ADSORPTION OF FATTY ACID SOAPS ON HEMATITE

by

Michael Uriel Oko

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FOREWORD

With the rising importance of iron ore beneficiation, a great deal of research has been conducted over the past few years in order to better understand its flotation characteristics. Although hematite in ore deposits is generally loosely associated with gangue and, therefore, presents a relatively easy liberation problem, its flotation is difficult, since the gangue has flotation properties similar to the hematite. A gread deal of skill and knowledge is needed for the successful flotation of this mineral, and this makes the choice of a collector particularly critical.

Carboxylic acids, seemingly simple in structure, are not yet fully understood as collectors since their adsorption on surfaces of minerals may be as dissociated anions or undissociated molecules depending on the conditions of the solution (12). This investigation was conducted to determine some of the adsorption characteristics of oleic and linoleic acid soaps in basic aqueous solutions on specularite hematite.

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HISTORICAL AND THEORETICAL

Introduction

Twenty years ago most of the iron ore was used unbeneficiated. Today, in North America, only ten percent of the ore mined is directly chargeable to the blast furnaces; the rest of the mined produce is being beneficiated to improve its physical characteristics and upgrade its iron content (4). This situation was caused by the large surplus capacity to produce iron ore which existed throughout the world. The lack of demand forced mining companies to improve their products to meet steelmakers specifications. Although this situation changed with the increase in world demand (1), all the iron ore presently used is marketed to rigid specifications. In 1963, out of the 73.564.000 long-tons of ore shipped from mines in the U. S., 78 percent was beneficiated. In Canada, the proportions of beneficiated iron ore have been steadily increasing since 1958. Preliminary estimates revealed that in 1964 the proportion will be 73 percent out of the total of 35.857.000 long tons mined, up five percent from the previous year. (2).

With the gradual depletion of our high grade ore reserves, increasing importance is attributed to the various ore upgrading techniques. In the case of iron ore, these are:

1 - heavy media separation
2 - spiral treatment
3 - tabling
4 - magnetic, electrostatic and high intensity separation
5 - flotation

Presently the technique of flotation occupies a minor role and

most of the ore processed in Canada is beneficiated by gravity concentration, of which the first three methods comprise. Gravity concentration, although relatively inexpensive, is best applied to coarsely agglomerated material of high specific gravity. With finely disseminated materials, such as taconite and some ores of hematite, the unit capacity of this process is low, making it necessary to build large plants requiring a high initial investment.

Magnetic separation cannot be applied to hematite ores in which the proportions of magnetics is low and a unit capacity problem exists for the other electrical separation methods. For instance, high intensity dry magnetic and electrostatic high tension methods proved useful in the concentration of some specularite Labrador ores in the size range of 14-35 mesh but they were applicable for finer ore concentration provided multi unit separators were used and thus cannot yet compete with the more conventional means of iron ore concentration (5).

In 1954, the first commercial flotation plant operated by Humbolt Mining Company opened in Marquette County, Michigan. The plant, with a capacity of 250.000 long tons per year, processed ore averaging 34 percent specularite hematite which was upgraded to a concentrate containing 62.5 percent (3). The success of this plant prompted the opening of another in 1956. By 1960 other plants opened in Michigan and the estimated iron ore flotation capacity for that year was 2.1 million tons. In 1963 this capacity was estimated to have doubled to 4.6 million tons per year (4).

In the case of Canadian practice, gravity concentration is exclusively used. In the future it is expected that flotation will become more important for the recovery of finely disseminated hematite.

Adsorption

Flotation is a process utilizing the ability of some chemical reagents to selectively attach themselves to surfaces of specific mineral particles in an aqueous pulp. rendering these specific minerals water repellent. By bubbling air through the pulp, these minerals attach themselves to the bubbles and rise with them to the surface where they are removed from the mineral aggregate. The adhesion of the mineral particle to an air bubble can be considered as a three stage process:

1 - selective attachment of chemical reagents on the mineral

2 - collision between the bubble and the mineral particle

3 - establishment of a finite contact between the air and the solid by replacement of the solid water interface by an air solid interface.

The main function of these chemical reagents, otherwise called collectors, is to concentrate at the surfaces of the mineral particles which are to be floated thus making them water repellent.

The mode of attachment of the collectors which are mostly thought to be dissociated in water, serves to divide the collectors into two groups. Anionic collectors which, after dissociation, have the anionic portion attach itself to the

mineral surface, and cationic collectors which do likewise with their cationic portion.

The mechanism of the adsorption of the collector is generally divided into two types: chemisorption and physical adsorption. Some of the differences between the two are: 1) the free energy of chemisorption is great, whereas that of physical adsorption is low, 2) chemisorbed films are hard to remove from the surface of the solid, whereas physically adsorbed molecules are not, 3) physically adsorbed molecules are held onto the solid by weak Van der Vaal's forces, whereas chemisorbed particles are held by chemical or electrostatic bonds.

In the flotation of most minerals where chemisorption is established, the collectors are attracted to the mineral surfaces electrostatically. The occurrence of the electrostatic attraction is best explained by the double layer theory.

The Double Layer on Hematite in Aqueous Solutions

The mechanism by means of which a surface charge is established on hematite in an aqueous solution is discussed by Parks and de Bruyn (8) and occurs in two stages (Figure 1):

1 - a surface hydration stage

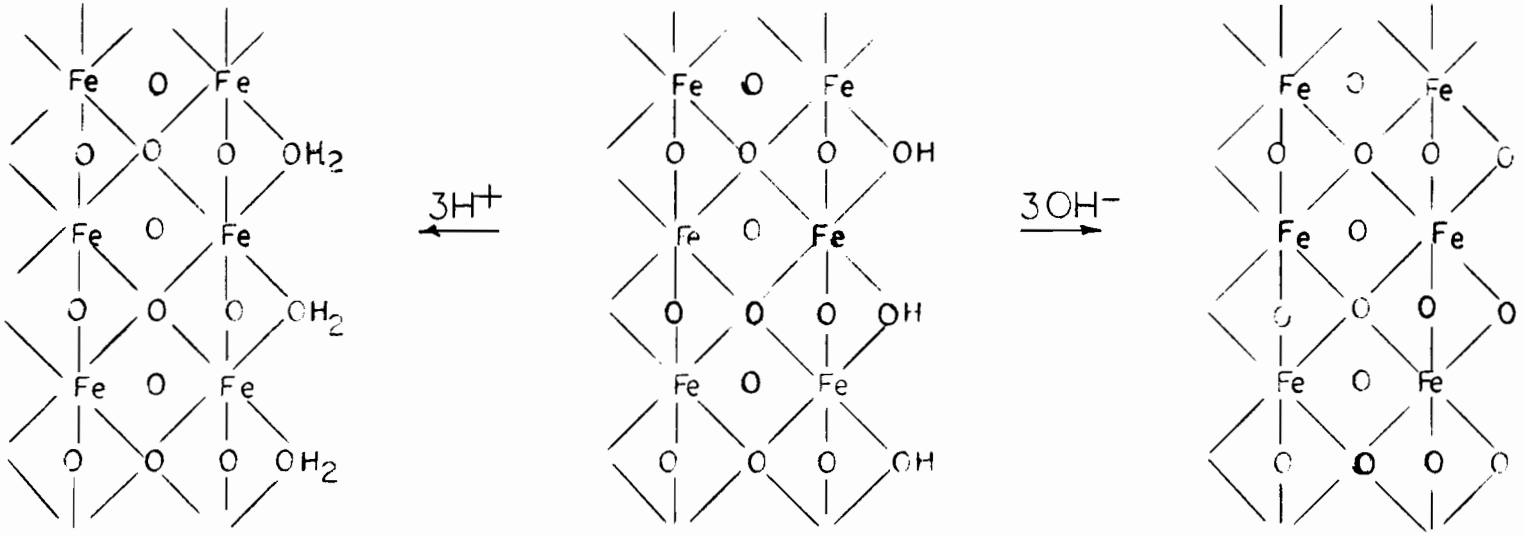
2 - adsorption of potential determining ions.

When the hematite is placed in water, its exposed surface atoms of oxygen complete their coordination shell by attracting H^+ ions from the solution and the iron atoms complete theirs by attracting OH^- ions. This hydrated layer, which is neutral in charge, acquires either a positive or a negative charge

FIGURE 1

ELECTROSTATIC CHARGE OF HEMATITE

IN AQUEOUS SOLUTIONS



POSITIVELY CHARGED

NEUTRAL

NEGATIVELY CHARGED

depending on the pH of the solution. The H^+ and OH^- ions are the potential determining ions, regarded by some investigators as part of the solid lattice (7), and are neutralized by oppositely charged ions called counter ions, attracted from the solution. Some counter ions are held directly on the surface in a place only a few angstroms in thickness (7), called the Stern plane, and the rest surround this plane and form an atmosphere called the diffused or Gouy layer. As shown in Figure 2, the surface potential ψ_o across the double layer abc can be divided into two parts, the drop across the diffused layer and the steeper drop across the Stern layer. The surface potential ψ_o is determined by the concentration of potential determining ions in the solution only (6). At a certain concentration of these ions, the surface is uncharged and no double layer exists. The pH of the solution at which the surface potential is 0, is called "the zero point of charge". On each side of the zero point of charge on the pH scale, the mineral's surface is oppositely charged.

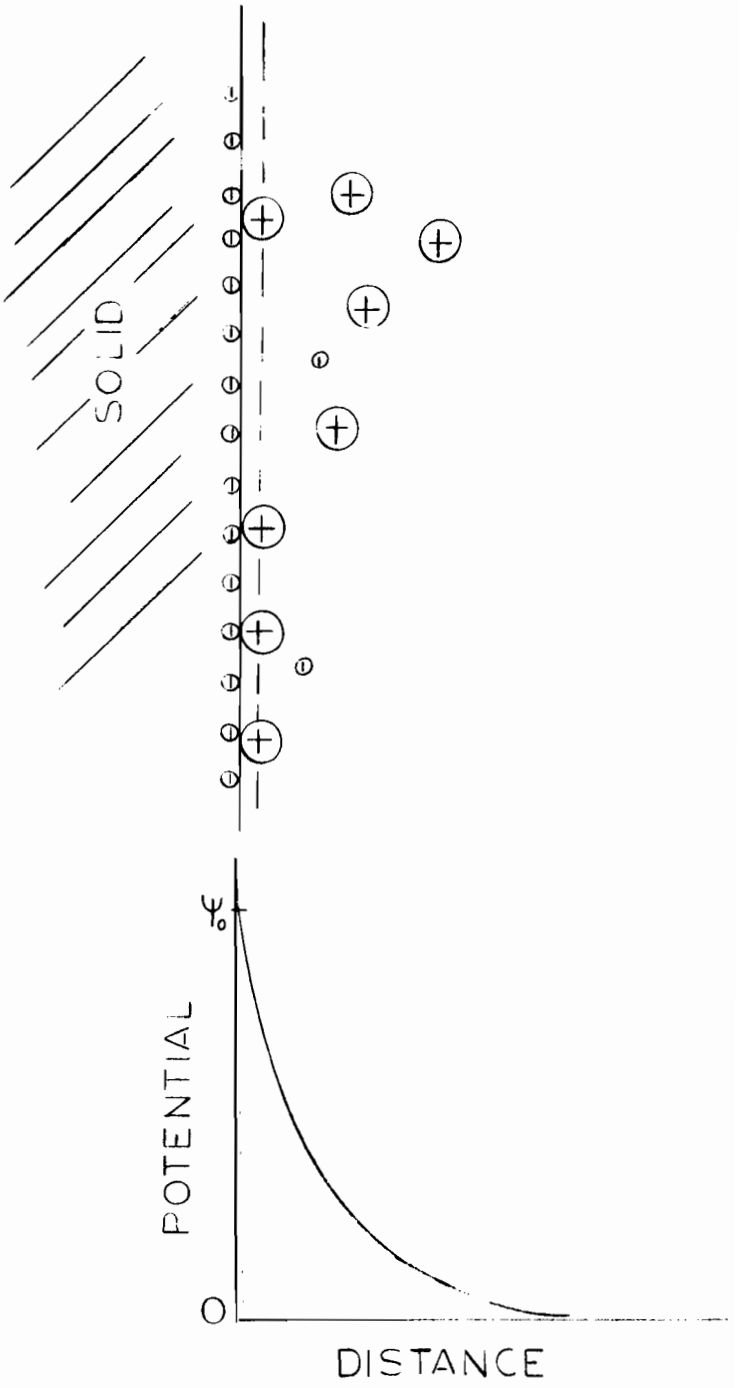
By having counter ions in the solution capable of adsorbing to the electrical double layer and rendering the surface of the mineral water repellent, flotation may be accomplished.

Fatty Acid Collectors

In 1939 Keck (10), through a series of flotation tests in basic solutions, proved that sodium oleate was a flotation reagent superior to other fatty acids such as ammonium palmolate, ammonium limoleate and potassium myrestate in basic solutions.

FIGURE 2

THE STRUCTURE OF THE DOUBLE LAYER
AND THE POTENTIAL DISTRIBUTION
IN AQUEOUS SOLUTIONS (7)


SOLID
POTENTIAL
Ψ_o
0
DISTANCE

In acidic solutions, he proved that oleic acid is a collector superior to lauric, myristic, palmitic, caprylic and valeric acids, all of which are saturated aliphatic monocarboxylic acids and also that the highest flotation recovery of hematite occurred between the pH of 7 and 8. The indication of the flotation efficiency of the 18 carbon aliphatic monocarboxylic acids and their ready availability prompted an investigation into the effects of the unsaturation on their flotation efficiency by Purcell and Sun (17, 19) Iwasaki, Cooke and Choi (18) and Buckenham and Mackenzie (20).

The structural formulae of oleic and linoleic acid may be represented as follows:

Oleic acid $CH_3-(CH_2)_7-CH = CH-(CH_2)_7-COOH$

Linoleic acid $CH_3-(CH_2)_4-CH = CH-CH_2-CH=CH-(CH_2)_7-COOH$

Both are abundant in vegetable oils, the oleic acid in its cis-form and the linoleic in its cis 9 cis 12 form (13). These belong to the eighteen carbon aliphatic monocarboxylic acids homologous series which contain stearic acid which is completely saturated, oleic with one unsaturated double bond linoleic with two and linolenic acid with three non conjugated double bonds.

The dissolution of the fatty acids in water is accompanied by dissociation of the molecule into ions in a manner similar to inorganic acids. Their dissociation occurs to a much lesser degree in this case and in general the following has been concluded:

1 - with increasing length of the carbon chain, there is a decrease in the dissociation of the acids in water (14),

2 - the increase in unsaturation causes an increase in the solubility of these acids in water. This is attributed to the affinity of the double bonds to water (19),

3 - the critical micelle concentration (cmc) in water of the acid soaps decreases as the carbon chain length increases. Since increased unsaturation results in properties equivalent to the reduction in the length of the hydrocarbon chain, the critical micelle concentration of the soaps of monocarboxylic acids containing the same number of carbon atoms is expected to decrease with increasing unsaturation (17),

4 - the hydrolysis of the soaps decreases with the increase in saturation. Thus, sodium linoleate hydrolyses to a lesser extent than sodium oleate (20).

The double bonds of the carboxylic acids are prone to air oxidation which affects the flotation efficiency of the acids. Gaudin and Cole (28) established that the air oxidation effects in flotation are very small in the case of oleic and linoleic acid but that the linolenic acid gets oxidized and its flotation efficiency is measurably affected.

Several investigators reached the general conclusion that the more unsaturated the 18 carbon monocarboxylic acid is, the more efficient a flotation reagent it becomes from the point of view of flotation kinetics (19) and effective pH range (18, 20). The very nature of the double bond and its effect on the shape of the aliphatic chain helps to explain this phenomenan. It is generally acknowledged that, in most cases, the dissociated anionic portion of the acid or its soap adsorbs in the electrical double layer with the polar part of the chain closest to the mineral and the nonpolar part oriented towards the water (21). At low adsorption concentrations in the

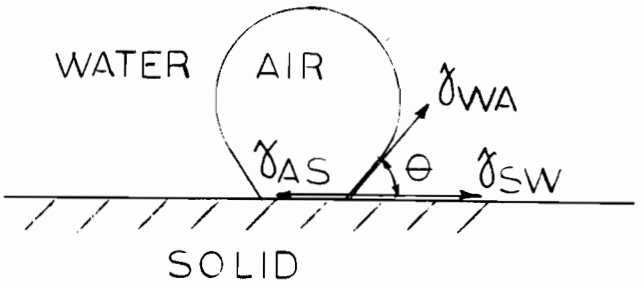
double layer, when the adsorbed species are not compressed by close neighbouring species into a fixed position, the hydrocarbon chain will most likely choose a horizontal orientation with respect to the surface (15). This orientation will be imposed on it by the surrounding hydrogen bonded water molecules into the structure of which the hydrocarbon chain does not easily fit. Flexible models of 18 carbon aliphatic monocarboxylic acids show that the carbon chain of stearic acid is straight, of the oleic acid is bent once and that of the linoleic acid is bent twice. Thus, when adsorbed on a mineral, the area occupied by each acid increases with increasing unsaturation (20). When the adsorption concentration of the fatty acid ions is high, the hydrocarbon chains have to assume a more vertical orientation with respect to the surface of the mineral so that more anions may be accommodated on it (21).

The Contact Angle

Tenacity of adhesion between air and a collector adsorbed may be examined by a contact angle measurement. Figure 3 shows a mineral, the surface of which was rendered water repellent by a collector in an aqueous solution. An air bubble attached to its surface displaced the water surrounding the mineral.

FIGURE 3

THE CONTACT ANGLE



If γas, γsw and γaw are the surface tensions in dynes/cm, equivalent to surface energies at the interfaces of air solid, solid water and water air respectively, it may be shown thermodynamically that a necessary condition for a bubble adhesion is that there will be a reduction in the surface free energies as adhesion takes place.

Thus:

$$\triangle F = -W = \gamma as - \gamma sw - \gamma aw$$

where W is the work done by the system during the change called the work of adhesion (21), and

$\triangle F$ is the change in free energy of the system.

From Figure 3, at equilibrium,

$$\gamma as = \gamma sw + \gamma aw \text{ Cos } \theta$$

Substituting

$-W + \gamma aw = \gamma as - \gamma sw$ in this equation γsw and γas are eliminated and the following expression obtained:

$$W = (1 - \text{Cos } \theta)\, \gamma aw$$

The quantity W is a measure of the tenacity of adhesion by which the mineral will attach itself to the surface of the bubble (9).

The Scope of Work

The main purpose of this investigation was to determine the adsorption isotherms of oleate and linoleate ions on hematite. By conducting the adsorption trials at pH of 10 two purposes were achieved: the adsorption of oleate and linoleate ions at the range of solution concentrations tested on the surface of the mineral was ascertained since, at this pH, the soaps of these acids are largely hydrolyzed (12, 47, 20) and the pH control was easily exercised by addition of NaOH. This avoided the contribution of other foreign ions which may have been needed to control the pH if adsorption at a lower pH value was to be studied.

The effects of oleate and linoleate ions on the surface tension of water and the contact angle of air bubbles on hematite were investigated. These effects were correlated to the adsorption studies emphasizing their influence on the floatability of the hematite in basic solutions. Practical verification of some of the findings of the investigation were achieved by flotation tests of hematite in solutions of various soap concentrations at the pH of 10 in the modified Hallimond Tube.

EXPERIMENTAL

Scintillation Apparatus

The concentration of the soap solution was determined by tracer techniques. The liquid scintillation apparatus used for counting purposes was Model 314 AX Tri Carb spectrometer of Packard Instrument Company, La-Grange, Illinois which was equipped with a freezer unit operating at 10°C. to reduce backgrown radiation (Appendix 2).

Agitation Adsorption Apparatus

Adsorption trials on hematite were conducted in 22 milliliter capacity sample vials supplied by The Canadian Laboratory Supplies. These were filled with soap solution and a pre-weighed amount of the sample. The vials were then mounted on a 12 inch disk which was rotated at 20 RPM for the duration of the adsorption test. The agitation apparatus was the same as the one used by Lapointe (22).

Agitation Desorption Equipment

Soap ions adsorbed to the surface of the solid hematite were desorbed in an apparatus similar to the one used by Gaudin and Bloecher in their adsorption experiments (23). The apparatus consisted of a filter flask on which a fritted glass filter was mounted. The solids were placed in solution in a filter and mechanically agitated by a mechanical mixer, using a glass rod as an agitator. By keeping a good seal between the filter flask and the glass filter, the solution was prevented from dripping into the flask. Upon completion of the desorption cycle, the seal was broken and the solution

allowed to filter into the flask.

Contact Angle Apparatus

The construction of the contact angle apparatus was based on the one designed by Taggart, Taylor and Ince (24). It consisted of a microscope with its stage and objective horizontally mounted. A transparent plastic container, in which the solution and the specimen were contained, was set on the stage. The bubble holder consisted of a glass capillary tubing mounted on an independent mechanical stage positioned on top of the microscope stage. The mineral specimen with a horizontal surface was placed in the flotation solution in the plastic container of the microscope stage and an air bubble was injected on its horizontal surface through the capillary tubing. The angle of contact of the gas solid liquid interfaces was observed as a magnified image through the microscope's eyepiece, which was provided with graduations enabling contact angle estimation to the nearest degree.

The Flotation Apparatus

A Hallimond Tube as modified by Fuerstenau, Metzger and Seele (25) was used for the flotation tests. The inlet gas flow was accurately controlled by using a rotameter type gas flowmeter. The only agitation applied to the pulp in the cell was through the bubbling action of the gas in it.

The B.E.T. Apparatus

Surface area measurements using krypton gas were performed on the Department of Metallurgical Engineering of McGill University B.E.T. apparatus (Appendix 1).

Hematite Sample Preparation

The mineral used for this investigation was -10 mesh specularite hematite spiral concentrate supplied by the Quebec Cartier Mining Company. The -150 +200 mesh portion represented the greater part of the concentrate, hence, it was used throughout the experiment. The preparation of the sample consisted of size separation, the removal of silica (SiO_2) and other low specific gravity minerals, the removal of magnetite and the washing of the hematite.

The concentrate was screened and the -150 +200 mesh portion retained. The silica and other low specific gravity solids were removed using a Richards Laboratory type free settling classifier (27). The product was considered silica free when on microscopic inspection less than 5% silica particles were present in the field of view. The magnetic portion was removed using a Ding Laboratory magnetic separator, after which the non magnetic portion was tested with a strong hand magnet to ensure the complete removal of the magnetics.

Since surface impurities greatly affect the sorption of collectors and the floatability of the mineral, the sample was washed twice following the scheme used by Iwasaki, Strathmore and Kim (38), with 10% hydrochloric acid solution. The sample was then decanted with distilled water and subsequently with de-ionized conductivity water. When the conductivity measurements of the wash effluent disclosed little change in the specific conductance, the surface of the hematite was considered clean. The sample was dried at 75°C.,

mixed thoroughly and kept in a closed glass jar. The specific surface as determined by krypton adsorption B.E.T. technique was found to be 1035 cm^2/gm. (Appendix 1).

Chemical Reagents

The oleic acid used in this investigation was a purified grade purchased from Fisher Scientific Company. With formula weight of 282.47 it was also reported to contain maximum of 5% pulyunsaturated. The purity of the acid was checked and the results are:

TABLE I

PURITY OF OLEIC ACID

	Pure Oleic Acid (13)	Oleic Acid Used
iodine value (wij's) (26)	89.87	89.2
Freezing point	4°C	4°C
Index of refraction n_D^{18}	1.463	1.461

The linoleic acid, purchased from the Hormel Institute of the University of Minnesota was reported to have an iodine value of 181.0 (theoretical 181.03) and an overall estimated purity greater than 99%.

The labelled 1-C14 oleic and linoleic acids were purchased from the Radiochemical Centre, Amersham Buckinghamshire, England, and were reported to be 97% pure (29). The linoleic acid, however, contained approximately 10% cis-trang isomer content and the oleic approximately 3%. These isomers were not

considered impurities. Each of the labelled acids was supplied dissolved in a benzene solution.

All the other chemicals were commercially available and only the purest grades were purchased and used.

PROCEDURE

Adsorption Tests

The soap solutions used for the adsorption tests were prepared by saponification of labelled oleic and linoleic acids. For each adsorption trial 100 milligrams of fatty acid weighed out in a weighing bottle were labelled with 2.5 microcuries of labelled acid in benzene solution. To drive out the benzene, the weighing bottle was placed in a rubber stoppered beaker in which two 1 mm. capillary tubings were inserted. A gentle stream of purified nitrogen was passed through one capillary onto the surface of the acid and exhaused through the second capillary. This operation was conducted in 50°C. water bath to ensure the complete benzene evaporation (29). The labelled acid was saponified with an equivalent amount of 0.1 normal solution of NaOH added to the weighing bottle which was then sealed air tight in a beaker and placed at 60°C. water bath for an overnight digestion.

Adsorption tests were performed on 5.000 gm. portions of hematite in 22 ml. glass sample vials. The vials, supplied with plastic covers, were cleaned in glass cleaning solutions. To avoid contact between the plastic cover and the soap solution, the inside of the covers were lined with aluminum foil, also washed in glass cleaning solution. The glass vials, aluminum linings and plastic covers were thoroughly rinsed with distilled water to prevent foreign ion contamination. It was found that no detectable change in the soap concentration occurred provided the liquid gas interface was eliminated by

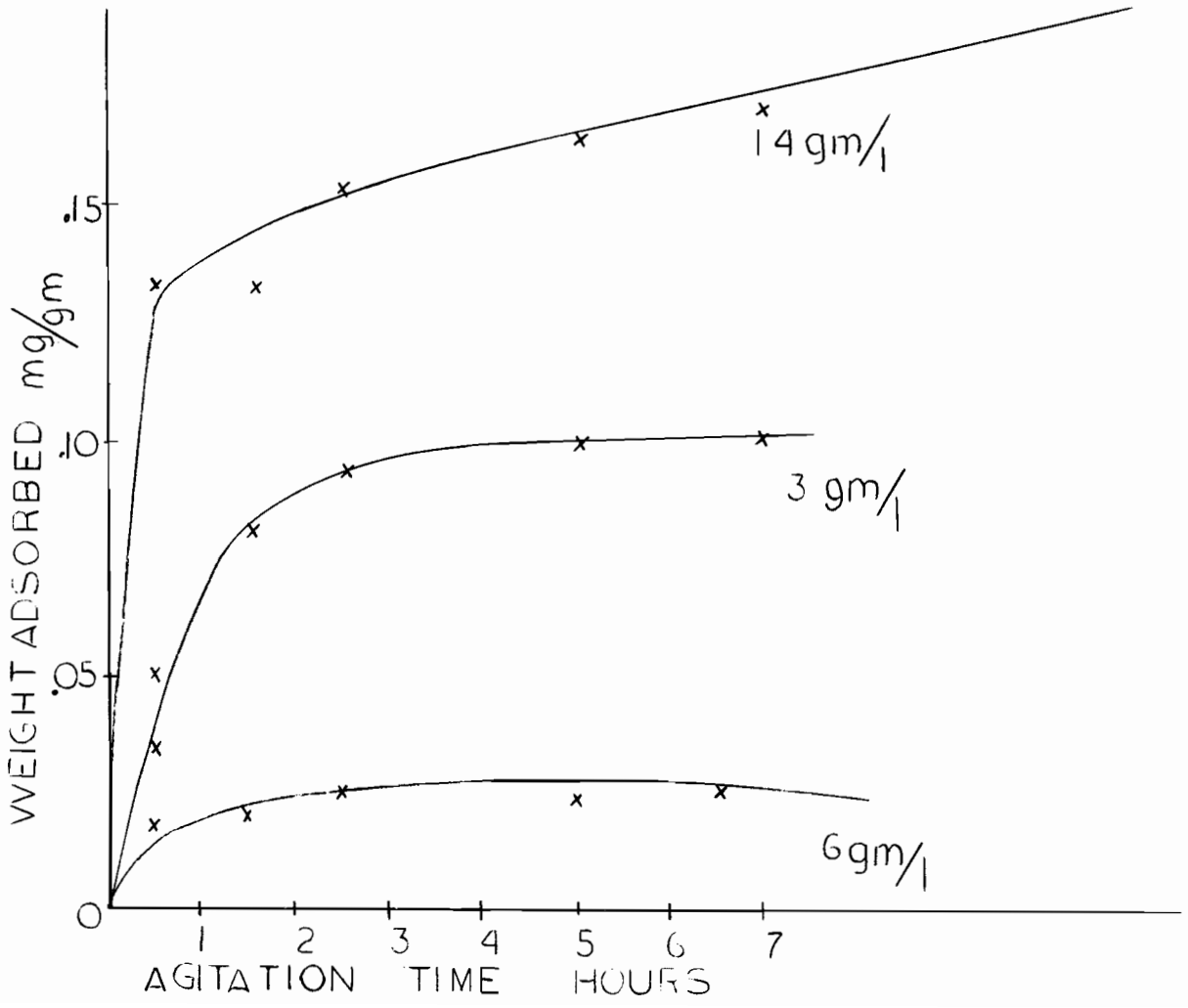
completely filling the vial up with soap solution.

For the adsorption tests, a master soap solution of 1.00 gm/l anion concentration was prepared by diluting the saponified labelled acid to 100 ml. with conductivity water. The accurate determination of the rate of radioactive disintegrations of this master solution by scintillation counting served as a base for the soap concentration determination of subsequent solutions prepared from it (Appendix II) The prepared glass vials containing the hematite sample portions were filled through a burette with soap solutions diluted from the master solution with their pH adjusted to 10 by addition of NaOH solution. The quantity of soap solution added to each vial and its concentration, as determined by scintillation counting, were carefully recorded. Thus, the change in concentration of the soap solution after the adsorption trial disclosed the exact weight of carboxylic anion adsorbed.

The period of agitation required for adsorption equilibrium conditions to be attained on the hematite sample in the vials was determined by withdrawing small equal quantities of solution from the vials for soap concentration determination by scintillation counting. The results disclosed that, after one half hour at the agitation rate of 20 RPM, most of the adsorption was complete and that a 2 hour agitation was required to bring the adsorption to equilibrium. From the shape of the curves (Figure 4) it was deduced that, at high soap concentration ranges, equilibrium is achieved more slowly. It was, therefore, decided to establish a period of agitation of four hours at 20 RPM for equilibrium state in this investigation.

FIGURE 4

ADSORPTION EQUILIBRIUM TIME DETERMINATION


14 gm/l
3 gm/l
6 gm/l
.15
.10
.05
0
WEIGHT ADSORBED mg/gm
1
2
3
4
5
6
7
AGITATION TIME HOURS

Desorption Tests

The sample on which labelled soap ions were adsorbed was placed in a fritted glass filter and a known quantity of water of pH 10 (adjusted by NaOH solution) was added. The sample was agitated in the water by a glass rod rotated at a high speed by a mechanical mixer. Every four hours the solution was filtered through the fritted glass and analyzed by scintillation counting. A fresh known quantity of water at pH 10 was placed in the fritted glass filter over the sample and the cycle repeated. By consistently analyzing the effluent, the amount of the ions removed from the surface of the hematite was estimated. To confirm the removal of the carboxylic ions after desorption, the hematite was dried and a .500 gm. portion was scintillation counted for the extimation of the amount of soap remaining on the surface.

Contact Angle Measurements

The contact angle measurements were performed on large crystals of specularite hematite supplied by the Quebec Cartier Mining Company. The crystals were washed in a manner identical to the preparation of the hematite sample. Contact angles were taken on flat, freshly cleaved surfaces of the hematite in solutions containing variable concentrations of unlabelled soaps at pH of 10.

To ensure that the flat faces of the hematite crystals are horizontal prior to the bubble deposition on the surface, the crystals were placed on a small mandrel in the plastic cell, the soap solution poured over, and the adsorption allowed to come to equilibrium, after which the contact angles were measured.

Surface Tension Measurements

Surface tension of oleate and linoleate soap solutions at pH of 10 were determined using the glass capillary method described by Harkins and Brown (39). The glass capillary was cut into 5 inch sections. The diameter of the bore was determined by filling it with distilled mercury, weighing the mercury and measuring the length of the bore. Prior to the surface tension measurements all the capillaries were thoroughly cleaned with a glass cleaning solution and rinsed with distilled water.

The surface tension measurements were performed on the falling meniscus in the vertical capillary tubings dipped into the soap solutions of various concentrations. The equilibrium height of the capillary was determined by a cathatometer following the method of Richards and Carver (41). The surface tension of the solution was calculated using

$$\gamma = \tfrac{1}{4}\ hgdm$$

where γ is the surface tension in dynes/cm.

h is the height of the meniscus in cm.

g is the gravity acceleration constant (980cm/sec^2)

d is the diameter of the capillary in cm.

m is the density of the soap solution (assumed to be 1 gm/cm^3)

Flotation Tests

Comparative flotation tests in the modified Hallimond tube (25) were conducted on 2.000 gm. of hematite sample, which was allowed to adsorb as previously described in 100 ml. of

soap solution (pH of 10) of known concentration. The inlet rate of flow of purified nitrogen gas was kept at 200 milliliters per minute. This rate of flow was sufficient to keep most of the sample in constant agitation. The flotation period was arbitrarily set to 30 seconds for each test.

RESULTS

Adsorption Tests

The results of the adsorption tests conducted at room temperature (23°C. - 28°C.) were tabulated in Tables II and III. In the construction of Table II, six master solutions and in Table III, two master solutions were used. Each master solution of 1.00 gm/l concentration and the solutions prepared from it were scintillation counted before and after adsorption tests. From this count, the solution concentrations before and after adsorption were deduced and the carboxylic anion contents of the vials calculated. The difference in the anion contents before and after agitation was the weight of the carboxylic group adsorbed on the hematite in mg/gm. The adsorption density in mg/cm^2 was then calculated.

The equilibrium solution concentration in gm/l of carboxylic anion versus the weight of the anion adsorbed in mg/cm^2 are given in Figures 5 and 6. The reproducibility of the isotherms was confirmed by independent adsorption tests each represented by a different master solution. In low equilibrium concentration ranges, the results were reproducible, whereas at high concentration ranges, especially in the case of linoleate soap, unexplainable scatter was observed.

There was an interesting phenomenon at concentrations higher than .4 gm/l. A light brown colour was observed in the solution. In this case, one such solution was qualitatively analyzed and found to contain dissolved iron (44). This might have been due to the reaction

TABLE II

SODIUM OLEATE ADSORPTION TEST RESULTS

SOLUTION pH 10.0

Counts per Minute			Solution Concentration			Vial Anion Contents			
1 mg/ml	Before Adsorption	After Adsorption	Before Adsorption	After Adsorption	Vial Contents	Before Adsorption	After Adsorption	Anions per 1 gr.	Adsorbed per cm^2
			mg/ml	mg/ml	ml	mg	mg	mg	x 10^{-3}
27185	879	185	.00323	.0068	21.3	.069	.015	.0108	.0104
27185	524	353	.0193	.0130	21.6	.417	.281	.027	.026
27185	1018	796	.0375	.0293	21.7	.814	.636	.036	.035
27185	1539	1223	.0566	.0450	21.6	1.223	.972	.050	.048
27185	2054	1711	.0756	.0622	21.7	1.640	1.349	.059	.057
27185	6848	5969	.2520	.2195	21.4	5.392	4.697	.139	.134
27185	19536	18397	.7189	.6770	21.2	15.240	14.352	.178	.174
27185	25118	25096	.9235	.8337	21.2	19.578	17.674	.382	.369
11750	2210	1927	.1888	.1642	21.2	3.990	3.480	.102	.099
11750	1082	960	.0922	.0818	21.7	2.000	1.770	.046	.044
36238	24338	22913	.6721	.6327	21.1	14.181	13.350	.166	.160
35732	26539	24600	.7427	.6900	21.4	15.894	14.417	.295	.285
34165	17220	15945	.5042	.4674	21.5	10.836	10.004	.166	.160
34165	8392	7313	.2456	.2141	21.3	5.232	4.559	.134	.130
34165	10621	9514	.3109	.2778	21.3	6.622	5.917	.141	.136
34165	23026	21613	.6740	.6326	21.3	14.355	13.475	.176	.170
36386	28722	26891	.7894	.7390	21.4	16.893	15.815	.216	.208

TABLE III

SODIUM OLEATE ADSORPTION TEST RESULTS

SOLUTION pH 10.0

Counts per Minute			Solution Concentration			Vial Anion Contents		Anions Adsorbed	
1 mg/ml	Before Adsorption	After Adsorption	Before Adsorption	After Adsorption	Contents	Before Adsorption	After Adsorption	mg/gm	mg/cm^2
			mg/ml	mg/ml	ml	mg	mg	mg	x 10^{-3}
41855	1395	1189	.0333	.0284	21.1	.700	.600	.020	.019
41855	2797	2383	.0668	.0569	21.8	1.460	1.240	.044	.043
41855	5459	4890	.1304	.1168	21.5	2.800	2.510	.058	.056
41855	9416	8672	.2250	.2072	21.2	4.770	4.390	.076	.073
41855	25639	23988	.6126	.5731	21.0	12.860	12.030	.166	.160
41855	41855	39170	1.0000	.9358	21.4	21.400	20.030	.275	.266
41557	25843	24730	.5835	.6097	21.4	13.048	12.486	.112	.108
12808	1800	1650	.1405	.1288	21.5	3.022	2.770	.051	.049
12808	3576	3317	.2792	.2580	21.5	6.003	5.568	.087	.084
12808	5508	5227	.4300	.4081	21.7	9.332	8.856	.095	.092
12808	7267	6825	.5674	.5389	21.5	12.199	11.457	.148	.143
12808	8459	8074	.6605	.6304	21.0	13.869	13.238	.126	.122
12808	9484	8993	.7405	.7021	21.5	15.920	15.096	.165	.160
12808	11152	10539	.8707	.8229	21.3	18.546	17.528	.204	.197
12808	12505	11530	.9763	.9002	21.4	20.894	19.265	.325	.314

FIGURE 5

OLEATE SOAP ADSORPTION ISOTHERM

AT pH 10

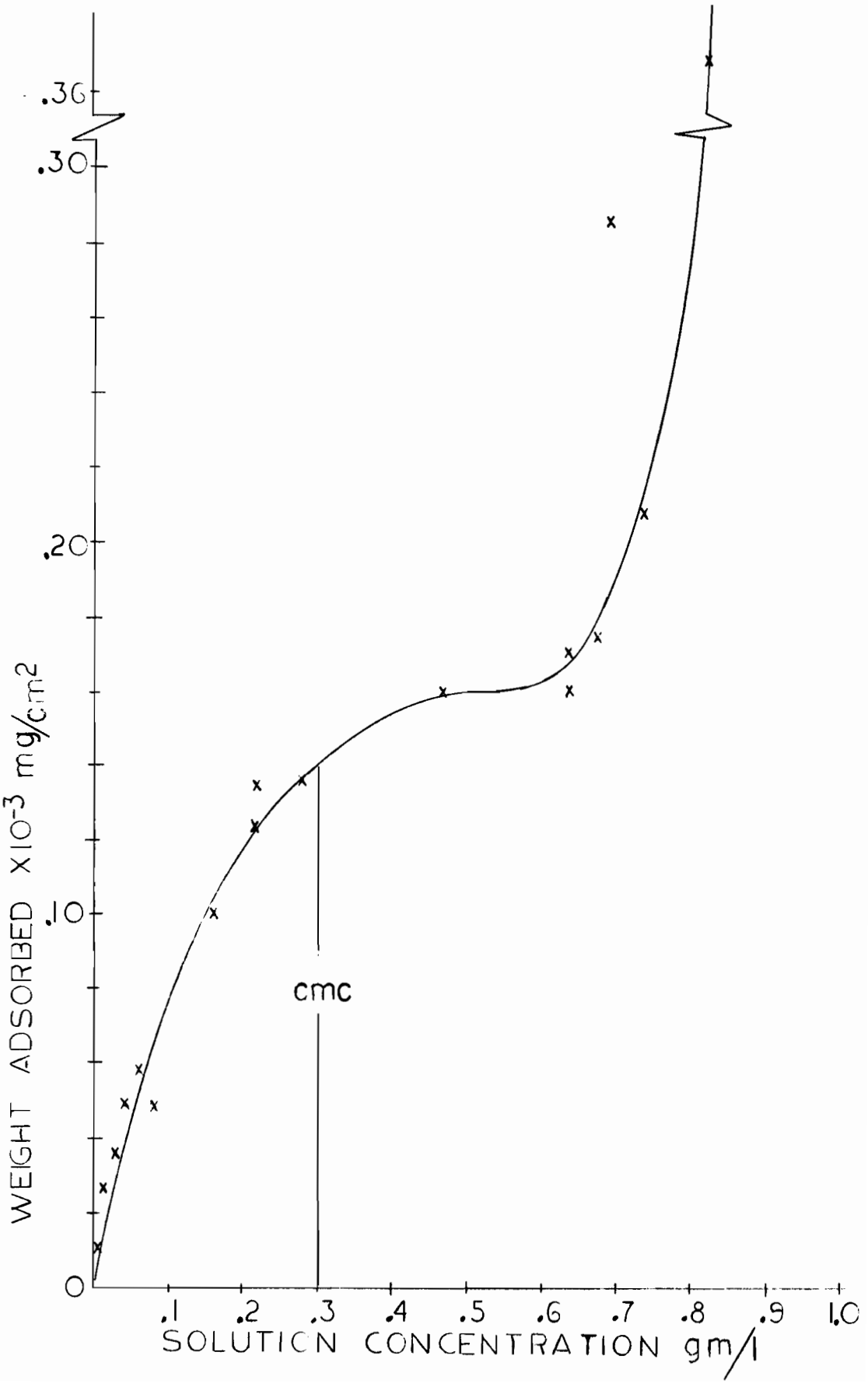
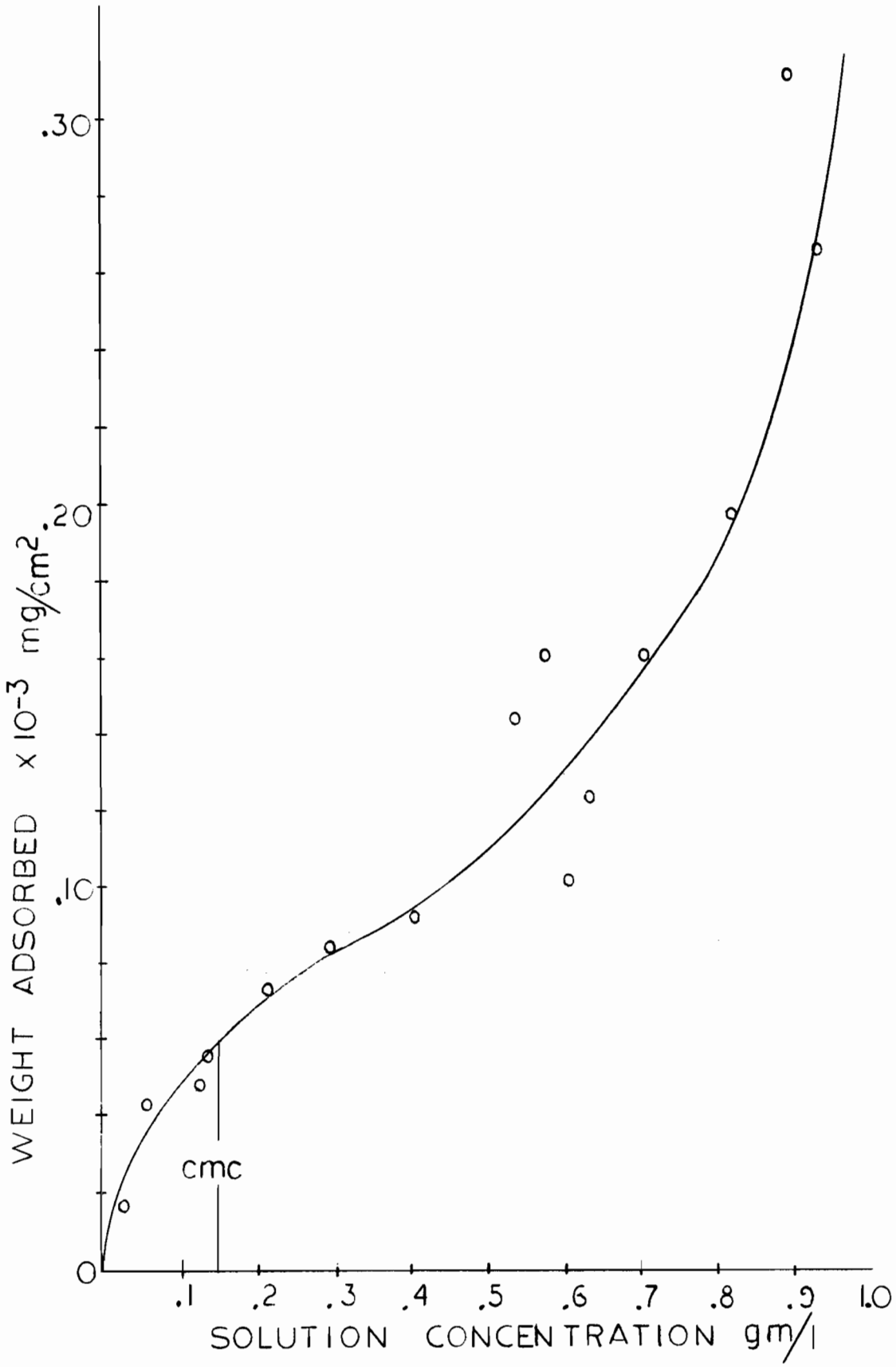

.30
.20
.10
0
WEIGHT ADSORBED X10-3 mg/cm2
cmc
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
SOLUTION CONCENTRATION gm/l

FIGURE 6

LINOLEATE SOAP ADSORPTION ISOTHERM

AT pH 10


.30
.20
.10
0
WEIGHT ADSORBED x 10-3 mg/cm2
cmc
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
SOLUTION CONCENTRATION gm/l

$$Fe(OH)_{3\ surface} + OH^- \rightleftharpoons Fe(OH)^-_{4\ aqua}$$

which has a considerable equilibrium constant, pK = 5, (45). The phenomenon could have been due to a secondary reaction between the negative complex and the dissociation products of the soaps.

Desorption

Tables IV and V summarize the results obtained in the desorption of oleate and linoleate soaps from hematite using water. The tests disclose that there are two stages in the desorption process. In the first stage, soap molecules or anions, at relatively high effluent concentrations, desorbed easily and in the second stage great difficulty was encountered in removing the adsorbate from the solids. For oleate adsorption, at pH of 10, 50% of the carboxyl groups were removed in a continuous test of 20 hours, and 60 hours were required to remove most of the balance from the solid. In the case of linoleate soap, 8 hours were required for the first stage desorption and 72 hours for the second. In both cases, to accelerate the desorption in the second stage, it was necessary to increase the pH of the solution to 11. This suggests that, during the first desorption stage, soaps which were physically adsorbed were removed whereas, in the second stage, carboxyl ions which presumably were attached more strongly to the Stern layer were desorbed.

Contact Angle Measurements

Contact angle measurements were taken on the freshly cleaved surfaces of relatively large sized hematite crystals.

TABLE IV

OLEATE ION DESORPTION

Step No.	Agitation Hours	pH	CPM of Effluent	Effluent Concentration gm/l	mg/gm Desorbed	Remarks
1	4	10	1673	.0490	.039	
2	4	10	984	.0288	.041	Steps 1 to 5, 5 gm. hematite treated
3	4	10	818	.0239	.038	Steps 6 to 12, 3.973 gm. hematite treated
4	4	10	431	.0126	.020	
5	8	10	522	.0153	.024	Stage 1 desorption
6	4	10	157	.0046	.007	Step 1 to 5 .162 mg/gm.
7	4	10	80	.0017	.003	
8	12	11	400	.0117	.071	Stage 2 desorption
9	8	11	94	.0027	.005	Step 6 to 12 .097 mg/gm.
10	8	11	32	.0009	.004	
11	8	11	29	.0008	.003	Left adsorbed on solids
12	8	11	34	.0010	.004	after desorption .002 mg/gm.
		TOTAL DESORBED mg/gm.			.259	
		Estimated Adsorbed by Liquid Scintillation Counting mg/gm.			.217	

TABLE V

LINOLEATE ION DESORPTION

Step No.	Agitation Hours	pH	CPM of Effluent	Effluent Concentration gm/l	mg/gm Desorbed
1	4	10	2117	.0484	.102
2	4	10	575	.0132	.028
3	4	10	381	.0087	.018
4	4	10	105	.0024	.008
5	4	10	39	.0009	.002
6	4	10	32	.0007	.002
7	4	11	94	.0022	.005
8-18*	44	11	44-10*	.0008-.0002	.013
19	4	11	11	.0003	.000
20	4	11	8	.0002	.000
		TOTAL DESORBED mg/gm.			.178
		Estimated adsorbed by liquid scintillation counting mg/gm			.166

* Sum of 11 desorption tests

Remarks

Weight of hematite treated 3.823 gm.

Stage 1 desorption
Step 1 and 2 .130 mg/gm.

Stage 2 desorption
Step 3 to 20 .048 mg/gm.

Left adsorbed on solids after desorption .002 mg/gm.

This method was specifically adopted to avoid the possibility of changing the adsorption characteristics of the hematite surfaces during mounting and polishing. The results plotted on Figure 7 are comparable to angles obtained by Taggard and Arbiter (50) for oleate soap. No comparable results were found for the linoleate soap.

A comparison between the two soaps is given in Table VI.

TABLE VI

CONTACT ANGLE VALUES OF SOAPS AT pH 10

	Oleate Soap	Linoleate Soap
Maximum contact angle	94°	110°
Solution concentration at maximum contact angle	.16 gm/l	.10 gm/l
Concentration limit of the bubble adherance	.20 gm/l	.40 gm/l

The results indicate that, beyond a certain collector concentration limit, no contact is established between the air and hematite.

Surface Tension Measurements

The effects of soap concentration on the surface tension of the aqueous solution are shown in Figure 8. With increased concentration, the surface tension drops rapidly for both soap solutions to a constant value of 20 dynes/cm for the linoleate and 5 dynes/cm for the oleate soap. The steady values of the surface tensions were obtained at the concentration of .15 gm/l and .30 gm/l for the linoleate and oleate soaps respectively. These values confirm those obtained by Buckenham

FIGURE 7

THE EFFECT OF SOAP ION CONCENTRATION
ON THE CONTACT ANGLE ON HEMATITE
AT pH 10

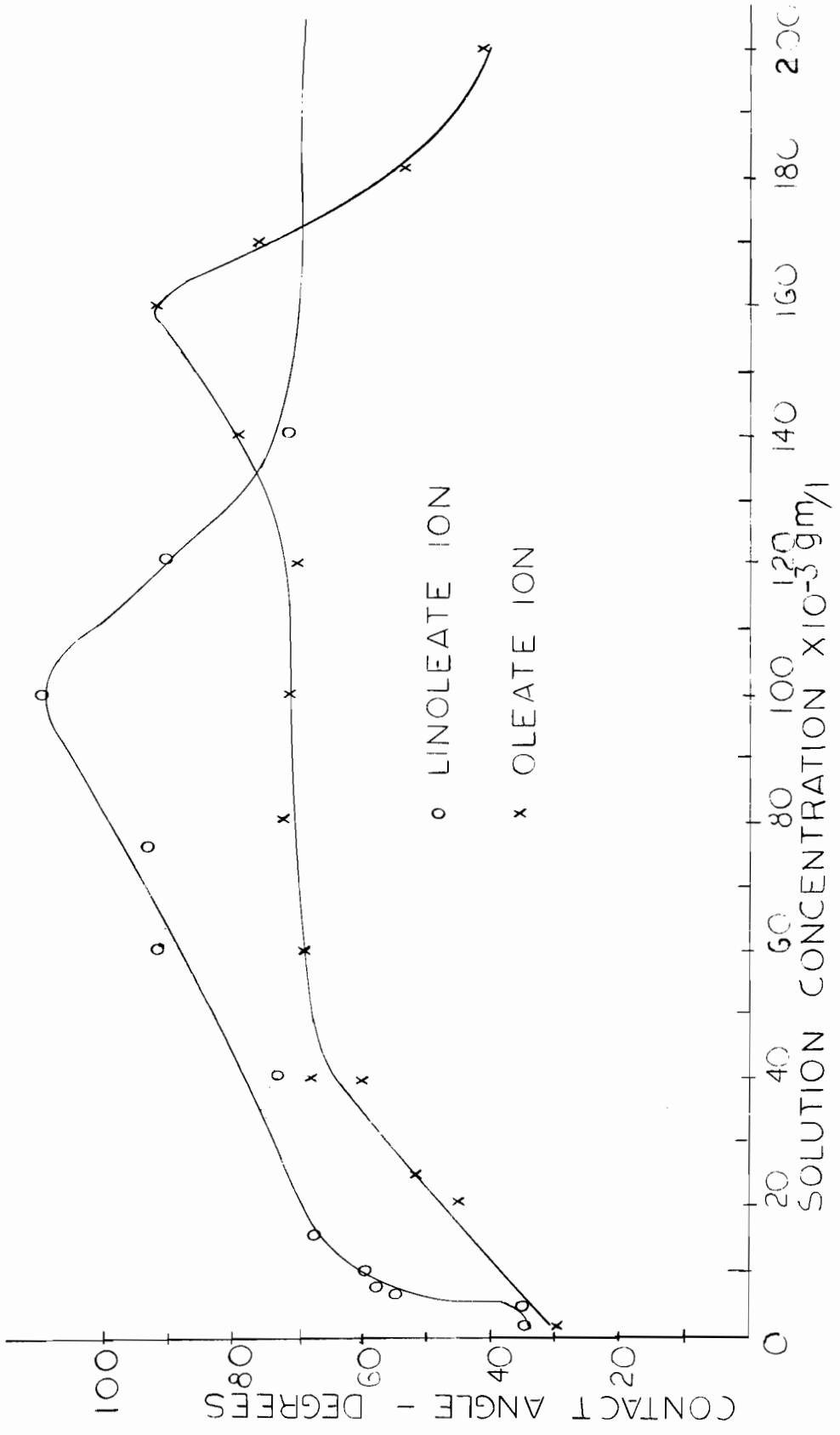
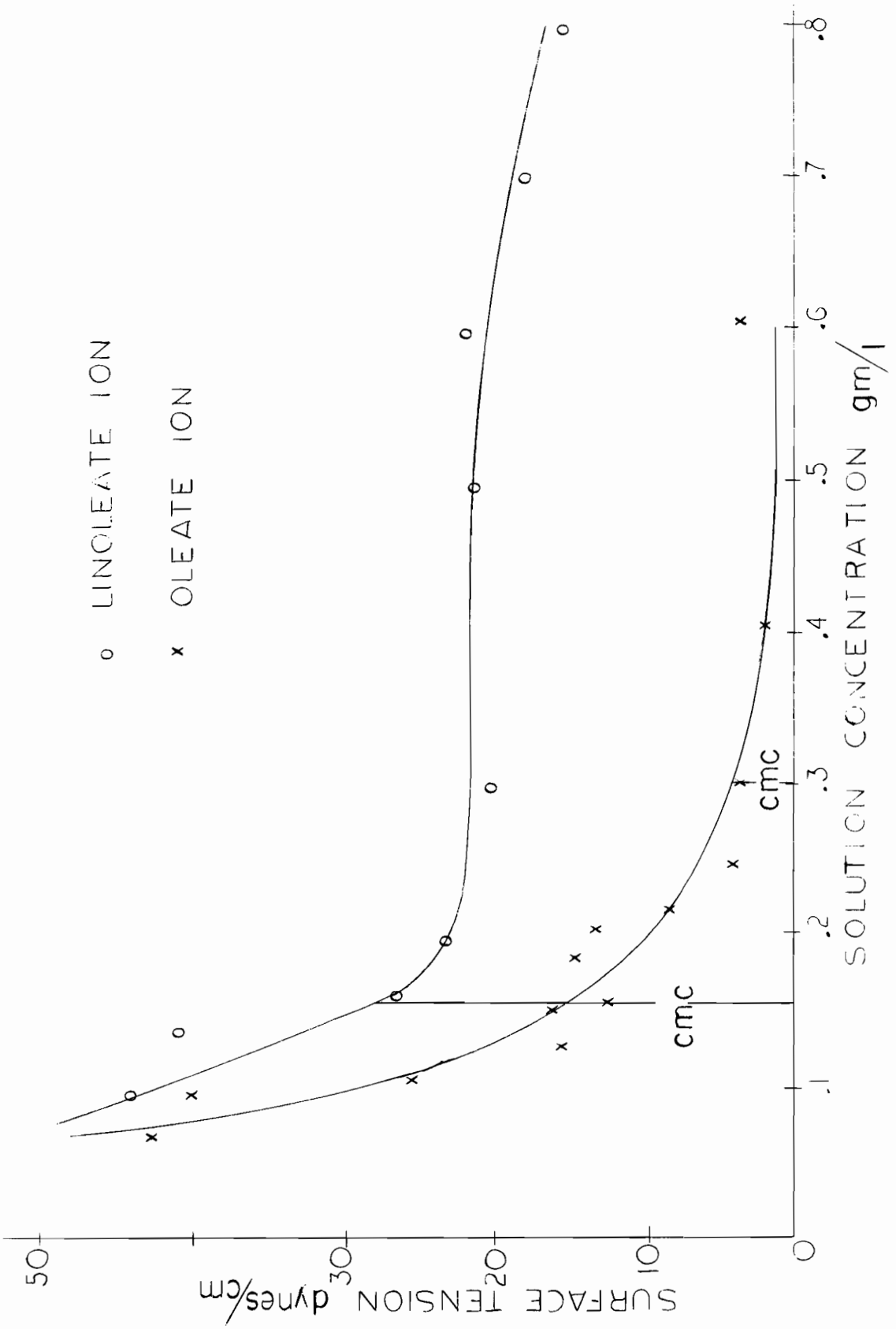

CONTACT ANGLE - DEGREES
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
SOLUTION CONCENTRATION X10-3 gm/l
o LINOLEATE ION
x OLEATE ION

FIGURE 8

THE EFFECT OF SOAP ION CONCENTRATION
ON SURFACE TENSION OF WATER
AT pH 10


o LINOLEATE ION
x OLEATE ION
SURFACE TENSION dynes/cm
SOLUTION CONCENTRATION gm/l
cmc
cmc
0
10
20
30
50
.1
.2
.3
.4
.5
.6
.7
.8

and MacKenzie (20) for the approximate collector concentrations at which micelles begin to form in appreciable quantities.

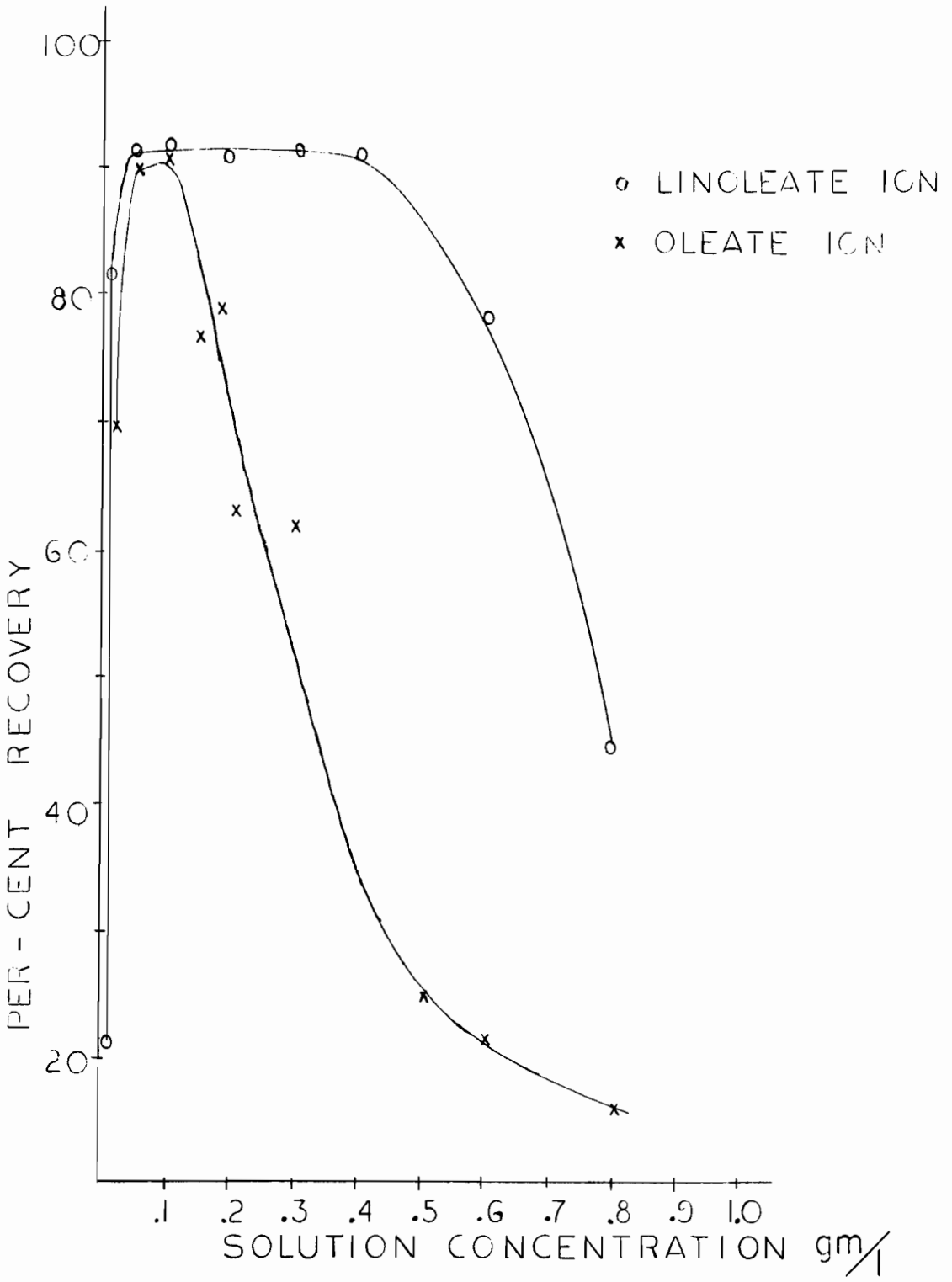
Flotation Tests

The flotation tests carried out in the Hallimond Tube show that maximum recoveries are obtainable at low soap anion concentrations. A plot of the solution concentration versus the percent recovery is shown in Figure 9. It indicates that the mineral recovery falls drastically in the case of oleate solutions of concentration higher than .2 gm/l. In the case of the linoleate soap a gradual drop in the recovery occurs at a much higher concentration of .4 gm/l.

FIGURE 9

HALLIMOND TUBE FLOTATION TEST RESULTS

pH 10


100
80
60
40
20
PER - CENT RECOVERY
o LINOLEATE ION
x OLEATE ION
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
SOLUTION CONCENTRATION gm/l

DISCUSSION OF RESULTS

The adsorption isotherms of oleate and linoleate soaps represented in Figures 5 and 6 show some similarities and their differences may be attributed to the effect of the extra double bond of the linoleic acid on the adsorption and the critical micelle concentration (cmc). At low soap concentrations, the slopes of both adsorption isotherms is high but it tends to decrease near the cmc. In the case of oleate soap, this is more pronounced, as the curve between the concentration of the cmc (.3 gm/l) and .65 gm/l tends to be almost horizontal, whereas, the linoleate soap curve assumes a constant slope of approximately 1 between the same concentration limits. When the concentration - contact angle curves (Figure 7) are compared, the linoleate soap has a higher contact angle on hematite (110^{o} versus 92^{o} of the oleate) at a lower solution concentration (.10 gm/l versus .16 gm/l) and after a 35^{o} drop between .10 - .14 gm/l its value remains constant up to the limit of bubble adherance at .4 gm/l. The contact angle on hematite in oleate soap solution drops 50^{o} between .16 gm/l and the limit of adherance at .20 gm/l.

The soap solutions can be considered completely dissociated to sodium cations and fatty acids anions and to behave at 1:1 ideal electrolytes in solutions more dilute than the cmc (52, 53, 58). Like all other surface active agents in aqueous solutions, these soaps are strongly polar. At gas liquid interface, the soap anions will orient their paraffin chain towards the gaseous phase and at liquid solid interface the hydrophillic carboxyl portions of the anions will be

attached to the polar sites on the solid leaving the paraffin chain portions oriented towards the water phase. When all the polar sites on the solid have been occupied, forming a possible monolayer, anions subsequently adsorbed, are said to be attached with the paraffin chains inserted between the chains of the monolayer, thus exposing the hydrophillic carboxyl parts to the aqueous phase (54).

Assuming a uniform coverage of soap anions on the surface of the hematite, subsequent layers of soap anions, adsorbed with a reversed orientation will cause a more hydrophillic surface. It follows that, when the monolayer is complete, the hydrophobicity of the surface is at its peak and that the larger the area occupied by the anion on the surface, the lesser is the quantity required to make the surface hydrophobic. Thus, a maximum contact angle is obtained at a lower surface adsorption density and a lower solution concentration in the case of linoleate soap. On the other hand, because of the tendency of the linoleate soap to form micelles is greater than that of the oleate, a smaller proportion of its anions will tend to adsorb to the surface with rising solution concentration past the monolayer capacity, making this soap effective as a collector over a larger range of concentrations. Therefore, it may be expected that the monolayer will be completed at a lower concentration of linoleate soap and that the surface will become hydrophillic at a lower concentration in the case of the oleate soap.

The following values are compared in Table VII: the areas occupied by oleic and linoleic acids on air water interfaces (21, 12, 46), their calculated surface densities when a uniform monolayer coverage is assumed, the respective equilibrium soap solutions concentrations to the adsorption isotherms, the contact angles and the flotation recoveries. Considering the contact angle measurements, the maximum flotation recoveries and the difficulty encountered in the removal of the soap anions in the second stage of the desorption tests, $47A^2$ for the oleate and $104A^2$ for the linoleate may be taken at the most likely areas occupied by each anion under the conditions of this investigation. The area of $47A^2$ was previously confirmed by Wilson, Miller and Roe (47) as being the most probable value for the area occupied by the oleate anion on latex. Unfortunately, no similar direct reference was found for the linoleate in the reviewed literature.

The zero point of charge of the natural hematite used in this investigation has been found to be at the pH of 8.5 (11) and, therefore, is negatively charged at the pH of 10. Thus, negative ions are observed to adsorb to a negative surface, with an appreciable proportion being firmly attached to the surface as indicated by the last stages of the desorption tests. A similar case was noted by Purcell and Sun (58) in their investigation of the zeta potential of rutile in aqueous solutions of oleate and linoleate soaps. It is likely that the adsorption occurs by an exchange mechanism between the hydroxyl and the carboxylic acid ions forming a monolayer and a subsequent adsorption in multilayers. The desorption of the multilayers

TABLE VII

MONOLAYER CAPACITIES ON HEMATITE

	Monolayer Acids on Water				Soap Anions	
	Oleic			Linoleic	Oleate	Linoleate
Limiting Areas A^2 *	56.6(46)	20.5(12)	25.2(12)	59.9(46)	47.0(47)	104.0
Monolayer Density $mg/cm^2 \times 10^{-3}$	.0826	.228	.184	.078	.0995	.050
Monolayer Density from Desorption Tests $mg/cm^2 \times 10^{-3}$					.099	.050
Soap Solution Equilibrium Concentration gm/l	.11	.76	.69	.27	.16	.10
Contact Angle, Degrees	73	nil	nil	72	92	110
Percent Flotation Recovery	90	17	21	92	75	92

* Bracket indicates reference number.

with ease and the monolayer with difficulty seems to suggest the possibility of physical non-selective adsorption in the diffused layer and a more selective adsorption on the Stern layer.

When the results of the adsorption isotherms are plotted on a logarithmic scale, the curves (Figure 10) show that up to the concentration range of .65 gm/l, the slope of the lower part of the curve is .5. An adsorption equation can be derived for the mode of adsorption in a manner identical to the one proposed by Gaudin and Morrow (51) for the lower part of the adsorption isotherm of dodecylammonium acetate on hematite and quartz:

$$\Gamma = K\sqrt{c}$$

where c is the solution concentration,

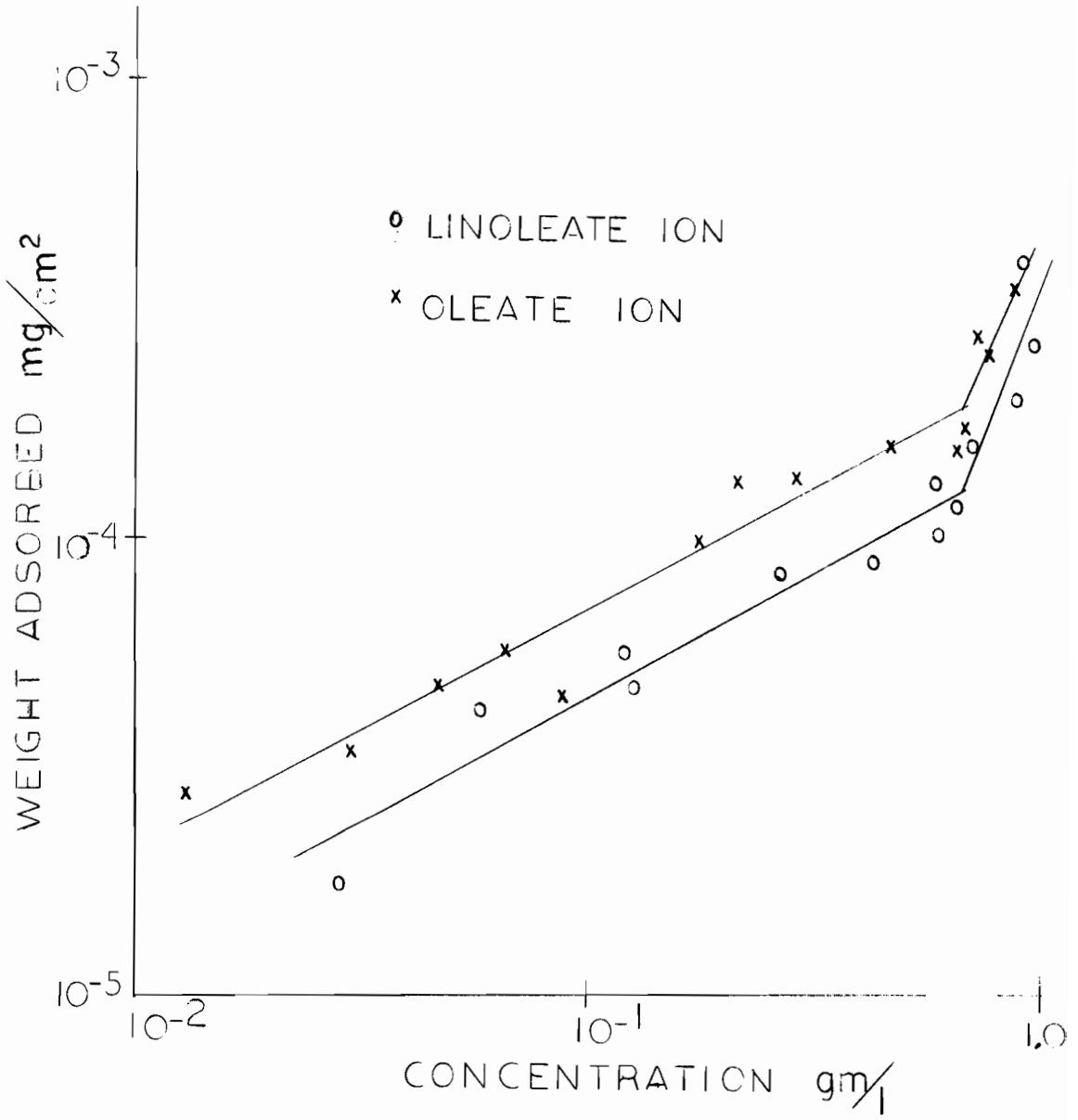
Γ is the adsorption density,

K is a constant.

At the concentration of .65 gm/l the curves on Figure 10 change their slope and the above equation is no longer valid. It seems that beyond this concentration anions no longer adsorb singularly at the liquid solid interfaces, as the adsorption is very large and the solution remains practically constant in concentration. A direct deposition of soap micelles probably occurs on the solid liquid interfaces. A similar case was noted by Vold (55) in his discussion of the adsorption of sodium dodecyl sulphate on carbon in solutions at concentrations higher than the cmc.

FIGURE 10

LOGARITHMIC PLOT OF THE ADSORPTION ISOTHERMS

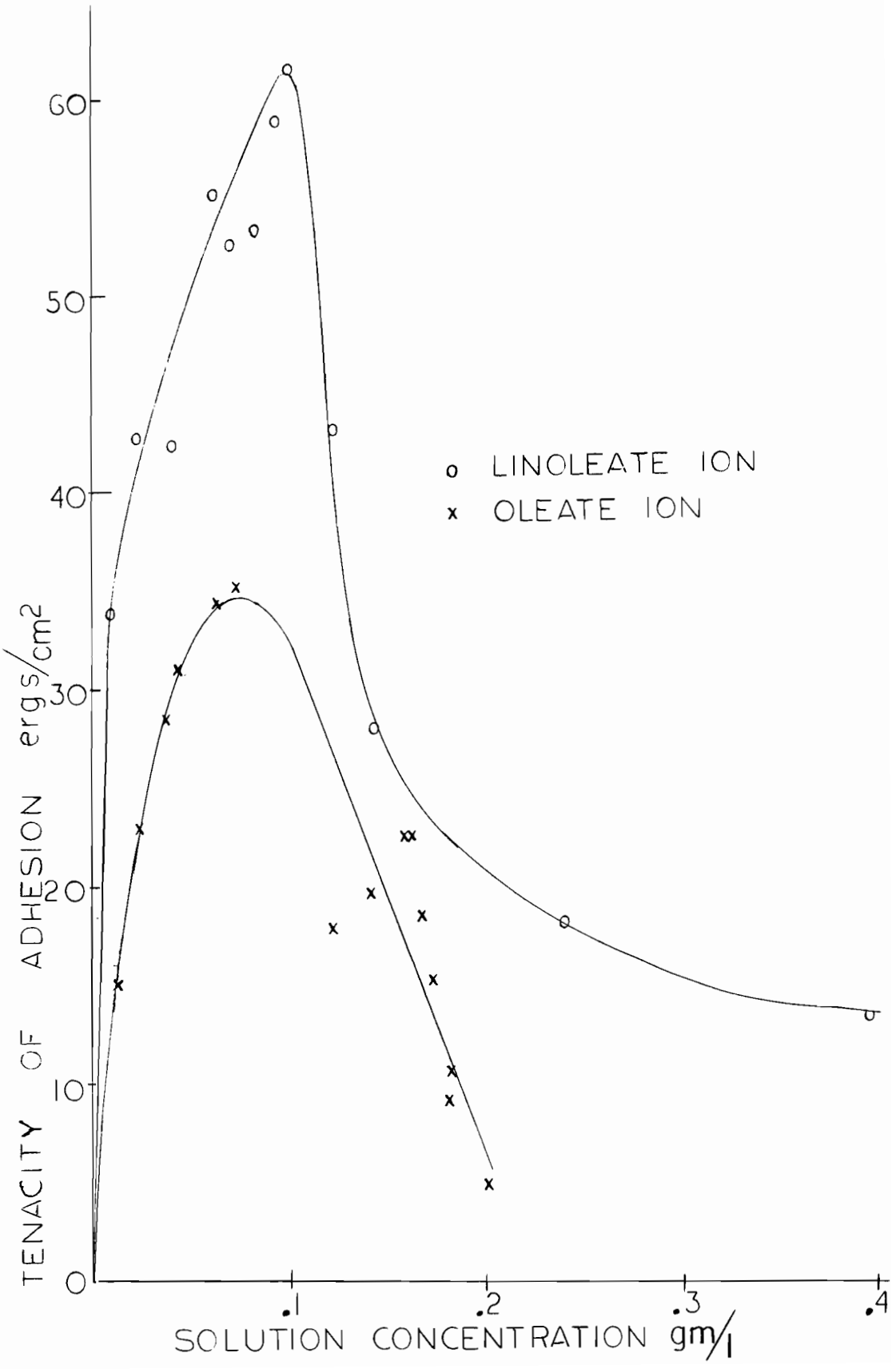

o LINOLEATE ION
x OLEATE ION
WEIGHT ADSORBED mg/cm²
10⁻³
10⁻⁴
10⁻⁵
10⁻²
10⁻¹
1.0
CONCENTRATION gm/l

The values of the work of adhesion W in ergs/cm^2, were plotted against the equilibrium soap concentration (Figure 11). The curve indicates a makedly higher tenacity of the air bubbles to the hematite in linoleate soap. It may be significant that the maximum of each curve occurs in both cases at the same concentration range of .1 gm/l, and that an abrupt drop in the value of W past that maximum occurs as the concentration increases. This steep decline corresponds to the drastic reduction at the same concentration range in the values of the solution surface tension (Figure 8). At the concentration range of .1 gm/l, the estimated monolayer capacity of the linoleate anion on hematite, the work of adhesion and the flotation recoveries (Figure 9) are at their maximum. At the estimated monolayer capacity of the oleate anion (.16 gm/l), however, the flotation recovery and the work of adhesion are lower than the maximum.

The marked differences in the features of the oleate and the linoleate solutions and their affect on the flotation of hematite can only be attributed to the existance of the additional double bond of the linoleate anion which renders it a better collector for hematite under the conditions of this investigation.

FIGURE 11

THE TENACITY OF AIR BUBBLE TO HEMATITE


60
50
40
30
20
10
0
TENACITY OF ADHESION ergs/cm²
o LINOLEATE ION
x OLEATE ION
.1
.2
.3
.4
SOLUTION CONCENTRATION gm/l

SUMMARY

The adsorption isotherms of oleate and linoleate soaps on hematite at the pH of 10 were determined and correlated with the effects of the cmc to the contact angle measurements and the floatability of the mineral. Also, by using the results of the desorption tests, an attempt had been made to determine the surface areas covered by each soap anion.

The following were the conclusions which were derived from this investigation:

(1) Maximum floatability under the conditions of the investigation occurred at soap anion concentration of .05 gm/l and, with increasing concentration of oleate anions, the floatability and contact angle of hematite rapidly decreased due to its high cmc. On the other hand, the same values for the linoleate solution over higher ranges of concentration, remained constant due to its low cmc.

(2) The linoleate soap was a better collector for hematite from the point of view of air-mineral tenacity and effective concentration ranges.

(3) The adsorption of the soap anions on the surface of the hematite was largely physical with the possibility of a more selective adsorption on the Stern layer.

Further investigation along parallel lines can be carried out to determine the effects of the solution pH on the adsorption of oleate and linoleate soaps to natural hematite. Very useful information of the possible separation methods of hematite from the associated gangue may be gathered by subjecting

minerals, such as, quartz for the same type of investigation and making a comparison between the adsorption isotherms at various solution conditions.

The adsorption of the carboxylic anions to the negative mineral surface by means of ion exchange needs further investigation. This may be accomplished by using tritiated heavy water as a tracer (42), a procedure similar to the one discussed for adsorption-desorption tests.

APPENDIX I

THE SURFACE AREA DEPERMINATION OF THE HEMATITE

THE SURFACE AREA DETERMINATION OF THE HEMATITE

The B.E.T. theory, developed by Brunnauer, Emmett and Teller (16) extended Langmuir's theory of monomolecular adsorption and rendered its usefulness in estimating surface areas of finely crushed solids. The derivation of the B.E.T. equation involves a detailed balancing of evaporation and condensation in adjacent layers and the assumption used is that in physical adsorption the forces of condensation are predominant in the adsorption of the first layer of molecules on the solids (21). The B.E.T. relationship is

$$\frac{P}{V_a\ (P_o - P)} = \frac{1}{V_m c} + \frac{(c-1)\ P}{V_m c\ \ P_o}$$

where V_a is the volume of gas adsorbed at the equilibrium pressure and temperature,

P is the equilibrium pressure,

P_o is the saturation pressure

V_m is the quantity of gas required to form a monolayer,

c is a constant.

Thus, when V_m is found and the average area occupied per adsorbate molecule is known, the specific area of the solid may be calculated.

For surfaces having a high constant (c) values, the B.E.T. plot passes through the origin of the P/P_o versus $P/V_a\ (P_o-P)$ plot and the slope is inversely proportional to the monolayer capacity V_a and thus one experimental point is required for the area determination (37). The full description of the apparatus, procedure and calculations are given elsewhere (48).

The experimental results were as follows:

(1) Free Space Determination:

Line	Gas	Burrette	Sample Stopcock	Pressure mm.	Temperature °C
1	He	3ȣ	Closed	86	20
2	He	2ȣ	Closed	139	20
3	He	2ȣ	Open	106	19
4	He	3ȣ	Open	72	19

The mercury density correction factor is:

$$\frac{Hg_{10}}{Hg_0} = \frac{12.5487}{13.5955} = .9966$$

$P_c = 106 \times .9966 = 105.6$ $\quad V = 24.197 \times \frac{86}{293.56} = 7.09$

$P_c = 72 \times .9966 = 71.8$ $\quad V = 14.93ȣ \times \frac{13.9}{293.56} = 7.07$

$F_s \quad \frac{1.67}{105.6} = .01581$

$F_s \quad \frac{1.13}{71.8} = .01574$

Average $F_s = .01578$ cc/mm Hg.

Observations and Calculations for V_a:

Line	Gas	Manometer mm.	P	P_o	P/P_o
5	Kr	70	1.49		
6	Kr		.95	2.50	
7	Kr			2.50	.3800
8	Kr	64		2.50	
9	Kr		1.65	2.50	.6600

Room Temperature 23°C.

Line 5: $V_D = V_t = .6633 \times \frac{70}{296.16} = .156ȣ$

Line 7: $V_s = P_c \times F_s \qquad P_c = .95 \times .9966 = .9468$

$V_s = .95 \times .9966 \times .01578 = .01494$ cc.

$V_{mc} = 32.6236 \times \frac{.01494}{296.16} = .00164$

$V_a = V_t - V_{mc} - V_s = .1402$

Line 8: $V_D = .6633 \times \frac{64}{296.16} = .1433$

$V_t = .1568 \times .1433 = .3001$

Line 9: $P_c = 1.65 \times .9966 = 1.644$

$V_s = P_c \times F_s = 1.644 \times .01578 = .02594$

$V_{mc} = 32.6236 \times \frac{.02594}{296.16} = .002858$

$V_a = V_t - V_m - V_s = .2713$

Legend:

F_s Free space factor

P_c Calibration pressure

V_t Sum total of all krypton additions

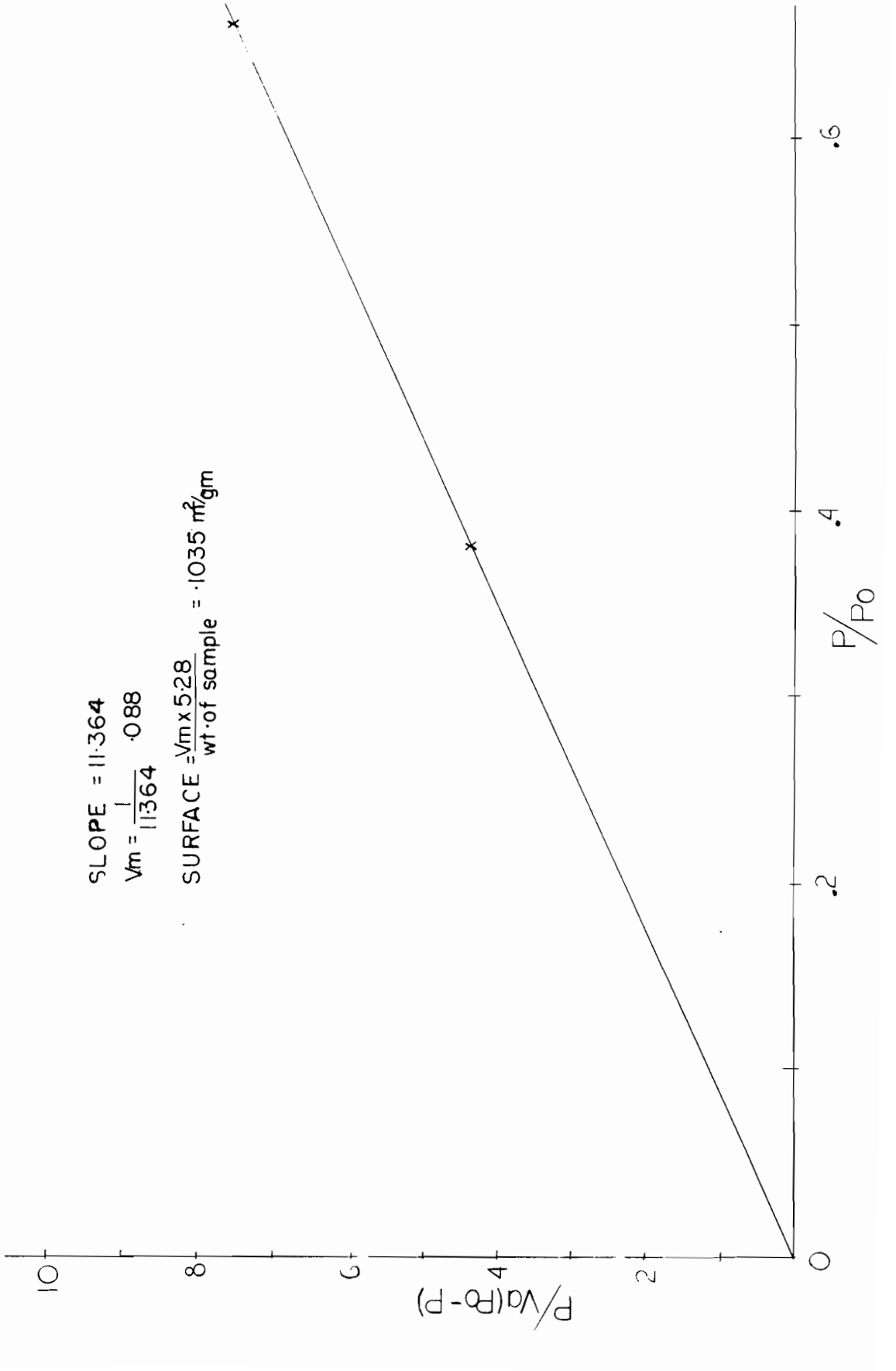
V_s Volume gas remained in the sample tube

V_{mc} Volume gas remained in the McLeod gauge

FIGURE 12

B.E.T. SURFACE AREA MEASUREMENTS

OF THE HEMATITE SAMPLE


SLOPE = 11.364
Vm = 1/11.364 = .088
SURFACE = Vm x 5.28 / wt. of sample = .1035 m²/gm
P/Va(Po-P)
P/Po
0
2
4
6
8
10
.2
.4
.6

APPENDIX II

SCINTILLATION COUNTING

SCINTILLATION COUNTING

The disintegration product of the labelled 1-c14 oleic and linoleic acid is β rays. When the compound is mixed with a suitable scintillation solution, these rays produce light flashes in the solution which can produce photoelectrons in a photosensitive electrode of a photomultiplier tube. The impulses recorded are directly proportional to the quantity of the active C-14 in the scintillation solution.

Since water of low soap concentration was analyzed for C-14, a dioxane base scintillation solution capable of dissolving 1 ml. of water was used. This system was recommended by Butler (42) and consisted of 1000 ml. of dioxane containing:

7 gm. of 2, 5 diphenyloxazole (PPO)

.05 gm. of 1, 4-bis-2-(phenyloxazolyl benzene) (PoPop)

120 gm. of naphthalene

For soap concentration determination, 1.00 ml. of labelled soap solution was pipetted into a scintillation vial containing 15 ml. of the solution and the count of disintegrations observed per minute (CPM) was recorded and compared with CPM observed in a solution of known concentration and radioactive activity. Thus, as the master solution was counted, a CPM count of each solution diluted from it enabled calculation of its soap carboxyl concentration.

In calibration of the Tri-Carb Spectrometer a simple procedure was followed which consisted of setting the freezer's temperature to a minimum limited by the scintillation solution freezing point (9 - 10°C. for the dioxane mixture used), then selecting the photomultipliers voltage and the discriminators settings. Selecting the photomultipliers voltage required counting an active vial of scintillation solution. The best photomultiplier voltage was set for maximum counting rate by trial and error. Subsequent to the voltage selection, the discriminators were set for the elimination of the background radiation count by substituting the active vial with a blank one containing 15 ml. of scintillation solution and 1 ml. of distilled water. Since not all the background radiation could be eliminated without reducing the counting efficiency, the soap concentration of each solution was determined using the formula:

$$\text{Concentration} = \frac{\text{CPM of sample} - \text{CPM background}}{\text{CPM of master} - \text{CPM background}}$$

For the determination of the amount of soap adsorbed on solid hematite a different procedure was followed. The solids for counting were dried at 75°C. in a steam oven and a .500 gm. was suspended in a toluene scintillation solution jellified with a thixotropic gel powder (43) in a glass vial. This scintillation solution consisted of 1 liter of toluene containing .1 gm. of PoPcp and 5 gm. of PPO and sufficient gel powder was added to keep the solids in suspension. The background count was done on a .500 gm. of unadsorbed solids suspended in this scintillation solution after the Tri-Carb

Spectrometer had been set for maximum counting efficiency as above. To determine the counting efficiency of the system, an amount of C-14 labelled toluene of known radioactivity was added to a blank vial, the background count of which had been predetermined. The counting efficiency of the system was therefore:

$$\frac{\text{CPM of Standard - blank CPM}}{\text{Disintegration rate of standard}} \times 100$$

In this case, the counting efficiency was determined to be 24%.

Since the counting efficiency of the liquid scintillation system was known (as it was determined in an identical manner) to be 60%, the amount of soap adsorbed on 1 gm. of solids was calculated using the relationship

mg. of soap anion adsorbed =

$$\frac{(\text{CPM of Sample - CPM of background}) \times .60 \times 2}{.24\ (\text{CPM of master - CPM of background})}$$

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