Colloids and Surfaces, 1 (1980) 387—405

FLOTATION CHEMISTRY OF HEMATITE/OLEATE SYSTEM

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(Received March 8th, 1980; accepted March 25th, 1980)

ABSTRACT

Oleate flotation characteristics of hematite have been investigated in this study under a wide range of experimental conditions of pH, temperature, ionic strength and collector concentration. The study revealed the following major features of this system which include: (a) a maximum in floatability in the neutral pH range; (b) an increase in the flotation response of hematite with increase either in solution ionic strength at room tempera ture or in temperature at low ionic strengths; (c) marked temperature—ionic strength interactions yielding an inversion of the above effect under elevated temperature and high ionic strength conditions. None of these features can be satisfactorily explained by classical theories of collector adsorption based on electrostatic or chemisorption model. In this paper, the flotation results are explained taking the adsorption kinetics and the solution chemistry of the oleate into consideration. It is shown that the unique solubility characteristics of oleate, together with its tendency to form ionomolecular complexes, is largely responsible for the observed complex flotation behavior.

INTRODUCTION

Currently beneficiation of hematite ores is conducted using either direct flotation (hematite flotation) or indirect flotation (quartz flotation) techniques depending upon the nature of the available ore bodies. In direct flotation, iron bearing mineral, mostly hematite, is floated using oleate as collector leaving siliceous gangue, usually quartz, in the tailings. Kick et al. [1] were among the first to investigate the utility of various collectors in hematite flotation from quartz. In their extensive study, they concluded that fatty acids and their soaps are superior collectors for hematite flotation and among these, sodium oleate is the best collector. Rietz [2], Kihlstedt [3] and Kivalo et al. [4] have demonstrated the successful use of tall oil in hematite flotation.

Although the interest in the beneficiation of hematite ores by flotation dates back to the thirties, no systematic or exhaustive fundamental study on the behavior of this flotation system has been reported. Nevertheless, independent studies [1, 3—13] carried out in the past have pointed out several features peculiar to the hematite/oleate system with some attempt to explain

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these findings. Thus it has been shown that the hematite flotation using oleate as collector is highly sensitive to pH [10] and that the best flotation recoveries are obtained in the pH range of 6—8 [1, 3—8, 10—12]. Also, increase in the conditioning temperature has been reported to significantly improve the hematite flotation response [5]. Recently we have shown that an increase in the solution ionic strength can also markedly increase the flotation of hematite using oleate [8].

The importance of oleate solution chemistry in the flotation process results from the fact that the oleic acid in aqueous solution undergoes hydrolysis and forms complex species which exhibit markedly different solubility and surface active characteristics [13, 14]. Among various oleate species, acid—soap, a complex of oleate ion and oleic acid, deserves special mention. It is prevalent in the neutral pH range and can be expected to be highly surface active. A change in pH or other variables such as temperature, changes not only the chemical state of the oleate, but also the amount of it dissolved in water as well as its effective surface activity at various interfaces. Since flotation process involves solid/liquid, solid/gas and liquid/gas interfaces, it is expected that the above-stated changes in the oleate properties would influence oleate flotation response.

Our study of flotation chemistry of hematite/oleate system is formulated on the basis of the above considerations and is directed towards the understanding of the fundamentals. This study involved investigation of the flotation of hematite using oleate, under a wide range of experimental conditions of pH, ionic strength, temperature and oleate concentration along with the determination of bulk as well as interfacial properties of oleate and those of hematite in aqueous solution, and analysis of the dependence of these properties on solution conditions.

EXPERIMENTAL

Materials

Minnesota massive (red) hematite lumps purchased from Ward's Natural Sciences Establishment were crushed to −35 mesh, sieved and stored dry in polyethylene bags. X-ray analysis showed the ore to be mostly hematite with minor amounts of quartz and magnetite. Dissolution of a representative ore sample in hot concentrated hydrochloric acid, left 6.45% of the original weight as insoluble residue, which was identified using X-ray diffraction analysis to be mostly quartz with traces of hematite. Over 85% of this residue was - 400 mesh, suggesting that quartz is finely dispersed in the hematite matrix. Streaming potential studies on 35/65 mesh hematite and the electrophoretic mobility studies on hematite fines (−400 mesh) showed the isoelectric point (IEP) of these samples to be around pH 3.0. However, the titration technique yielded a value of pH 7.1 for PZC* which is closer to the reported

*PZC = point of zero charge.

value of pH 8.2 for synthetic hematite [15]. The differences in the values obtained using electrokinetic and the titration technique can be explained on the basis of the hematite surface contamination of silicate. Such a contaminated surface is expected to yield an average IEP that lies between that for pure hematite and that for pure silicate. For a given sample, the basis for averaging will differ depending upon the measuring technique. For example, the electrokinetic technique may show an average IEP based on the relative surface area while in titration technique, in addition, microscopic pore area will also play an important role. Since hematite is known to exhibit porous surface structure, the titration technique can be expected to give a value closer to that of pure hematite than the electrokinetic technique.

Radioactive oleic-1-^{14}C acid of 2.6 mc g^{-1} activity with 99+% purity, used for the adsorption studies, was supplied by the Applied Science Laboratories in ampoules sealed under nitrogen atmosphere, and was used without further purification after saponification. The stock solution so prepared was preserved under nitrogen at 2°C. Required dilute solutions were made daily from a stock solution of potassium oleate at a pH of $\sim$11.2 and maintained under nitrogen at 2°C.

All chemicals such as KNO_3, KOH, and HNO_3 were either reagent or AR grade and were used without further purification. Triple distilled water of conductivity 10^{-6} to $10^{-7}\,\Omega^{-1}\,cm^{-1}$, prepared in pyrex still and collected and stored in Teflon bottles, was used for all experiments.

RESULTS

Flotation

A modified Hallimond cell with automatic control of flotation time and stirring intensity and time, was used for all flotation experiments. The flotation procedure consisted of desliming 0.8 gram of a sample till free of visible fines and transferring it to a cylinder to which the desired collector solution is added. It was then conditioned by stirring for ten minutes in a constant temperature bath. After conditioning, the pH of the pulp supernatant was measured and the pulp was transferred to the cell. Flotation was conducted for ten seconds at a nitrogen flow rate of 20 ml min^{-1}.

The effect of pH on the Hallimond cell flotation of natural hematite is shown in Fig. 1. A strong dependence of flotation on pH is evident from this figure. Maximum flotation is obtained around the neutral pH range and this is in agreement with the results reported in the literature [10]. In the past, the maximum around the neutral pH range has been attributed to the location of PZC in this pH region. As mentioned earlier, it has been proposed that oleic acid preferentially adsorbs on the neutral surface sites which are present in high concentration near the PZC. It has been found earlier [8], however, that the pH of maximum flotation response, pH*, shifted to higher pH values with increase in oleate concentration. If surface characteristics of hematite alone are responsible for the flotation behavior, such a change in the pH of

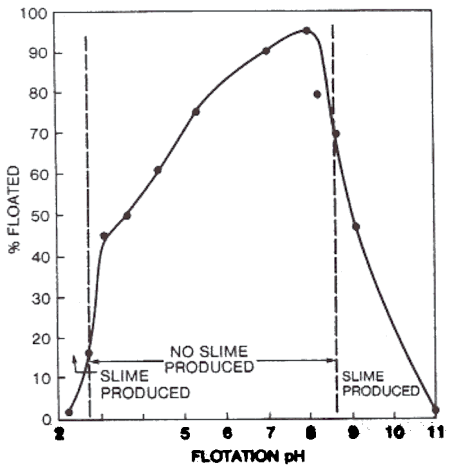


Fig. 1. Hematite flotation using 3×10^{-5} M oleate at 100°C.

maximum flotation should not have occurred. From a mechanistic view point, this result is very significant as it sheds doubt on the concept that the maximum flotation response around neutral pH range is due to the existence of PZC of hematite in that pH range [10].

It has also been observed that under low ionic strength conditions, the increase in conditioning temperature improves the flotation response significantly while the opposite is true under high ionic strength conditions [8]. Also, while at room temperature the increase in ionic strength from 8×10^{-5} to 2×10^{-1} M increased the recovery from 30 to 90%, at 94°C the recovery decreased from 80 to 35%. The significance of this result to the actual flotation practice should be noted since it suggests that variation of temperature or ionic strength can contribute to either an increase or a decrease of the flotation depending upon other solution conditions. These results are also interesting from a fundamental view point since they are opposite to what one would expect on the basis of a flotation model based on the electrostatic interactions alone.

Conditioning is a very critical step in flotation using oleate. Prolonged conditioning with intense agitation is required in this case. As can be seen from Table 1, at low pH levels, 10 minutes of conditioning is found not to be adequate for obtaining maximum flotation response. However, at pH 8.1, even 3 min of conditioning appears to be nearly adequate. It should be noted that prolonged conditioning requirement is not unique to hematite/oleate system but is characteristic of all the flotation systems employing oleate as collector, such as feldspar/oleate or wolfromite/oleate, again indicating the role of oleate chemistry in flotation.

The flotation response of hematite using 3×10^{-5} M oleate is shown in Fig. 2 as a function of pH under two different experimental conditions. In one

TABLE 1

Hematite/oleate flotation
Effect of agitation

	Agitation time	Recovery (%)
pH 7.3/75°C	0	15
	10	73
	30	88
pH 3.7/100°C	0	5
	3	20
	10	50
pH 8.1/100°C	0	67
	3	75
	10	78

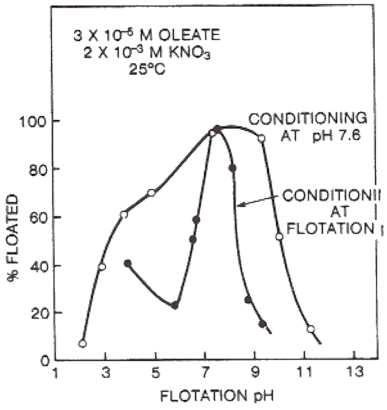


Fig. 2. The effect of adjusting pH after conditioning on hematite flotation at 25°C and 2×10^{-5} M KNO_3 using 3×10^{-5} M oleate, collector.

case, the conditioning is carried out at the pH of the flotation (Condition A) while in the other case, the conditioning is carried out at pH 7.6 (Condition B). In the latter case, after conditioning, the pH of the supernatant solution is quickly changed to a predetermined value and the flotation is carried out within 30 s. In this case, although the solution is equilibrated with respect to pH, solid particles can be assumed not to have had an opportunity to completely adjust to the new pH conditions. Such an assumption is consistent with our observation that desorption of oleate is dictated by relatively slow kinetics [7, 15]. It can be seen from this figure that the flotation response is measurably different under the two conditions. Much higher flotation is realized under condition B. The data in the above-stated Fig. 2 can be better under-

stood if one invokes the role of liquid/air interface. The sharp fall in the flotation above pH 10 under condition B can be attributed to the increasing repulsion between the negatively charged gas bubble and the similarly charged hematite particle. This is further substantiated by the fact that the decreased flotation response at pH 11 under condition B is improved significantly by simply washing the unfloated sample with water (pH 5.8) and floating it in it. The decrease in the flotation in the acid pH range on the other hand is the result of reduced adsorption of oleate at the liquid/air interface as indicated by the lower surface pressure of oleate solutions under these conditions [16].

Surface tension

A dynamic surface tension measuring technique was developed utilizing the Wilhelmy plate method and a microbalance. Details of this technique along with results on the surface tension behavior of oleate system have already been described elsewhere [16]. It was shown [16] that a definite correlation exists between the dynamic surface tension property and equilibrium surface tension lowering and flotation characteristics of this system. Such correlation was thought to be 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.

Oleate adsorption on hematite

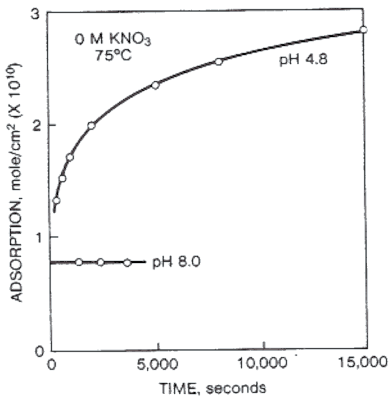
Adsorption of potassium oleate on hematite was estimated by determining the change in the oleate concentration due to the hematite addition in a known volume of solution. The adsorption cell used was similar to the one used earlier [17] with minor modifications. In a typical experiment, a 0.5-g hematite sample is mixed with 100 ml of oleate solution under desired conditions and the oleate disappearance is monitored by periodically withdrawing 1.5-ml alliquotes of suspensions, centrifuging it and determining the oleate concentration in the supernatant using radioactive tracer technique.

The process of adsorption of oleate on hematite was found to be strongly time dependent, with the equilibration time being a function of solution pH, ionic strength, oleate concentration and temperature. A detailed account of the adsorption behavior of this flotation system is presented elsewhere [7]. A summary of the major characteristics is presented here.

Typical results for the kinetics of oleate adsorption on the natural hematite at 75°C under varying pH conditions are given in Fig. 3. The strong pH dependence of equilibration time and the total adsorption is evident from this figure. For example, while less than 100 s are required for equilibration

at pH 8.0, it takes more than 15,000 s at pH 4.8. Also, the total oleate adsorption increases with decrease in pH. The pH dependence is more clearly seen in Fig. 4 where equilibrium adsorption is plotted as a function of pH. It should be noted that only the initial oleate concentration is kept constant in this case. The equilibrium oleate concentration is indeed dependent on the extent of oleate loss due to adsorption.

It should be pointed out that under low pH conditions oleate will exist in



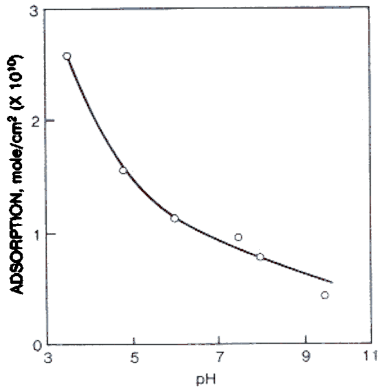


Fig. 3. Effect of pH on the kinetics of oleate adsorption on hematite with 1.5×10^{-5} M potassium oleate at 75°C.

Fig. 4. Effect of pH on oleate adsorption with 1.5×10^{-5} M potassium oleate at 75°C.

solution as a dispersion. Under such conditions, disappearance of oleate from the solution can be due to phase separation and/or heterocoagulation with hematite particles. To clarify whether significant phase separation occurred, several control experiments were conducted. In these experiments, normal test procedure was used except that no hematite was added. The decrease in oleate concentration can be attributed in such a case to the phase separation. These experiments revealed no significant loss of oleate from the solution even after eight hours of agitation. Alternatively, another set of experiments was conducted with 0.5- and 0.25-g hematite samples in 100-ml oleate solutions. It was found that the reduction of hematite amount from 0.5 to 0.25 g reduced the rate of loss of oleate from solution to half, without altering the kinetics of oleate adsorption. These experiments clearly confirmed that the loss of oleate from the solution was due to its transfer to the hematite surface.

The effect of oleate concentration on the equilibrium adsorption density at pH 8.0 and under different experimental conditions of ionic strength and temperature is presented in Fig. 5. It is seen that the oleate adsorption on

hematite is strongly dependent on solution pH, ionic strength, oleate concentration and temperature. The effect of the above variables except pH is similar to that observed for hematite flotation. For example identical temperature—ionic strength interactions are observed in adsorption (see Fig. 6) and in flotation [8]. Under lower ionic strength conditions, the increase in temperature increases oleate adsorption at pH 8.0, but decreases it at pH 4.8. Under high ionic strength conditions, on the other hand, the increase in temperature decreases the oleate adsorption under all pH conditions. The increase in ionic strength increases oleate adsorption density. The adsorption rate is also enhanced by increase in ionic strength, temperature or pH [15]. Under all conditions, the intensity of agitation has been found not to affect the kinetics of oleate adsorption suggesting that the process is not diffusion controlled [7].

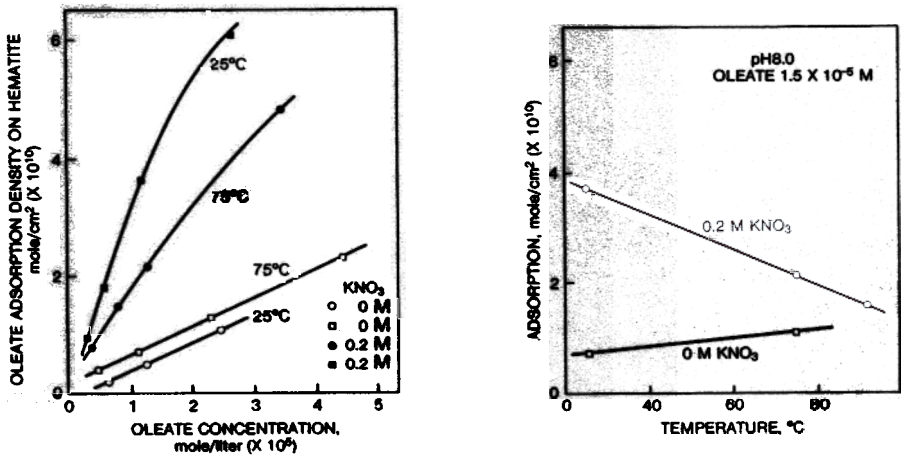


Fig. 5. Effect of ionic strength and temperature on the oleate adsorption isotherms on hematite at pH 8.0.

Fig. 6. Temperature—ionic strength interactions in oleate adsorption on hematite at pH 8.0 and 1.5 x 10^{-5} M oleate concentration.

Oleate adsorption in relation to hematite flotation

The flotation response of a system is generally correlated with its adsorption properties with the increase in the flotation attributed to increased collector adsorption density on the mineral.

In this investigation, all the flotation experiments were conducted with 10 minutes of conditioning under varying experimental conditions. The adsorption tests, however clearly indicated that, under certain experimental conditions, 10 min of conditioning is insufficent to attain equilibrium adsorp-

tion. Hence it was considered appropriate to correlate flotation results with the oleate adsorption density at 10 min of conditioning rather than with the equilibrium adsorption density. Figure 7 depicts the variation in the flotation response as well as adsorption characteristics of this flotation system as a function of pH. It is clearly seen that the flotation characteristics do not follow the adsorption behavior of this system. It is clearly seen that while flotation is decreasing below pH 7.5, the adsorption density is continuously increasing with decrease in pH.

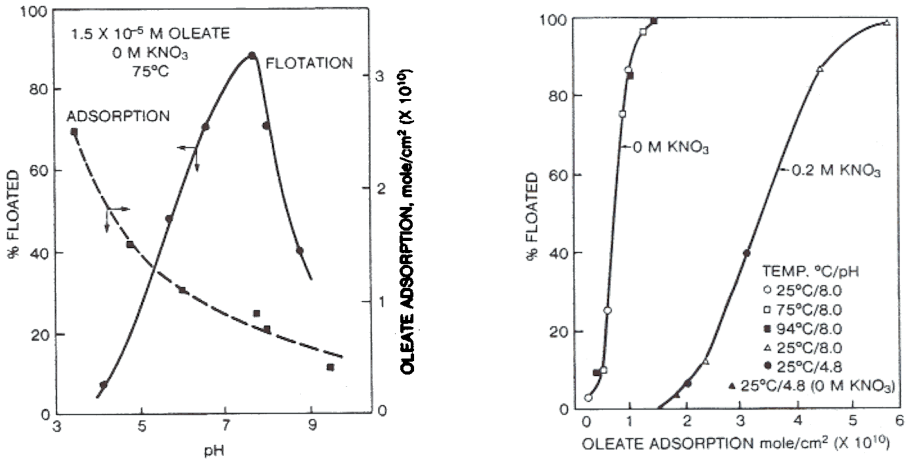


Fig. 7. pH dependence of flotation and adsorption in hematite—oleate system with 1.5 X 10^{-5} M potassium oleate at 75°C.

Fig. 8. Flotation—adsorption correlation.

The relationship between flotation recovery and adsorption density at pH 8.0 and 4.8 is illustrated in Figure 8. It is seen that at pH 8.0 an increase in adsorption density sharply increases flotation recovery. It should be noted that under the stated conditions, a similar adsorption—flotation correlation is obtained at 25 and 94°C conditioning temperatures. In other words, at pH 8.0, increase in temperature increases flotation by increasing the oleate adsorption density.

The change in pH from 8.0 to 4.8 and/or increase in solution ionic strength to 2 X 10^{-1} M at 25°C yields an entirely new adsorption—flotation curve indicating that the degree of dependence of floatability on adsorption is not universally constant and that it is a function of at least pH and ionic strength. Under lower pH and higher ionic strength conditions, much higher adsorption is required to obtain the same flotation as that at pH 8.0 under low ionic strength conditions.

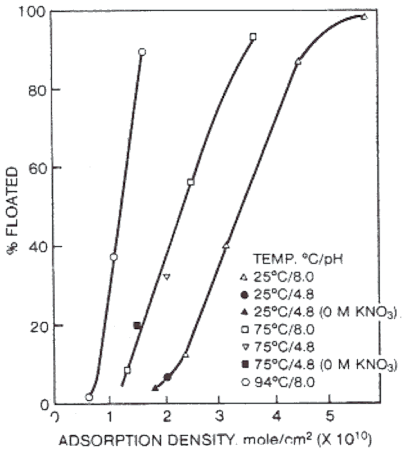


Fig. 9. Flotation—adsorption correlation. Effect of pH, temperature and ionic strength.

The effect of temperature on flotation-adsorption correlation at 0.2M KNO_3 is illustrated in Fig. 9. It is noted that the increase in conditioning temperature also produces a significant shift in the degree of correlation. Thus to obtain a given flotation recovery, much lower adsorption density is required under elevated temperature conditions.

All the curves plotted in these figures are of elongated S shape, with linear increase in recoveries in 10—80% range with increase in adsorption densities. Under these conditions the resulting flotation response can be related to adsorption through the following relation

$$R = \alpha \Gamma + \beta \qquad (4)$$

Where α and β are constant under a given set of pH, ionic strength and temperature conditions. α essentially represents the dependence of recovery on adsorption density. The values of α and β are estimated for each curve and are tabulated in Table 2. It is seen that while the value of β remains essentially constant, the value of α is strongly dependent on pH, ionic strength and temperature. For example, at 2×10^{-1} M ionic strength the change in temperature from 25 to 94°C changes α from 35×10^{10} to 124×10^{10} and β from - 69 to - 71. It is proposed that the values of α and β will reflect among other factors, the role of oleate adsorbed on the bubble as well as that of other surface active agents present in the system, for example, as an impurity.

Hematite slime behavior

Several visual observations were made on the sliming behavior of hematite particles during conditioning and flotation step. Hematite by itself, in the absence of any collector, tended to slime considerably producing red or orange colored slimes.

TABLE 2

Values of the coefficients α and β in the equation $R = \alpha\Gamma + \beta$

Conditions			α cm mole^{-1} ($\times 10^{18}$)	β
pH	Temp. (°C)	KNO_3		
8.0	25—94	0	165	-77
4.8—8.0	25	0.2M	35.3	-69
4.8	25	0		
4.8—8.0	75	0.2M	50.4	-70
4.8	75	0		
4.8—8.0	94	0.2M	124	-71

In general, the presence of oleate significantly modified the sliming tendency of hematite. Excellent hematite slime aggregation was observed even at as low an oleate concentration as 3×10^{-6} M, provided the solution pH was below 7.0. The conditioning time required to get good aggregation was found to be dependent on the pH, ionic strength, oleate concentration and temperature. Above pH 7.0 generally inferior slime aggregation was observed.

An increase in ionic strength or oleate concentration and/or a decrease in pH was always helpful in improving and accelerating aggregation. For example using 1.5×10^{-5} M oleate solution in absence of KNO_3, no noticeable aggregation was observed at pH 8.0 while excellent aggregation was obtained at pH 4.8 in 2×10^{-1} M KNO_3 after just two minutes of conditioning.

An increase in temperature also produced a significant enhancement of hematite slime aggregation under lower pH conditions. At pH levels above 8.0 however no noticeable temperature effects were observed.

The hematite slime aggregates were observed to be quite stable and changes in the experimental conditions did not appreciably alter the aggregation behavior. For example a well-aggregated hematite slime at pH 4.8 remained aggregated even after agitating it at pH 8.8 for several hours, even though at pH 8.8 minimum aggregation was normally obtained.

DISCUSSION

On the basis of the above results major features of this flotation system can be stated as follows:

1. Hematite flotation response and the oleate adsorption characteristics are very sensitive to pH especially in the neutral pH range; however while maximum hematite floatability is observed around pH 7 to 8, no such maximum is observed for oleate adsorption density in this pH range. In fact, the oleate adsorption density is found to continuously decrease with increase in pH. Nevertheless, one does observe a maximum in the dynamic surface ten-

sion and the actual surface activity of oleate species at liquid/air interface under these conditions [7, 16]. The pH of maximum flotation response (pH*) is dependent on the oleate concentration and follows the relation log C_T = 0.5 pH* + const. This phenomenon cannot be explained by considering the properties of hematite surface alone.

2. A direct correlation between hematite flotation and oleate adsorption density exists only under a given pH and ionic strength condition. Decrease in pH or increase in ionic strength increases the oleate adsorption density, but results in lower sensitivity of flotation to adsorption density so that for a given flotation higher oleate adsorption is required under these conditions.

3. Increase in temperature under low ionic strength conditions increases oleate adsorption on hematite and leads to the improvement in hematite flotation response. The improvement in the flotation response is, however, much more significant in the acidic pH range [7]. Under similar conditions, although the dynamic surface tension property of oleate improves, its surface activity, as measured by surface pressure actually decreases under acidic pH conditions and only marginally increases under basic pH conditions [7].

4. Increase in ionic strength at lower temperatures improves the oleate adsorption characteristics, its surface activity at liquid/air interface as well as hematite flotation characteristics while only marginally affecting the dynamic surface tension property of oleate solutions.

5. Like other oleate flotation systems, hematite/oleate system also needs prolonged conditioning time especially under pH levels below 8.0 where oleate adsorption at liquid/air interface as well as at hematite surface is rather slow.

6. Conditioning is a critical step in the flotation operation of this system. Once properly conditioned, one can obtain effective flotation under much wider pH conditions. Under similar conditions, oleate desorption from hematite surface was also observed to be very slow [7]. However, under extreme pH conditions although the oleate desorption is not significant, the flotation recovery falls to lower values owing perhaps to the changes in properties of the liquid/air interface.

7. Under high pH conditions, i.e. above pH 10, the low flotation recovery is considered to be due to decreased oleate adsorption as well as the unfavorable particle bubble interaction, owing to identical electrical charge on particles and bubbles.

The above-stated results clearly demonstrate the complex nature of this flotation system. As stated earlier, several theories have been developed in the past to explain some of the special features of this flotation system. However, none of them are considered satisfactory for explaining all the above properties. The failure of these models is attributed to two reasons:

(a) They have not taken into consideration the changes in the chemical state of the oleate in the solution under different experimental conditions.

(b) The role of other interfaces particularly the solution/gas interface has been ignored.

In order to properly evaluate the role of these two factors in flotation, it is necessary to first consider the chemical equilibria of oleate in solution.

OLEATE CHEMISTRY

Oleic acid is a weakly acidic insoluble compound in aqueous solution, which forms highly soluble salts with monovalent alkali metal ions such as sodium or potassium. These soluble salts, under appropriate solution pH conditions can undergo series of hydrolysis reactions yielding complex oleate species [18]. The species that have been considered are oleate ion (R^-), oleic acid ($\underline{RH}$), acid—soap (R_2H^-), acid—soap salt (R_2HNa) and oleate dimer (R_2^{2-}). The relative proportion of these species in aqueous solution is strongly dependent on the total oleate concentration, pH, temperature and ionic strength.

The chemical equilibria between these oleate species can be represented in the following manner [18]:

$$RH \xrightarrow{K_1} \underline{RH} \qquad pK_1 = 7.6 \qquad (5)$$

$$\underline{RH} \underset{}{\overset{K_2}{\rightleftharpoons}} R^- + H^+ \qquad pK_2 = 4.95 \qquad (6)$$

$$\underline{RH} + R^- \underset{}{\overset{K_3}{\rightleftharpoons}} R_2H^- \qquad pK_3 = -4.95 \qquad (7)$$

$$2R^- \underset{}{\overset{K_4}{\rightleftharpoons}} R_2^{2-} \qquad pK_4 = -4.0 \qquad (8)$$

$$R_2H^- + Na^+ \underset{}{\overset{K_5}{\rightleftharpoons}} R_2HNa(\text{precipitate}) \qquad pK_5 = -9.35 \qquad (9)$$

These equations suggest that at a given total oleate concentration, the decrease in pH increases the oleic acid concentration and decreases the oleate ion concentration, the oleate complex species being stable mostly in the neutral pH range. The behavior of this system is rather complex, especially because of the different solubilities of these species in water. For example at room temperature while oleic acid exhibits equilibrium solubility of only 2.51×10^{-8} M, the oleate ions are highly soluble [19], and the acid soap ions exhibit intermediate solubility. Besides, the salt of acid soap in its undissociated form is expected to show least solubility. In general, true oleate solutions are obtained only in the basic pH range. The neutral and acidic pH solutions are turbid containing stable fine dispersion of various oleate species.

A phase diagram describing the concentrations of various oleate species in solution as a function of pH at 25°C is given in Fig. 10. This diagram has been constructed on the basis of eqns (5)—(9) for 3×10^{-5} M total oleate solution containing 8×10^{-5} M sodium nitrate. It is observed from the diagram that: (a) acid—soap is present in significant amounts in the neutral pH range, with a maximum at pH 7.8. Its concentration rapidly decreases as

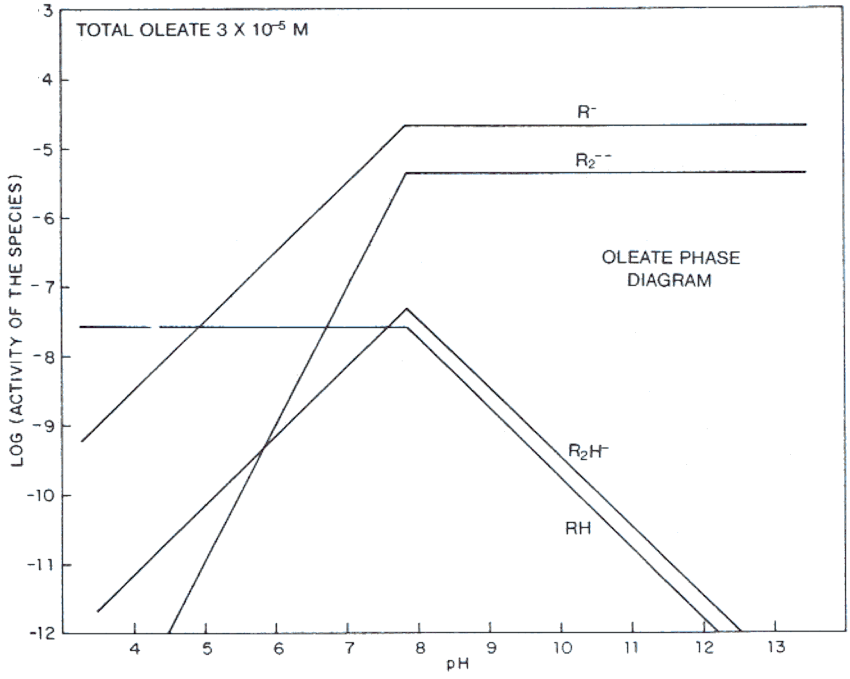


Fig. 10. Activities of various oleate species in solution as a function of pH for a total oleate concentration of 3×10^{-5} M. (calculated values.)

the pH is changed from 7.8. (b) Acid—soap precipitation does not occur at any pH conditions. However, such precipitation will occur at neutral pH if the oleate concentration exceeds 10^{-4} M. (c) The pH of oleic acid precipitation and the pH of maximum acid—soap formation are identical. (d) At any given pH, the concentration of R_2^{2-} is lower than that of R^-. However, its concentration is expected to increase rapidly with increase in total oleate concentration. (e) At pH 7.8 oleic acid precipitates and thus below this pH a second phase appears which will be present as dispersion. The amount of this dispersed phase will increase with decrease in pH.

It should be noted that among the various forms of oleate discussed above, acid—soap complex essentially represents a larger surfactant and thus can be expected to be highly surface active.

The surface activity of these oleate species can be investigated by monitoring the dynamic as well as static surface tension behavior of oleate solutions under different pH conditions. Surface tension results obtained here show that the oleate solution demonstrates maximum surface activity under conditions where acid-soap species are more prevalent.

Mechanistically, depending upon the experimental conditions, oleate can transport itself to the hematite surface in two distinct manners: (a) In a molecular or ionic state (solute form) which is possible under high pH and/or un-

der high temperature conditions, i.e. under conditions where oleate exists as soluble species such as R^- or RRH^-; (b) In a fine droplet state which is likely under high ionic strength and/or under low pH conditions. Under conditions (b) oleate will be present as a dispersion of oleic acid, and the adsorption of it on the hematite surface would be similar to the process of heterocoagulation involving positively charged hematite particles and negatively charged oleic acid droplets. These two modes of adsorption, i.e. solute adsorption and droplet adsorption, can be expected to lead to different magnitude and kinetics of adsorption and, most importantly, different type of adsorption, i.e. the solute adsorption would be much more uniform and homogeneous over the hematite surface as compared to the droplet adsorption which can occur in patches.

Examination of the adsorption and flotation data suggests that the solute adsorption is characterized by faster adsorption kinetics, lower adsorption density and higher flotation recoveries while the droplet adsorption is characterized by slower adsorption kinetics, higher adsorption density and lower flotation response.

The forces responsible for oleate adsorption could be chemical such as those responsible for the formation of iron oleate or physical such as electrostatic. In the neutral or basic pH range, the electrical interaction is not favorable and thus only the formation of iron oleate bond appears possible. In such a case, adsorption would take place in spite of the electrical repulsive interaction between negative oleate species and negatively charged hematite surface. In the lower pH regions (below 8) however, some degree of electrostatic interaction is possible since at least part of the hematite particle may exhibit positive charge and thus be oppositely charged to the oleate—oleic acid droplets. It has been shown [20—22] that the incipient condition of heterocoagulation requires only some differences in the magnitude of charge between two dissimilar surfaces so that one surface is positive in relation to other. Such electrical interaction would of course become more significant as the pH of the system is lowered below 8.0. Below pH 3.5, i.e. below the apparent PZC of hematite used in the present study, the surface will be positive and will interact with oleate droplet. This is possibly the reason for the sudden increase in flotation or the presence of a hump around pH 4 in the flotation—pH curves observed in most cases [7, 16].

The transition of adsorption mechanism from solute state (fast) to the droplet state (slow) in the neutral pH range can account for the prolonged conditioning required in this flotation system. These requirements would indeed be characteristic of the oleate system irrespective of the type of mineral being floated. Increase in temperature, which not only increases the molecular transport but also increases solubility of various oleate species, can be expected to increase adsorption kinetics and hence lower the conditioning time.

The above discussion clearly indicates that oleate chemical equilibria play a complex role in influencing the hematite flotation behavior. One can essen-

tially view oleate as a mixture of three collectors, i.e. oleate ions, acid—soap and oleic acid. The relative concentrations of these three collectors will be dependent on the experimental conditions of pH, total oleate concentration, temperature and ionic strength. Since these three collectors differ significantly in their polarity, surface activity and solubility, they are expected to respond also differently to hematite and to lead to different degrees of flotation. On the basis of this consideration, one can explain the variation in flotation under different conditions, where different degrees of flotation response is observed, at a given oleate adsorption density. Explanation is summarized below:

Oleate adsorption density Γ on hematite can be written as:

$$\Gamma = \Gamma_{R^-} + \Gamma_{RRH^-} + \Gamma_{RH} \qquad (10)$$

where

Γ_{R^-} = adsorption density of oleate ions
Γ_{RRH^-} = adsorption density of acid—soap
$\Gamma_{\underline{RH}}$ = adsorption density of oleic acid

Each state of oleate is expected to have a different value for α. The term α as described earlier represents the flotation response of the collector at a given adsorption density and is defined as $dR/d\Gamma$ where R is flotation recovery. One cannot evaluate α experimentally since unfortunately, the individual adsorption densities Γ_{R^-}, Γ_{RRH^-} and $\Gamma_{\underline{RH}}$ cannot be determined directly since the adsorption experiments yield only net oleate adsorption. One can, however, obtain values of these functions by selecting extreme conditions where only one of the three species is expected to predominate. For example at pH 4.8, oleic acid is expected to predominate in the solution. Under such conditions, the total adsorption can be attributed to a single component. Thus:

$$\frac{dR}{d\Gamma}\Big|_{\substack{\text{pH } 4.8 \\ 25^\circ C}} = \frac{dR}{d\Gamma_{\underline{RH}}} = \alpha_{\underline{RH}}$$

$$\frac{dR}{d\Gamma}\Big|_{\text{pH } 8.0} = \frac{dR}{d\Gamma_{RRH^-}} = \alpha_{RRH^-}$$

$$\frac{dR}{d\Gamma}\Big|_{\text{pH } 12.0} = \frac{dR}{d\Gamma_{R^-}} = \alpha_{R^-}$$

The value of these constants were evaluated from the experimental results as:

$\alpha_{RH} = 35.3 \times 10^{10}$ cm^2 mole^{-1}
$\alpha_{RRH^-} = 165 \times 10^{10}$ cm^2 mole^{-1}

The values of α_{R^-} could not be evaluated since at pH 12.0 no appreciable flotation or adsorption was observed.

The present treatments suggest that the hematite flotation might be more sensitive to the presence of acid—soap in the solution than oleic acid. This is directly evidenced from Fig. 11 where the hematite flotation is plotted as a function of pH along with the estimated concentration of acid—soap at a constant total oleate concentration of 3×10^{-5}M. It is remarkable that the maximum in flotation corresponds closely to that of acid—soap concentration. The above correlation clearly suggests the possibility of a major role by acid—soap in hematite flotation.

Alternatively, a parameter "reduced adsorption density" ($\overline{\Gamma}$) may be defined as:

$$\overline{\Gamma} = \alpha \Gamma$$

such that the eqn (4) reduces to

Limit

$$10 < R < 90 \qquad R = \overline{\Gamma} + \beta \tag{13}$$

Since reduced adsorption density $\overline{\Gamma}$ involves the term α, it takes into account the influence of the chemical state of the collector in the solution.

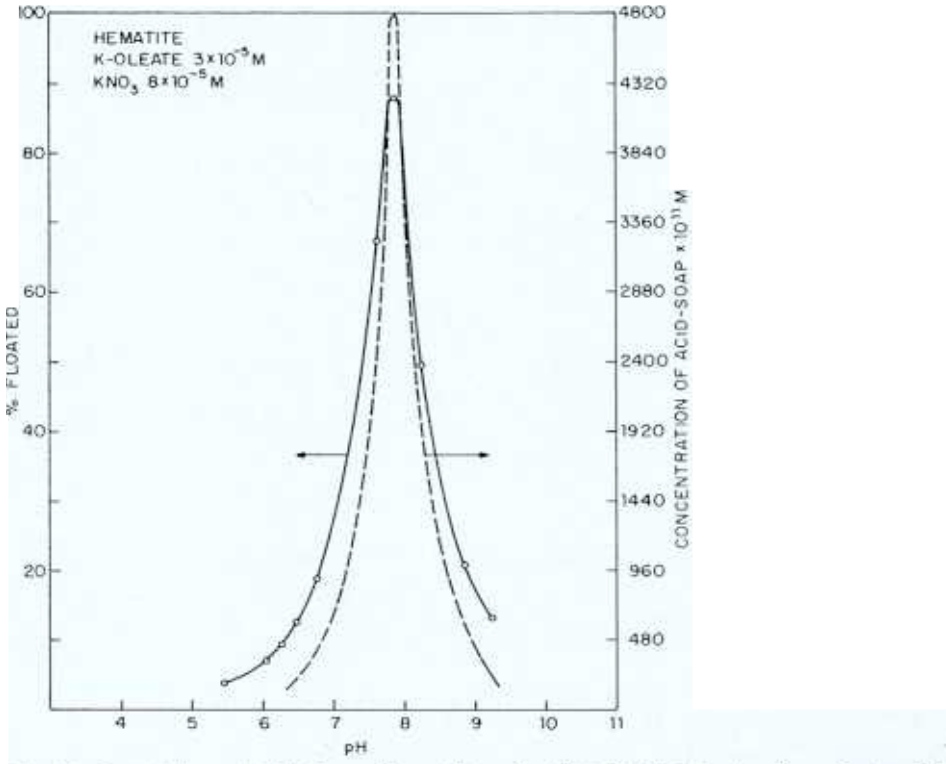


Fig. 11. Correlation of flotation of hematite using 3×10^{-5} M of potassium oleate with the concentration of acid—soap complex.

Equation (13) contains only one constant (which is a true constant under all experimental conditions) and represents a general correlation which is independent of experimental conditions. Flotation response is plotted in Fig. 12 as a function of reduced adsorption density $\bar{\Gamma}$ under a wide range of experimental conditions. It is to be noted that a general correlation between flotation and reduced adsorption that is valid under all conditions of pH, ionic strength, temperature and oleate concentration, has resulted from the above analysis based on oleate chemical equilibria.

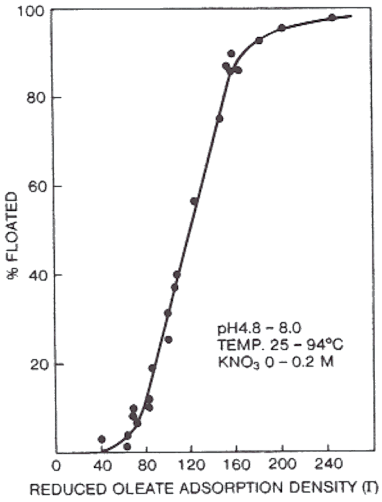


Fig. 12. Hematite flotation as a function of reduced adsorption density of oleate on hematite under various experimental conditions.

ACKNOWLEDGEMENT

The authors wish to acknowledge the National Science Foundation (ENG-78-25213) and the American Iron and Steel Institute (23-279).

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