid., 59, 2189, (1937).
12. Smith, H.A., and Fusek, J.F., Ibid., 68, 229, (1946).
13. Adam, N.K., 'Physics and Chemistry of Surfaces', Oxford University Press, London, (1941).
14. Russel, A.S., and Cochran, C.N., Ind.Eng.Chem., 42, 1332, (1950).
15. Hirst, W., and Lancaster, J.K., Research (London), 3, 336, (1950).
16. Glueckauf, E., J.Am.Chem.Soc., 73, 849, (1951).
17. MaxNestlar, F.H., and Cassidy, H.G., Ibid., 72, 680, (1950).
18. Ito, K., and Fukao, K., Kagaku Kenkyusho Hokoku, 33, 41, (1957).
19. Kinnosuke, H., Nippon Kagaku Zasshi, 88, 1044, (1967).

20. Smith, H.A., and Hurley, R.B., J. Phys. Colloid Chem., 53, 1409, (1949).
21. Morrison, J.L., and Miller, D.L., Can. J. Chem., 33, 330, (1955).
22. Suito, E., Arakawa, M., and Arakawa, T., J. Chem. Soc. Japan Pure Chem. Sect., 75, 596, (1954).
23. Loomis, A.G., Procedures monthly, 18(11), 19, (1954).
24. Tamaki, K., Nippon Kagaku Zasshi, 78, 1151, (1957).
25. Medvedeva, A.P., Ogneupory, 25, 134, (1960).
26. Tovarov, V.V., Tsement, 13(3), 15, (1947); Ibid., 13(7), 12, (1947).
27. Ries, H.E. Jr., Johnson, M.F.L., and Melik, J.S., J. Phys. Colloid Chem., 53, 638, (1949).
28. Kordecki, M.C., and Gandy, M.B., Intern. J. Appl. Radiation and Isotopes, 12, 27, (1961).
29. Kravchenko, I.I., Genkina, B.I., and Kovalenko, E.K., Tr. Ufinsk. Neft. Nauchn.-Issled. Inst., 13, 109, (1964).
30. Jankovics, L.R., Proc. Pa. Acad. Sc., 30(2), 323, (1966).
31. Korenev, A.D., and Lunina, M.A., Zh. Fiz. Khim., 43(6), 1605, (1969).
32. Kipling, J.J., and Wright, E.H.M., J. Chem. Soc., (1964), 3535.
33. Ibid., (1962), 855.
34. Hasegawa, M., and Low, M.J.D., J. Colloid Interface Sc., 30, 378, (1969).
35. Tyler, A.J., Hambleton, F.H., and Hocky, J.A., Catalysis, 13, 35, (1969).

36. Bertoluzza, A., Fabbri, G., and Farne, G., Atti Accad. Nazl. Lincei, Classe Sci. Fis., Mat. Nat., 37(6), 424, (1964).
37. Lorenzelli, V., and Gesmundo, F., Ann. Chim., 56(6), 628, (1965).
38. Serratos, J. M., Nature, 208(5011), 679, (1965).
39. Sugimura, T., and Kitahara, A., Nippon Kagaku Zasshi, 86(10), 1025, (1965).
40. Matsen, F. A., Makrides, A. C., and Hackerman, N., J. Chem. Phys. 22, 1800, (1954).
41. Waksmundzki, A., Oscik, J., Rozylo, J., and Nasuto, R., Przem. Chem., 46(5), 287, (1967).
42. Low, M. J. D., and Rao, V. V. S., Can. J. Chem., 46(20), 3255, (1968).
43. Chukin, G. D., and Ignat'eva, L. A., Zh. Prikl. Spektrosk., 8, 872, (1968).
44. Bandiera, J., and Maccache, C., Bull. Soc. Chim. Fr., 8, 2637, (1969).
45. Kubelkova, L., and Jiuru, P., Z. Phys. Chem., 80, 140, (1972).
46. Chukin, G. D., and Khrustaleva, S. V., Zh. Fiz. Khim., 47(8), 2055, (1973).
47. Nishimura, M., Nagoya-Shi Kogyo Kenkyusho Kenkyu Hokoku, 55, 24, (1976).
48. Hirokawa, T., Ohno, K., Kimura, T., and Murata, H., Chem. Lett., 5, 457, (1977).

49. Naono, H., Moori, K., and Norimoto, T., Bull.Chem.Soc., 49(7), 1772, (1976).
50. Kozlov, N.S., Tarasevich, V.A., Akulich, N.A., and Moiseenok, L.I., Vestsi Akad, Navuk B.SSR, Ser, Khim.Navuk, 4, 5, (1976).
51. Rendal, H.M., and Smith, A.L., J.Chem.Soc., Faraday Trans.1, 73(1), 101, (1977).
52. Miller, A.H., J.Inst.Petr., 59(565), 27, (1973).
53. Appeldoorn, J.K., and Tao, F.F., Wear, 12, 117, (1968).
54. Rudston, S.G., and Whitby, R.D., J.Inst.Petr., 57(556), 189, (1971).
55. Goldblatt, I.L., Ind.Eng.Res.Develop., 10(3), 271, (1971).
56. Beerbower, A., and Goldblatt, I.L., Wear, 18, 421, (1971).
57. Vogel, A.I., 'A text book of quantitative inorganic analysis', The Eng.Lang.Book Soc. & Longman, London, 3rd ed., pp-468.
58. Ibid., pp-523.
59. Rahman, M.A., and Ghosh, A.K., Bang.Pharm.J., 6, 12, (1977).
60. Rahman, M.A., Ghosh, A.K., and Basu, S.K., Ibid., (accepted).
61. Kipling, J.J., and Peakall, D.B., J.Chem.Soc., (1956), 4828.
62. Groszek, A.J., Proc.Intern.Symp.on Surface Area Det., held in Bristol, U.K., 313, (1969).
63. Schomaker, V., and Pauling, L., J.Am.Chem.Soc., 61, 1769, (1939).
64. Bonino, G.B., Lorenzelli, V., Randi, G., and Gesmundo, F., Ann.Chim., 54, 1187, (1964).

65. Bandiera, J., and Stanislas, T.J., Bull.Soc.Fr., 841, (1973).

APPENDIX - 1

TABLE 1 - 1

A P P E N D I X - A

T A B L E S I V - X I X

Table-IV. Data for the calibration curve for the estimation of iron(III) and Pyridine.

Fe ⁺³ in water		Pyridine in n-heptane	
Concentration mg/lit.	Absorbance	Concentration mg/lit.	Absorbance
0.5	0.11	1.5	0.03
1.0	0.21	3.0	0.08
1.5	0.32	4.8	0.12
2.0	0.42	7.8	0.20
2.5	0.53	10.2	0.25
3.0	0.63	12.0	0.30

Absorbances taken at 480 and 251 mμ for iron(III) and pyridine respectively.

Table-V. BET nitrogen gas adsorption measurements at liquid N₂ temperature, -196°C.

Adsorbent	Weight of adsorbent (w) g	Degassing Conditions			Pressure Volume			Limiting Value	
		Temp °C	Vacuum mm Hg	Time hr	(P) cm Hg	of N ₂ adsor-	of N ₂ adsor-	of Volume of N ₂ bed at bed at NTP (V _m)	
						NTP(V _w) NTP(V)		c.c/g c.c/g	
CuO	0.5043	150	10 ⁻⁵	4	24.44	1.57	3.12	2.12	
	0.4972	150	10 ⁻⁵	4	23.80	1.65	3.33	2.26	
	0.4892	150	10 ⁻⁵	4	24.15	1.46	3.00	2.05	
Fe ₂ O ₃	0.5218	350	10 ⁻⁵	3	25.50	1.63	3.13	2.08	
	0.4874	350	10 ⁻⁵	3	23.80	1.41	2.89	2.11	
	0.5028	350	10 ⁻⁵	3	24.30	1.56	3.12	2.12	
Al ₂ O ₃	0.1239	350	10 ⁻⁵	3	23.70	4.85	38.78	27.15	
	0.1055	350	10 ⁻⁵	3	25.50	4.37	41.45	27.52	
	0.1065	350	10 ⁻⁵	3	24.82	4.35	40.88	27.55	

Table-VI. Flow micro-calorimetric measurements for CuO powder.

Change in solute concentration M $\times 10^{-3}$ From(C ₁) To(C)		Cumulative heat evolved (q) mcal/g	10 ⁶ X C/q M mc ⁻¹ g	Amount of stearic acid adsorbed (x) mol $\times 10^{-5}$ /g	C/x M mol ⁻¹ g $\times 10^2$
0	0.5	216	2.31	1.5	0.33
0.5	1.0	280	3.57	1.6	0.63
1.0	1.5	360	4.17	1.9	0.79
1.5	3.0	404	7.42	2.2	1.36
3.0	7.0	424	16.51	2.3	3.04
7.0	12.0	430	27.91	2.4	5.00

At monolayer coverage,

heat evolved (q₀)
mcal/g 439

integral energies
of adsorption
Kcal/mole 17.9

integral heat per
unit surface (q₀/S)
mcal/m² 47.2

Table-VII. Flow micro-calorimetric measurements for Fe_2O_3 powder.

Change in solute concentration From(C_1) To(C) $\text{M} \times 10^{-3}$		Cumulative heat evolved (q) mcal/g	$10^6 \text{XC}/q$ $\text{M} \text{mcal}^{-1} \text{g}$	Amount of stearic acid adsorbed (x) $\text{mol} \times 10^{-5} / \text{g}$	C/x $\text{M} \text{mol}^{-1} \text{g} \times 10^2$
0	0.5	232	2.16	1.6	0.31
0.5	1.0	302	3.31	1.6	0.63
1.0	1.5	406	3.69	1.7	0.88
1.5	3.0	445	6.74	1.8	1.67
3.0	7.0	466	15.02	2.1	3.33
7.0	12.0	469	25.59	2.2	5.45

At monolayer coverage,

heat evolved (q_0)

mcal/g 485

integral energies

of adsorption

Kcal/mole 21.3

integral heat per

unit surface (q_0/S)

mcal/ m^2 55.3

Table-VIII. Flow micro-calorimetric measurements for Al_2O_3 powder.

Change in solute concentration $\text{M} \times 10^{-3}$ From(C_1) To(C)		Cumulative heat evolved (q) mcal/g	$10^6 \text{XC}/q$ $\text{M} \text{mcal}^{-1} \text{g}$	Amount of stearic acid adsorbed (x) $\text{mol} \times 10^{-5} / \text{g}$	C/x $\text{M} \text{mol}^{-1} \text{g} \times 10^2$
0	0.5	2412	0.21	22.9	0.02
0.5	1.0	3740	0.27	24.3	0.04
1.0	1.5	5024	0.30	27.6	0.05
1.5	3.0	5796	0.52	29.4	0.10
3.0	7.0	6124	1.14	30.9	0.22
7.0	12.0	6146	1.95	31.2	0.38

At monolayer coverage,

heat evolved (q_0)
mcal/g 6184

integral energies
of adsorption
Kcal/mole 19.6

integral heat per
unit surface (q_0/S)
mcal/ m^2 51.8

Table-IX. Effect of shaking time on adsorption of stearic acid.

Adsorbent	Concentration of stearic acid solution, $\text{mM} \times 10^{-3}$	Amount of stearic acid adsorbed, $\text{mM} \times 10^{-5}/\text{g}$.					
		Shaking time, min.	10	20	30	45	60
CuO	10		1.85	1.90	1.95	2.00	2.00
	40		2.14	2.25	2.40	2.42	2.40
Fe_2O_3	10		1.85	1.90	1.95	2.00	2.00
	40		2.08	2.16	2.21	2.20	2.20
MgO	20		16.50	18.90	20.29	22.80	22.80
	75		17.08	20.47	23.60	23.60	23.60
Al_2O_3	25		24.10	27.05	28.50	29.00	29.00
	75		25.73	31.16	32.09	32.00	32.00
Silica gel	75		53.90	55.40	56.50	58.00	58.00
	300		84.20	87.95	91.00	91.00	91.00

Table-X. Determination of adsorption of stearic acid on CuO powder by adsorption from solution method.

Concentration of stearic acid solution, $\text{M} \times 10^{-3}$		Amount of stearic acid adsorbed (x)	C/x
Before adsorption (C)	After adsorption (C_1)	$\text{mol} \times 10^{-5} / \text{g}$	$\text{M mol}^{-1} \text{g} \times 10^2$
5	4.1	1.8	2.8
10	9.0	2.0	5.0
15	13.9	2.2	6.8
20	18.8	2.4	8.3
30	28.8	2.4	12.5
40	38.8	2.4	16.7

Adsorbent powder 5 g ;

Solution 100 ml.

Table-XI. Determination of adsorption of stearic acid on Fe_2O_3 powder by adsorption from solution method.

Concentration of stearic acid solution, $\text{M} \times 10^{-3}$		Amount of stearic acid adsorbed (x) $\text{mol} \times 10^{-5} / \text{g}$	C/x $\text{M mol}^{-1} \text{g} \times 10^2$
Before adsorption (C)	After adsorption (C_1)		
5	4.1	1.8	2.8
10	9.0	2.0	5.0
15	14.0	2.0	7.5
20	18.9	2.2	9.1
25	23.9	2.2	11.4
30	28.9	2.2	13.6
40	38.9	2.2	18.2

Adsorbent powder 5 g ;

Solution 100 ml.

Table-XII. Determination of adsorption of stearic acid on MgO powder by adsorption from solution method.

Concentration of stearic acid solution, $\text{M} \times 10^{-3}$		Amount of stearic acid adsorbed (x) $\text{mol} \times 10^{-5} / \text{g}$	C/x $\text{M mol}^{-1} \text{g} \times 10^2$
Before adsorption (C)	After adsorption (C_1)		
5*	3.5	15.0	0.33
10*	8.0	20.0	0.50
15	4.1	21.8	0.69
20	8.6	22.8	0.88
25	13.4	23.2	1.08
30	18.3	23.4	1.23
40	28.2	23.6	1.69
50	38.1	23.8	2.10
75	63.2	23.6	3.18

Adsorbent powder 5 g, * 1 g ;

Solution 100 ml.

Table-XIII. Determination of adsorption of stearic acid on Al_2O_3 powder by adsorption from solution method.

Concentration of stearic acid solution, $MX10^{-3}$		Amount of stearic acid adsorbed (x) $molX10^{-5}/g$	C/x $M mol^{-1}gX10^2$
Before adsorption (C)	After adsorption (C_1)		
10*	7.4	26.0	0.38
15*	12.3	27.0	0.56
20*	17.1	28.9	0.69
25	10.5	29.0	0.86
30	15.0	30.0	1.00
40	24.5	31.0	1.29
50	34.0	32.0	1.56
75	59.0	32.0	2.34
100	84.0	32.0	3.13

Adsorbent powder 5 g, * 1 g ;

Solution 100 ml.

Table-XIV. Determination of adsorption of stearic acid on Silica gel powder by adsorption from solution method.

Concentration of stearic acid solution, $\text{MX}10^{-3}$		Amount of stearic acid adsorbed (x) $\text{molX}10^{-5}/\text{g}$	C/x $\text{M mol}^{-1}\text{gX}10^2$
Before adsorption (C)	After adsorption(C_1)		
18.5	16.5	20	0.93
30.0	26.8	32	0.94
45.0	40.8	42	1.07
60.0	54.6	54	1.11
75.0	69.2	58	1.29
90.0	83.6	64	1.41
105.0	97.9	71	1.48
120.0	112.5	75	1.60
150.0	141.6	84	1.79
180.0	171.2	88	2.04
210.0	201.1	89	2.36
240.0	230.9	91	2.64
270.0	260.8	92	2.94
300.0	290.9	91	3.30
330.0	320.9	91	3.63

Adsorbent powder 5 g ; Solution 500 ml.

Table-XV. Determination of adsorption of pyridine on CuO powder by adsorption from solution method.

Concentration of pyridine solution, $\text{MX}10^{-3}$		Amount of pyridine adsorbed (x)	C/x
Before adsorption (C)	After adsorption (C_1)	$\text{molX}10^{-5}/\text{g}$	$\text{M mol}^{-1}\text{gX}10^2$
3.12	2.75	3.7	0.84
6.32	5.82	5.0	1.26
9.48	8.91	5.7	1.66
12.64	12.02	6.2	2.04
15.80	15.17	6.3	2.51
18.96	18.33	6.3	3.01
22.12	21.49	6.3	3.51
38.35	37.72	6.3	6.08

Adsorbent powder 5 g ;

Solution 500 ml.

Table-XVI. Determination of adsorption of pyridine on Fe_2O_3 powder by adsorption from solution method.

Concentration of pyridine solution, $\text{M} \times 10^{-3}$		Amount of pyridine adsorbed (x)	C/x
Before adsorption (C)	After adsorption (C_1)	$\text{mol} \times 10^{-5}/\text{g}$	$\text{M mol}^{-1} \text{g} \times 10^2$
3.12	2.74	3.8	0.82
6.32	5.82	5.0	1.26
9.48	8.90	5.8	1.63
12.64	12.01	6.3	2.01
15.80	15.16	6.4	2.47
18.96	18.31	6.5	2.92
22.12	21.48	6.4	3.46

Adsorbent powder 5 g ;

Solution 500 ml.

Table-XVII. Determination of adsorption of pyridine on MgO powder by adsorption from solution method.

Concentration of pyridine solution, $\text{M} \times 10^{-3}$		Amount of pyridine adsorbed (x) $\text{mol} \times 10^{-5} / \text{g}$	C/x $\text{M mol}^{-1} \text{g} \times 10^2$
Before adsorption (C)	After adsorption (C_1)		
6.32	4.82	18.2	0.35
9.48	6.87	26.1	0.36
15.80	12.30	35.0	0.45
22.12	17.84	42.8	0.52
30.16	25.33	48.3	0.62
38.35	33.09	52.6	0.73
50.35	44.61	57.4	0.87
63.82	57.79	60.3	1.06
80.28	74.25	60.3	1.33

Adsorbent powder 5 g ;

Solution 500 ml.

Table-XVIII. Determination of adsorption of pyridine on Al_2O_3 powder by adsorption from solution method.

Concentration of pyridine solution, $\text{MX}10^{-3}$		Amount of pyridine adsorbed (x) $\text{molX}10^{-5}/\text{g}$	C/x $\text{M mol}^{-1}\text{gX}10^2$
Before adsorption (C)	After adsorption(C_1)		
12.64	9.63	30.1	0.42
25.56	20.63	49.3	0.52
38.35	32.01	63.4	0.60
63.82	56.61	72.1	0.88
110.66	102.32	83.4	1.33
164.34	155.74	86.0	1.91
200.42	191.82	86.0	2.33
240.25	231.65	86.0	2.79

Adsorbent powder 5 g ;

Solution 500 ml.

Table-XIX. Determination of adsorption of pyridine on Silica gel powder by adsorption from solution method.

Concentration of pyridine solution, $\text{MX}10^{-3}$		Amount of pyridine adsorbed (x) $\text{molX}10^{-5}/\text{g}$	C/x $\text{M mol}^{-1}\text{gX}10^2$
Before ads- orption (C)	After ads- orption(C_1)		
12.64	1.39	112.5	0.11
25.56	9.01	165.5	0.15
38.35	19.60	187.5	0.20
63.82	41.81	220.1	0.29
110.66	86.69	239.7	0.46
164.34	139.79	245.5	0.67
200.42	175.64	247.8	0.81
240.25	215.47	247.8	0.97

Adsorbent powder 5 g ;

Solution 500 ml.

APPENDIX - B

THE FLOW MICRO-CALORIMETER

1. Description of apparatus.

The calorimeter (Fig.18) consists essentially of a metal block (A) surrounding a cylindrical cavity in which the Teflon calorimeter cell (B) is situated. The diameter and height of the cell are 0.623 cm and 0.55 cm respectively. The bottom of the cell is closed by 500 mesh stainless steel gauze (C) attached to a metal outlet tube (D) which can support granulated solids (E) (adsorbent). The top of the cell adheres tightly to the bottom walls of a central channel in the metal block forming a continuation of the cell cavity. The interior of the cell is thus accessible either from the top of the metal block or after removal of the outlet tube from the bottom of the block. Liquids or gases can percolate freely through the cell, after flowing along the walls of the central channel (F).

The temperature of the adsorbent is measured by two thermistors (G) protruding from the walls of the cell at a height of 0.232 cm from the gauze. The thermistors are connected in a wheatstone bridge circuit and are opposed by two reference thermistors (H) embeded in the metal block. The four thermistors construct the arms of the bridge, its output being fed to a potentiometric recorder.

For use at an ambient temperature, the carrier liquid can flow along the walls of the central channel from

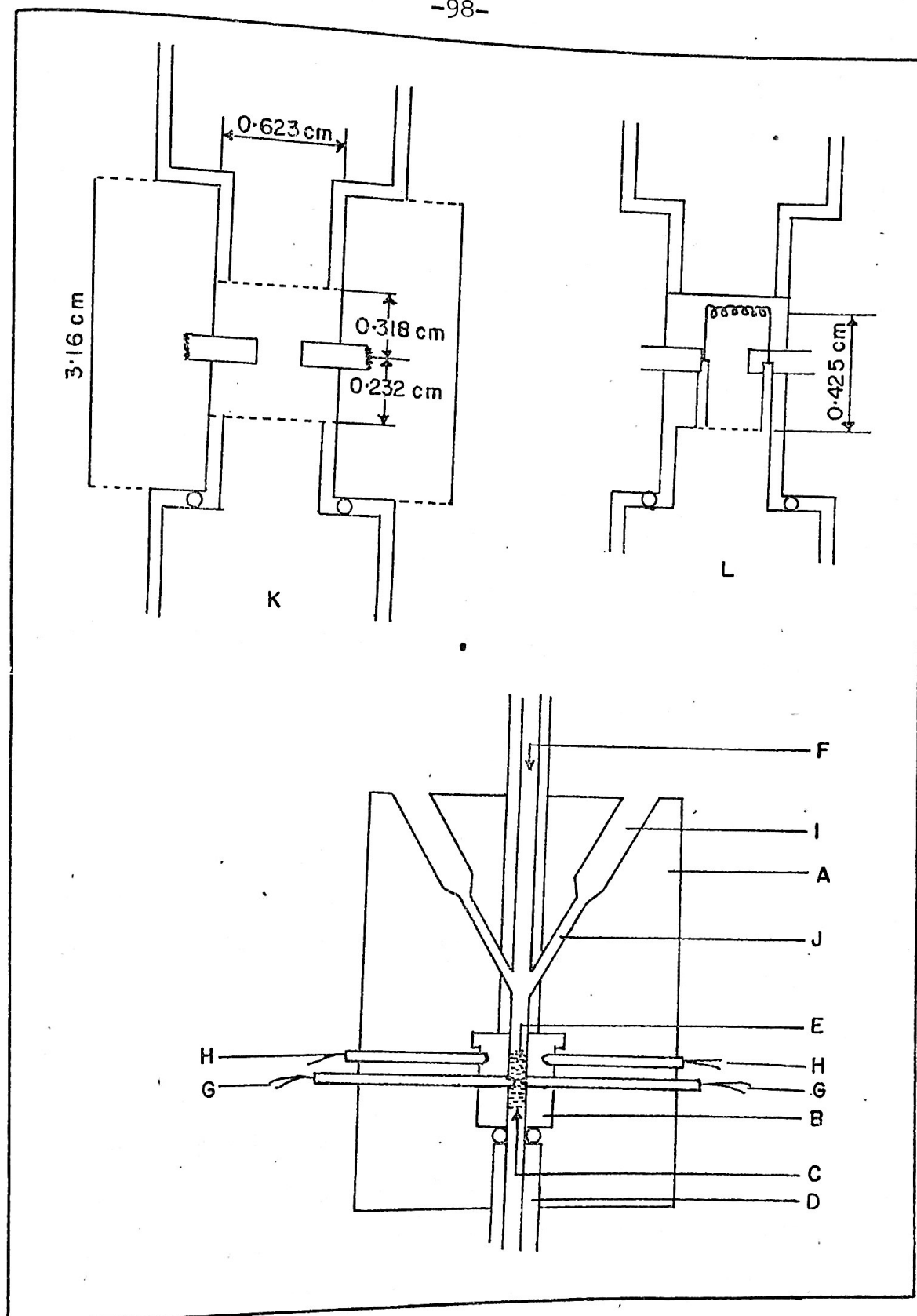


Fig.18. Representational diagram and dimension of calorimeter cell and position of heating coil in calorimeter cell.

a container situated above the metal block, ultimately contacting the adsorbent (E). However, the top half of the metal block contains two cylindrical side cavities (I) which can accommodate containers with carrier liquid or solution to be percolated through the adsorbent in the cell. Narrow channels (J) extend from the bottom of the side cavities and contact the central channel in the block above the walls of the Teflon cell. When the calorimeter is used at an elevated temperature, containers with the carrier liquid are placed in the side cavities so that when the liquid drains down the channels it attains a temperature close to that of the cell contents. The dimension of the calorimeter cell (K) and the position of the heating coil (L), for calibration purposes are shown in the same Figure.

2. Accessories (Fig.19).

(i) Calibration unit :

The calibration unit (A) is similar to the outlet tube except that a heat generating coil made of nichrome wire is fitted at a height of 0.425 cm above the gauze. The two ends of the small coil are sealed with the terminals(TT) termed as the calibration leads. During calibration the calibration leads are connected with the power producing battery (1.5 volt battery) placed inside the calorimeter chassis.

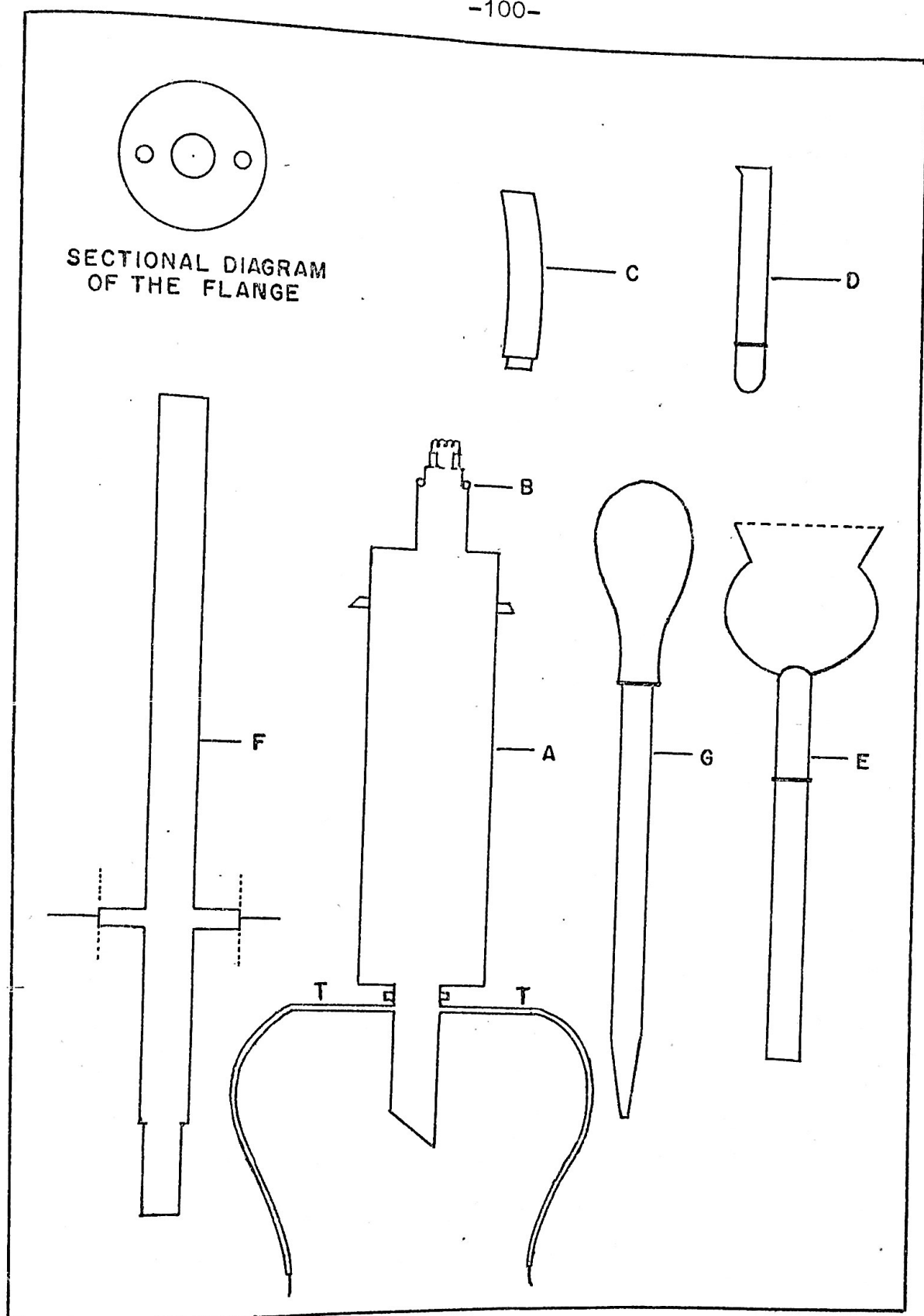


Fig.19. Accessories of the flow micro-calorimeter.

The black rubber ring (B) fixed on the outlet tube prevents leakage of solvent and powder from the bed by percolation around the outer wall of the outlet tube.

A rubber blank (C), a small rubber tube closed at one end by a metal piece, when fitted tightly at the end of the outlet tube serves the purpose of holding up the solvent in the calorimeter cell.

(ii) Measuring tube :

It is a small tube (D) with a black rubber band. The powder is weighed into the measuring tube and then poured into the calorimeter cell. The correct amount of powder required to fill the cell is determined by trial and error method. Once the correct amount of powder required is determined, it is poured into the tube and tapped gently until no decrease of volume occurs. The rubber band is now moved to the appropriate position on the measuring tube, so as to reduce the tedium of repeatitive weighing of a given powder for several experiments.

(iii) Powder delivery funnel :

The powder from the measuring tube is introduced into the calorimeter cell by a long stem glass funnel (E). Before introducing the powder the calorimeter cell is filled

with a carrier liquid (usually hydrocarbon) and it is ensured that the tip of the stem of the funnel remains just above the surface of the liquid. This is achieved by positioning correctly a rubber band provided with the stem of the funnel. If the stem touches the liquid, the powder will adhere on the wall of the stem.

(iv) Carrier liquid inlet tube :

Experiments are carried out under continuous flow of carrier liquid through the bed of powder in the calorimeter cell. The carrier liquid is introduced with a stainless steel tube (F) extending upto the powder bed. The inlet tube is provided with a flange having two screw holes. To prevent movement the inlet tube is fixed with the metal block of the calorimeter by inserting two long knurled screws through the screw holes.

(v) Glass dropper :

After each experiment a long stem glass dropper (G) is used for washing the calorimeter cell, inlet tube, wire gauze and all other parts where powder adheres during operations.

(vi) Agla micro-meter syringe outfit (Fig.20) :

When adsorption experiments are carried out using pulse or injection method the adsorbate is introduced by a microsyringe. The microsyringe is specially suitable for use in experimental technique requiring the accurate measurement of very small volume of fluid. It is composed of an all-glass hypodermic syringe (A) shown in Figure-20, the barrel is made of borosilicate glass. The syringe can be attached by a rigid holder (B) to a micro-meter screw gauge (C) which operates the plunger. The ratchet device (D) used at the end of the micro-meter screw gauge (C) will prevent damage to the glass plunger should the syringe be improperly assembled. A small screw (E) at the other end of the micro-meter may be used to lock the head in any desired position. The maximum amount of liquid that can be delivered with the micro-meter is 0.5 ml and the least count of the micro-meter is such that 0.2 l of liquid can be delivered to the smallest.

(vii) Liquid reservoir :

The carrier liquid is run into the inlet tube from a separating funnel (F) (Fig.20). The outlet of the separating funnel is a capillary. Hypodermic needles of different dimensions can be attached to the outlet of the separating funnel. The flow-rate of the liquid is fixed by the diameter

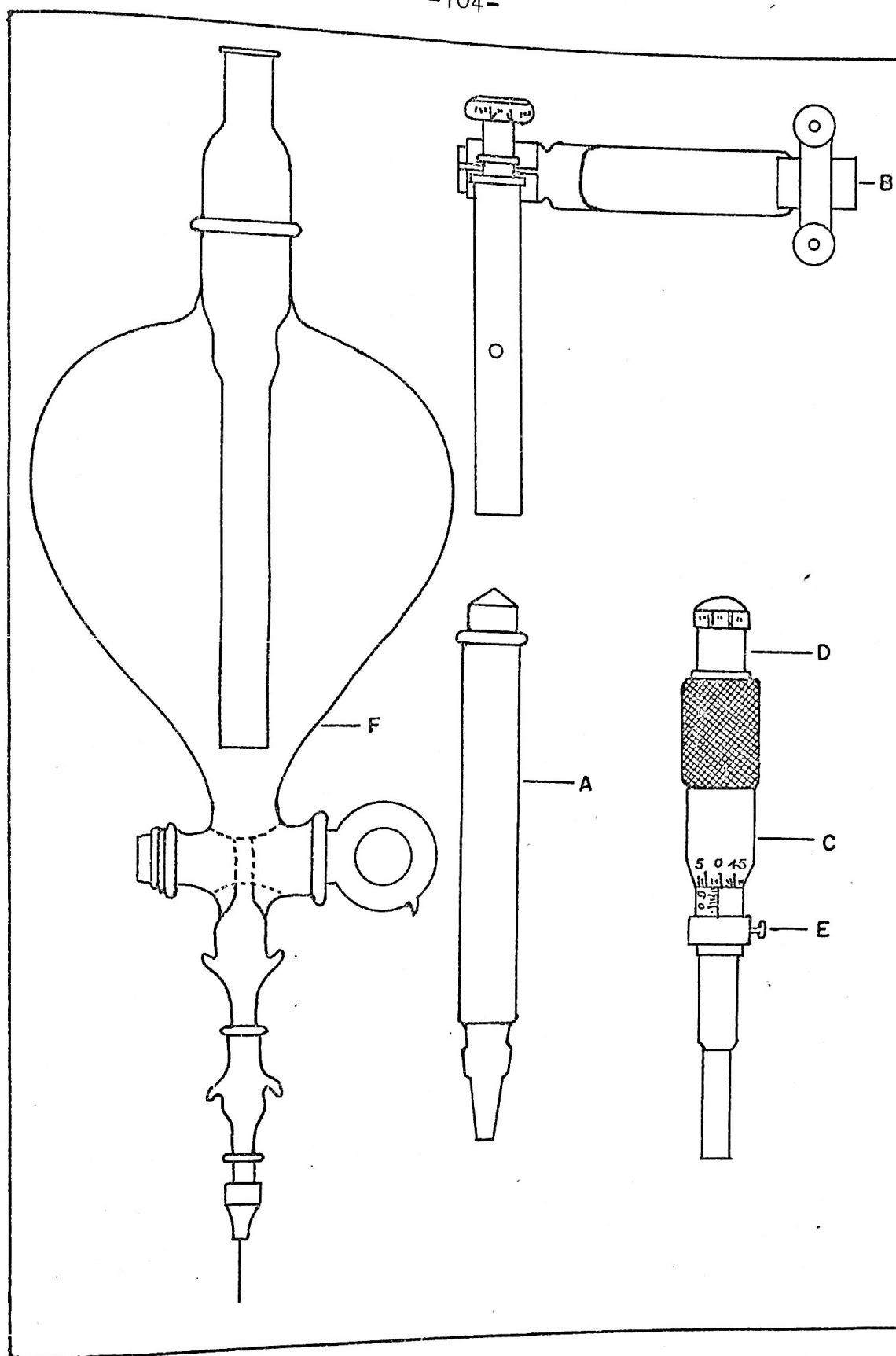


Fig.20. Carrier liquid reservoir and micro-syringe of the flow micro-calorimeter.

of the needle, the diameter of the wire inserted into it, and the liquid head in the reservoir. Changes of flow-rate can be achieved by attaching different needles and adjustment of the position of the wire inside them. To prevent evaporation of the solvent a ground joint stopcock having a long tube to dip down into the solvent is fitted on the mouth of the dropping funnel.

(viii) Pen recorder :

The output of the calorimeter is recorded in terms of milli (or micro) voltage in a Leeds & Northrup Recorder. The sensitivity of the calorimeter can be varied by changing any of the following :

(a) Calorimeter range switch - by changing the position of the switch from 1 to 4 the sensitivity can be increased by a factor of 4.

(b) Calorimeter reduced sensitivity switch - by switching on this the calorimeter sensitivity can be reduced by a factor of 8.

(c) D.C. amplifier 5000/100 V - the sensitivity of the calorimeter can be increased by a factor of 50 by changing the amplifier switch to the following selected position :
100 μ V, 200 μ V, 500 μ V, 1000 μ V, 2000 μ V and 5000 μ V.

3. Calibration.

Before carrying out an adsorption experiment the calorimeter is calibrated. The flow micro-calorimeter is provided with a calibration circuit (Fig.21) through which a known quantity of heat can be supplied to the powder bed in the calorimeter cell to give a peak area in the recorder chart. A plot of quantity of heat vs peak area serves as a calibration chart.

The calibration circuit consists of :

- (i) The dry battery giving 1.5 volts nominal output.
- (ii) The potentiometer R_2 can be set to any position between 100 ohms and 1000 ohms.
- (iii) The calibration unit itself has a resistance of 5-6 ohms. The leads attached to the calibration coil offers a resistance of 0.21 ohms which should be deducted from the resistance of the calibration unit to give the coil resistance.

The heat supplied to the powder bed by the calibration coil can be calculated as follows :

According to Ohms Law, $V = i(R+r)$,

where, V = the measured battery voltage, R = the resistance offered by the potentiometer R_2 , i = the current in amperes for value R of R_2 , r = the resistance of the calibration coil.

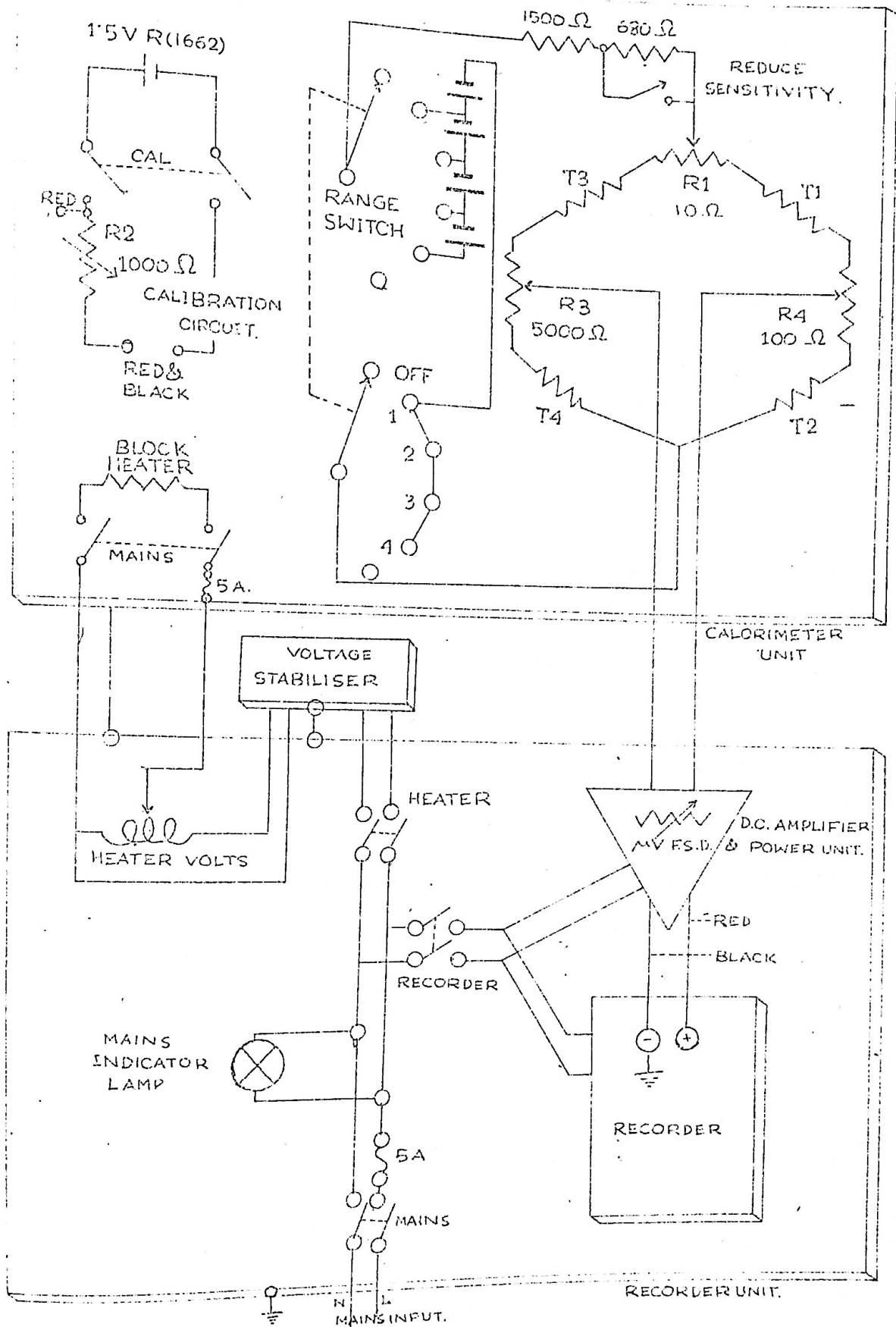


Fig.21. Circuit diagram of the flow micro-calorimeter.

Therefore,

$$i = \frac{V}{R+r} \quad (i)$$

Power, W, dissipated by the calibration coil is given by,

$$W = i^2 r \quad (ii)$$

Substituting the value of i from equation (i),

$$W = \frac{V^2 r}{(R+r)^2} \text{ watts.}$$

The power is usually converted into millicalories (H) and for a calibration time of t seconds :

$$H = \frac{V^2 r t}{(R+r)^2} \times \frac{1000}{4.2} \text{ millicalories} \quad (iii)$$

By varying R_2 and time, t, the quantity of heat supplied to the powder bed can be varied. Thus different amounts of heat corresponding peak areas in the chart-recorder are obtained. The calibration of the flow micro-calorimeter can be carried out at different sensitivity levels by changing the position of the D.C. amplifier switch in the recorder.

Procedure :

To carry out the calibration experiments the resistance of the calibration unit was measured. The calorimeter was drawn out of the draught proof case. The voltage of the power producing battery (Fig.21) was also measured between

the pair of Red/Black terminals ; with R_2 rotated anticlockwise and switching on the calibration switch. The calibration unit was inserted in from below the calorimeter and locked. This unit was fitted very carefully using the guides provided below the calorimeter in order to avoid contact between the coil and thermistor bulb protruding into the cell. The potentiometer R_2 was adjusted to a value between 150 - 350 ohms, measured between the all Red and the left hand Red/Black terminal with the calibration switch off. Calorimeter bridge current was switched on by turning the range switch to range 1 (Fig.21). The calorimeter cell was then filled with the appropriate amount of activated powder using the procedure described in the last section. Calibration leads were then connected to the Red/Black terminals and the calorimeter was pushed inside the draught proof case. The output lead of the calorimeter was plugged into the recorder unit. The inlet tube was introduced into the calorimeter through the aperture in the top of the case and held tightly by inserting two screws. Carrier liquid with a flow-rate of 0.1 ml/minute was allowed to pass through the bed along the wall of the inlet tube from a reservoir fixed at the top of the draught proof case. When a steady flow of the carrier liquid of 0.1 ml/min. was obtained from the outlet tube the mains of the recorder and the recording switch was switched on. The D.C. amplifier

was set at 500 V and the chart switch was also pushed on. When a steady trace in the pen recorder chart was obtained, power was supplied to the calibration coil by switching on the calibration switch in the calorimeter. After the elapse of a period of time the calibration switch was switched off. The recorder gave a trace of peak in the chart. Heat supplied to the bed of the powder was calculated (equation (iii) in this section). The calibration experiments were repeated by using various values of the resistance R_2 in the calibration circuit and also by varying time of power supply. The heat supplied in each experiment was calculated and the corresponding peak area was read off from the recorder chart. To determine the peak area an arbitrary unit which was followed throughout the work was chosen. Finally the calibration graph was obtained by plotting heat supplied vs peak area.

A P P E N D I X - C
P U B L I C A T I O N S

Determination of Specific Surface Area of Ferric Oxide and Alumina Powders

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(Paper received 8 December 1976 and accepted 5 May 1977)

Methods for measuring the surface areas of powdered solids are considered and the specific surface areas of ferric oxide and alumina powders using adsorption of stearic acid from benzene solution are determined. It has been found that the value of the specific surface area of both powders agree with the BET nitrogen gas adsorption area if it is considered that the area occupied per molecule of stearic acid on the powder surface is of the order of $60\text{--}70\text{\AA}^2$. This finding shows that orientation of the stearic acid molecule on the solid/liquid interface takes place so that stearic acid molecules lie neither completely perpendicular nor completely parallel to the surface. Possible orientations of stearic acid chains on the surface are envisaged.

1. Introduction

The determination of the surface area of powdered solids is of immense industrial importance and a wide range of methods is available for this purpose of which static calorimetric, flow calorimetric, gaseous adsorption and adsorption from solution methods are the most common. All these methods require the knowledge of either (1) the amount of solute adsorbed or (2) the amount of heat evolved to give a monolayer coverage of solute on to the powder surface.¹⁻⁵ Both the static calorimetric method and nitrogen gas adsorption method are tedious and need skilled operators and drastic conditions for degassing of powders. Recently, the flow microcalorimeter has proved itself to be a useful tool for the determination of the surface area of powdered solids. But this apparatus is expensive and the reliability of the flow microcalorimetric results has recently received criticism.⁶ On the other hand, the method based on adsorption from solution is simple and does not involve much instrumentation. In this work a method based on the adsorption from solution of stearic acid is studied.

Literature shows a large volume of work on the adsorption of stearic acid from solution on powdered solids.^{1-5,7-16} In the early work the area occupied by one molecule of stearic acid on the adsorbent surface was assumed to be $17\text{--}20\text{\AA}^2$. It is seen that the specific surface area of a powder calculated on the above assumption agrees with the BET nitrogen gas adsorption area only for some limited cases, for example, for solids like hydrated alumina⁷ and calcium phosphate.¹⁶ On the other hand, an examination of Medvedeva's¹³ findings show that the specific surface area of alumina powder determined by the method of adsorption of stearic acid from solution agrees with the BET nitrogen gas adsorption area if it is considered that the area occupied by one molecule of stearic acid is about $60\text{\AA}^2$. This result has been supported by the recent flow microcalorimetric studies that for alumina and ferric oxide powders the area occupied per molecule of stearic acid is in the range of $60\text{--}70\text{\AA}^2$. It is interesting to note that hydrated alumina and calcium phosphate powders are non-porous, and alumina and ferric oxide powders are porous. Therefore, a hypothesis may be put forward that the area occupied per molecule of stearic acid on non-porous powders is different from that on porous powders. To substantiate this hypothesis adsorption of stearic acid on a number of porous and non-porous powders is to be studied. The present study is, however, limited to the determination of the specific surface area of two porous powders, namely, alumina and ferric oxide.

2. Materials used

1. Ferric oxide, prepared in the laboratory, 99.5%; BET nitrogen gas adsorption area $9.2 \pm 0.6 \text{ m}^2/\text{g}$.
2. Extrapure Alumina, M. Woelm Eschwage, Germany; BET nitrogen gas adsorption area $120 \pm 5 \text{ m}^2/\text{g}$.
3. Benzene, BDH Chemicals Ltd, London, 99.9%.
4. Methanol, BDH Chemicals Ltd, London, 99.9%.
5. Stearic acid, BDH Chemicals Ltd, London, 99.9%.
6. Sodium methoxide, prepared and standardised in the laboratory.

3. Experimental procedure

Dried ferric oxide or alumina (1 or 5 g) was weighed accurately and was placed in a clean, dry 250 ml glass-stoppered flask. 100 ml of 0.05 molar stearic acid in benzene were added and the flask held in a constant temperature bath for 1 h with intermittent shaking; the solution was allowed to settle for 2 h. Unless otherwise stated 10 ml of the supernatant solution were pipetted carefully into a small beaker. The solution was then evaporated slowly at room temperature and the stearic acid remaining in the beaker was dissolved in 10 ml benzene-methanol mixture. The amount of stearic acid was estimated by potentiometric titration with standardised sodium methoxide solution. The amount of stearic acid adsorbed was found from the amount of stearic acid present before and after the adsorption. Similarly, experiments were carried out taking different concentration of the acid solution.

4. Results and discussions

For adsorption from a solution of a given concentration duplicate experiments were carried out and for each experiment the concentration of stearic acid after adsorption was determined by titrating three samples of supernatant liquid. For duplicate adsorption no noticeable difference in the concentration of stearic acid after adsorption was observed, although the titration of replicate samples for a given experiment showed variation of concentration in the order of $\pm 1\%$. Concentrations of stearic acid below 0.01 M could not be accurately determined and, therefore, for determining the concentration of stearic acid after adsorption for solution of lower concentrations 20 ml of supernatant liquid was withdrawn, evaporated and the residue was dissolved in 10 ml benzene methanol mixture and then titrated.^{19,20} Concentrations of stearic acid after adsorption quoted in Table 1

Table 1. Adsorption of stearic acid on alumina (at 30°C) and ferric oxide (at 35°C) powders

Concentration of stearic acid before adsorption (M)	Concentration of stearic acid after adsorption (M)	
	Alumina powder	Ferric Oxide powder
0.005	—	0.004
0.010	0.007 ^a	0.009
0.015	0.012 ^a	0.014
0.020	0.017 ^a	0.019
0.025	0.010	0.024
0.030	0.015	0.029
0.040	0.025	0.039
0.050	0.034	0.049
0.075	0.059	—
0.100	0.084	—

^a 1 g of powder was used as adsorbent. In all other experiments 5 g of powder were used as adsorbent.

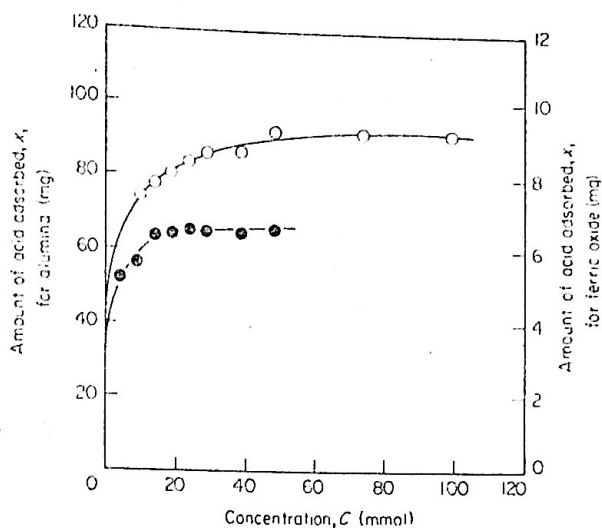


Figure 1. Relation between amount adsorbed, x , and concentration, C , of stearic acid. ●, Fe_2O_3 ; ○, Al_2O_3 .

are averages of the replicate measurements mentioned above. In Figure 1 the amounts of stearic acid, x , adsorbed are plotted against its initial concentration, C , in benzene solutions. It is seen from the figure that the amount of stearic acid adsorbed on alumina is very large in comparison with that on ferric oxide. A plot of C/x vs x shown in Figure 2 gives a straight line, thus showing Langmuir type of adsorption both on ferric oxide and alumina. However, the ferric oxide surface becomes saturated by very dilute solutions of stearic acid compared with that of alumina. From the slope and intercept of the straight line of Figure 2 the appropriate amount of stearic acid adsorbed at monolayer coverage may be obtained. This monolayer value may also be read from the value at the plateau of the curve in Figure 1.

The determination of surface area from the amount of stearic acid adsorbed requires the area occupied per molecule of the solute to be known. If stearic acid molecules lie perpendicular to the surface with carboxyl groups resting on the solid/liquid interface area occupied per molecule would be approximately $18\text{\AA}^2$ whereas, according to the Courtauld model of paraffin, area occupied per molecule of stearic acid would be approximately $100\text{\AA}^2$, if the molecules are to lie parallel to the

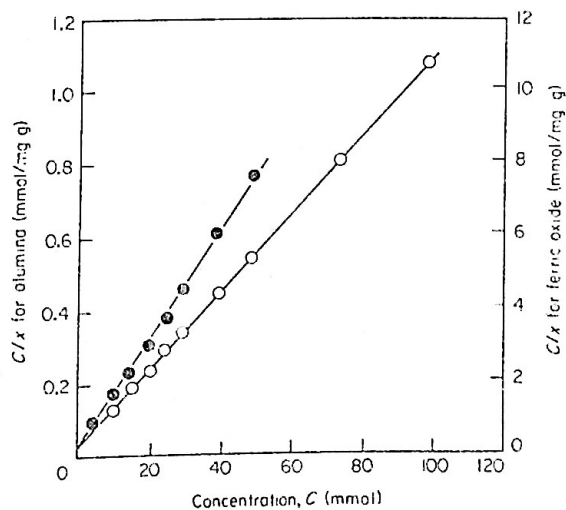


Figure 2. Langmuir plots. ●, Fe_2O_3 ; ○, Al_2O_3 .

surface with the whole chain resting on it. Considering the area occupied by one molecule of stearic acid to be $18\text{\AA}^2$, the surface area of ferric oxide and alumina powders are found to be 2.5 and $36.6\text{ m}^2/\text{g}$, respectively. Although the surface area of alumina powder obtained under similar consideration by Medvedeva agrees with the present result for alumina the values for both ferric oxide and alumina are far too low compared with the corresponding BET nitrogen gas adsorption surface area. If the total BET gas adsorption area is to cover, the area occupied per molecule of stearic acid in the present case comes out to be 60 and $67\text{\AA}^2$ respectively for alumina and ferric oxide powders. It is interesting to note that although the BET nitrogen gas adsorption area of alumina powder is about 12 times greater than that of ferric oxide powder, the powders are very similar in the sense that the area occupied per molecule of stearic acid on them is in the same range.

It may, therefore, be concluded that on both the surfaces of alumina and ferric oxide the position of stearic acid molecules is almost the same, and the molecules lie neither completely perpendicular nor completely parallel to the surface. It is believed that the polar head of stearic acid, that is the carboxyl group, rests on the powder surface but the precise position of the rest of the chain on the solid/liquid interface is not known. The following possible positions can be envisaged:

1. The stearic acid chain forms a strong attachment to the surface through the carboxyl group and all the adjacent methylene groups lie on the surface and the tail, containing about six carbon atoms, of the chain rests in the liquid phase.
2. Primary attachment is through the carboxyl group and methylene groups after every six carbon atoms attach themselves to the surface so that a spiral arrangement occurs.

The findings of Allen and Patel⁵ tend to support arrangement 2. Arrangement 1 is supported by the fact that the normal hydrocarbon chain lies flat on to the polar surface.²¹ In fact alumina and ferric oxide powders are polar in nature, and the stearic acid molecule consists of a long hydrocarbon chain.

References

1. Groszek, A. J. *Chem. Ind.* 1965, 2003.
2. Groszek, A. J. *Chem. Ind.* 1966, 1765.
3. Rahman, M. A. *Bangladesh Journ. Sci. & Ind. Res.* (in press).
4. Allen, T.; Patel, R. M. *Powder Technol.* 1968/69.
5. Allen, T.; Patel, R. M. *J. Colloid and Interface Science* 1971, 35, 647.
6. Parfitt, G. D., B. P. Symposium on the Significance of the heats of adsorption at solid/liquid interface. (Groszek, A. J. ed.), 1971.
7. Russel, A. S.; Cochran, C. N. *Ind. Eng. Chem.* 1950, 42, 1332.
8. Hirst, W.; Lancaster, J. K. *Research (London)* 1950, 3, 336.
9. Smith, H. A.; Hurley, R. B. *J. Phys. and Colloid Chem.* 1949, 53, 1409.
10. Suito, E.; Arakawa, M.; Arakawa, T. *J. Chem. Soc. Japan, Pure Chem. Sect.* 1954, 75, 596.
11. Loomis, A. G. *Procedures monthly* 1954, 18, No. 11, 19.
12. Tamaki, K., *Nippon, Kagaku Zasshi* 1957, 78, 1151.
13. Medvedeva, A. P. *Ogneupory* 1960, 25, 184.
14. Kordecki, M. C.; Gandy, M. B. *Intern. J. appl. Radiation and Isotopes* 1961, 12, 27.
15. Jankovic, L. R. *Proc. Pa. Acad. Sci.* 1966, 30(2), 323.
16. Korenev, A. D.; Lunina, M. A. *Zh. Fiz. Khim. (Russ)* 1969, 43(6), 1605.
17. Groszek, A. J., SCI Monograph No. 28.
18. Allen, T.; Patel, R. M. A Paper presented to the Particle Size Analysis Conference, held at Bradford, 1970.
19. A. K. Ghosh, M.Sc. Thesis. Rajshahi University, 1976.
20. Rahman, M. A.; Ghosh, A. K. *Bangladesh Pharmaceutical Journal* 1977, 6 (1), 12.
21. Groszek, A. J. *Proc. Roy. Soc.* 1970, A314-498.

Surface area of cupric oxide and magnesium oxide by adsorption of stearic acid and pyridine*.

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Abstract

Specific surface area of CuO and MgO powders are determined using adsorption of stearic acid and pyridine from solution. In agreement to the earlier works involving Fe_2O_3 , Al_2O_3 and silica gel it has been found that surface area of CuO and MgO powders obtained assuming area occupied per molecule of stearic acid to be $65 \text{ \AA}^2$ closely agrees respectively with that obtained assuming area occupied per molecule of pyridine to be $24.7 \text{ \AA}^2$, the molecular area. In view of these results it is concluded that stearic acid and pyridine may be used as standard solutes for the determination of surface area of powdered solids.

1. Introduction

The specific surface area of cupric oxide and magnesium oxide have been determined by gas adsorption (1-5), x-ray diffraction (1), and the adsorption of fatty acids from solution (6).

* Paper has been accepted for publication in the APPLICATIONS OF SURFACE SCIENCE (U.S.A). The acceptance letter is enclosed at the end of this paper.

The method based on adsorption of fatty acids from solution is simple but to evaluate surface area by this method the area occupied per molecule of acid is required to be known. This may customarily be determined by equating BET nitrogen gas adsorption area to the total area occupied by the solute molecules at equilibrium adsorption to form monolayer coverage. In earlier communications (7,8) it has been reported that the specific surface area of ferric oxide, alumina and silica gel powders determined by adsorption of stearic acid from benzene solution corresponds respectively to the BET nitrogen gas adsorption area if area occupied by one molecule of stearic acid is considered to be of the order of $60-70 \text{ \AA}^2$. Whereas specific surface area of the same powders determined by adsorption of pyridine from n-heptane solution (9) corresponds respectively to the BET nitrogen gas adsorption area if it is assumed that the area occupied per molecule of pyridine to be of the order of 23.0 to $24.6 \text{ \AA}^2$. In the present work specific surface area of cupric oxide and magnesium oxide has been determined using adsorption of stearic acid from benzene solution and pyridine from n-heptane solution with a view to examine the possibility that these two solutes could be used as standards for determining specific surface area of powdered solids.

2. Experimental

Methods of adsorption of stearic acid and pyridine from solution were described elsewhere (7,9). Oxide powders were extra-pure. Benzene (99%) was kept in contact of sodium wire for at least 24h. n-Heptane (99%) was further purified by percolating through a mixed column of silica gel and alumina, kept in contact of molecular sieve for 3 days and then distilled in contact of sodium wire; fraction boiling between 98-98.5°C was collected and the stock kept in contact of sodium wire.

3. Results and Discussions

Adsorption of stearic acid and pyridine respectively from solution in benzene and n-heptane on cupric oxide and magnesium oxide were carried out at 30°C. The adsorption isotherms shown in Figure-1 are composite isotherms, but at the low range of concentrations studied they approximate very closely to the individual isotherms (10,11). From each isotherm it is possible to obtain a limiting value of adsorption from plateau. Straight line relationship between C/x and C shown in Figure-2 indicates that Langmuir type of adsorption takes place on both the powders. The appropriate amount of stearic acid and pyridine adsorbed at monolayer coverage has been obtained from the slope and intercept of each of these curves using Langmuir equation (12,13); these values are found to be

2.4×10^{-5} and 23.6×10^{-5} mol of stearic acid per gram for cupric oxide and magnesium oxide respectively and the corresponding values are 0.63×10^{-4} and 6.03×10^{-4} mol of pyridine. considering that one molecule of stearic acid occupies $65 \text{ \AA}^2$ (7,8) the surface area of CuO and MgO have been evaluated to be 9.4 and $92.4 \text{ m}^2/\text{g}$ respectively.

The same powders give surface area of 9.4 and $89.7 \text{ m}^2/\text{g}$ for CuO and MgO respectively, assuming area occupied by one molecule of pyridine to be $24.7 \text{ \AA}^2$, the molecular area. In confirmation of the earlier works (7-9) involving Fe_2O_3 , Al_2O_3 and silica gel close agreement of surface area of CuO and MgO obtained by using stearic acid and that using pyridine is observed.

It is, therefore, concluded that for a wide range of adsorbents stearic acid and pyridine may be used as standard solutes for determination of surface area of powdered solids.

References

- (1). A.C.Zettlemoyer and W.C.Walker, J.Phys.Colloid Chem., 31 (1947) 763.
- (2). Ibid., Ind.Eng.Chem., 39 (1947) 69.
- (3). W.Wendt, Fette-Seifen-Anstrichmittel, 57 (1955) 910.
- (4). T.Oyama and J.Shimoizaka, J.Mining Inst.Japan, 69 (1953)

- (5). G.Kraus, J.W.Ross and L.A.Girifalco, J.Phys.Chem., 57 (1953) 330.
- (6). G.D.Modica and S.Tira, Ann.Chim.(Rome), 46 (1956) 21.
- (7). M.A.Rahman and A.K.Ghosh, J.appl.Chem.Biotechnol., 27 (1977) 529.
- (8). Ibid., J.Chem.Technol.Biotechnol., submitted for publication.
- (9). Ibid., J.Colloid Interface Sc., submitted for publication.
- (10). J.J.Kipling and E.H.M.Wright, J.Chem.Soc., (1962) 855.
- (11). Ibid., (1964) 3535.
- (12). A.K.Ghosh, M.Sc Thesis, Rajshahi University, 1976.
- (13). T.Allen and R.M.Patel, J.appl.Chem., 20 (1970) 165.

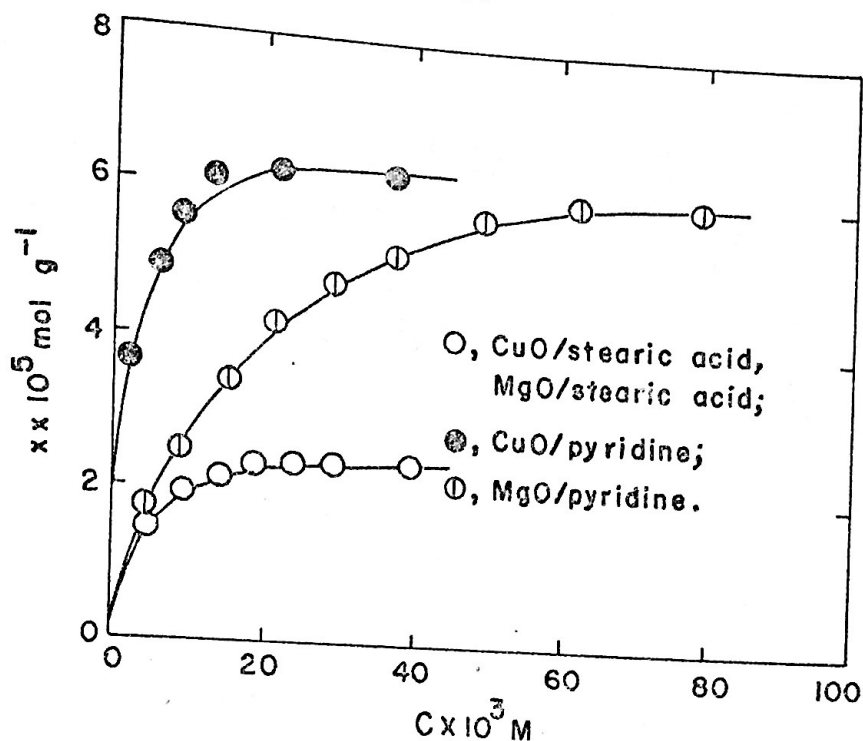


Figure-1. Relation between amount adsorbed (x) and concentration of solute solution (C). (for MgO ordinate should be multiplied by 10).

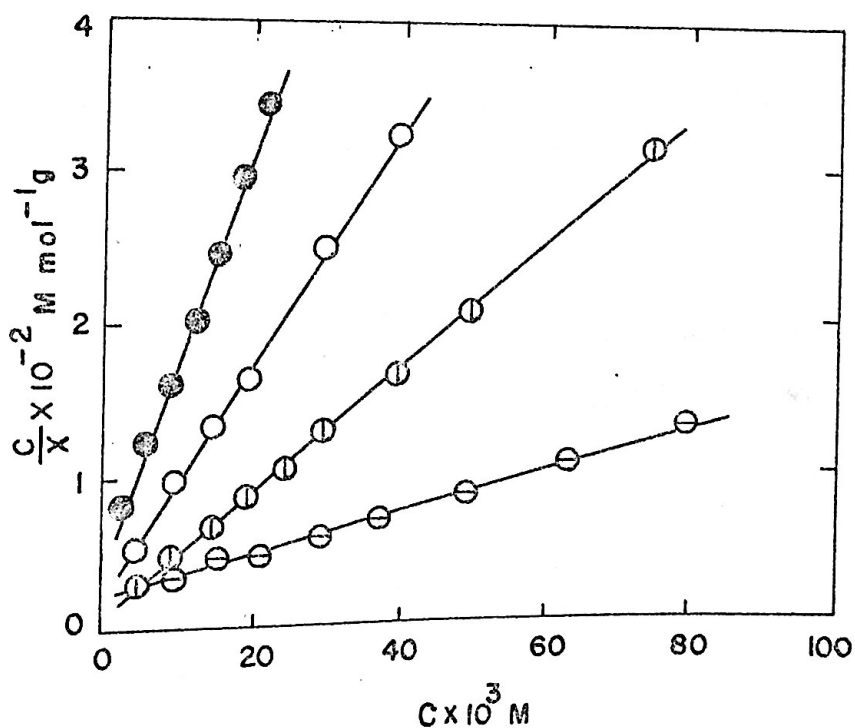


Figure-2. Langmuir plots.
 $\bigcirc$ CuO/Stearic acid (ordinate should be multiplied by 5),
 $\bigodot$ MgO/Stearic acid, $\bullet$ CuO/Pyridine, $\oplus$ MgO/Pyridine.

APPLICATIONS OF SURFACE SCIENCE

*A Journal Devoted to the Technological Implications
of the Microscopic Force Laws that Govern the
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September 25, 1979

Dr. M. A. Rahman
Department of Applied Chemistry
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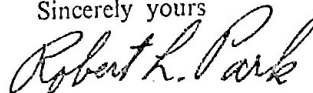
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on: Surface Area of Cupric Oxide and Magnesium Oxide
by Adsorption of Stearic Acid and Pyridine

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Determination of Specific Surface Area of Ferric Oxide, Alumina and Silica Gel Powders using Adsorption of Pyridine from n-Heptane Solutions*.

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Abstract

Adsorption of pyridine from n-heptane solution on ferric oxide, alumina and silica gel powders has been studied. The Langmuir type of adsorption was followed although some departure noticeable especially in the case of alumina. However, specific surface area of ferric oxide, alumina and silica gel powders evaluated on the assumption of a close-packed monolayer gave values within 6.6% of the respective BET nitrogen gas adsorption surface area.

I. Introduction

In the determining specific surface area of powdered solids using the method of adsorption of solute from solution the area occupied per molecule of solute on the solid surface must be known. Although adsorption from n-hexane, cyclohexane and benzene solutions of n-fatty acids and organic bases - speci-

* Paper has been accepted for publication in the Journal of Colloid and Interface Science (U.S.A.).

ally stearic acid and pyridine - on oxide adsorbents has been extensively studied, relatively little is known about the orientation of the solute molecules on the adsorbed layers and the area occupied per molecule of the solute can not be predicted. In the earlier publications (1,2) it has been reported that the BET nitrogen gas adsorption surface area of porous powders - ferric oxide, alumina and silica gel - agreed well with the respective specific surface area if the area occupied per molecule of stearic acid was considered to be $60-70 \text{ \AA}^2$. This finding has been interesting in view of the fact that the BET nitrogen gas adsorption surface area of alumina powder was 13 times and that of silica gel was 40 times greater than that of ferric oxide powder, and there has been evidence that the mechanism of adsorption of stearic acid on alumina and silica gel differs (3). The object of the present work was to examine the validity of the method of determination of specific surface area by adsorption of pyridine from solution.

II. Experimental

Material. Ferric oxide, prepared in the laboratory, 99%, BET nitrogen gas adsorption surface area $9.2 \pm 0.6 \text{ m}^2/\text{g}$. Aluminium oxide Woelm neutral, activity grade I, (M. Woelm Eschwage, Germany), BET nitrogen gas adsorption surface area

$120 \pm 5 \text{ m}^2/\text{g}$. Silica gel, BDH laboratory reagent, BET nitrogen gas adsorption surface area $370 \pm 3 \text{ m}^2/\text{g}$. n-Heptane, BDH laboratory reagent, 99.5 % (GLC), further purified by percolating through a mixed silica gel and alumina column and distilled to collect the fraction boiling between $98-98.5^\circ\text{C}$. Pyridine AnalAR, BDH Chemicals Ltd., 99.5 %.

Adsorption experiment. Ferric oxide, alumina and silica gel were dried at 110°C and 5 g each was placed in a 1 litre glass-stoppered flask. 500 ml solution of pyridine in n-heptane was added and the flask was held in a water bath at 30°C for 48 hours with intermittent shaking; the solution was then allowed to settle for 2 hours.

Analysis of the solution. The supernatant solution from the adsorption flask was pipetted into a flask, diluted with n-heptane and the concentration of the pyridine was measured spectrophotometrically at 251 m μ using a Double Beam Beckman Spectrophotometer.

III. Results and Discussions

For adsorption from solution of a given concentration duplicate experiments were carried out, and for each experiment, concentrations of pyridine both before and after adsorption were determined. In duplicate adsorptions the differences in

the concentration of pyridine after adsorption were observed to be in the range of $\pm 1\%$. In Figure-1 the amounts (x) of pyridine adsorbed are plotted against the initial concentrations (C). It is seen from Table-I and Figure-1 that silica gel adsorbs the most pyridine. Plots of C/x vs C shown in Figure-2 give straight lines, showing the Langmuir type of adsorption in general, although the results for alumina tend to depart from the Langmuir adsorption indicated by the dashed line for alumina in Figure-2. From the slopes and intercepts of the straight lines in Figure-2 the appropriate amounts of pyridine adsorbed at the monolayer coverage were determined; these could also be read from the values at the plateau of the curves in Figure-1.

Assuming a close-packed monolayer to cover the whole of the BET nitrogen gas adsorption surface area the area occupied per molecule of pyridine was found to be 23.7, 23.0 and 24.6 $\text{\AA}^2$ respectively for ferric oxide, alumina and silica gel surfaces. From the data of Pauling and Schomaker (4), Kipling and Peakall (5) found the molecular area of pyridine to be 24.7 $\text{\AA}^2$; the latter authors used this value to determine the maximum amount of chemisorption possible on boehmite. Formation of a monolayer is thus clearly shown, although some bilayer formation may have occurred on alumina when a large excess of pyridine was present. This finding agrees with the

previous results for silica gel (6-9) and alumina (10,11).

The fact that the area occupied per molecule of pyridine on ferric oxide, alumina and silica gel is of the same order suggests the orientation of pyridine molecules in all the cases studied to be the same; so that adsorption of pyridine molecules takes place through nitrogen atom probably via perpendicular approach of the molecules. This mechanism has also been envisaged by Miller (12) during his study of wear in steel-on-steel system using pyridine as an anti-wear agent.

Our results show that the specific surface area of ferric oxide, alumina and silica gel powders evaluated on the assumption of close-packed monolayers so that an area of $24.7 \text{ \AA}^2$ occupied per molecule of pyridine, gives an estimate of specific surface area not more than 6.6% greater than determined by the BET nitrogen gas adsorption method. However in the case of dehydroxylated oxide surfaces, such as on pyrogenic silica or powders that have been heated, e.g., to 1000°C , this method may not be suitable since there are insufficient hydroxyl groups on the surface to hold a monolayer of pyridine molecules.

Acknowledgement

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References

1. Rahman, M.A., and Ghosh, A.K., J.appl.Chem.Biotechnol., 27, 529, (1977).
2. Rahman, M.A., and Ghosh, A.K., J.Chem.Tech.Biotechnol., submitted for publication.
3. Hasegawa, M., and Low, M.J.D., J.Colloid Interface Sci., 30, 378, (1969).
4. Pauling, L., and Schomaker, V., J.Am.Chem.Soc., 61, 1769, (1939).
5. Kipling, J.J., and Peakall, D.B., J.Chem.Soc., (1958), 184.
6. Waksmundzki, A., Oscik, J., Rozlyo, J., and Nasuto, R., Przem.Chem., 46, 287, (1967).
7. Bertoluzza, A., Fabbri, G., and Farne, G., Atti.Acad.Nazl. Lincei Rend, Classe Sci.Fis., Mat.Nat., 37, 424, (1964).
8. Bonino, G.B., Lorenzelli, V., Randi, G., and Gesmundo, F., Ann.Chim., 54, 1187, (1964).
9. Lorenzelli, V., and Gesmundo, F., Ann.Chim., 56, 628, (1965).
10. Bandiera, J., and Naccache, C., Bull.Soc.Fr., (1969), 2637.
11. Bandiera, J., and Stanislas, T.J., Ibid., (1973), 841.
12. Miller, A., J.Inst.Petr., 59, 27, (1973).

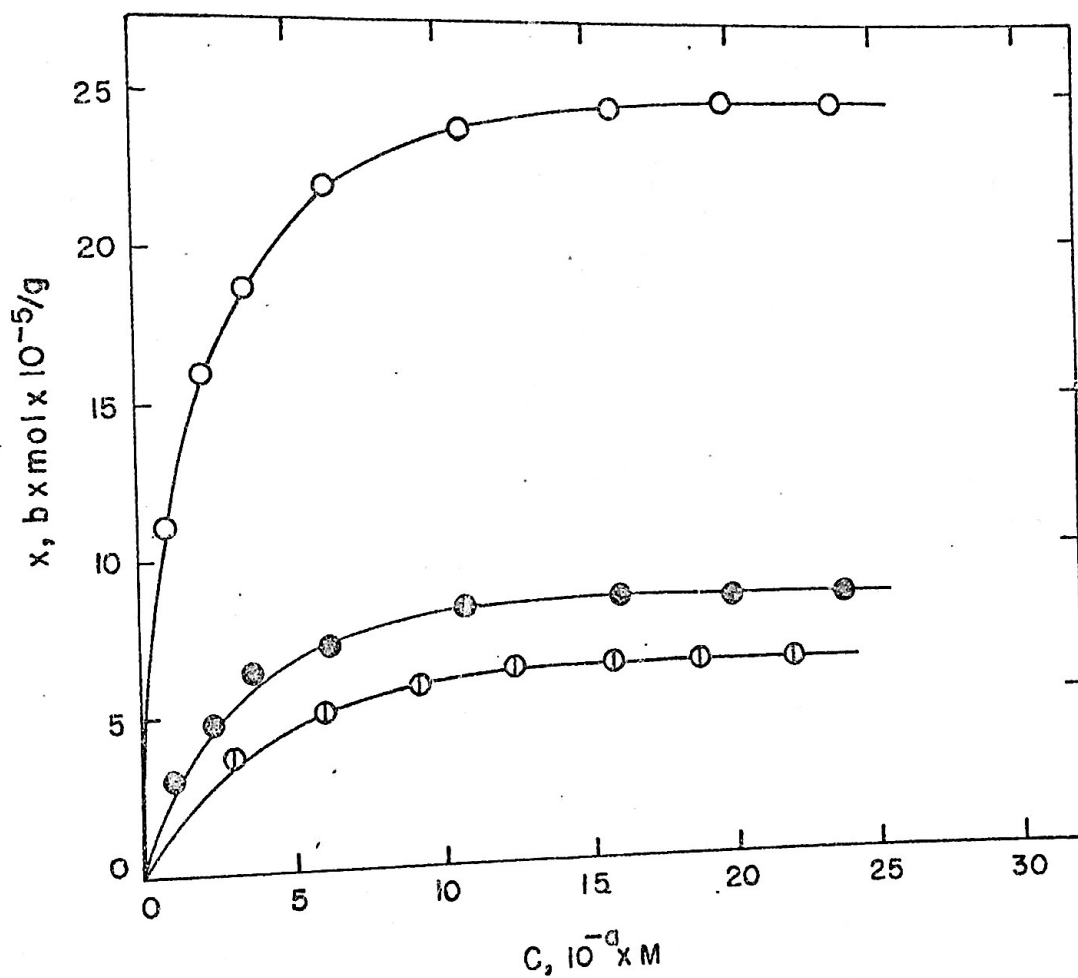


Figure-1. Variation of the amount of pyridine adsorbed (x) on powders with concentration of pyridine solution (C).
 $\odot$ Fe₂O₃ ($a = 3, b = 1$), $\bullet$ Al₂O₃ ($a = 2, b = 10$),
 $\circ$ Silica gel ($a = 2, b = 10$).

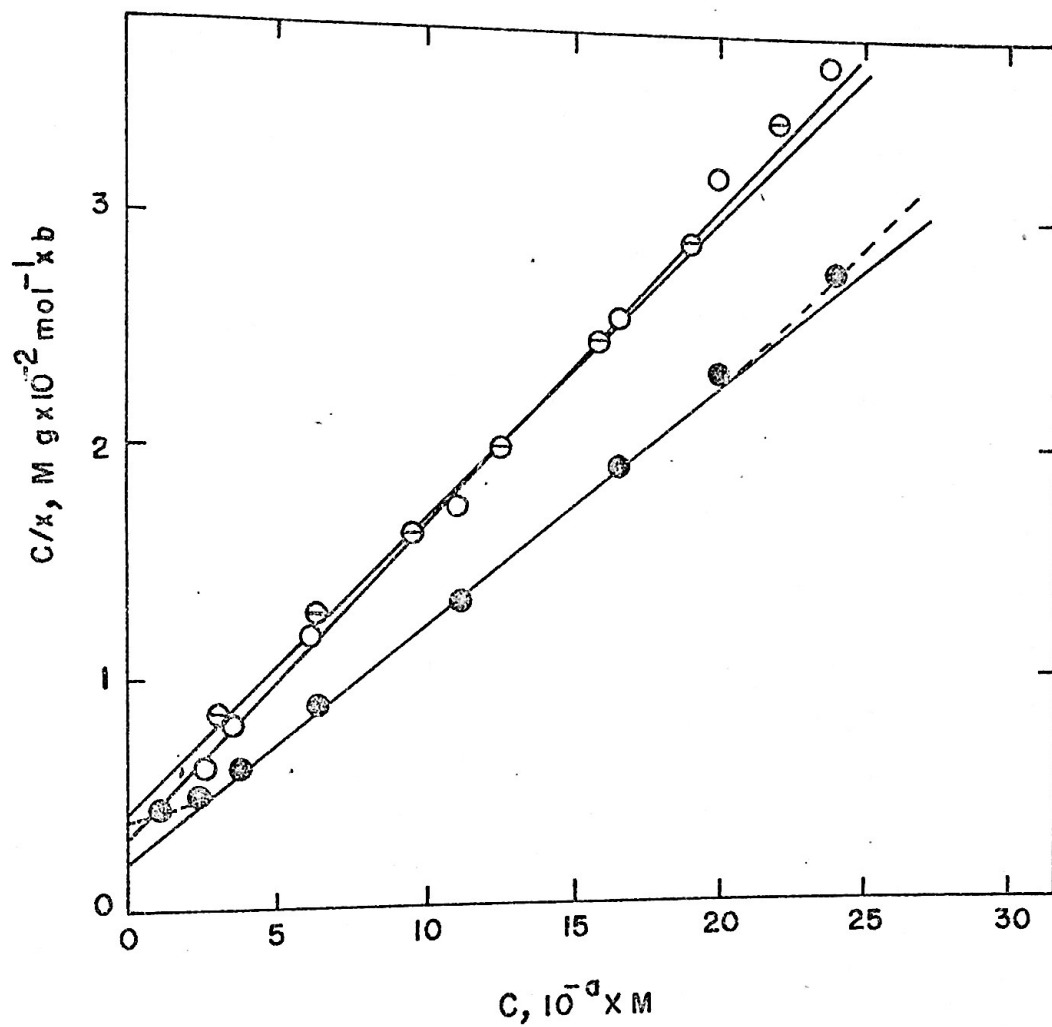


Figure-2. Langmuir plots.
 $\ominus \text{Fe}_2\text{O}_3$ ($a = 3$, $b = 1$), $\bullet \text{Al}_2\text{O}_3$ ($a = 2$, $b = 1$),
 $\circ$ Silica gel ($a = 2$, $b = 0.25$).

Table-I. Adsorption of Pyridine on Fe_2O_3 , Al_2O_3 and Silica gel Powders.

Conc of Pyridine soln, $\text{MX}10^{-2}$				Amt.of Pyridine adsorbed (x)		
Before	After adsorption			mol $\text{X}10^{-4}/\text{g}$		
adsorp- tion(C)	Fe_2O_3	Al_2O_3	Silica gel	Fe_2O_3	Al_2O_3	Silica gel
0.312	0.274	-	-	0.38	-	-
0.632	0.582	-	-	0.50	-	-
0.948	0.890	-	-	0.58	-	-
1.264	1.201	0.963	0.139	0.63	3.01	11.25
1.580	1.516	-	-	0.64	-	-
1.896	1.831	-	-	0.65	-	-
2.212	2.148	-	-	0.64	-	-
2.556	-	2.063	0.901	-	4.93	16.55
3.835	-	3.201	1.960	-	6.34	18.75
6.382	-	5.661	4.181	-	7.21	22.01
11.066	-	10.232	8.669	-	8.34	23.97
16.434	-	15.574	13.979	-	8.60	24.55
20.042	-	19.182	17.564	-	8.60	24.78
24.025	-	23.165	21.547	-	8.60	24.78

Adsorbent 5 g, Solution 500 ml.

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Alumina and Silica Gel Powders using Adsorption of Pyridine from n-Heptane Solution

Authors M. A. Rahman and A. K. Ghosh

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Determination of Specific Surface Area of Silica gel Powder*.

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Abstract

The specific surface area of silica gel powder is determined using adsorption of stearic acid from benzene solution. It has been found that the value of specific surface area agrees with the BET nitrogen gas adsorption surface area if area occupied per molecule of stearic acid is considered to be $67\text{\AA}^2$.

Introduction

Recent infra-red and thermogravimetric studies^{1,2} reveal that the model of adsorbed layer of stearic acid on alumina and silica powders differs from that of Kipling and Wright who assumed long chain fatty acids to be physically adsorbed on the surfaces as dimers parallel to the plane of the surfaces^{3,4}. Although it has been evidenced that on both these powders the adsorption layer consisted predominantly of monomers at low degrees of coverage, and weak and reversible dimers forming at high concentration of solution orientation of the adsorbed molecules could not be ascertained by the infra-red

*Paper has been submitted for publication in the Journal of Chemical Technology and Biotechnology (London).

studies. It is, therefore, required that the method of determination of surface area of powdered solids using long chain fatty acids be tested experimentally.

Examinations of published experimental results have shown that the BET nitrogen gas adsorption surface area of powdered solids agree with those determined by the method of adsorption of stearic acid from benzene solution if area occupied by one molecule of stearic acid is considered to be $17-20 \text{ \AA}^2$ on non-porous solids and $60-70 \text{ \AA}^2$ on porous solids⁵. In the present work surface area of a chromatographic grade silica gel has been determined by adsorption of stearic acid from benzene solution and compared with that determined by BET nitrogen gas adsorption method.

Experimental

The purity of solvent and adsorbate, experimental procedure and method of estimation of stearic acid were same as reported earlier^{5,6}. The chromatographic grade silica gel (BDH Chemicals Ltd.) having BET nitrogen gas adsorption surface area of $370 \pm 3 \text{ m}^2/\text{g}$ was used as adsorbent. The adsorption experiments were carried out using 5 g of silica gel in 500 ml solution.

Results and Discussions

The data in Table-I and Figure-1 show that the isotherm exhibits limiting adsorption at an equilibrium solution concen-

tration of $24.0 \times 10^{-2} M$ and above to give adsorption of 9.1×10^{-4} mol g^{-1} of stearic acid per gram of silica gel. These values are much too high compared with the corresponding values for ferric oxide and alumina powders reported earlier⁵. A plot of C/x vs C shown in Figure-2 yields a straight line, thus showing Langmuir type of adsorption. In contrast to the results obtained for characterized silica⁷ limiting adsorption in the present case appears to give a close-packed monolayer so that the area occupied by one molecule of stearic acid is $67 \text{ \AA}^2$ if the total BET nitrogen gas adsorption surface area is to cover. This value compares well with those for ferric oxide and alumina powders⁵. It is interesting to note that in spite of the wide difference of the BET nitrogen gas adsorption surface area of ferric oxide, alumina and silica gel powders area occupied by one molecule of stearic acid on them is of the same order. This finding shows that stearic acid molecules lie neither completely perpendicular nor completely parallel to the surface of silica gel.

References

1. Hasegawa, M.; Low, M.J.D., J. Colloid Interface Sc., 1969, 30(3), 378.
2. Tyler, A.J.; Hambleton, F.H.; Hockey, J.A., Catalysis, 1969, 13, 35.

3. Kipling, J.J.; Wright, E.H.M., J.Chem.Soc., 1964, 3535.
4. Kipling, J.J., 'Adsorption from Solution of Non-electrolytes', Academic Press, London, 1965, pp-106.
5. Rahman, M.A.; Ghosh, A.K., J.appl.Chem.Biotechnol., 1977, 27, 529.
6. Rahman, M.A.; Ghosh, A.K., Bang.Pharm.J., 1977, 6, 12.
7. Armistead, C.G.; Tyler, A.J.; Hockey, J.A., Trans.Faraday Soc., 1971, 67(578 pt-2), 493.

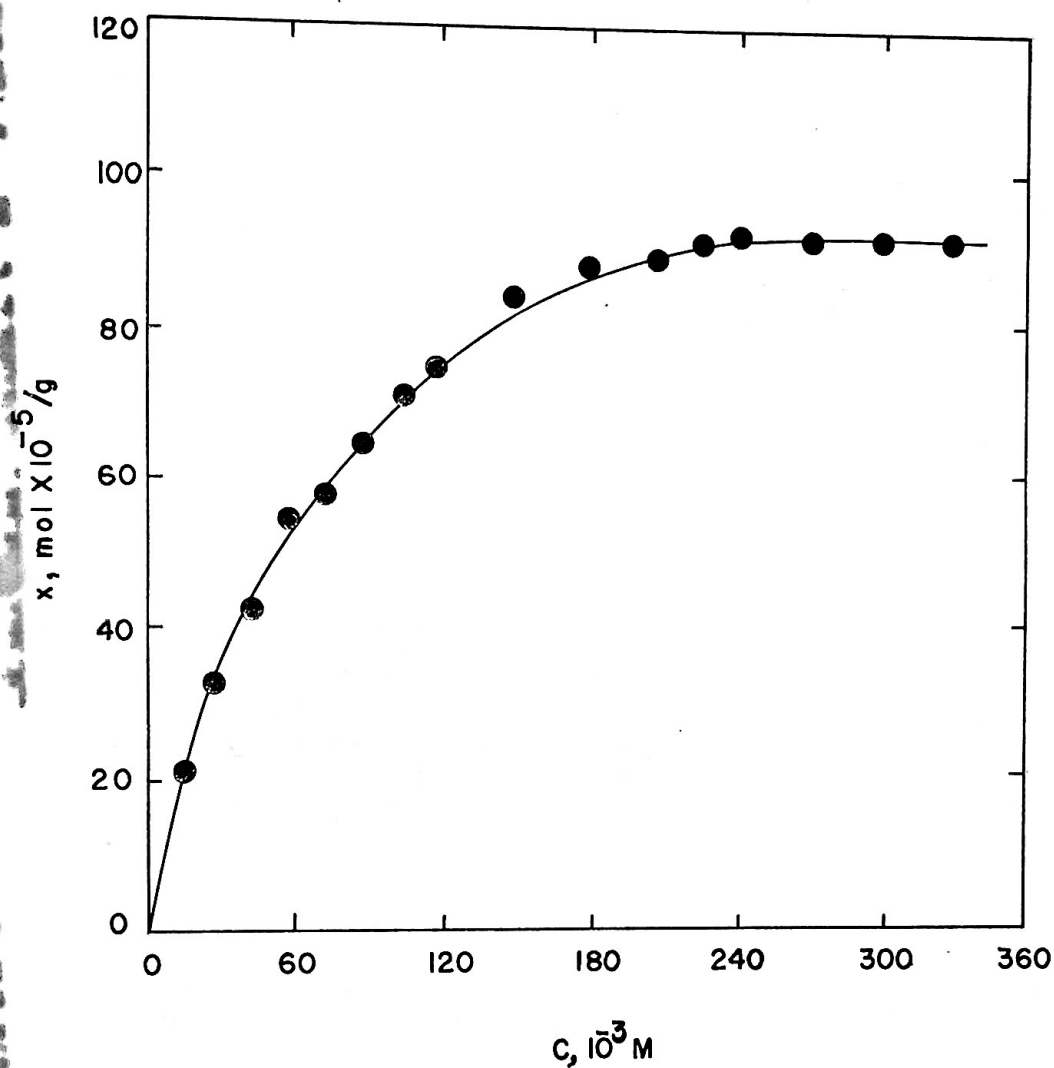


Fig.1. Relation between amount adsorbed (x) and concentration (C) of stearic acid solution on silica gel.

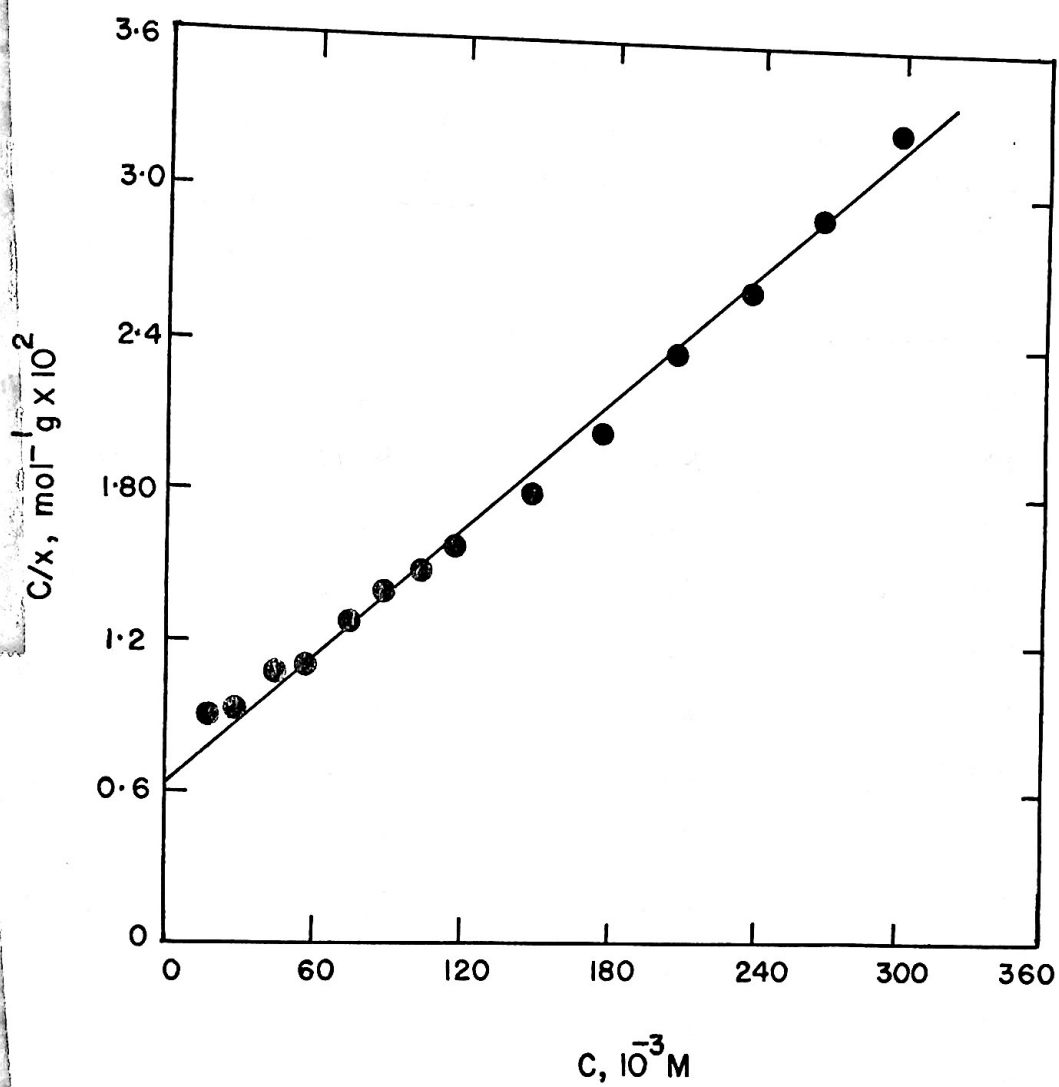


Fig.2. Langmuir plots.

Table-I. Adsorption of Stearic Acid on Silica gel at 30°C.

500 ml solution, 5 g silica gel.

Concentration of stearic acid solution ($\text{M} \times 10^{-3}$)		Amount of stearic acid adsorbed, x $\text{mol g}^{-1} \times 10^{-4}$	C/x $\text{M mol}^{-1} \text{g}$
Before adso- rption, C	After adso- rption		
18.5	16.5	2.0	92
30.0	26.8	3.2	94
45.0	40.8	4.2	107
60.0	54.6	5.4	111
75.0	69.2	5.8	129
90.0	83.6	6.4	141
105.0	97.9	7.1	148
120.0	112.5	7.5	160
150.0	141.6	8.4	179
180.0	171.2	8.8	204
210.0	201.1	8.9	236
240.0	230.9	9.1	264
270.0	260.8	9.2	294
300.0	290.9	9.1	330
330.0	320.9	9.1	363

Comparison of BET gas adsorption, Flow micro-calorimetric and Adsorption from solution methods of Determination of Surface Area of Powdered Solids*.

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Abstract

Using CuO , Fe_2O_3 and Al_2O_3 powders as adsorbents BET gas adsorption, flow micro-calorimetric and adsorption from solution measurements have been carried out. It has been found that adsorption of nitrogen gas on all the adsorbents is physical in nature but stearic acid employed in the flow micro-calorimetric and adsorption from solution methods gives mostly chemisorption of the molecules on the adsorbent powders. Surface areas determined by the flow micro-calorimetric and adsorption from solutions have been found to be identical for the respective powders. Despite the difference in mechanism of adsorption of N_2 and stearic acid molecules the flow micro-calorimetric and adsorption from solution surface areas agree fairly well with the BET nitrogen gas adsorption surface areas of the adsorbents if it is assumed that the area occupied per molecule of stearic acid to be of the order of $60-70 \text{ \AA}^2$.

* Paper has been submitted for publication in the Powder Technology (Bradford, U.K.).

Introduction

The determination of surface area of powdered solids is of scientific and technological importance. Consequently much interest has been shown in this field to give a wide range of methods of which BET gas adsorption method, static calorimetric method, flow micro-calorimetric method and method of adsorption from solution are the most common. Both BET gas adsorption and static calorimetric methods are well established but tedious and they need drastic conditions of degassing of the powders. Flow micro-calorimetric heat of adsorption has been compared with the heat of immersion measured by static calorimeters (1-3). Compared with the static calorimetric method the flow micro-calorimetric method is rapid and the latter has the added advantage that the amount of solute adsorbed may be determined (3,4). But flow micro-calorimetry needs skilled operators. The method based on adsorption of solute from solution (5) is simple and does not require much instrumentations.

The aim of the present work has been to compare results of BET gas adsorption, flow micro-calorimetric and adsorption from solution methods with a view to examine the validity of the method of adsorption from solution as a standard. Whereas nitrogen gas has been chosen for the BET method

stearic acid, a commonly employed solute, has been used for the flow micro-calorimetric and adsorption from solution measurements.

Experimental

Materials. Spectroscopic grade of CuO , Fe_2O_3 and Al_2O_3 powders were used as adsorbents. Compressed nitrogen gas, liquid nitrogen and benzene were of analytical grade. Benzene was dried by keeping sodium wires immersed in it. Stearic acid was 99.9 percent pure.

Procedures.

(a) Determination of BET nitrogen gas adsorption surface area. The sample tube containing a known weight, w , of adsorbent was fitted to the BET apparatus. The sample was then degassed slowly by using first a rotary pump and finally a water jacketed mercury diffusion pump to give vacuum of 10^{-5} mm Hg. The sample tube was then covered by a thermostatically controlled heater. Power input into the heater was adjusted by a 'Variac' set at a predetermined point. Degassing was continued for 3-4 hours at the preset temperature. After the degassing was over the sample tube was slowly cooled first by switching off the heater, then as the temperature fell down to about 150°C the heater was removed and the sample was allowed to air cool. Volume, V_w , of N_2 gas adsorbed at liquid

N_2 temperature, $-196^{\circ}C$, was then determined at an equilibrium pressure, P , so that P/P_0 lies between 0.3 and 0.35 where P_0 is the vapour pressure of the gas at that temperature, value of P_0 being 76 cm Hg at $-196^{\circ}C$. The limiting value of the volume in c.c of N_2 gas adsorbed per gram of adsorbent, V_m , was determined by the 'one point' method using the expression,

$$V_m = V(1-P/P_0) \quad (1)$$

where V is the volume of nitrogen gas adsorbed per gram of adsorbent, being equal to V_w/w .

BET surface area of the adsorbent was obtained from the expression,

$$S_w = NA_m w V_m / V_0 \quad (2)$$

where N = Avogadro's number, A_m = area occupied by one molecule of N_2 and $V_0 = 22400$ c.c, molar volume of gas at NTP.

Specific surface area of the adsorbent was given by

$$S = \frac{S_w}{w} \quad (3)$$

(b) Determination of flow micro-calorimetric surface area.

A flow micro-calorimeter (Mark II, Microscal Ltd., London) has been used for determination of heat of adsorption and amount of solute adsorbed. The apparatus has been illustrated elsewhere (4,6).

The integral heats of adsorption at different concentrations of solute were determined by the saturation method as follows. The solvent, benzene, was percolated through the bed of the adsorbent in the calorimeter cell and sufficient time was allowed to obtain a steady base-line in the recorder chart. The whole of the solvent stream was then replaced by a stream of equal flow-rate of a solution of stearic acid in benzene. The solution stream was allowed to run until the concentration of the solute on the powder bed came into equilibrium with that in the solution. This resulted in the evolution of heat and produced a peak in the recorder chart. By replacing the stream step-wise with solutions of increasing concentrations it was possible to saturate the adsorbent. The cumulative heat in this process is known as integral heat of adsorption. The heat of adsorption at monolayer, q_0 , was obtained from the Langmuir plots of integral heats. The specific surface area of the adsorbent may be given by the expression,

$$S = Kq_0 \quad (4)$$

where q_0 = heat of adsorption per gram of adsorbent at monolayer coverage, and K = proportionality constant. The value of K for different adsorbent was determined by equating the flow calorimetric specific surface area to the BET nitrogen gas adsorption specific surface area.

The amounts of stearic acid adsorbed by different adsorbents in flow micro-calorimetric measurements were determined by the pre-column method as follows. The adsorbent was placed in a pre-column, a glass tube having the same internal diameter as the 'Teflon' cell in the calorimeter. The solvent, benzene, was then percolated through the powder bed in the pre-column before it was referred to adsorbent in the calorimeter. After a steady base-line was obtained in the recorder chart the solvent stream was replaced by a stream of solution of same flow-rate. The amount of solute adsorbed by the powder bed in the pre-column was computed using the equation,

$$x = tCf/w \quad (5)$$

where x = amount of solute adsorbed in milligram per gram of adsorbent, t = retention time of solute in minute, C = concentration of solute in milligram per millilitre, f = flow-rate of solution in millilitre per minute, and w = weight of adsorbent in the precolumn in gram (7).

Experiments were repeated by using solutions of different concentrations and the monolayer value of the amount of solute adsorbed, x_m , by a given adsorbent was determined from the Langmuir plots. Specific surface areas of adsorbents were obtained from the expression,

$$S = \frac{NA_m x_m}{M} \quad (6)$$

where N = Avogadro's number, A_m = area occupied per molecule of stearic acid, and M = molecular weight of stearic acid.

(c) Method of adsorption from solution.

Dried adsorbent powder (1 or 5 g) was weighed accurately and was placed in a clean, dry 250 ml glass-stoppered flask. 100 ml of 0.05 molar stearic acid in benzene were added and the flask was held in a constant temperature bath for 1 hour with intermittent shaking; the solution was allowed to settle for 2 hours. 10 ml of the supernatant solution were pipetted carefully into a small beaker. The solution was then evaporated slowly at room temperature and the stearic acid remaining in the beaker was dissolved in 10 ml benzene-methanol mixture. The amount of stearic acid was estimated by potentiometric titration with standardised sodium methoxide solution. The amount of stearic acid adsorbed was found from the amount of stearic acid present before and after the adsorption. Similar experiments were carried out taking solutions of different concentrations. The values of x_m were obtained from the Langmuir plots and specific surface areas of the adsorbents were obtained from equation (6).

Results and Discussions

Nitrogen gas adsorption measurements have been carried out using a BET apparatus. These results are summarized in Table-1. It is seen from Table-1 that the limiting volume, V_m , of nitrogen gas adsorbed per gram of adsorbent are close to one another for CuO and Fe_2O_3 powders but this value is about 13 times greater in the case of alumina powder. For all the adsorbents repeated evacuation and adsorption of nitrogen gas on a sample gave the value of V_m within the range of experimental error. This reversibility of adsorption of nitrogen gas on the adsorbents indicates that the process of adsorption is physical in nature. To compute specific surface area the commonly used values of area per molecule of nitrogen are 16.2 and $16.8 \text{ \AA}^2$, the molecular area of nitrogen based on solid and liquid nitrogen densities. Values as high as $20.2 \text{ \AA}^2$ have been used for adsorption on Sterling MTG powder (8).

Both integral heat of adsorption, q , and amount adsorbed, x , of stearic acid on the adsorbents have been measured by the flow calorimetric method. These results are given in Table-2. Figure-1 shows the isotherm obtained by plotting q vs C . Straight line relationships of the plots of C/q vs C shown in Figure-2 indicates that the adsorption is

of Langmuir type in all the cases. It is possible to measure heat of desorption by the flow micro-calorimeter by exchanging the flow of a solution with a solvent. After the adsorbent surfaces have been saturated the flow of solutions were replaced by solvent; these produced peaks in the recorder chart indicating negative heat effects. The desorption heats were found to be 35, 30 and 28 percent respectively of the adsorption heat due to CuO , Fe_2O_3 and Al_2O_3 powders. The fact that the adsorption of stearic acid on CuO , Fe_2O_3 and Al_2O_3 powders are only partially reversible indicates that unlike nitrogen molecules stearic acid molecules are mostly chemisorbed on these adsorbents. This is supported by their high values of integral energies of adsorption. Infra-red and thermogravimetric studies (9,10) revealed that stearate are predominantly formed on the Al_2O_3 surface. Integral heat evolved per unit surface has been found to be 47.2, 53.3 and 51.8 mcals/m² respectively for CuO , Fe_2O_3 and Al_2O_3 powders. Allen and Patel (7) has found this value to be 24.7 mcals/m² for Fe_2O_3 using n-octadecanol. Reciprocals of the values of integral heat evolved per unit surface are equal to constant K in equation (4) for the respective powders. The value of K depends upon the nature of the adsorbent surface and adsorbate molecules. Therefore, for practical purposes the use of equation (4) to compute surface area is limited. However, the

fact that the values of integral heat evolved per unit surface of CuO , Fe_2O_3 and Al_2O_3 powders are close to one another indicates that the nature of the surfaces of these powders are approximately identical. An average value of K based on these data would, therefore, give good estimate of specific surface area of CuO , Fe_2O_3 and Al_2O_3 powders, being 8.6, 9.5 and $121.7 \text{ m}^2/\text{g}$ respectively.

Results obtained by the method of adsorption from solution are summarized in Table-3. Comparison of the results in Table-2 and Table-3 shows that in contrast to the flow method the adsorbents get saturated at higher concentrations. Isotherms obtained by plotting amount of solute adsorbed, x , vs concentration of solution, C , using the results of method of adsorption from solution is shown in Figure-3. Straight line relationships of the plots of C/x vs C shown in Figure-4 indicates that adsorption of stearic acid on all the adsorbents studied are of Langmuir type. From the slope and intercept of this plot the limiting values of amount of stearic acid adsorbed, x_m , to give monolayer coverage are obtained. An examination of the flow calorimetric results in Table-2 would reveal that the limiting value of stearic acid adsorbed, x_m , are the same for respective adsorbents as that of adsorption from solution method. Specific surface area of the adsorbents determined by these two methods would, therefore, be

found to be identical.

In the early works area occupied by one molecule of stearic acid, A_m , was taken to be around $18 \text{ \AA}^2$ assuming that the molecules rested on the adsorbent surfaces perpendicularly (11-13). Examinations of Medvedeva's results (11) and recent flow calorimetric studies (3,7,14) gave the value of A_m to be of the order $60-70 \text{ \AA}^2$. Whereas according to the Courtauld model of paraffin the value of A_m would be approximately $100 \text{ \AA}^2$ if the molecules are to lie parallel to the surface with the whole chain resting on it. Using the above values of A_m the specific surface areas of the adsorbents have been computed. These results are tabulated in Table-4 along with the results obtained by BET nitrogen gas adsorption method. It is seen from Table-4 that the specific surface areas of the adsorbents obtained by the flow micro-calorimeter and adsorption from solution agree fairly well with that obtained by BET nitrogen gas adsorption method if it is considered that the area occupied per molecule of stearic acid to be of the order of $60-70 \text{ \AA}^2$ and that of nitrogen to be 16.2 or $16.8 \text{ \AA}^2$. Assumption that area occupied per molecule of stearic acid to be 18 and $100 \text{ \AA}^2$ are found to give very low and very high estimate respectively indicating that stearic acid molecules lie neither completely perpendicular nor completely parallel to the surfaces studied.

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References

1. G.D.Parfitt, BP Symp. on the Significance of Heat of Adsorption at the Solid/Liquid Interface, ed. A.J.Groszek, March 5, 1971.
2. M.W.Tideswell, Ibid.
3. M.A.Rahman, Bang.J.Sc.Ind.Res., 12,151,(1977).
4. A.J.Groszek, Soc.Chem.Ind.Monograph No. 28,174.
5. M.A.Rahman and A.K.Ghosh, J.appl.Chem.Biotechnol., 27,529, (1977).
6. M.A.Rahman, Bang.J.Sc.Ind.Res., 12,147,(1977).
7. T.Allen and R.M.Patel, J.appl.Chem., 20,165,(1970).
8. A.J.Groszek, Proc.Intern.Symp. on Surface Area Determination held in Bristol, U.K., 313,(1969).
9. M.Hasegawa and M.J.D.Low, J.Colloid Interface Sci., 30,378, (1969).
10. A.J.Tyler, F.H.Hambleton and J.A.Hockey, Catalysis, 13,35, (1969).
11. A.P.Medvedeva, Ogneuporg, 25,184,(1960).

12. A.S.Russel and C.N.Cochran, Ind.Eng.Chem., 42,1332,(1950).
13. W.D.Harkins and D.M.Gans, J.Am.Chem.Soc., 53,2804,(1931).
14. A.J.Groszek, Chem.Ind., 2003,(1965); Ibid, 1765,(1966).

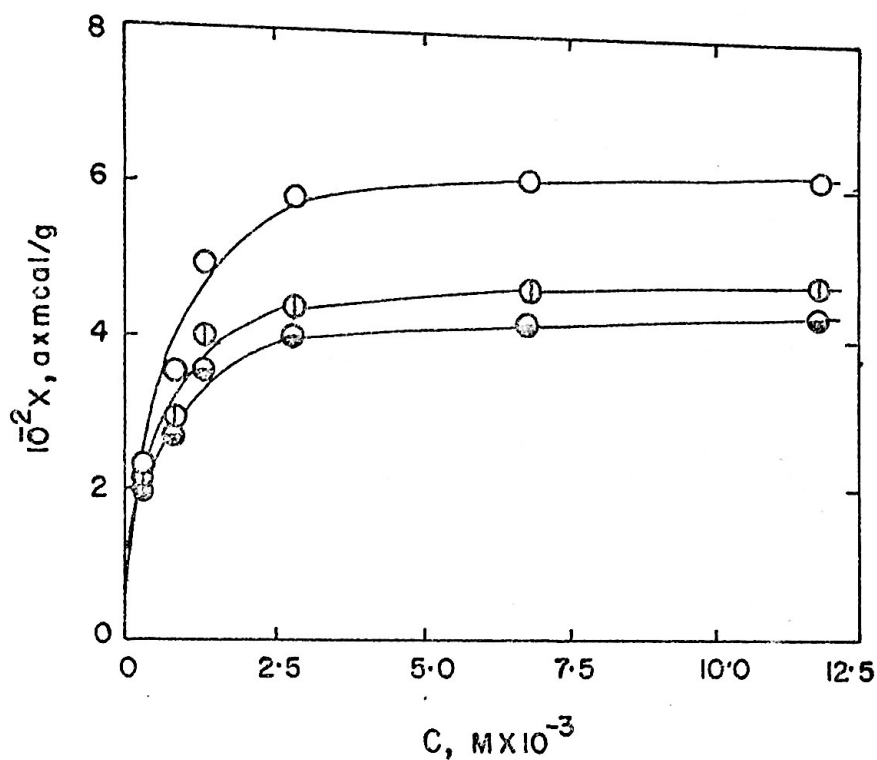


Fig. 1. Variation of Integral heat evolved with concentration of stearic acid solution. $\bullet$ CuO ($a = 1$), $\odot$ Fe_2O_3 ($a = 1$), $\circ$ Al_2O_3 ($a = 10$).

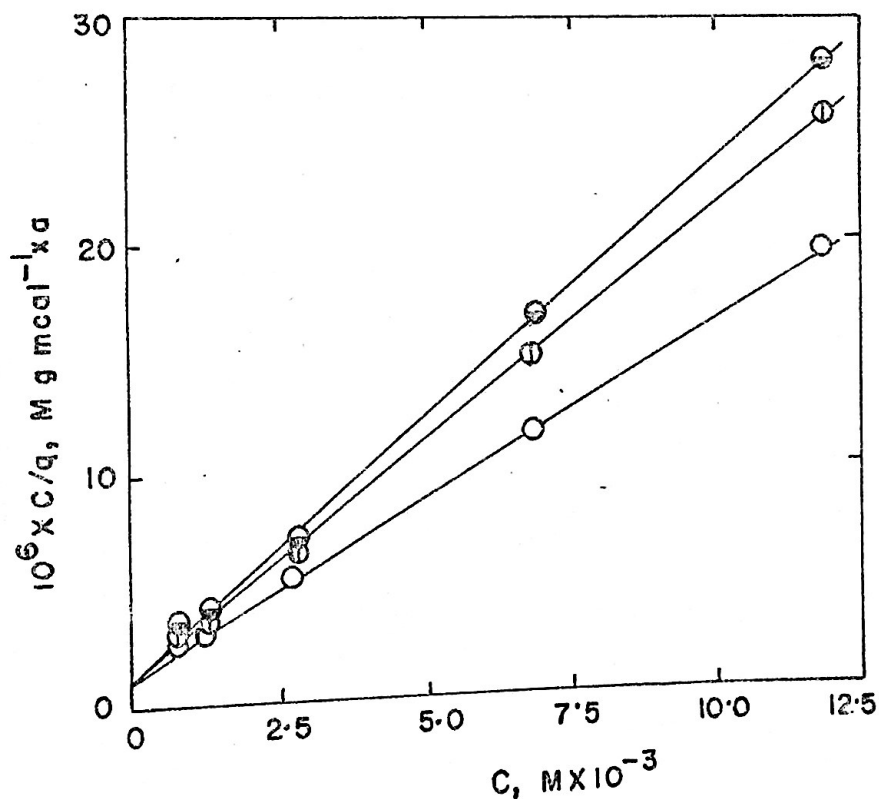


Fig. 2. Langmuir plots of the flow micro-calorimetric results. $\bullet$ CuO ($a = 1$), $\odot$ Fe_2O_3 ($a = 1$), $\circ$ Al_2O_3 ($a = 0.1$).

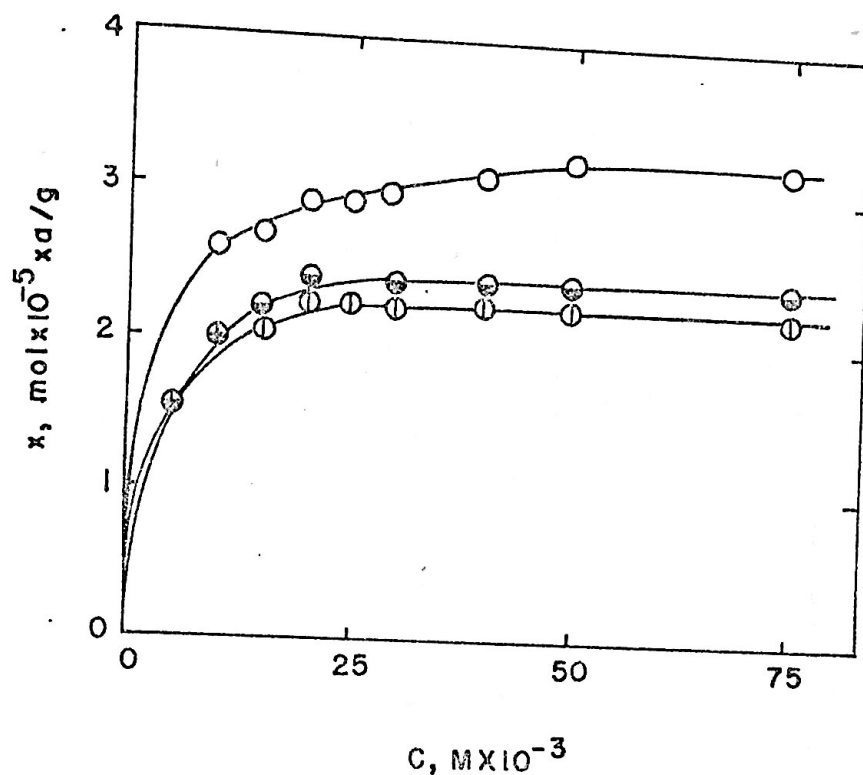
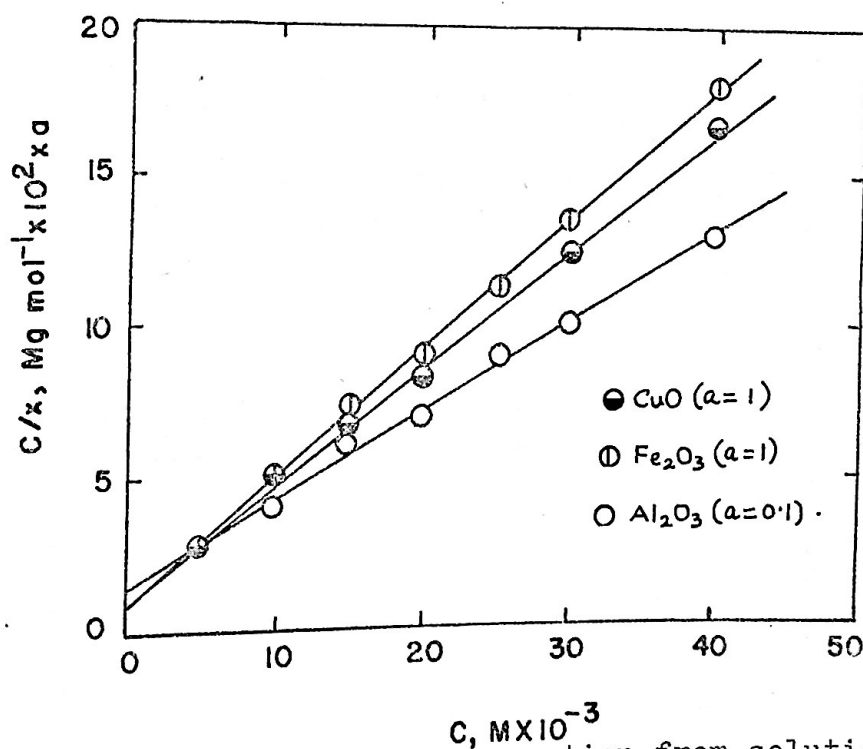


Fig.3. Variation of amount adsorbed with the concentration of stearic acid solution. $\bullet$ CuO ($a = 1$), $\odot$ Fe_2O_3 ($a = 1$), $\circ$ Al_2O_3 ($a = 10$).



data of the adsorption from solution results.

Table-1. BTP nitrogen gas adsorption measurements at liquid N₂ temperature, -196°C.

Adsorbent	Weight of adsorbent (w) g	Degassing Conditions			Pressure (P) cm Hg		Volume of N ₂ adsorbed at bed at NTP (V _w)		Volume of N ₂ adsorbed at bed at NTP (V _m)		Limiting Value of Volume of N ₂ adsorbed at NTP (V _∞)	
		Temp °C	Vacuum mm Hg	Time hr								
CuO	0.5043	150	10 ⁻⁵	4	24.44	1.57	3.12		2.12			
	0.4972	150	10 ⁻⁵	4	23.80	1.65	3.33		2.26			
	0.4892	150	10 ⁻⁵	4	24.15	1.46	3.00		2.05			
Fe ₂ O ₃	0.5218	350	10 ⁻⁵	3	25.50	1.63	3.13		2.08			
	0.4874	350	10 ⁻⁵	3	23.80	1.41	2.89		2.11			
	0.5028	350	10 ⁻⁵	3	24.30	1.56	3.12		2.12			
Al ₂ O ₃	0.1239	350	10 ⁻⁵	3	23.70	4.85	38.78		27.15			
	0.1055	350	10 ⁻⁵	3	25.50	4.37	41.45		27.52			
	0.1065	350	10 ⁻⁵	3	24.82	4.35	40.88		27.55			

of N₂ adsorbed at bed at NTP (V_w)
 of N₂ adsorbed at bed at NTP (V_m)
 of Volume of N₂ adsorbed at NTP (V_∞)
 c.c/g c.c/g c.c/g

Table-2. Flow micro-calorimetric measurements.

Change in solute concentration $\times 10^{-3}$	Cumulative heat evolved, q mcal/g	Amount of stearic acid adsorbed, x $\text{mol} \times 10^{-5}/\text{g}$			$10^6 \chi_c/q$ M g/mcal					
		From (C ₁)	To (C)	CuO	Fe ₂ O ₃	Al ₂ O ₃	CuO	Fe ₂ O ₃	Al ₂ O ₃	
0	0.5	216	232	2412	1.5	1.6	22.9	2.31	2.16	0.21
0.5	1.0	280	302	3740	1.6	1.6	24.3	3.57	3.31	0.27
1.0	1.5	360	406	5024	1.9	1.7	27.6	4.17	3.69	0.30
1.5	3.0	404	445	5796	2.2	1.8	29.4	7.42	6.74	0.52
3.0	7.0	424	466	6124	2.3	2.1	30.9	16.51	15.02	1.14
7.0	12.0	430	469	6146	2.4	2.2	31.2	27.91	25.59	1.95

At monolayer coverage,

Heat evolved (q_0)	439	485	6184
mcal/g			
Integral energies of adsorption	17.9	21.3	19.6
kcal/mole			
Integral heat per unit surface (q_0/s)			
mcal/m ²	47.2	53.3	51.8

Table - 5. Measurements of Adsorption from Solution.

Concentration of stearic acid solution	Before adsorption			After adsorption			Amount of stearic acid adsorbed, x			C/x		
	MX10 ⁻³			mol X10 ⁻⁵ /g			M gX10 ² /mol					
	CuO	Fe ₂ O ₃	Al ₂ O ₃	CuO	Fe ₂ O ₃	Al ₂ O ₃	CuO	Fe ₂ O ₃	Al ₂ O ₃			
Before adsorption (C)												
5	4.1	4.1	-	1.8	1.8	-	2.8	2.8	-			
10	9.0	9.0	7.4*	2.0	2.0	26.0	5.0	5.0	0.4			
15	13.9	14.0	12.3*	2.2	2.0	27.0	6.8	7.5	0.6			
20	18.8	18.9	17.1*	2.4	2.2	28.9	8.3	9.1	0.7			
25	-	23.9	10.5	-	2.2	29.0	-	11.4	0.9			
30	28.8	28.9	15.0	2.4	2.2	30.0	12.5	13.6	1.0			
40	38.8	38.9	24.5	2.4	2.2	31.0	16.7	18.2	1.3			
50	-	-	34.0	-	-	32.0	-	-	1.6			
75	-	-	59.0	-	-	32.0	-	-	2.3			
100	-	-	84.0	-	-	32.0	-	-	3.1			

Solution 100 ml, Adsorbent 5 g, *1 g.

Table-4. Surface Area of Adsorbents.

Adsorbent	Surface Area, m ² /g						
	BET method (N ₂ adsorption)			Flow calorimetric and Adsorption from solution method (Stearic acid adsorption)			
	Area per molecule of N ₂ , Å ²			Area per molecule of stearic acid, Å ²			
	16.2	16.8	20.2	18	60	70	100
CuO	9.3	9.7	11.6	2.6	8.7	10.1	14.5
Fe ₂ O ₃	9.1	9.5	11.4	2.4	8.0	9.3	13.3
Al ₂ O ₃	119.4	123.8	148.9	34.7	115.6	134.9	192.7