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THE NATURE OF MOLECULAR FILMS OF OLEIC ACID ON QUARTZ

BY

KENNETH L. KEATING

A

THESIS

submitted to the faculty of the SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

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1950

Approved by

Associate Professor of Mineral Dressing

Preface

Most investigators in flotation research, when studying the contact angles on reagent coated minerals, assume that a monomolecular layer of the collector "plates out" on the mineral surface if it is conditioned in a solution of the desired collector. Little mention is made of the fact that there might be more than a monomolecular layer, or possibly less. It is true that the surface is altered as shown by the change in the contact angle before and after treatment. This research was done in the hope that some proof or other enlightenment might come from an investigation of these molecular layers and there nature on a mineral surface.

It was the author's privalege a few years ago to witness a lecture-demonstration by Dr. Kathryn Blodgett on the application of monomolecular films to a glass surface. The possibility immediately presented itself that this might be a good method of checking the original hypotheses, namely, that of there being a monomolecular layer of collector on a mineral surface. Sometime later, it was observed in the flotation mill of the National Lead Company, Titanium Division, Tahawus, New York, that excessive amounts of oleic acid in the flotation circuit would "poison" the pulp to a point where recovery of the desired mineral was impaired. This phenomenon suggested that, possibly, a di-molecular layer was being formed on the mineral resulting in a polar outer surface instead of the desirable non-polar, air avid

surface.

With these observations in mind, a research topic was evolved concerning the general nature of these coatings and how they "appeared" on the mineral surface. Four techniques of attack presented themselves: (1) X-ray diffraction studies of these films; (2) Electron diffraction studies of the films; (3) Heat of reaction between reagent and mineral surface; (4) Film transference and ultimate contact angle measurement of the trasferred films.

The X-ray technique was abandoned when it was found that the panetrating power of the X-ray was too great to obtain a clear picture of these thin films.

The electron diffraction method offered a good possibility. Dr. N. S. Gingrich of the University of Missouri, Columbia, Missouri, confirmed the supposition that a diffraction picture could be made of a thin film, but stated that there would be no way of interpreting such pictures with our present knowledge. Furthermore, the work would have to have been done at Columbia where the electron diffraction instrument is available.

Measuring the heat of reaction of the collector "absorbing" on the mineral surface would have necessitated the building and calibration of an extremely sensitive calorimeter which would have left little if any time for experimental work.

Thus, the film deposition technique was adopted as the most plausible method of attacking the problem. The usefulness of this technique may seem vague, even though it is a better way of discovering more about the coated surface

with which the researcher deals.

The author wishes to express his gratitude to Professor A. Legsdin, thesis supervisor, for his aid and helpful suggestions while carrying out the work.

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Introduction

The purpose of this research was to show the nature of oleic acid on quartz mineral by transferring calcium oleate films, known to be monomolecular and of a definite orientation, to the surface of a piece of quartz, and measuring the resulting coated mineral by contact angle technique.

If a contact angle could be shown to exist for a monomolecular layer of collector on a mineral surface, it could
then be concluded that flotation could take place with only
enough collector to form a monolayer. On the other hand, if
a di-molecular layer showed no tendency to form a contact
angle, we could conclude that too much reagent would be
equally as ineffective as too little reagent.

Chemists have long been familiar with oil films on water and the pressures they exert. The literature has many examples where the chemist has measured this spreading force of floating oils and other organic liquids. Dr. Irving Langmuir, who has done some extensive work in this field, found that there were a large number of oils and fats which spread out to form extremely thin films of the order of 10⁻⁷ cm in thickness when placed on water. (1)

⁽¹⁾ Langmuir, I., Fundamental Properties of Solids and Liquids, J. Am. Chem. Soc., Vol. 39, p. 1863, (1917)

It was found that the general characteristics of all such substances is that they contain in their molecules certain

groups which have an affinity for water and are therefore called hydrophilic. The most common of these groups is the -OH group or the -COOH group. If such a group is substituted for one of the hydrogen atoms in the molecules of a pure hydrocarbon, the effect is to increase the solubility of the substance in water.

Langmuir reasoned that the substances that spread as thin films upon water, are substances whose molecules possess a composite structure with most of the molecule having little affinity for water, thus being hydrophobic, whereas, another portion of the molecular surface is hydrophilic. By spreading on the water surface, the molecules are able to arrange themselves so that the hydrophilic portion of each molecule comes into contact with water without bringing the hydrophobic portion into contact with water. In most of the fatty acids the -COOH group is at the end of a long hydrocarbon chain. Thus, when the molecules spread over the water surface they become arranged on the water with the heads (hydrophilic groups) in the water and their tails (hydrophobic groups) packed side by side above the layer that contains the heads.

Because of the affinity of the hydrocarbon parts of the molecules for each other, the molecules spread out on the surface of the water just enough to enable their heads to come in contact with the water. By measuring the volume of oil required to form a monomolecular film covering a given area, experimenters have been able to calculate the thickness of the film. The experimenters assumed this

thickness to be the length of the molecules since these are arranged approximately vertically in the film. The cross-sectional area of each molecule was calculated by knowing the number of molecules on the surface and measuring the area to which the film spread.

Through using this simple technique, experimenters have been able to calculate the shapes of many molecules of this type.

Langmuir found through his experiments that the area of a monomolecular film decreases elastically with applied force until it reaches a yield point at which the film crumples. (2)

(2) Langmuir, I., Two Dimensional Gases, Liquids, and Solids., Science, Vol. 84, p. 379, (1936)

The area decreases considerably with slight additions of force as the crumpled monomolecular film begins to form a double layer. With some films he achieved a second elastic range where, presumably, the double layer was being compressed to a yield point. The compression strength of a multilayer was not as great as that of a monomolecular film due to the complexity of bonding forces present in multilayer films.

Langmuir found the crumpling force for a single layer of cleic acid to be about 36 dynes/cm. (3) As the number of

⁽³⁾ Langmuir, I., Fundamental Properties of Solids and Liquids, J. Am. Chem. Soc., Vol. 39, p. 1865, (1917)

double bonds in the carbon chain is increased, the required compressive force is increased due, probably, to the adherence

of the more active chain to the water surface. The more active parts of the chain also decrease the ultimate compressive strength of their monomolecular films proportionally.

Langmuir (4) showed, in 1919, that a monomolecular oil

film could be deposited on a solid surface by dipping the solid beneath a water surface covered with a compressed monomolecular film and withdrawing the solid slowly. After the water peeled away from the solid surface, or evaporated, the oil film was left on the solid, with the molecules in the film retaining the orientation which they had on water.

This method has been developed further for depositing fatty acids on glass. (5) The most satisfactory experimental

⁽⁴⁾ Langmuir, I., Mechanism of Surface Phenomena of Flotation, Trans. Farad. Soc., Vol. 15, p. 62, (1920)

⁽⁵⁾ Langmuir, I., Fundamental Properties of Solids and Liquids, J. Am. Chem. Soc., Vol. 39, p. 1879, (1917)

procedure is that, in which water peels completely off the glass as the glass is withdrawn from the water-bath. This occurs when molecules of the fatty acid, which are spread on the water surface, leave the water and attach themselves to the edges of the glass slide as soon as one end of the slide emerges from the bath. Water then peels away from this coated area, and as the water recedes, the oil film soated area, and as the water is displaced.

Films which attach themselves to glass in the manner just described are formed only under special conditions. Fatty acids form these films if the film on the water surface is under surface pressure and the water-bath is slightly basic. Stearic acid gives excellent results used on an alkaline water-bath at a surface pressure of 20 dynes/cm.

Stearic acid may be deposited in successive layers, with the layers of odd number oriented with the -CH₃ groups away from glass, and the layers of even number with the -CH₃ groups toward the glass. The former orientation occurs when glass is raised through an oil film spread on water, and the latter when glass coated with a glass-adhering layer is lowered slowly through a similar film. As the glass is lowered, the film on the water surface attaches itself tightly to the slide, but since water makes a contact angle of approximately 90° with a coated slide, the film is turned upside down as the slide carries it down into the water. The phenomenon is striking when the motion of the film is observed by means of scattered talc particles. Blodgett has been able to deposit up to 300 layers on glass very easily by using this technique.

Films deposited on glass with the molecules oriented so that only -CH groups are exposed at the upper surface form a surface which water and oils will not wet. (6) Films

⁽⁶⁾ Blodgett, K. B., Deposition of Successive Monomolecular Layers, J. Am. Chem. Soc., Vol. 57, p. 1008, (1935)

oriented in the opposite direction with all -COOH groups

on the outer surface are completely wetted by water.

In this work, an attempt was made to use and apply Blodgett's technique in the deposition of monomolecular films of calcium oleate onto a quartz surface. In the field of mineral flotation, several experimenters have made the hypothesis that quartz will not float using soap unless the surface of the quartz mineral is first activated with multi-valent cations such as calcium, magnesium, aluminum, copper, iron, lead, etc. (7) If this be so, and all

⁽⁷⁾ Gaudin, A. M. and Rizo-Patron, A., The Mechanism of Activation in Flotation, Mining Technology, May, 1942

experimental evidence leads one to believe that it is so, a film of calcium oleate transferred to a quartz surface would have properties very similar to those of floatable quartz in a flotation machine, with one exception. The transferred film would have a known orientation on the quartz surface and, possibly, a known area concentration. In order to evaluate the surface, contact angle measurements would be made of single and multi-layered films.

Apparatus and Equipment

For the film deposition work a trough as described by Blodgett was made from an aluminum cake pan coated on the

(8) Blodgett, K. B., op.cit., p. 1010

inside with a thick layer of paraffin. The paraffin was necessary to keep aluminum ions from getting into solution and also to aid in the formation of a convex meniscus where the surface of the water touched the side of the pan. A waxed thread was placed across the center of the trough as suggested by Blodgett to keep the transfer film away from the oil used to maintain a constant pressure. Films were transferred by this apparatus and measured, although the method seemed to be crude.

A Cenco Hydrophil Balance (Fig. 1) was borrowed from the Chemistry Department of the Missouri School of Mines and Metallurgy and put into use. This apparatus is expressly designed for film pressure work and was much more amenable to the delicate work of transferring films.

The balance is made with fine hairs supporting the stationary barrier and strips of platinum foil sealing the spaces between the ends of the barrier and the sides of the trough. This arrangement was found unsatisfactory from the start and minor alterations were made in the instrument. The platinum foil was replaced by waxed hairs cemented on with Duco Cement. This arrangement was found satisfactory for the prevention of leakage of the film around the ends of the

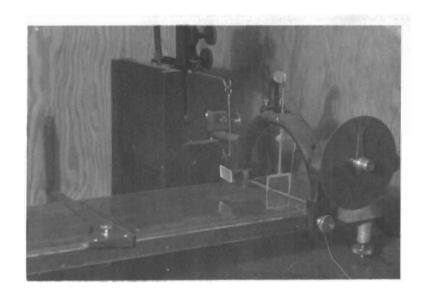


Figure 1

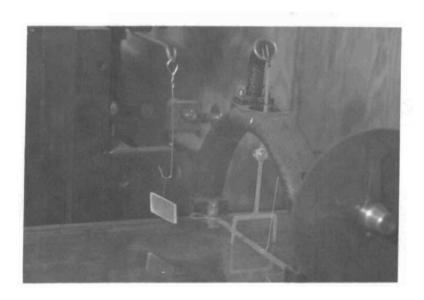


Figure 2

stationary barrier, but the hairs would frequently break or the cement would not hold, and a great deal of time was consumed in merely keeping the apparatus in running order. The waxed hairs were finally discarded and waxed thread used in their place. The thread was satisfactory as far as the film work was concerned, and it was more substantial so that several tests could be made without repairing the balance.

A dipping apparatus (Fig. 1) was made using a rack and pinion device to raise and lower the slide through the compressed film. For holding the quartz slide, a saddle of very fine stainless steel wire was made (Fig. 2).

Contact angles were measured in a conventional bubble machine as described by Taggart. (9) Accuracy was sufficient

⁽⁹⁾ Taggart, A. F., Handbook of Mineral Dressing, pp.19-176, Wiley and Sons, (1945)

to permit contact angle measurements to be made within one half of one degree.

Materials and Reagents

The oleic acid used in the experiments was Eastman Kodak Technical grade. This acid was of a clear, light amber color.

The stearic acid used was U.S.P. grade. This acid was in the form of white flakes.

The benzene used to make the dilute solutions of the fatty acids was U.S.P. grade.

A quartz crystal was cut and ground to dimensions 3.20 cm. long, 1.35 cm. wide, and 0.20 cm. thick. This gave a final surface area of 10.46 square centimeters. The final polish was done on a cloth wheel using alumina for an abrasive.

Tap water was used in all cases except where otherwise stated. The pH of the tap water varied between 7.65-7.7. The tap water furnished an abundant supply of calcium and magnesium ions with which the oleic acid formed the respective hard water soaps. Inasmuch as calcium ion was the most abundant ion in the tap water, the films are called calcium oleate films in the discussion to follow.

Procedure

Initial work was done in trying to duplicate the technique of Dr. Blodgett (10) by depositing calcium cleate films

(10) Blodgett, K. B., op.cit., p. 1010

onto a glass surface from the aluminum trough. A waxed thread was placed slack across the clean water surface and benzene solutions of oleic and stearic acids were placed on either side of the thread. A glass slide was passed through the calcium oleate film and a film was deposited. Contact angles were measured on this surface. It was later found that much more than a monolayer was floating on the water when deposition was made. Since more than a monolayer was deposited, the measurements were invalid. It was thought that the technique was faulty and so this method of film transfer was given up in favor of using the Cenco Hydrophil Balance. It is believed now that this method, if conducted correctly, possibly, is superior to the Hydrophil Balance method.

After obtaining and standardizing the Hydrophil Balance, experiments were begun to find the force required to crumple a monomolecular film of calcium oleate on water. Inconsistent values were obtained at first, but as skill developed crumpling pressures averaged between 27.5 and 32.5 dynes/cm (Fig. 3). This compared favorably with 36 dynes/cm as given in the literature.

⁽¹¹⁾ Langmuir, I., op.cit., p. 1879

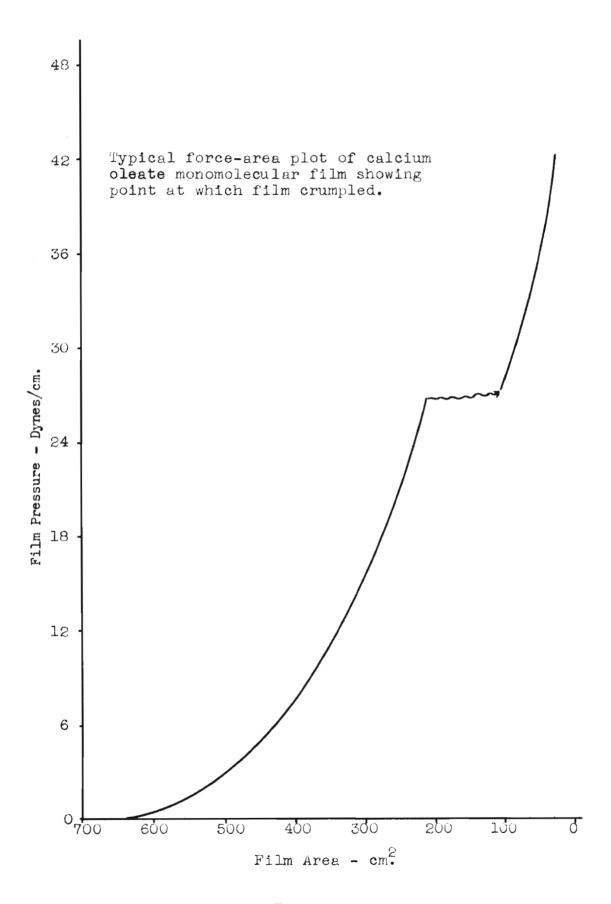


Figure 3

If a monomolecular film crumpled at pressures above 27.5 dynes/cm, all film transfer work would have to be done at pressures of 20 to 25 dynes/cm. With this in mind, an attempt was made to transfer a film to the surface of the quartz slide. The trough was filled with water and the surface was swept clean with chromium plated rods. The quartz slide. after being cleansed in hot cleaning solution, was placed in a stainless steel wire saddle and then immersed in the trough until covered by the water. A few drops of a benzene solution containing 0.1% oleic acid were added to the surface of the water between the two barriers (Fig. 1) and allowed to spread evenly on the surface. After giving the benzene a few minutes to evaporate, the movable barrier was closed upon the stationary barrier until the film began to exert a force against the latter barrier as evidenced by the indicating needle. At this point back pressure was begun on the stationary barrier in order to counter the force of the film. Thus, by skillful handling, it was possible to keep the film pressure balanced against this back pressure while decreasing the area between the two barriers. When the film pressure reached a value close to 25 dynes/cm the closing action was stopped, and the slide was slowly raised through the film. As the slide emerged from the trough, the pressure was seen to relax slightly, indicating that some of the film was being pushed off onto the slide. The slide emerged almost completely dry.

Contact angle measurements were made on the film covered slide immediately after it emerged from the trough. A technique differing slightly from that of Taggart and others was used to do this. Whereas, the more common way of measuring contact

angles is to submerge the solid in the water and bring the air bubble down to the solid surface, the method followed here was to place a drop of water on the surface of the air surrounded solid. Placing the quartz slide under water as in the former method would necessitate passing the slide through the surface of the water where the attached film might possibly be stripped off in the opposite way in which it was deposited. Therefore, it became necessary to keep the quartz slide in air and place a drop of water on its surface—the drop assuming the customary contact angle at the juncture of the air, water, and solid. The conditions of measurement are somewhat reversed, but as long as the angle is measured across the water phase, the resulting contact angle should be similar regardless of the method. The average contact angle of a monomolecular layer of calcium oleate on quartz was found to be 18.2°.

Using the same technique as that described for depositing a single layer, two, three, four, and five layers were deposited in succession, measuring the contact angle of each layer. Because the odd numbered layers were always formed by bringing the quartz slide up through the floating film, only the one, three, and five layer deposits were available for contact angle measurement in the bubble machine. The even numbered layers were formed by passing the quartz slide down through the floating film, and, therefore, these existed only under water. Contact angle measurements of two and four layer deposits were done beneath the surface of the water with the aid of a small dental mirror and an eye dropper. With the quartz slide lying on the bottom of the trough, the eye

dropper was brought down close to the quartz surface and an air bubble squeezed out. With the aid of the dental mirror it was observed that the bubble showed no affinity to the quartz surface for either the two or the four layer film deposit. Thus, it can be said that the contact angle for two and four layer deposits is substantially zero.

The average contact angle of three molecular layers of calcium oleate on quartz was 32.5° and for five molecular layers 33.5°.

In order to ascertain the adhesive power of multi-layered films to the quartz surface, tests were made passing
filmed quartz through a water-air interface, noting any
alterations of the film by contact angle measurements. The
quartz slide was raised and lowered through a floating film,
placing two layers on the quartz surface and ending under the
surface of the water. The water surface was then swept clean
with the chrome-plated rods and the slide raised through the
water-air interface. The average contact angle after such
treatment was 13.6°. When the same technique was used on a
four layered surface, the contact angle averaged 16.4°.

Discussion

From a comparison of the contact angle measurements made on the various layers of calcium oleate on crystalline quartz, it can be seen that a single layer has, roughly, half the water repellency of either three or five layers. (18.2° for a single layer, 32.5° for three layers, and 33.5° for five layers) Presumably, for all subsequent odd numbered layers the contact angle would not increase appreciably above that for five layers. Consequently, it may be assumed that for three and subsequent odd numbered layers the surface is saturated with non-polar ends of calcium oleate molecules. On an area basis the same amount of calcium oleate was removed by the quartz slide on the first, third, and fifth layers. Therefore, the difference in contact angle, and ultimately the wettability of the surface, cannot be attributed to area concentration. If the first and third monomolecular layers have the same area concentration, the only reason that can be given for their having different contact angles is that the orientation of some of the molecules in the first layer must be altered. For an explanation of this phenomenon it would be well to consider stepwise the construction of these films on the quartz.

Cooke and Digre (12) have shown that quartz abstracts

⁽¹²⁾ Cooke, S. R. B. and Digre, M., Studies on the Activation of Quartz with Calcium Ion, Transaction A.I.M.E.
Vol. 184, pp. 299-305 (1949)

calcium ion from solution, and that flotation with oleic acid is possible after calcium ion is abstracted from the solution. It has been proposed that calcium or other multivalent cations form a positive bridge between the negative partial valencies protruding from the quartz crystal lattice and the negative oleate ion. The number of oleate ions that are firmly bonded to the surface will depend upon the number of calcium ions underneath, and this in turn will depend upon the number of available partial valencies protruding from the crystal lat-The monomolecular film that was forced upon the quartz surface is a packed array of calcium oleate molecules, whereas the available bonding spaces are not continuous, but spotty. The resulting layer is likened to a crowded subway car carrying 100 people and supplying only 50 straps on which to hold. The 50 people who do not have straps from which to hang are very unstable just as the unbonded calcium oleate molecules are unstable in the packed monomolecular layer. The unstable molecules do not leave the surface because the first film exists only in air and there is no place for these molecules to go. By the time a second and a third layer is placed on top of them, the unstable molecules are sealed in place and they cannot dissolve away. The third layer of molecules is held in place by crystallographic forces shared between the second and third layers. Therefore, it is being held by more uniform forces than the first layer.

When a drop of water is placed on the first monomolecular layer for a contact angle determination, the environment of the surface molecules is changed. Evidently, the forces holding

the bonded calcium oleate to the quartz crystal are fairly strong as these molecules are unaffected by the water surroundings. The unstable calcium cleate molecules, however, are not bonded to the quartz surface and are free to react to any forces of attraction set up by the water phase. Inasmuch as carbon atoms are free to rotate about single bond linkages, it is possible for the unstable molecules to reverse their position in the film by having their ends double back on the oleate chain until the polar end of the molecule is outermost and in close proximity to the water phase. The water repellency of non-polar ends of the bonded calcium oleate molecules is somewhat moderated by the water avid character of these reversed molecules. Whereas paraffin has a completely non-polar surface and presents a 110° contact angle, the first layer on the quartz slide has a mixture of non-polar and polar molecule ends resulting in a greatly reduced contact angle (18.2°).

By the time three or more layers are built up onto the surface of the quartz, the forces holding the molecules in place are much more uniform and fewer molecules are reversed in their positions resulting in a greater contact angle than is measured for the single layer. There must be some molecular reversal in the third layer or else the contact angle would be the same as that measured for the completely non-polar surface of paraffin.

When the quartz slide carrying the two and the four layer deposit was raised through a clean surface of water, probably all of the calcium oleate was stripped off except for the firmly

bonded molecules on the quartz surface. All the other layers, including the unstable molecules in the first layer, left the slide as it passed through the water-air interface. Water molecules might have filled up the vacant spaces, resulting in a contact angle slightly less than that for a single, complete monomolecular layer.

In 1920, Langmuir (13) coated several mineral surfaces by

(13) Langmuir, I. The Mechanism of Surface Phenomena in Flotation, Trans. Farad. Soc., Vol. 15, p. 62, (1920)

the same technique as was used in this work to coat quartz. He did not go beyond a single layer, but he did show that the contact angle varied appreciably for the various minerals, proving that the contact angle for these monomolecular films is definitely a function of the solid under the film. The results of his work are tabulated here.

<u>Mineral</u>	Contact Angle
Mica	18•
Glass	45•
Platinum	65•
Calcite	70•
Sphalerite	82•
Galena	86•

The reason Langmuir gives for each mineral having a different contact angle is, that the number of unsaturated bonds available on each surface varies. Those molecules in the monomolecular film that are not rooted to an unsaturated bond are free to dissolve away when adjacent to a water phase. On an area basis there is, probably, a greater percentage of unsaturated bond positions on the galena surface than on any of the other minerals tested.

When a mineral is conditioned for flotation in the conventional way, it is recognized that the surface will not be covered by a complete monomolecular film as were the samples used by Langmuir and the quartz filmed in this research. Instead, a molecule is fastened onto the surface only wherever there is an unsaturated valence which the molecule can satisfy either alone, or by sharing.

Gaudin and his associates have shown by other methods (14)

that flotation collectors coat mineral surfaces in an incomplete monolayer. Through a geometric analysis of the atomic arrangements of both the mineral and the collector, Gaudin has shown that the collector molecules adhere to the mineral surface to form an orderly pattern with voids between the collector molecules. From an analysis of the data in this research, it would indicate that Gaudin is correct.

⁽¹⁴⁾ Gaudin, A. M. and Preller, G. S., Surface Areas of Flotation Concentrates and the Thickness of Collector Coatings, Mining Technology, May, 1946

Conclusions

From the data obtained from this set of experiments the following may be concluded to be true:

1. The contact angles measured for a quartz surface filmed with various layers of calcium oleate are as follows:

	Contact angle
One layer	18.2
Two layers	zero
Three layers	32.5
Four layers	zero
Five layers	33•5

2. By virtue of the difference in the contact angle of the first and subsequent odd numbered layers, and because approximately equal amounts (areas) of calcium cleate were present in each layer, it can be said that there was a distinct difference as to air avidity between the layer adjacent to the quartz surface and the subsequent odd numbered layers.

Postulates

From the data obtained in this set of experiments the following postulations may be made:

- l. Depending on the lattice structure of the quartz, certain molecules in the first calcium oleate layer are bonded to the quartz, while others are not. The latter molecules are free to respond to forces set up by their environment. When surrounded by water, they may turn about in their places, bringing their polar ends outward and they may possibly, dissolve away into the water phase. Thus, calcium oleate can exist on the surface of quartz in a spotty non-continuous layer during a flotation process.
- 2. Three and five layers of calcium oleate can be assumed to be nearly equally held to the second and fourth layers by crystallographic forces of the calcium eleate alone. They expose, therefore, a nearly continuous non-polar surface.
- 3. Two and four layers of calcium oleate can be assumed to be held in the same fashion as three and five layers.

 They expose a nearly continuous polar surface.

Discussion of Experimental Errors

Much difficulty was encountered in keeping the compressed film on the Cenco Hydrophil Balance from leaking around the ends of the barrier, despite the efforts taken to prevent it. This is the reason why no accurate data could be collected for the change in film area with film deposition on the quartz slide.

The much discussed technique of Patek (15) was used in

(15) Patek, J. M., Relative Floatability of Silicate Minerals,
A.I.M.E. Milling Methods, p. 486, (1934)

taking the contact angles. Critics have stated that his technique of using a dry surface and observing the contact angle of a drop of water placed upon the surface is open to contamination from the atmosphere. However, it is pointed out that the contact angle of a clean quartz slide remained zero even after thirty minutes exposure to the atmosphere. The conclusion that must be drawn is that the bubble machine used in this experiment is not accurate enough to detect such slight amounts of contamination.

Suggestions for Further Work

In regard to continuing experiments on transferring films to mineral surfaces, the next step might easily be the accurate determination of the amount of film per unit area transferred to the mineral surface. To avoid the difficulties encountered due to leakage with the Cenco Hydrophil Balance, it is suggested that the simplified balance used by Blodgett be tried again.

It would also be interesting to note how tenaciously the various films adhere to the surface if rinsed in clear water. As reported in the text of this thesis, this was tried on a restricted scale and only the firmly bonded first layer molecules seemed to remain on the surface.

The experimenter should be warned of the tedious and delicate technique that is required in this type of work.

Several attempts are usually necessary before a reproducable datum can be obtained.

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I was born in Chicago, Illinois on May 19th, 1923.

I attended the Proviso Township High School in Maywood,
Illinois (a suburb of Chicago) and graduated in June, 1941.

In September, 1941, through the aid of a scholarship, I enrolled at the Massachusetts Institute of Technology,
Cambridge, Massachusetts and began to study metallurgy.

My education at MIT was interrupted in 1944 by military service and resumed in 1946, so that I graduated in February,
1947. After graduation, I assumed duties as a Research
Assistant on the MIT Staff, working under Professor A. W.
Gaudin on flotation research.

I left MIT in September, 1947, to take a position as assistant Metallurgist for the National Lead Company, Titanium Division, Tahawus, New York. One year later I left the National Lead Company to come to the Missouri School of Mines and Metallurgy for graduate work. In September, 1949, I became an Instructor of Metallurgical Engineering in this School.

My present plans are to continue graduate study working toward the degree of Doctor of Philosophy in Metallurgical Engineering. I then hope to continue teaching extractive metallurgy.

Limital Lee Lealing