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KINETICS OF OLEATE ADSORPTION AT THE LIQUID/AIR INTERFACE AND ITS ROLE IN HEMATITE FLOTATION

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Dynamic surface tension properties of potassium oleate solutions have been investigated as a function of *p*H, surfactant concentration, ionic strength, and temperature in order to establish the role of these properties in determining the flotation response of hematite using oleate. Correlation of the results suggests a major role of the collector adsorption on the bubble and the related kinetics in determining the flotation response. Also, the role of oleate solution chemistry is examined as a function of *p*H. Maximum flotation response is found to occur under conditions of acid-soap formation.

Flotation of mineral particles is the result of adherence of air bubbles to the particles with which they come in contact in the flotation cell. In the past such adherence has been described to take place if the surface of the particle is naturally hydrophobic or if the surface is at least partially converted to that state owing to the adsorption of reagents that contain nonpolar parts. The role of the adsorption of these reagents on the bubble surface has been considered only rarely for interpreting the froth flotation behavior of minerals (*1* to *6*). It was proposed that the collector ions adsorbed on the bubble, in significantly larger amounts than on the solid/solution interface according to certain semi-empirical models, can migrate to the solid/gas interface upon contact with a charged mineral particle in order to satisfy the charge balance requirements at the interface and thus reduce the induction time sufficiently to cause attachment of the bubble to the particle and subsequent flotation (*1*). On the other hand, if the mineral surface and the bubble surface are similarly charged or if the mineral surface is fully covered with the collector, such adsorption at the bubble surface can increase induction time. It is thus important to consider that adsorption at the solution/gas interface in addition to that at the solid/liquid interface when studying froth flotation mechanisms.

Most importantly, however, it should be recognized that, at its time of contact with a mineral particle in the flotation cell, a bubble is only a fraction of a second old and adsorption on its surface can be different from that determined under equilibrium conditions. It therefore becomes necessary to determine the rate of collector adsorption on a fresh surface to establish the role of adsorption on the bubble in froth flotation. In this study we have examined the role of this adsorption and the kinetics involved by determining the dynamic surface tension of oleate solutions and flotation obtained using these solutions at various levels of collector concentration, *p*H, ionic strength and temperature.

The flotation characteristics of hematite using oleate have been studied in detail in the past (7 to *17*). It is reported that good flotation is obtained in the neutral *p*H range. The mechanism of this flotation is not, however, clearly established. Chemisorption of oleate on hematite has been proposed to be the major factor causing the flotation. However, there is no direct evidence to support such a mechanism. It must be noted that the dependence of flotation on *p*H can be due to the effect of *p*H on the surface characteristics of hematite in water as well as that on the oleate solution chemistry. The point of zero charge of massive hematite is reported to be around *p*H 4.5 to 5.0 (*18*). The sample used here did, however, seem to posess a lower point of zero charge (*19*) possibly due to the presence of finely dispersed silica in it. The effect of *p*H on the state of oleate in solution is significant. Under alkaline conditions oleate is present in solution in ionic form. Upon decreasing the *p*H, its state changes continuously from that of oleate to that of oleic acid (mostly precipitated)

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through an intermediate state of acid-soap. Furthermore, the hydrolysis of potassium oleate and acid-soap formation is expected to be a function of ionic strength and temperature. This *p*H-dependent surfactant characteristic can possibly influence the mineral flotation response. In this paper, this aspect of oleate flotation of hematite also will be discussed.

EXPERIMENTAL

MATERIALS

Massive red Minnesota hematite supplied by Wards Natural Sciences Establishment was used for flotation studies. The hematite was found to be 94% pure with quartz as the major impurity. The samples for flotation were prepared by crushing and sieving.

Oleic acid used was supplied by the Applied Sciences Laboratory in a number of sealed ampoules. It was specified to be 99+% pure and was used without further purification. The ampoules were kept refrigerated until use. A stock solution of 7.5 × 10^{-4} mole/liter potassium oleate was prepared by dissolving oleic acid in deaerated water containing potassium hydroxide to maintain a *p*H of 11.2 after saponification. This stock solution was stored at 2°C under nitrogen. Storage under nitrogen was found necessary in order to avoid any slow oxidation of oleic acid and consequent poor reproducibility. All the other chemicals used were Fisher's certified chemicals. Water triple distilled in a pyrex still and collected and stored in teflon bottles was used for making the solutions.

FLOTATION

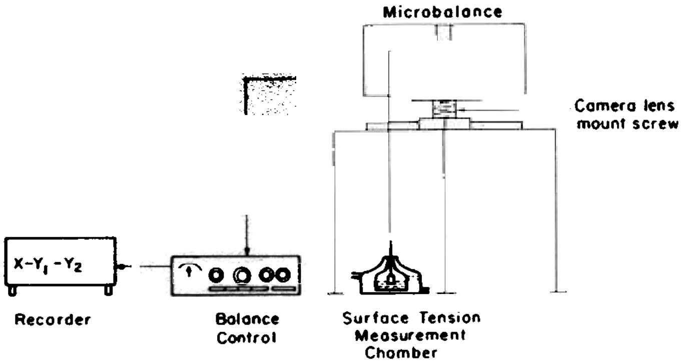
The flotation experiments were done in a modified Hallimond cell apparatus described elsewhere (*20*). A special feature of this apparatus is the automatic control of gas flow and stirring which yielded reproducible stirring rate and flotation time. For flotation tests, 0.8 g of 100 × 150 mesh size hematite was first deslimed till free of visible fines and then conditioned. This was done by transferring the deslimed hematite into a graduated cylinder containing 100 ml of the oleate solution at the desired *p*H and ionic strength. The cylinder is kept in a constant temperature bath for 10 min for the pulp to attain the bath temperature. The pulp is next agitated for 10 min at that temperature and then left unstirred outside the bath for 10 min for cooling to room temperature. The *p*H is then measured and the pulp is transferred to the Hallimond cell for flotation for 10 s at a nitrogen flow rate of 20 ml/min.

SURFACE TENSION

A dynamic surface tension-measuring technique was developed utilizing the Wilhelmy plate method and a microbalance (*21*). The cell containing the test solution is jacketed for circulation of water at the desired temperature (see Figure 1). A hole was provided on the side of the cell at a level above the solution in order to remove surface layers using a capillary connected to an aspirator and thereby to create a nascent surface. In order to test the nature of the contact of the solution surface with the sensor, the balance was mounted on a camera screw ring enabling smooth raising or lowering of the sensor. The output of the microbalance is fed to the Y-channel of an X-Y recorder with the X-axis for recording aging time.

In a series of tests to check the possible effects of air on the surface tension decay rate, an atmosphere of nitrogen was maintained above the solution in the cell. The solution itself was made using deaerated water.

For measurements of surface tension decay as a function of time, a thin surface layer is removed by suction and the surface tension recording is begun at the end of suction. The recording directly yields surface tension versus time plots. During the test it is necessary to ascertain the absence of air bubbles at the interface particularly near the sensor. It is also necessary to deaerate the test solution before use in order to prevent the evolution of bubbles during experiments at non-ambient temperatrues. The suction was uniformly applied for 30 s in all cases even though the surface tension values for pure water were obtained in less than 10 s. Repeated recordings followed by suctions obtained for most test solutions showed the reproducibility to be satisfactory.



'ig. A schematic diagram of the setup for surface tension measurement.

RESULTS

FLOTATION

Typical results obtained for the oleate flotation of hematite as a function of *p*H are given in Figure 2 for three oleate

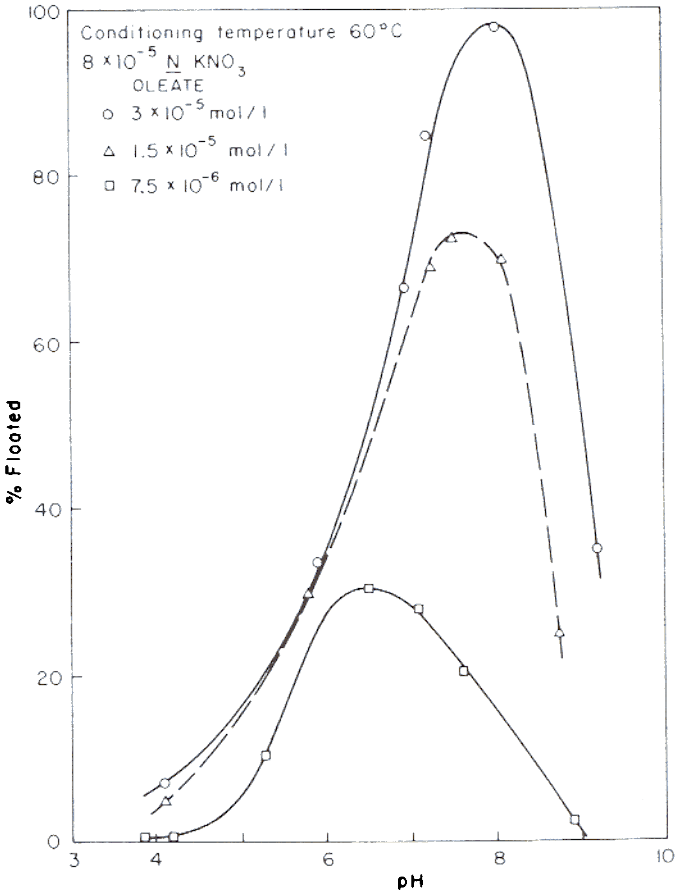


Fig. 2. Hematite flotation as a function of *p*H at different oleate concentrations.

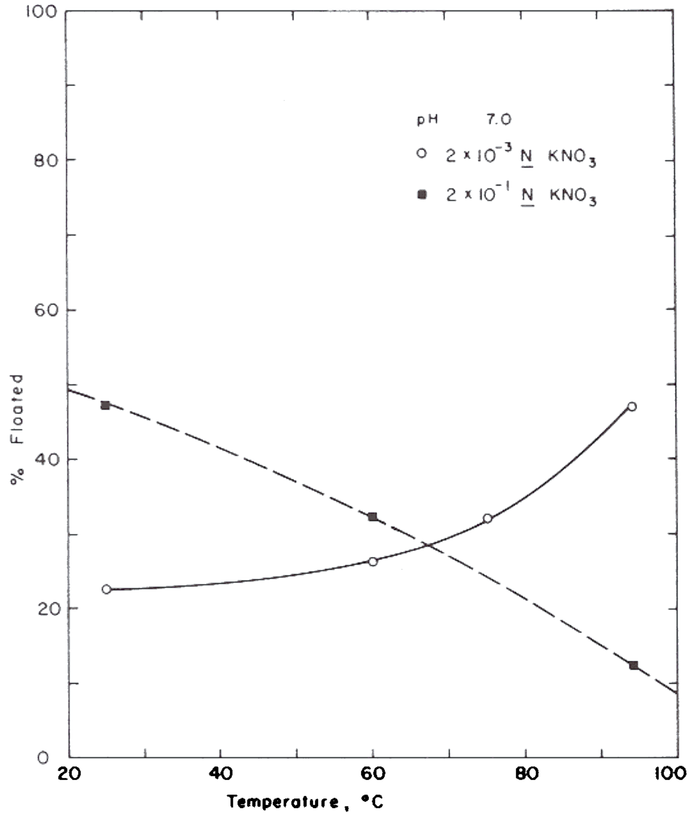


Fig. 3. Diagram illustrating the effects and interactions of conditioning temperature and ionic strength on hematite flotation using potassium oleate.

concentrations. KNO_3 concentration was maintained in this case at 8 X 10^{-5} N and the pulp was conditioned at 60°C. Flotation was done in all cases at room temperature. As reported in earlier literature (*7* to *16*) hematite flotation is highly sensitive to *p*H with maximum flotation around neutral *p*H. The effect of the conditioning temperature and ionic strength on the oleate flotation was described earlier (*22*). Typical results to show the effect are given in Figure 3. It was found that as the conditioning temperature was increased the flotation recovery increased significantly under low ionic strength conditions. Under high ionic strength conditions (above 10^{-2} N) the reverse effect was observed, the reasons for which are currently under investigation.

SURFACE TENSION

The results obtained for the dynamic surface tension of 3 X 10^{-5} mole/liter potassium oleate solutions at various *p*H values are shown in Figure 4. Effect of solution temperature and ionic strength on the nature of surface tension decay is illustrated in Figure 5. It is evident that the kinetics of surface tension lowering is highly sensitive to both ionic strength and temperature.

The surface tension curves in general exhibit three distinct regions. Region I in which there is negligible surface tension decrease, Region II characterized by a linear decrease in surface tension with time, and Region III characterized by an exponential-type decrease. While all the three regions exist at lower *p*H values, the plots for higher *p*H values are shown to exhibit only the latter regions. Also, the solutions attain equilibrium surface tension in a finite time which is dependent on the solution *p*H, temperature, and ionic strength.

The extent of maximum surface tension lowering obtained is dependent significantly on ionic strength and temperature. The effects are clearly seen in Figure 6 and 7 in which the equilibrium surface pressure (surface tension lowering) is plotted as a function of *p*H at two ionic strength conditions and two temperatures. At all *p*H values, an increase in ionic strength is found to yield increased surface pressure. Also maximum surface pressure is produced in the neutral *p*H range. The effect of temperature is seen to decrease the equilibrium surface pressure below about *p*H 8 and to increase it in basic solutions.

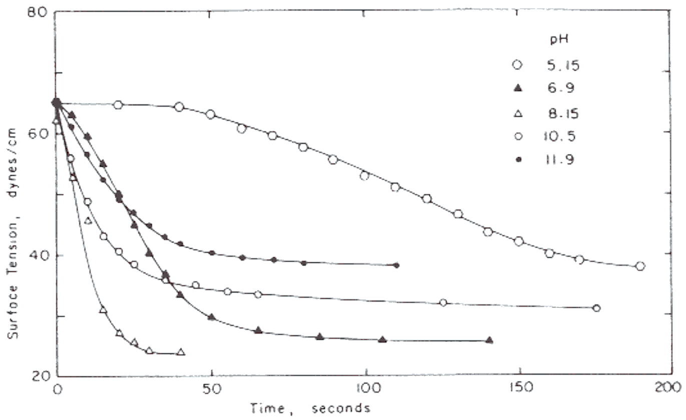


Fig. 4. Surface tension decay characteristics of 3 X 10^{-5} mole/liter potassium oleate solution at various *p*H values at 75°C. Supporting electrolyte is KNO_3 at an ionic strength of 2 X 10^{-1} N.

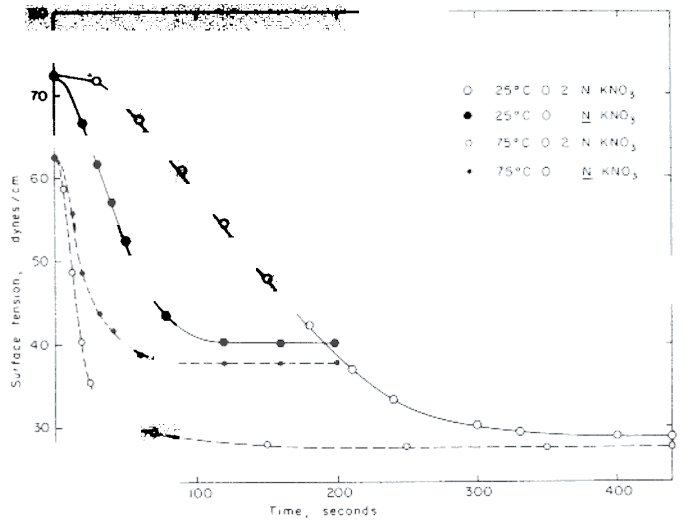


Fig. 5. Effect of temperature and ionic strength on the surface tension decay characteristics of 3 X 10^{-5} mole/liter potassium oleate solutions at *p*H 8.2.

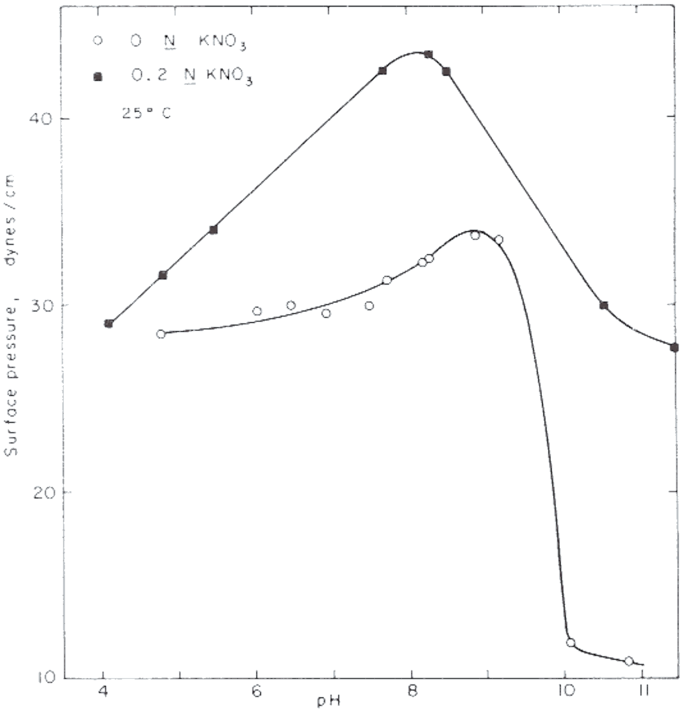
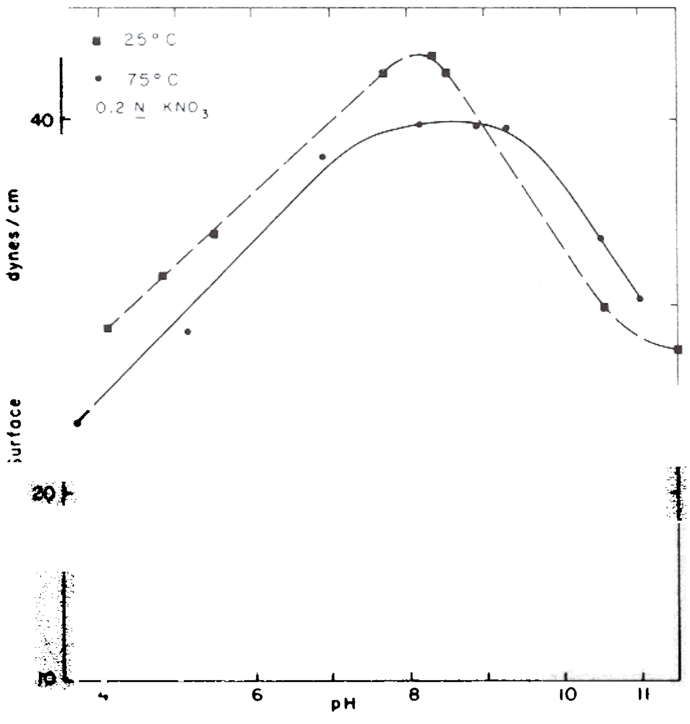


Fig. 6. Effect of ionic strength variation on the final surface pressure of 3×10^{-5} mole/liter potassium oleate solution at 25°C.



Effect of temperature on the final surface pressure of 3×10^{-5} potassium oleate solution. Supporting electrolyte is KNO_3 at an ionic strength of 2×10^{-1} N.

DISCUSSION

The results for the dynamic surface tension of potassium oleate solutions show the dependence of both the lowering of surface tension and the rate of lowering on the various solution properties such as *p*H to be complex. The effects are in several ways as complex as that obtained for flotation (*22*). The complex surface tension effects are mainly the result of the changes produced in the chemical state of the fatty acid with change in solution *p*H. As the solution *p*H is lowered from basic values, in addition to the hydrolysis of oleate, complex formations also take place in a certain *p*H range. The hydrolysis that occurs when the *p*H of the aqueous solutions of the fatty acid salt is decreased leads to the formation of oleic acid, which due to its very low solubility precipitates in the form of fine dispersions. The amount of fatty acid salt present in the system therefore continuously decreases as the *p*H is decreased and the amount of precipitated fatty acid increases. This is further complicated by the formation of complex species in the intermediate *p*H range due to the association between the fatty acid molecule and its salt (*23*). These complexes known as acid-soaps exist in significant amounts around neutral *p*H and evidently are much more surface active than the other forms of oleate. The surface activity and the rate of transport to the surface as well as the effect of ionic strength and temperature on these properties can be expected to be different for various chemical forms of fatty acid. Major factors governing transport to the interface, in addition to any electrical barriers, are penetration into the monolayer and reorientation of the species in it (*24*). It has been recognized that for long chain fatty acids simple diffusion theory will not explain the dynamic surface tension results (*25*). The extent to which the transport of oleate, oleic acid, and acid-soap is governed by each of the above factors will determine the dependence of dynamic surface tension behavior on *p*H and on other solution properties, particularly ionic strength and temperature. The possible effect of impurities in the surfactant on the rate of surface tension changes must be noted at this point. The discussion of the transport of the fatty acid species to the interface and the model developed for this transport will be appropriately described in other publications.

CORRELATION OF OLEATE FLOTATION OF HEMATITE AND DYNAMIC SURFACE TENSION PROPERTIES OF POTASSIUM OLEATE SOLUTIONS

The flotation recovery of hematite using potassium oleate a as collector is plotted as a function of *p*H in Figures 8, 9, and 10 along with the slope of the linear portion of the corresponding surface tension decay plot in stage II that covers most of the decay. It is evident that both of these properties of the oleate solutions correlate well at 25° and 75°C, suggesting the possible role of the solution/gas interfacial adsorption kinetics in determining the flotation behavior. A correlation exists also between the total surface tension lowering and the flotation recovery. This is illustrated in Figures 11, 12, and 13. It must be noted here that similar to the rate of decay during stage II, the total surface tension lowering is also a measure of the solution/gas interfacial adsorption and it involves the processes that occur during all stages. The overlapping of the curves is not an essential correlation criterion because the flotation curve can be displaced with respect to the flotation axis by using a different flotation time. It is the

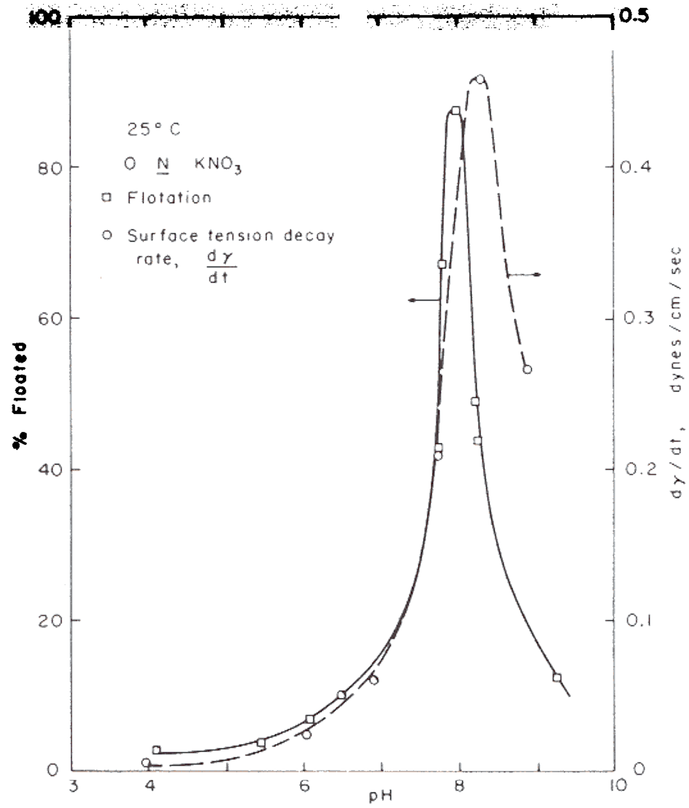


Fig. 8. Comparison of flotation properties of 3 × 10^{-5} mole/liter potassium oleate solution with its surface tension decay rate characteristics at 25°C, supporting electrolyte is not present.

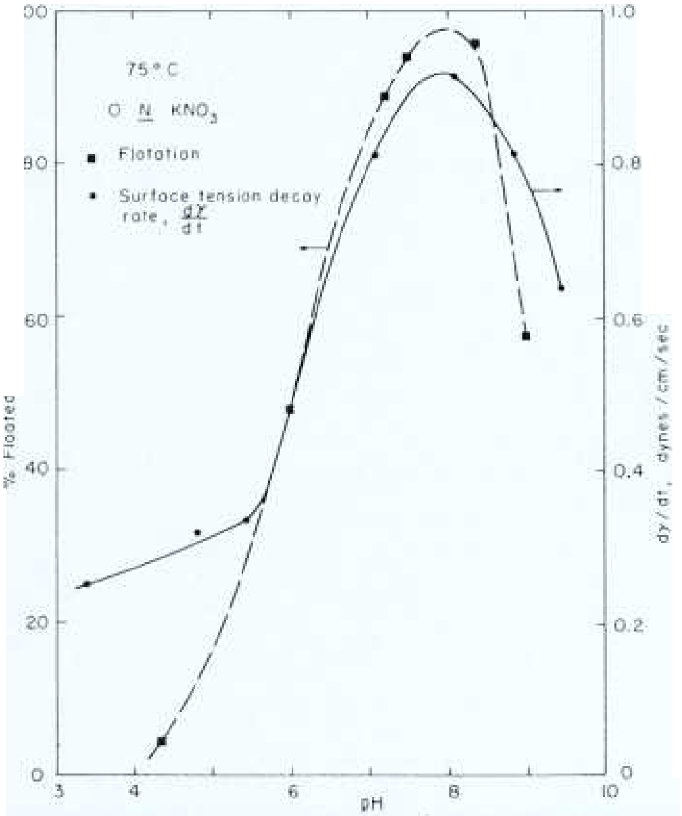


Fig. 9. Comparison of properties of 3 × 10^{-5} mole/liter potassium oleate solution with its surface tension decay rate characteristics at 75°C, supporting electrolyte is not present.

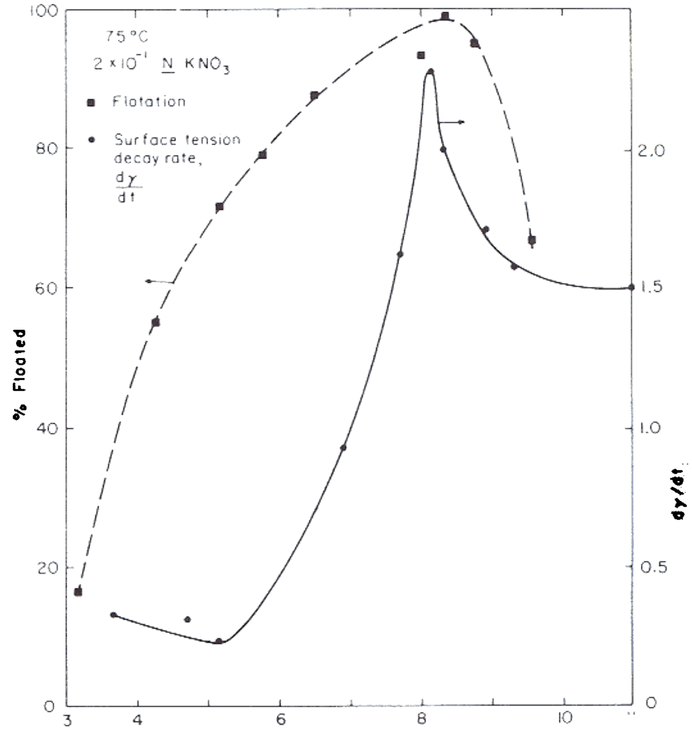


Fig. 10. Comparison of flotation properties of 3 × 10^{-5} mole/liter potassium oleate solution with its surface tension decay rate characteristics at 75°C. Supporting electrolyte (2 × 10^{-1} N KNO_3) is present.

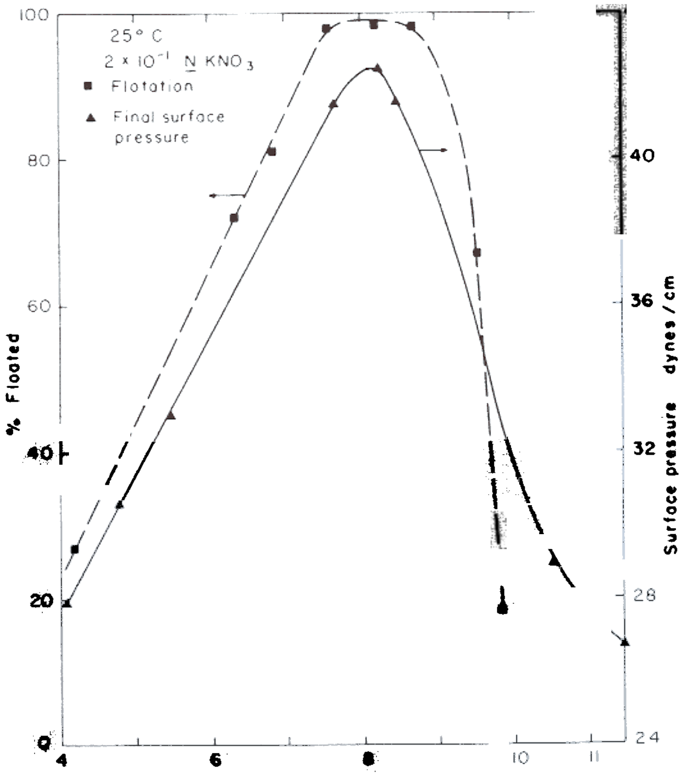


Fig. Comparison of flotation properties of 3 × 10^{-5} mole/liter potassium oleate solutions with final surface pressure obtained for it at 25°C. Supporting electrolyte (2 × 10^{-1} N KNO_3) is present.

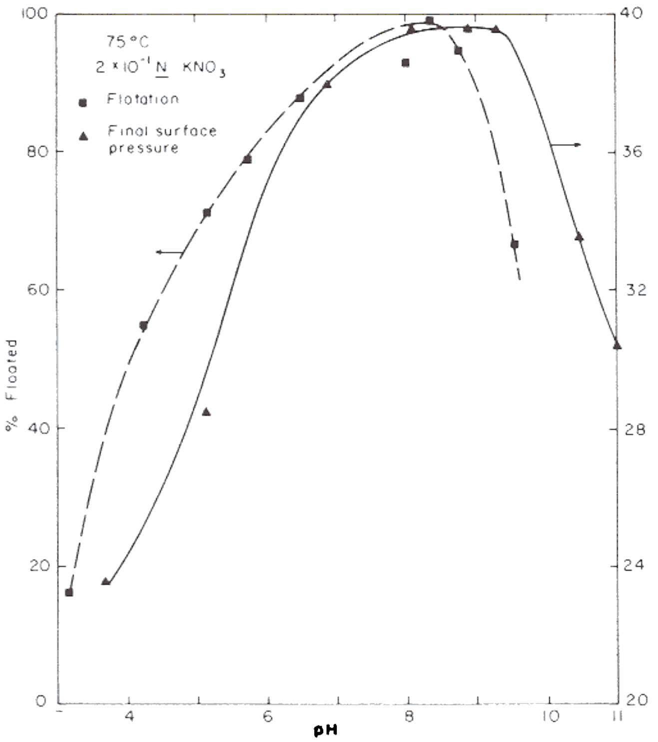


Fig. 12. Comparison of flotation properties of 3 × 10^{-5} mole/liter potassium oleate solutions with final surface pressure obtained for it at 75°C. Supporting electrolyte (2 × 10^{-1} N KNO_3) is present.

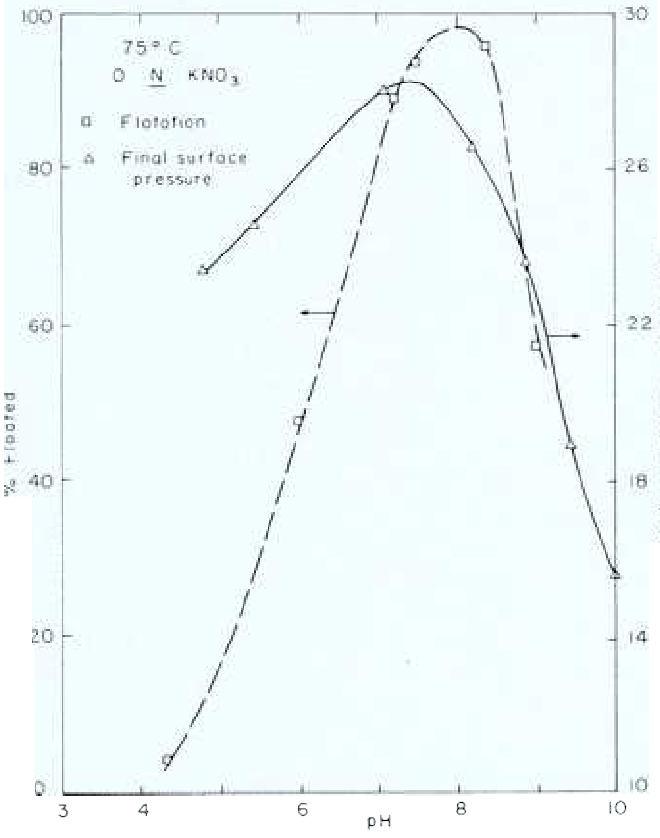


Fig. 13. Comparison of flotation properties of 3 × 10^{-5} mole/liter potassium oleate solutions with final surface pressure obtained for it at 75°C. Supporting electrolyte is not present.

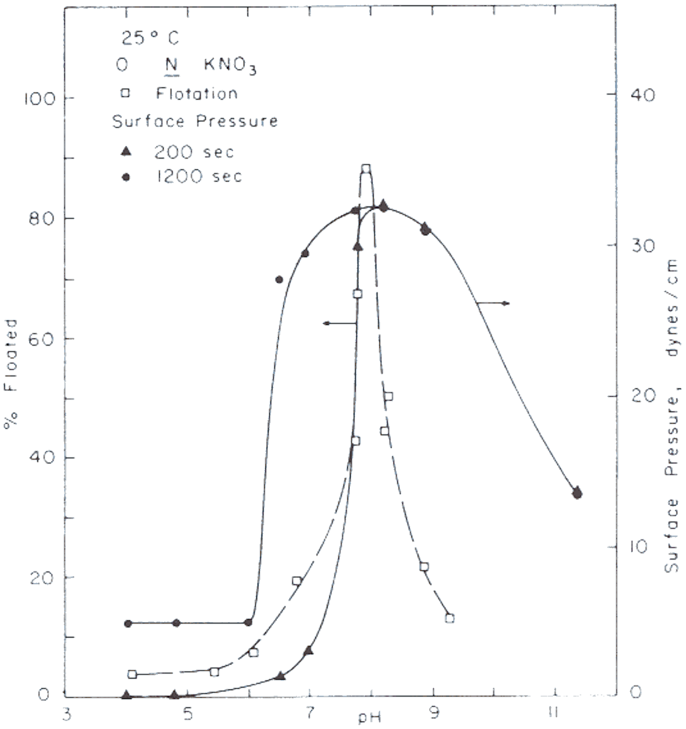


Fig. 14. Comparison of flotation properties of 3 × 10^{-5} mole/liter potassium oleate solutions with surface pressure at different decay time intervals. Supporting electrolyte not present.

presence of an increase or decrease in a given *p*H range or the *p*H of maximum response that is the primary correlation criterion. Another parameter for meaningful correlation with flotation is the surface tension reduction for a given initial period since this would essentially relate flotation to the adsorption density at the time of contact. (See Figures 14 and 15.)

A correlation between dynamic surface tension properties and flotation recovery is possible either because the collector adsorption density on the bubble is a major factor determining flotation or because of the similarity between the processes of collector adsorption at the solution/gas interface and other parameters such as adsorption at the solid/liquid interface that have been shown to be involved in determining flotation response. An examination of the flotation phenomena suggests that all the above mentioned factors can be possible causes for the correlation. In the Hallimond type cell except for the case of the first few bubbles, the bubbles' surface is only a fraction of a second old under normal agitation conditions when the bubble is making contact with the mineral particle. It can be clearly seen from Figures 4 and 5 that under these conditions only in a few instances does appreciable collector adsorption take place at the solution/gas interface to produce detectable surface tension lowering.* For example, only above about

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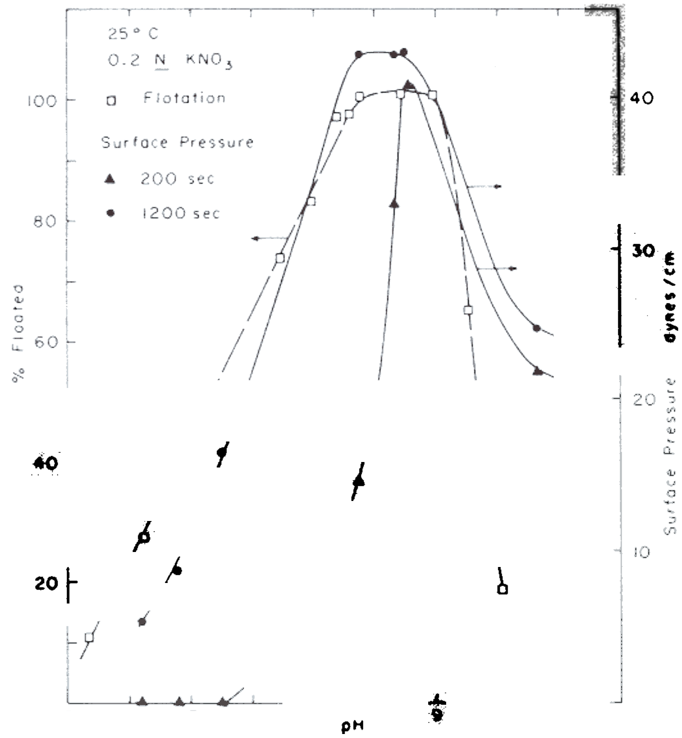
*Even though the plots in Figures 4 and 5 yield data for surface tension reduction during the first four seconds rather than during the first second, the initial rate of adsorption indicated by these plots can be assumed to apply also for the first second. This is particularly so since measurable surface tension reductions occur often only after a certain adsorption density at the solution/gas interface has been approached.



ig. 15. Comparison of flotation properties of 3×10^{-5} mole/liter potassium oleate solutions with surface pressure at different decay time intervals. Supporting electrolyte (2×10^{-1} N KNO_3) is present.

*p*H 7 is there significant lowering in surface tension of a 3×10^{-5} mole/l oleate solution at 25°C during the first few seconds. It must be pointed out that it is in this *p*H range that maximum flotation is obtained. Collector migration from the bubble surface onto the mineral/bubble/liquid contact region has been proposed earlier to be a mechanism for the rapid attainment of solid/gas interfacial adsorption density (*1*, *2*). Indeed if collector migration to the bubble surface itself is too slow to produce any significant adsorption by the time the bubble contacts the particle, there will be very little subsequent migration of it to the solid/gas solution contact area. Correlation of large solution/gas interfacial adsorption rates to good flotation recovery is expected on this basis.

In a real flotation cell there is turbulence which is absent in the surface tension apparatus. Collector adsorption can therefore be expected to take place at a higher rate than in the tests described here. A few surface tension tests done with agitation by stirring the bulk solution did not produce, however, a measurable increase in the surface tension decay rate. Since the penetration of the surfactant ions into the monolayer and subsequent orientation (rather than bulk diffusion) may be the slow steps in the collector adsorption at the solution/gas interface, agitation of the bulk is actually not expected to produce any significant effects. In this connection it might be stated here that a drop of concentrated oleate solution emptied carefully on a surface did produce instant lowering of the surface tension to the equilibrium value.

The correlation between surface tension decay rate and flotation recovery can also be due to similarity in mechanisms of transport of surfactant species to solution/gas interface and that of any other controlling interfacial phenomena such as adsorption at the mineral/solution interface. The effect of conditioning temperature on flotation response cannot of course be explained on the basis of dynamic surface tension phenomena since the aeration for flotation was always done at room temperature. This argument is based on the assumption that conditioning at high temperature has not produced any irreversible change in the oleate solution constitution. This assumption was tested and confirmed to be true for the present system. Correlation of the effect of temperature on the surface tension behavior to that on the flotation can then be due to similarities in mechanisms of the various adsorptions. Our recent experiments (*24*) have in fact clearly shown the presence of such similarities. For example, whereas adsorption at solid/solution interface is complete in less than two minutes at *p*H 8 where the surface tension decay rate is also very high; at *p*H 4.8 where the decay rate is very low it takes several hours for adsorption density on the solid to reach an apparently constant value.

It is interesting to note that the study of the surface tension decay rate does provide one with a tool for following the fast kinetics of adsorption of a given collector at the solid/liquid interface even though differences can exist between the two adsorptions. Adsorption kinetics at the solid/liquid interface for very short periods cannot be studied for practical reasons. Even though oleate adsorption in hematite could involve chemical reactions that do not necessarily take place at the liquid/air interface, extrapolation in the absence of data for the solid/liquid interfaces of indicated adsorption processes at the liquid/air interface can be helpful for elucidating the overall mechanisms of flotation. Oleate can absorb on hematite either in the form of oleate ions, oleic acid, or acid-soap, or any combination of these species. In this case it is convenient to recognize two types of adsorption that can be termed *primary adsorption* and *secondary adsorption*. Primary adsorption takes place due to physical, electrical, or chemical forces of attraction between the adsorbate species and the adsorbent species. The presence of other adsorbate species at the surface is not a necessary condition for primary adsorption to take place even though it can often be prevented due to that. The oleate ions can absorb on hematite due to any of the above reasons. Secondary adsorption is proposed to take place only in the presence of species that adsorb primarily. Thus oleic acid can co-adsorb with the oleate ions. In this case co-adsorption is due to van der Waals association between the organic species. (In addition, oleic acid could adsorb primarily due to chemical reaction with adsorbent species or due to any other force such as those due to hydrogen bonding). Such secondary adsorption should be expected to take place at the solution/gas interface also. For this reason, information from the surface tension experiments can be useful in understanding the overall process of adsorption. Results in Figures 8 to 13 show that the *p*H ranges for best flotation, highest surface tension decay rate, and maximum surface activity for oleate solutions are the same. This *p*H range is also the one in which acid-soap forms in the solution. This strongly surface active acid-soap can be expected to play an important role in the overall adsorption process including that which takes place at the solid/solution interface governing flotation. The actual concentration of acid-soap in solution is a complex function of *p*H. The following reactions determine the concentration of acid soap in the system:

$$R^- + H^+ \overset{K_1}{\rightleftharpoons} \underset{\substack{\text{oleic}\\ \text{acid}}}{RH} \qquad (2)$$

$$R^- + RH \overset{K_2}{\rightleftharpoons} \underset{\substack{\text{acid-}\\ \text{soap}}}{RRH^-} \qquad (3)$$

$$K_1 = \frac{[RH]}{[R^-]\,[H^+]} \qquad (4)$$

$$K_2 = \frac{[RRH^-]}{[R^-]\,[RH]} \qquad (5)$$

If C_t is the total concentration of the surfactant

$$C_t = 2[RRH^-] + [R^-] + [RH] \qquad (6)$$

Under the conditions of acid-soap precipitation $[RRH^-]$

$$K_2 = 1/[RH]\,[R^-] \qquad (7)$$

From (4) and (7)

$$K_1K_2 = 1/[R^-]^2\,[H^+]^* \qquad (8)$$

where $[H^+]^*$ is the concentration of H^+ at which acid-soap becomes precipitated.
From (8)

$$p\text{H}^* = \log\,(K_1K_2) + 2\log\,[R^-] \qquad (9)$$

The *p*H of acid-soap precipitation is related to the total oleate concentration in the manner described by Equation (9). Since pK_1 is - 4.7 (*13*), the surfactant will be present mostly in oleate ionic form in the basic *p*H region. Since the solubility of oleic acid and acid soap is negligible, C_t can be assumed to be approximately equal to R^- just before precipitation is initiated.
Then

$$pH^* = \log K_2K_1 + 2\log C_t \qquad (10)$$

At this *p*H, the acid-soap will begin to precipitate in the bulk solution. This precipitation could occur at the hematite/solution interface at a bulk *p*H value higher than *p*H* since the interfacial *p*H for a negatively charged hematite solution system will be lower than the bulk *p*H. Significance of *p*H* to flotation recovery owing to acid-soap precipitation at the interface or related adsorption can be tested by plotting the *p*H of maximum flotation recovery as a function of total surfactant concentration. Such a plot for flotation at a conditioning temperature of 25°C and 0 N KNO_3 (where flotation curves as a function of *p*H are sufficiently sharp for obtaining accurate values for the *p*H of maximum flotation recovery) is given in Figure 16. The slope of the line is 2.0 in agreement with Equation (10). Under other conditions where the flotation peaks are sufficiently sharp, the values obtained for the slope were in the range of 1.8 to 2.3. This correlation derived essentially from a knowledge of the bulk properties of oleate solutions and the experimental results for surface tension experiments provides an indication of a major possible mechanism governing fatty acid flotation of minerals. Whether the correlation is due to direct relationship between acid-soap precipitation at the interface or its adsorption there or is due to some other interfacial phenomena similarly related to oleate solution chemistry can be answered only with further experimentation and analysis. The importance of an accurate knowledge of surfactant solution chemistry and the properties of the bubble surface is strongly suggested by the present results.

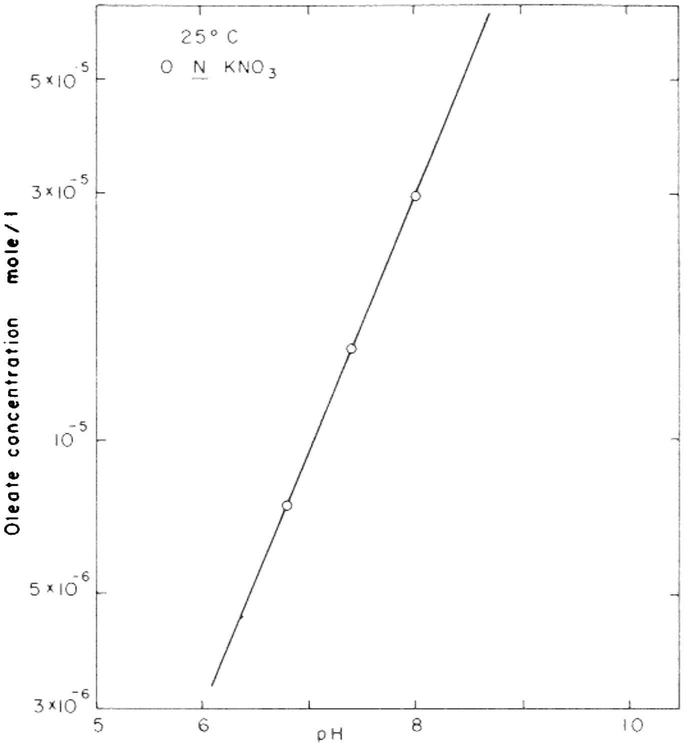


Fig. 16. Correlation between potassium oleate concentrations and *p*H of maximum flotation response.

The consideration of surface activity of the collector alone would require the *p*H of maximum flotation of all minerals with a given collector to be the same. It must, however, be noted that the location of this *p*H is dependent also upon the adsorption mechanisms of various forms of oleate including the complexes on the minerals and the role of *p*H in the adsorption mechanisms. The optimum *p*H for surfactant adsorption and hence flotation can also depend upon the mineral surface properties such as zeta potential that do control adsorption in some cases. Thus both the surface activity of the collector and the mineral surface characteristics should together be considered while studying the flotation behavior of any mineral-collector system.

SUMMARY

The role of collector adsorption on the bubble in froth flotation has been suggested in the past to be significant. At its time of contact with a mineral particle in a flotation cell, a bubble is, however, only a fraction of a second old and adsorption on its surface might be significantly different from that obtained under equilibrium conditions. In this study we have examined the role of oleate adsorption at the solution/gas interface and the kinetics involved by determining the dynamic surface tension of these solutions and hematite flotation obtained at various levels of oleate concentration, *p*H, ionic strength, and temperature.

Flotation of hematite and surface tension lowering are found to be highly sensitive to *p*H, temperature, and ionic strength. The actual dependence of surface tension decay on the above variables is rather complex mainly due to the changes produced in the chemical state of the fatty acid with change in solution *p*H. In addition to the hydrolysis of oleate to oleic acid when the *p*H is decreased, complex species also form particularly in the intermediate *p*H range. Transport of each of these species can be somewhat differently controlled by mechanisms involving penetration into the monolayer and reorientation in it.

Flotation recovery was compared with both the characteristic slope of the surface tension decay plot and the total surface tension lowering. Good correlation of flotation was obtained both at 25° and 75°C with the characteristic slope and with the total surface tension lowering under all ionic strength conditions. Maximum flotation and surface tension lowering occur around neutral *p*H where acid-soap is the predominant species. This strongly surface active species can also be expected to play an important role in the overall adsorption process governing flotation. The *p*H of bulk precipitation of acid-soap *p*H* is given by

$$pH^* = \log (K_2 K_1) + 2 \log C_t$$

where K_2 and K_1 are equilibrium constants of acid-soap formation from acid and soap and of acid formation from soap and H^+, respectively, and C_t is the total concentration of the collector. Significance of *p*H* to flotation recovery owing to acid-soap precipitation at the interface or related adsorption was tested by plotting the *p*H of maximum flotation recovery as a function of total surfactant concentration. Such a plot yielded a straight line with a slope of about 2 in agreement with the equation. This correlation, derived essentially from a knowledge of the bulk properties of oleate solutions and from the results of surface tension experiments, identifies a possible major mechanism governing fatty acid flotation of minerals. While the question of whether the correlation is due to direct relationship between acid-soap precipitation at the interface or its adsorption there or due to some other interfacial phenomena similarly related to oleate soltuion chemistry needs further study, the relevance of surfactant solution chemistry and the properties of the bubble surface is clearly shown by the present results.

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DISCUSSION

J. D. Miller: Will you comment on the experimental technique used to measure surface tensions specifically with regard to surface layer removal?

P. Somasundaran: The surface tension is measured (and recorded) by means of the Wilhelmy plate method using a sandblasted paltinum sensor. The surface layer is removed by allowing the tip of a capillary connected to an aspirator to just touch the surface of the solution. In the case of our oleate solutions this procedure elevated the surface tension to that of pure water in less than 5 s. We continued the suction for 30 s, however. Recordings obtained for surface tension reduction after the termination of the suction reflect the rate of arrival of surfactant species at the interface to create the surface excess. If excessive amount of bulk solution is removed by suction, care must be taken to lower the sensor for constant depth of immersion or to apply correction for any change in buoyancy effects. For those monolayers that might not spread or flow at the surface satisfactorily, it is helpful to force the surfactant towards the above capillary by means of a properly oriented gentle airstream. This technique is thus a powerful tool for studying kinetics of surfactant adsorption involving relatively short time intervals.