

SURFACE PRECIPITATION OF INORGANICS AND SURFACTANTS AND ITS ROLE IN ADSORPTION AND FLOTATION

K.P. ANANTHAPADMANABHAN and P. SOMASUNDARAN

Henry Krumb School of Mines, Columbia University, New York City, NY 10027 (U.S.A.)

(Received 18 May, 1984; accepted 10 July 1984)

ABSTRACT

Adsorption of surfactants and inorganics on minerals is influenced by the properties of the solid as well as various chemical equilibria involving such reactions as complexation, precipitation, and micellization. Analysis of the adsorption process from an overall chemical equilibrium point of view shows that in a number of mineral–reagent systems, the so-called chemisorption can, in fact, be viewed as a surface-precipitation process. The marked pH dependence of adsorption of metallic species on oxides, often speculated to be due to the chemisorption of hydrolyzed metal ions, can also be explained in terms of surface-precipitation processes. This precipitation in the interfacial region is essentially controlled by the solubility product for precipitation in the bulk solution and the activities of the species in the interfacial region. In this paper, the adsorption behavior of cobalt and calcium species on silica, and ferric species on alumina is examined in terms of surface precipitation. Also, the electrokinetic behavior of iron-oxide–octylhydroxamate and apatite–oleate systems, and the flotation characteristics of tenorite (CuO)–salicylaldoxime and calcite/apatite/dolomite–fatty-acid/sulfonate systems have been analyzed. Changes in electrokinetic and flotation behavior of these systems have been correlated with precipitation conditions.

INTRODUCTION

Adsorption of surfactants on hydrophilic minerals is an essential step in the surface hydrophobization and the consequent bubble-particle attachment leading to flotation. Adsorption on minerals may result from a direct interaction between the solid surface and the adsorbate species due to electrostatic, chemical or other forces, or from an indirect activation process. In the latter case, a third component, often referred to as activator, modifies either the solid surface or the surfactant to aid adsorption. These effects leading to adsorption are influenced in turn by interactions such as micellization and precipitation of surfactant, dissolution of the solids followed by hydrolysis of dissolved species, complexation and precipitation. When the adsorption process is examined in the light of various chemical equilibria that may occur in the system, it becomes evident that in a number of systems adsorption is the result of precipitation of the adsorbate on the mineral surface.

In this paper, a number of cases of adsorption reported in the literature are analyzed to determine the role of surface precipitation in the adsorption process. It is shown that reactions such as precipitation that occur in the interfacial region are controlled by the activities of the species in that region and that, often, such reactions may occur in the interfacial region before they occur in the bulk solution. A thermodynamic basis for surface precipitation is presented and the conditions for surface precipitation in selected systems are correlated with those for adsorption, flotation and electrokinetic effects.

SURFACE VERSUS BULK PRECIPITATION

The distribution of various species between the interfacial region of a solid and the bulk solution is governed by the electrochemical properties of the solid and the properties of the bulk medium. The existence of an electrical potential at the solid—liquid interface, for example, will lead to preferential partitioning of oppositely charged counter-ions in the interfacial region. In such systems, under conditions of electrochemical equilibrium, the activity in the interfacial region is related to that in the bulk by the equation [1]

$$a_{i-s} = a_{i-b} \exp \frac{\mu_{i-s}^{\circ} - \mu_{i-b}^{\circ}}{RT} \quad (1)$$

Where a_{i-s} and a_{i-b} represent the activities of species i in the surface and bulk regions, respectively. μ_{i-s}° and μ_{i-b}° represent the standard electrochemical potential of species i in the surface and bulk regions, respectively. The difference $\mu_{i-s}^{\circ} - \mu_{i-b}^{\circ}$ represents the adsorption energy. Note that the activity of a species can be higher in the interfacial region than in the bulk solution, if favorable free energy changes accompany such a redistribution. Many reactions involving the adsorbate species may take place as a result of such a redistribution. For example, aggregation of surfactants at the solid—liquid interface leading to hemimicellization can be shown to occur when the interfacial concentration of the surfactant attains values equal to the "CMC". Similarly, reactions involving cations released from the solid and the adsorbate anions may also take place preferentially in the interfacial region under conditions when the surface is positively charged. However, in the absence of any favorable electrostatic or other forces, such reactions might be expected to take place simultaneously in the interfacial region as well as in the bulk. Surface precipitation may predominate if the kinetics of release of metallic species are relatively slow.

Specific examples from the literature involving the above interactions are discussed in the following sections.

ADSORPTION OF METALLIC SPECIES AT OXIDE—WATER INTERFACE

Adsorption behavior of multivalent species on oxide surfaces has been the subject of several investigations in the past [2—5]. In general, adsorption of

multivalent species on oxide surfaces exhibits a sharp pH dependence. Adsorption increases markedly at pH values just below that required for the precipitation of the corresponding metal hydroxide. This has been attributed to the chemisorption of the first metal-hydroxy species which have been suggested to exist in significant amounts under those pH conditions [2]. A typical example, viz., the adsorption of Ca species on silica, is given in Fig. 1 [3]. Ca adsorption is found to remain almost constant in the pH region 4–10 and to increase markedly around pH 11. This sharp increase has been attributed to the chemisorption of CaOH^+ which begins to form in significant amounts around this pH [2]. The adsorption process in this pH region can be examined from another view point. Evidently, some Ca^{2+} ($\approx 3 \times 10^{-10}$ mol cm^{-2}) adsorbs in the interfacial region in the pH region of 4 to 10. Therefore, the interfacial concentration of Ca^{2+} is higher than that in the bulk solution. Assuming that the thickness of the adsorbed layer is about 35 Å (thickness of the electrical double layer), the pH of precipitation of Ca(OH)_2 is estimated to be 11.4. On the other hand, if the thickness is assumed to be 10 and 4 Å (contact adsorption), the respective pH values for precipitation are 11.15 and 10.96. Note that the surface region should attain the above pH value for precipitation to occur in the interfacial region. In the absence of any added Ca, the surface pH of silica can be expected to be lower than its bulk value. This difference can, however, be expected to decrease in the presence of adsorbed calcium. In fact, our estimates of equivalent negative sites of 4.2×10^{-10} mol cm^{-2} , based on the available information on the

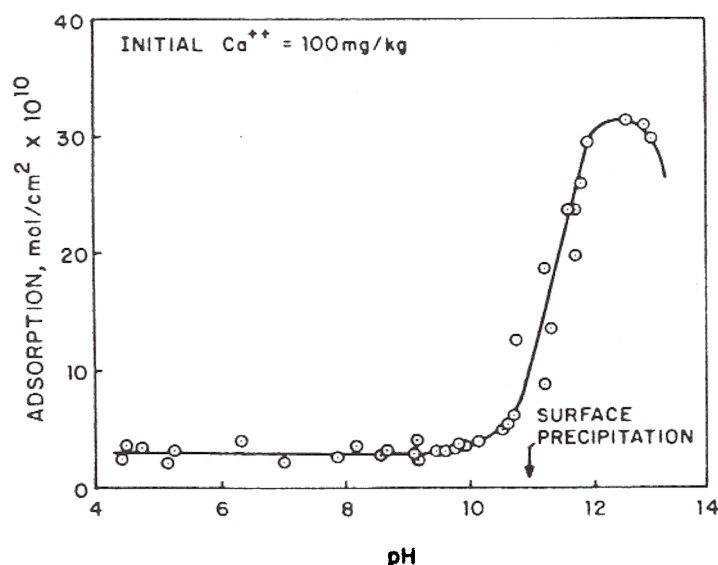


Fig. 1. pH dependence of Ca adsorption on quartz. $K_{sp}(\text{Ca(OH)}_2) = 10^{-5.3}$ [6]. pH of surface precipitation for different assumed values of adsorbed-layer thickness (δ): δ (35Å): pH = 11.4, δ (10Å): pH = 11.15, δ (4Å): pH = 10.96. (After Clark and Cooke [3].)

charge density of silica ($40 \mu\text{C cm}^{-2}$ at pH 11 and ionic strength $10^{-2} \text{ kmol m}^{-3}$) suggests that in the present case, the surface pH will not be significantly different from the bulk pH, since $3 \times 10^{-10} \text{ mol cm}^{-2}$ of calcium is reported to adsorb at this pH. Thus, it can be seen that the sharp increase in adsorption coincides with the conditions for the surface precipitation of $\text{Ca}(\text{OH})_2$.

Similar results for the adsorption of Co^{2+} on silica [5] and our estimate of pH of precipitation are given in Fig. 2. Again, the marked increase in cobalt adsorption around pH 7 can be attributed to surface precipitation of $\text{Co}(\text{OH})_2$.

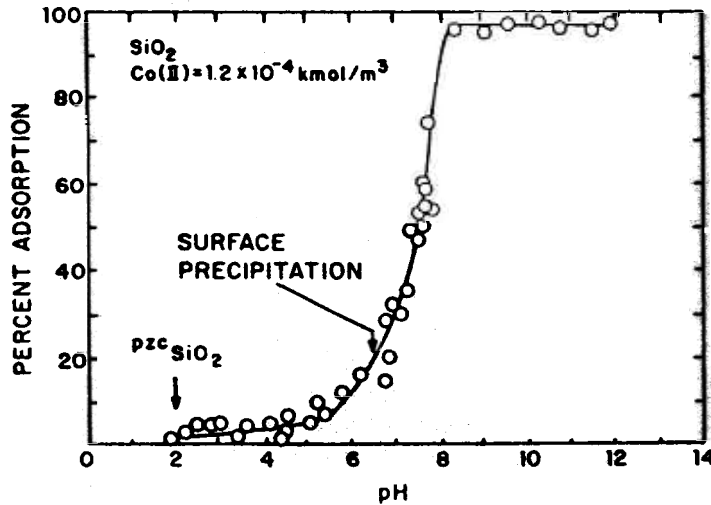


Fig. 2. Experimental adsorption isotherm for Co^{II} adsorption at $1.2 \times 10^{-4} \text{ kmol m}^{-3}$ on silica at 25°C . The available surface area is $75 \text{ m}^2 \text{ l}^{-1}$. $K_{\text{sp}}(\text{Co}(\text{OH})_2) = 10^{-15}$ [5]; pH of precipitation of $\text{Co}(\text{OH})_2$ for different values of adsorbed layer thickness (δ): δ (10Å): pH = 6.9, δ (4Å): pH = 6.7. (After James and Healy [5].)

Another interesting example of metal-ion adsorption, which is often quoted as a counter argument to surface precipitation [2], is that of the ferric species on alumina (Fig. 3). Adsorption of Fe^{3+} on alumina increases markedly around pH 2. It is argued in this case that the ferric species as well as ferric hydroxide are highly positively charged around pH 2 and hence precipitation of metal hydroxide on a positively charged alumina is unlikely [2]. However, it is to be noted that since alumina is positively charged around pH 2, the surface pH in this case will be higher than the bulk pH. The zeta potential of alumina at pH 2 is about 55 mV. An estimate of the surface pH can be obtained using the measured value of zeta potential and the equation [6]:

$$\text{pH}_s = \text{pH}_b + F\psi_d / 2.3 RT \quad (2)$$

According to this, when the bulk pH is 2, the surface pH can be as high as 2.8. The pH required for the precipitation of $\text{Fe}(\text{OH})_3$ ($K_{\text{sp}} = 10^{-38.7}$ [6]) at $10^{-4} \text{ kmol m}^{-3} \text{ FeCl}_3$ is only 2.4. In other words, when the bulk pH is 2, the

surface pH may be much higher than that required for the precipitation of $\text{Fe}(\text{OH})_3$. It is possible that a surface pH higher than 2.4, maybe as high as 2.8, is necessary for surface precipitation, because the concentration of ferric species in the interfacial region will be less than its value in the bulk solution. Thus, it is clear that the sharp increase in ferric uptake by alumina around pH 2 can also be considered to be the result of surface precipitation of $\text{Fe}(\text{OH})_3$.

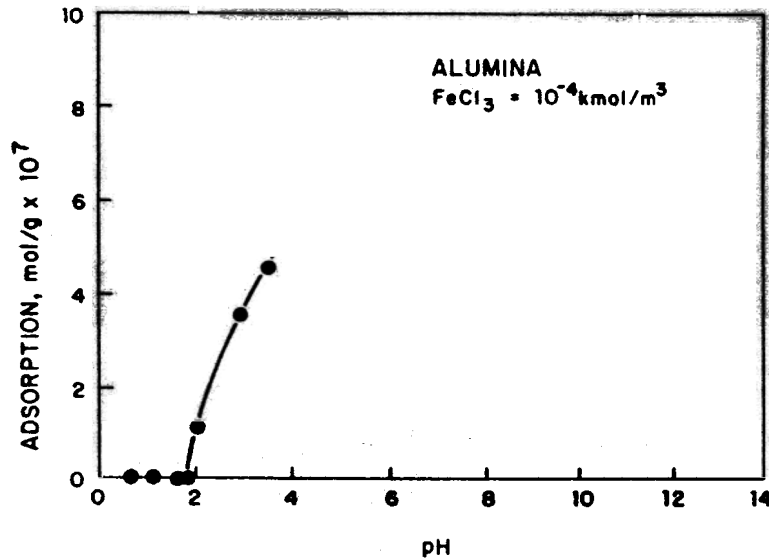


Fig. 3. pH dependence of adsorption of ferric species on alumina. $\text{FeCl}_3 = 10^{-4} \text{ kmol m}^{-3}$. $K_{sp}(\text{Fe}(\text{OH})_3) = 10^{-38.7}$ [6]. ξ (alumina, pH 2) = 55 mV [3], surface pH corresponding to bulk pH of 2 = 2.8, pH for $\text{Fe}(\text{OH})_3$ precipitation = 2.4. (After Fuerstenau and Palmer [2].)

As discussed earlier, the marked increase in cobalt adsorption on silica around pH 7 may be due to the surface precipitation of $\text{Co}(\text{OH})_2$. James and Healy [4], on the basis of their electrokinetic potential measurements, have shown that the surface of silica under these conditions becomes similar to that of $\text{Co}(\text{OH})_2$. According to these authors, oxide minerals in general in the presence of multivalent ions exhibit a characteristic zeta-potential dependence on pH. Such systems exhibit three charge reversals. The first charge-reversal pH (CR1) corresponds to the point of zero charge of the mineral oxide. The second charge reversal occurs around the pH where the "adsorption" exhibits its sharp increase. James and Healy [4] have attributed the second charge-reversal point (CR2) to the onset of surface precipitation of the adsorbate hydroxide on the original oxide surface. The third charge-reversal point (CR3) corresponds to the point of zero charge of the adsorbate hydroxide.

Based on the dependence of the second charge-reversal pH (CR2) on the

solids concentration in the case of the Co^{2+} —silica system, these authors have further argued that the surface precipitation is governed by a thermodynamic solubility product which is different from that for the bulk precipitation. The present analysis shows that it is not necessary to invoke a new thermodynamic constant for surface precipitation, if the interfacial activities of the species involved are considered. This is further examined below.

A plot of CR2 versus solids concentration for the Co^{2+} —silica system is given in Fig. 4. Note that the total concentration of Co species is constant and equal to $10^{-4} \text{ kmol m}^{-3}$. The solubility product of $\text{Co}(\text{OH})_2$ is 10^{-15} [5] and, therefore, the precipitation of $\text{Co}(\text{OH})_2$ in the bulk solution, in the absence of any solid, is expected only at pH 8.5. The second charge-reversal pH, which is indicative of the onset of surface precipitation, is found to decrease with decrease in the solids concentration. A decrease in solids concentration at constant total Co concentration should lead to higher adsorption, expressed per unit area of solid, but also to higher equilibrium concentration in the bulk solution because of lower depletion. Thus, as the solids concentration is decreased both the interfacial concentration and the bulk equilibrium concentration will increase. Consequently, the pH for surface precipitation will continue to decrease with decrease in solids concentration. If this point is extrapolated to zero solids concentration, the corresponding value of CR2 is 7.8. According to James and Healy [4], this value of CR2 should have corresponded to bulk precipitation of $\text{Co}(\text{OH})_2$. Since at $10^{-4} \text{ kmol m}^{-3}$ cobalt, bulk precipitation of $\text{Co}(\text{OH})_2$ is expected to occur only at pH 8.5, these authors postulated that the surface precipitation is controlled by a solubility product which is different from that for the bulk solution. This phenomenon can, however, be examined in the following manner also. Surface precipitation of $\text{Co}(\text{OH})_2$ occurs mainly because the surface concentration of Co^{2+} is higher than that in the bulk solution. Even at the pH corresponding to extrapolated zero solids, the Co concentration responsible for precipitation is the surface concentration. Thus, the extrapolated value of CR2 represents the bulk precipitation pH of a system which has a bulk cobalt concentration equal to the extrapolated value of the surface concentration of the present system. In other words, if the bulk solution had cobalt equivalent to the extrapolated value of surface concentration corresponding to zero solids, then the precipitation of $\text{Co}(\text{OH})_2$ would have occurred at pH 7.8. This value of surface concentration in fact corresponds to the adsorption density when the equilibrium Co^{2+} in the system is $10^{-4} \text{ kmol m}^{-3}$. Using the experimental result, given in Ref. [5], the adsorption density of cobalt at an equilibrium concentration of $10^{-4} \text{ kmol m}^{-3}$ and at a pH of 7.8 is $10^{-10} \text{ mol cm}^{-2}$. Assuming an adsorbed layer thickness of 300 Å (electrical double-layer thickness), the corresponding surface concentration is estimated to be $0.033 \text{ kmol m}^{-3}$. Using this concentration and the solubility-product value for bulk precipitation, the pH of precipitation is 7.2. Thus, at the extrapolated value of CR2, precipitation of $\text{Co}(\text{OH})_2$ would occur if the bulk solution has Co^{2+} equal to the extrapolated interfacial concentra-

tion corresponding to zero solids. The present calculations therefore show that, in the case of the Co^{2+} -silica system, the surface precipitation is governed by the same bulk-precipitation constant. Furthermore, these results suggest that the intrinsic reactivities of Co^{2+} and OH^- have not necessarily changed in the interfacial region and the observed surface precipitation at pH values below that for bulk precipitation is merely due to the higher concentration of Co^{2+} in the interfacial region.

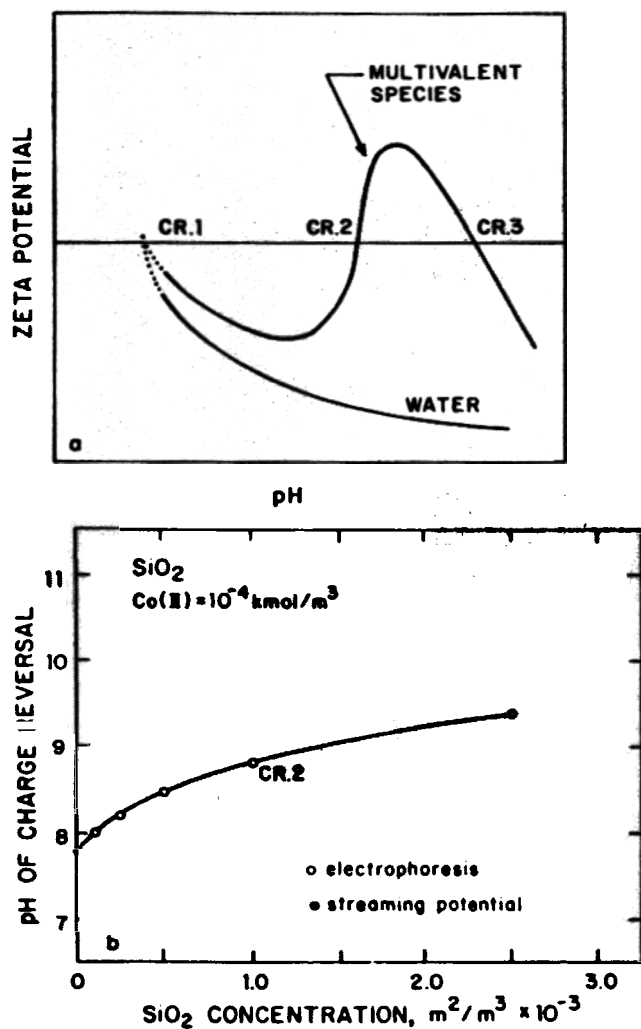


Fig. 4. (a) Schematic diagram illustrating the three charge-reversal points of SiO_2 in the presence of multivalent metallic species. (b) The pH of charge-reversal CR.2 of SiO_2 in $10^{-3} \text{ kmol m}^{-3}$ electrolyte, and $10^{-4} \text{ kmol m}^{-3}$ Co^{II} solutions as a function of the available surface area of the colloid per unit volume of suspension. (After James and Healy [4].)

ELECTROPHORETIC MOBILITY

If precipitation of adsorbate species occurs on the mineral, then its surface should behave similarly to that of the precipitate. A powerful tool which can be used to identify such surface alterations, without subjecting the samples to treatments used in spectroscopic techniques, is the measurement of electrophoretic mobility. A shift in the isoelectric point (IEP) of the mineral in the presence of surfactants has often been considered to indicate chemisorption [7]. Examples are, however, provided in this section to show that the solution conditions giving rise to such shifts in fact correspond to those for the precipitation of surfactant salts.

The results of Mishra et al. [8] for the electrophoretic mobility of apatite in oleate solutions (Fig. 5) show that the apatite surface becomes progressive-

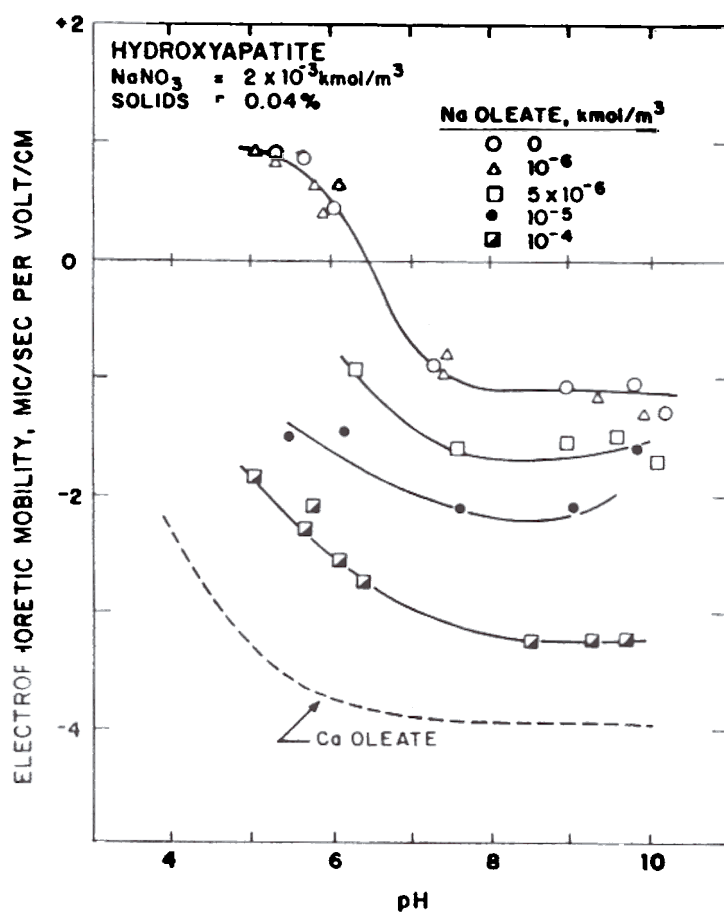


Fig. 5. Electrophoretic mobility—pH curves for hydroxyapatite for varying concentration of sodium oleate in $2 \times 10^{-3} \text{ kmol m}^{-3} \text{ NaNO}_3$. Significant shift occurs in isoelectric point at $5 \times 10^{-6} \text{ kmol m}^{-3}$ oleate. Precipitation of Ca—oleate (pH 6.5) occurs at $2 \times 10^{-5} \text{ kmol m}^{-3}$ oleate. (After Mishra et al. [8].)

ly similar to that of Ca-oleate with increase in oleate concentration. This is indicative of the formation of Ca-oleate on the mineral surface. The interesting point to note here is that, at 10^{-6} kmol m^{-3} oleate, the electrophoretic mobility of apatite is almost identical to its value in water. At 5×10^{-6} kmol m^{-3} oleate, however, a significant shift in the IEP is observed. Traditionally these results would be interpreted to suggest that chemisorption of oleate on apatite begins at some oleate level between 10^{-6} and 5×10^{-6} kmol m^{-3} oleate. Our calculations show that, at the IEP of the mineral ($pH_{IEP} = 6.5$ and Ca^{2+} in solution = 10^{-4} kmol m^{-3} [9]), the concentration of oleate required to precipitate Ca-oleate is 2×10^{-6} kmol m^{-3} . The first significant change in the apatite IEP can thus be seen to occur at oleate levels required for the precipitation of Ca-oleate. In another study, Wang and Somasundaran [10] have shown that minerals such as calcite, kaolinite and titania, in the presence of $CaCl_2$ and Na-oleate, exhibit identical zeta-potential values, suggesting the formation of Ca-oleate in all three systems.

Yet another system considered to involve chemisorption and exhibiting a shift in IEP is that of hematite-octylhydroxamate illustrated in Fig. 6 [11]. At a hydroxamate level of 2×10^{-5} kmol m^{-3} , a change in the IEP of hematite from 8.1 to 7 is observed. In this case also, with increase in the hydroxamate concentration, the surface is progressively becoming similar to that of ferric hydroxamate. Using the available thermodynamic data for the formation of ferric hydroxamate [11], the conditions for its precipitation have been determined and the results are given in Fig. 7. Evidently, at 2×10^{-5} kmol m^{-3} hydroxamate, ferric hydroxamate can be expected to precipitate in the entire pH region.

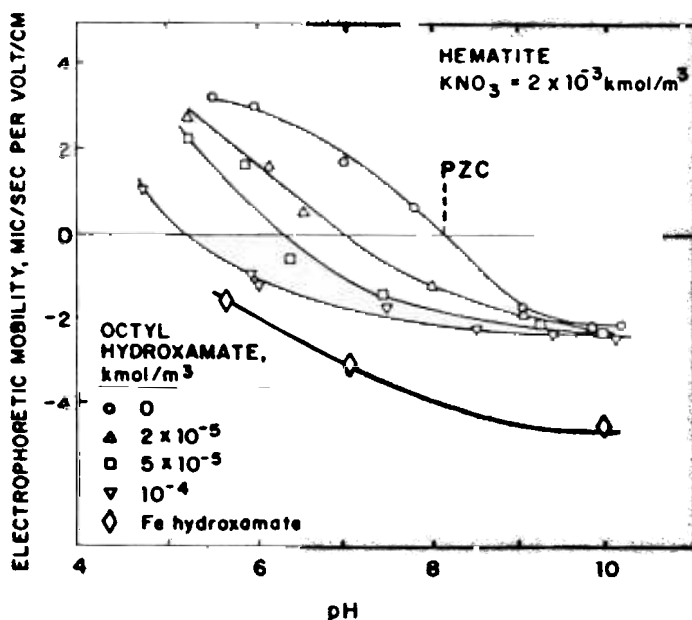


Fig. 6. Electrophoretic mobility of hematite at various levels of hydroxamate. See Fig. 7 for ferric hydroxamate precipitation conditions. (After Raghavan and Fuerstenau [11].)

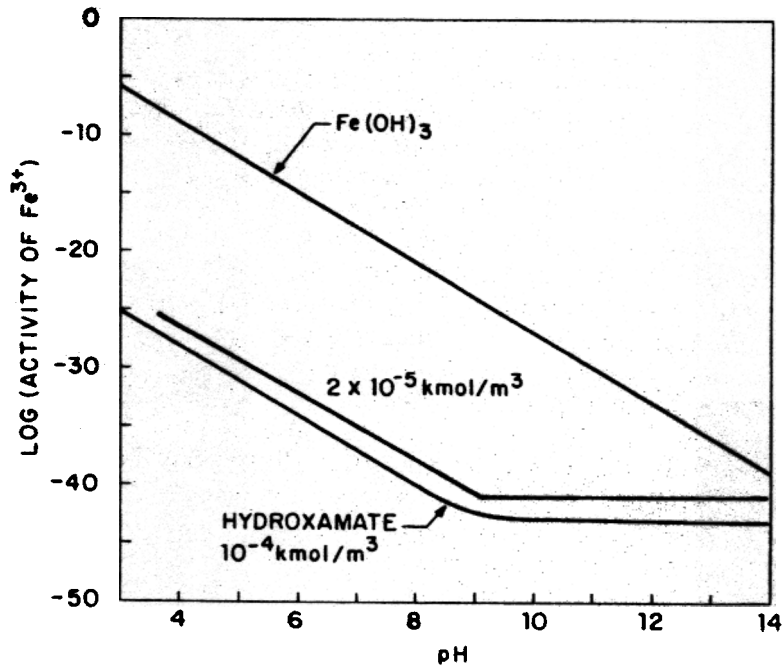
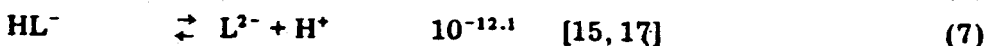
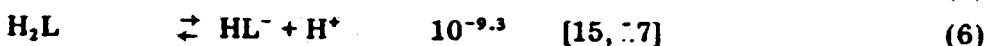
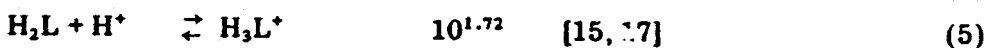
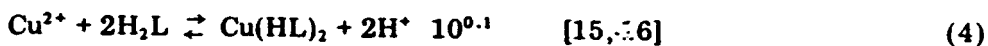
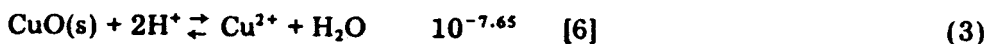


Fig. 7. Activity of Fe^{3+} in equilibrium with $\text{Fe}(\text{OH})_3$ and ferric hydroxamate. At 2×10^{-5} and $10^{-4} \text{ kmol m}^{-3}$ hydroxamate, Fe^{3+} from $\text{Fe}(\text{OH})_3$ can precipitate ferric hydroxamate.

FLOTATION

In this section, the so-called "chemisorption conditions" for the flotation of selected oxide, carbonate and phosphate minerals are shown to correspond to those for the precipitation of cation-collector salts in the interfacial region.

Chelating-type collectors such as hydroxamate and salicylaldoxime (SALO) are considered to chemisorb strongly on the mineral surface and cause their flotation [11–14]. Typical results for the flotation of tenorite (CuO) using SALO are given in Fig. 8 [13]. Flotation increases sharply above $2 \times 10^{-4} \text{ kmol m}^{-3}$. Using the equilibria given below, the SALO (H_2L) concentration required for the precipitation of $\text{Cu}(\text{HL})_2$ is estimated to be $1.7 \times 10^{-4} \text{ kmol m}^{-3}$.



Interestingly, the SALO flotation of CuO increases markedly just above this concentration. The calculations are for the precipitation of the Cu-SALO complex in the bulk solution. However, since at pH 4.8 almost all the SALO (>99.9%) is present in the neutral molecule form, both the surface and bulk precipitation can be expected to take place under identical conditions, and thus the conditions for flotation in this case are seen to correspond to that for the precipitation of Cu-SALO complex in the interfacial region.

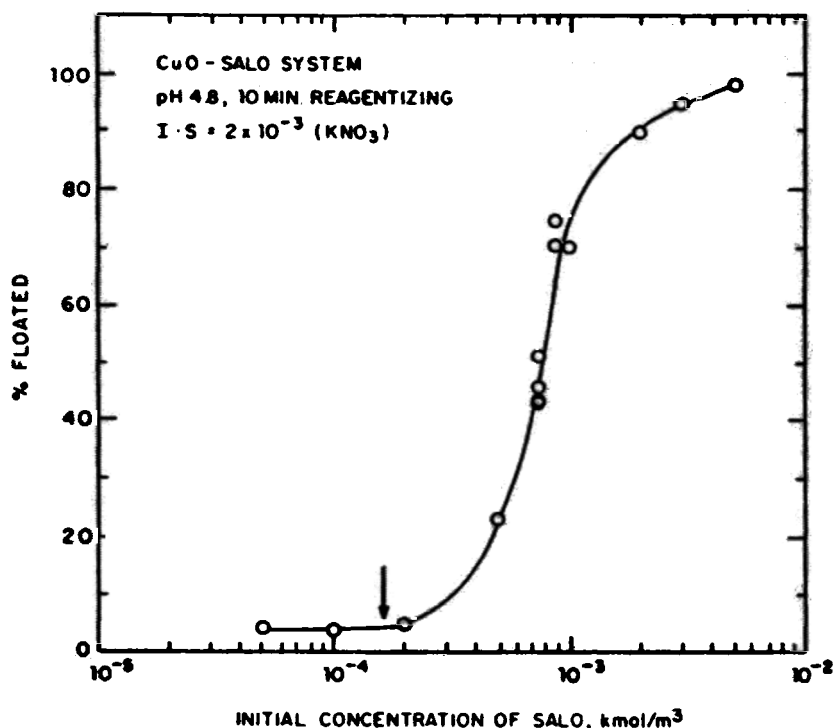


Fig. 8. Dependence of CuO flotation on SALO concentration. Arrow indicates the onset of precipitation of Cu-SALO complex. (After Nagaraj and Somasundaran [13].)

The above calculations may be extended to determine the pH range of flotation at a given level of SALO by computing the activity of Cu^{2+} in equilibrium with CuO and Cu-SALO complex. The results given in Fig. 9 show that the amount of Cu^{2+} released from the mineral in the pH range 1.2 to 9.8 is higher than that required to precipitate the Cu-SALO complex. Thus, the Cu-SALO complex is stable in the pH range 1.2 to 9.8 and hence both surface and bulk precipitation are expected to occur in this pH region. Flotation results given in Fig. 10 show the pH range of CuO flotation to be in excellent agreement with that predicted on the basis of experimentally determined surface precipitation [13]. The presence of a minimum in the flotation in the above pH region is related to the preferential bulk precipita-

tion in this region and the results of Nagaraj and Somasundaran [13] show good correlation between the chelate on the surface and the mineral flotation. It should be noted that in the latter work, the role of partitioning of the surfactant between the surface and the bulk precipitate was recognized for the first time and flotation was correlated with the formation of surface precipitate.

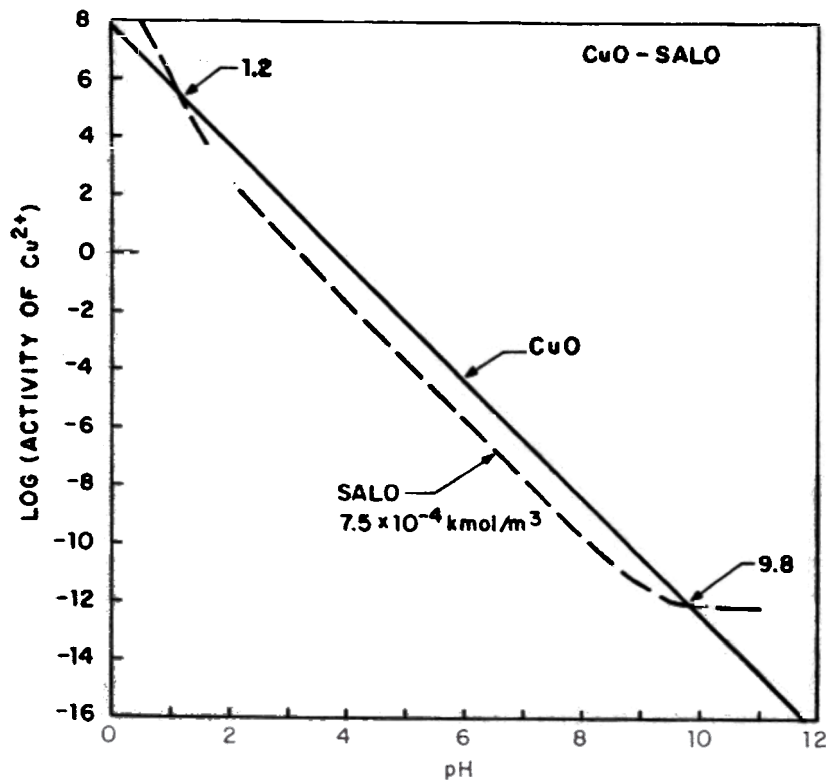


Fig. 9. Activity of Cu^{2+} in equilibrium with Cu-SALO complex and CuO . pH of precipitation of Cu-SALO complex = 1.2-9.8.

The combination of anionic surfactants and semi-soluble minerals represents another class of "chemisorption" system. The typical flotation behavior of calcite [18], dolomite [19] and apatite [19] using anionic surfactants is shown in Figs 11 and 12. Note that, under the pH conditions of flotation, the minerals have either zero charge or some negative charge. Electrostatic factors in these systems should, therefore, not result in measurable excess of surfactant in the interfacial region. The bulk-precipitation conditions should represent the lower limit of surface precipitation. This is obtained again by determining the Ca^{2+} activity in equilibrium with the minerals and the surfactant required to precipitate Ca-surfactant salt under the respective pH conditions [9]. The detailed procedure to determine the activity of Ca^{2+} in equilibrium with various minerals is given in Refs [6, 9,

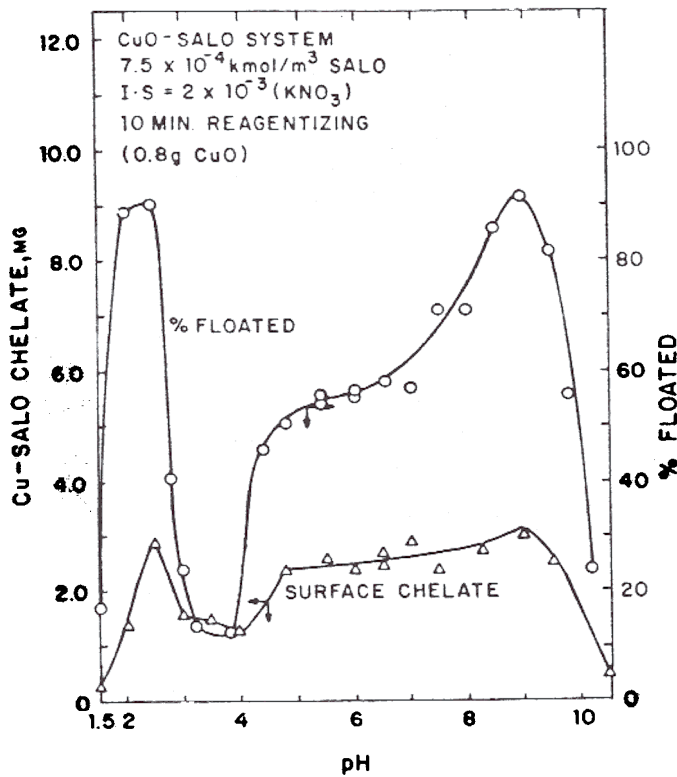


Fig. 10. pH dependence of flotation and surface chelation. Flotation pH range coincides with the precipitation range given in Fig. 9. (After Nagaraj and Somasundaran [13].)

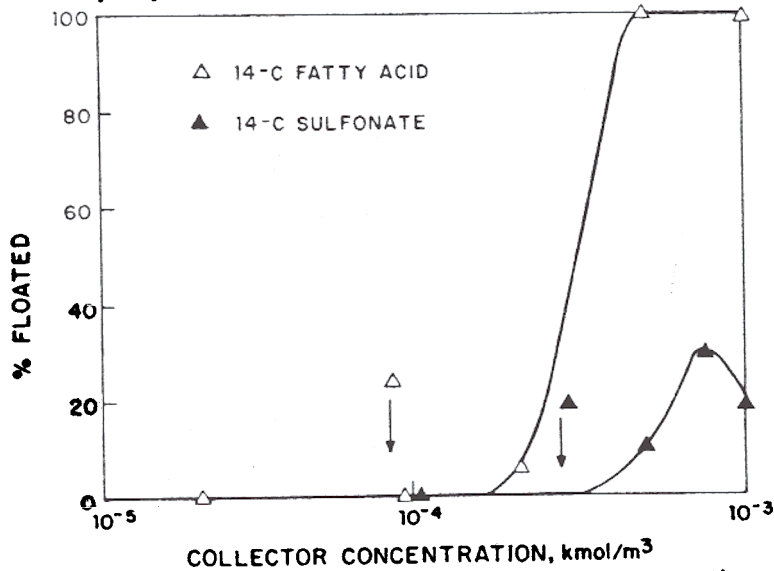


Fig. 11. Dependence of calcite flotation on collector concentration. Arrows indicate the onset of precipitation of Ca-surfactant salt ($\text{pH} = 9.7$). Estimated concentration of $\text{Ca}^{2+} = 4 \times 10^{-7} \text{ kmol m}^{-3}$ (system open to atmosphere). K_{sp} (C-14 fatty acid) = 2.5×10^{-15} [2], K_{sp} (C-14 sulfonate) = 2.9×10^{-14} . (After Fuerstenau and Miller [18].)

20]. The minimum concentration of the surfactant required to precipitate the Ca-salt in each of the above cases is indicated in Figs 11 and 12. The concentration at which flotation begins to occur can be clearly seen to correspond to the onset of Ca-surfactant-salt precipitation.

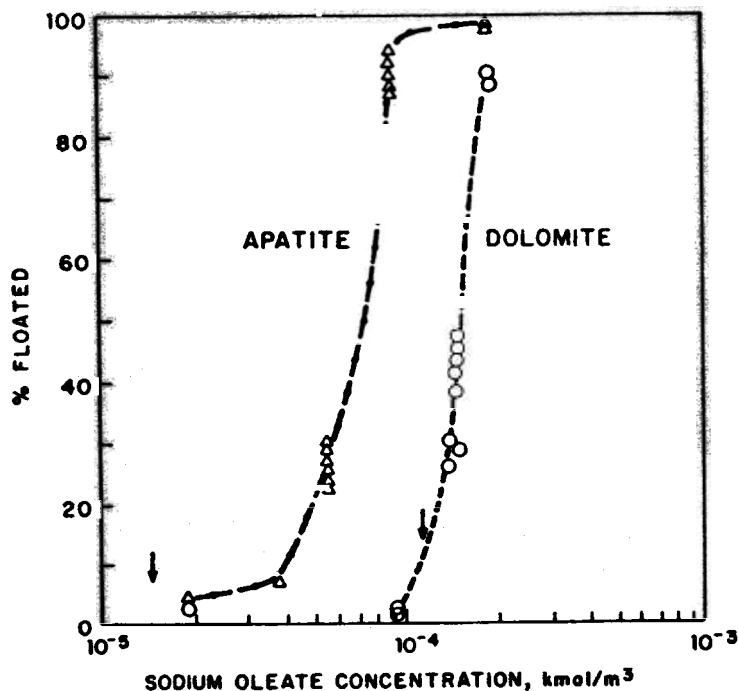


Fig. 12. Flotation of apatite and dolomite as a function of oleate concentration. Arrows indicate the onset of precipitation of Ca-oleate (pH = 10). Ca^{2+} (dolomite) = 2.8×10^{-4} kmol m⁻³, Ca^{2+} (apatite) = 2×10^{-6} kmol m⁻³, K_{sp} (Ca-oleate) = 4×10^{-16} [21]. (After Moudgil and Chanchani [19].)

In addition to the above, the possibility of surface precipitation has been considered also in dodecylbenzenesulfonate-Bereasandstone[22]/limestone-[22]/kaolinite[23] systems. In these systems, the experimentally observed adsorption maximum has been attributed to the surface precipitation of multivalent ion-surfactant complexes in the low concentration region and the redissolution of such precipitates in micellar solutions.

Unlike the situation in the systems examined above, if electrostatic factors are favorable for adsorption, then the surfactant concentration in the interfacial region will be higher than that in the bulk solution. The interactions that occur in the interfacial region will depend essentially upon the relative concentrations of the surfactant required to form hemimicelles [24, 25] and to precipitate the surfactant salt. If the HMC (hemimicelle concentration) is lower, then the formation of hemimicelles would be preferred over the salt precipitation. This can be illustrated using the alumina-dode-

cylsulfonate system in which adsorption has been established to be due to a combination of electrostatic and chain-chain-interaction forces, leading to hemimicellization [24, 25]. The activity of Al^{3+} in equilibrium with alumina as well as with Al-dodecylsulfonate is shown in Fig. 13. At 7.5×10^{-5} kmol m^{-3} sulfonate, the Al^{3+} concentration required to precipitate Al-sulfonate is much higher than that available from dissolved alumina. Even at a higher sulfonate monomer concentration equal to its bulk CMC (9.8×10^{-3} kmol m^{-3}), precipitation can occur only at pH values below 5.0. Thus under neutral pH conditions, precipitation of Al-sulfonate is not expected in the system. As the sulfonate concentration is increased, the interfacial concentrations can attain values corresponding to the bulk "CMC", and hemimicelle formation will begin. From calculations using the sulfonate-adsorption density at the onset of hemimicellization (2.7×10^{-12} mol cm^{-2} [27]) and assuming the adsorbed-layer thickness to be equal to the electrical double-layer thickness (67 Å, ionic strength = 2×10^{-3} kmol m^{-3} NaCl), the concentration in the interfacial region is estimated to be 4×10^{-3} kmol m^{-3} . If, on the other hand, the adsorbed-layer thickness is assumed to be 20 Å, the interfacial concentration will be 1.35×10^{-2} kmol m^{-3} . There will indeed be a distribution of sulfonate within the double layer. In any case, the sulfonate level in the interfacial region can be considered to be of the order

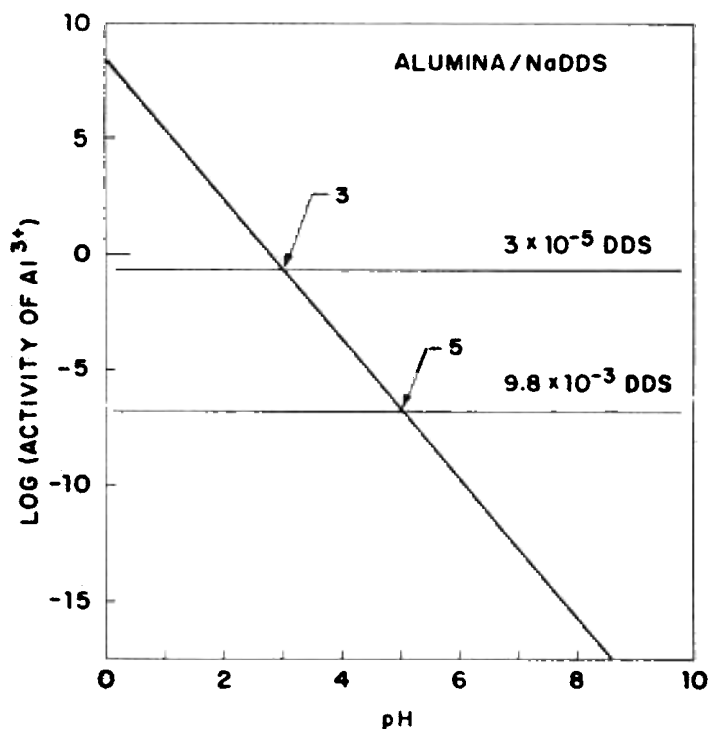


Fig. 13. Activity of Al^{3+} in equilibrium with alumina and aluminum dodecylsulfonate. $K_{sp}(\text{Al}(\text{OH})_3) = 3.2 \times 10^{-34}$ [6], $K_{sp}(\text{Al}(\text{DDS})_3) = 3.3 \times 10^{-14}$ [26].

indicated above and is close to the bulk CMC of dodecylsulfonate, 9.8×10^{-3} kmol m^{-3} . Thus, in this case, formation of hemimicelles occurs as opposed to precipitation of Al-sulfonate (hemimicellization itself can be considered to be a surface-condensation phenomenon).

SUMMARY AND CONCLUSIONS

Electrokinetic, adsorption and flotation behavior of a number of mineral/surfactant systems has been analyzed to show that the conditions of marked increase in "chemisorption" coincide with those for the precipitation of the cation-surfactant salt in the interfacial region. Adsorption of the surfactant in the interfacial region due to electrostatic or other forces, or accumulation of metallic species in the interfacial region due to slow release and transport of the dissolved species into the bulk, can lead to surface precipitation. In the absence of any favorable adsorption forces, both the surface and bulk precipitation may occur simultaneously. If, on the other hand, the concentration of metallic species released from the solid is not sufficient to cause precipitation, then above a critical interfacial concentration close to critical micelle concentration in the bulk solution, the surfactant may form hemimicelles at the solid-liquid interface.

The marked pH dependence of adsorption of metallic species such as calcium or cobalt on oxides may also be due to the surface precipitation of the hydroxide on the mineral surface. Evidently, it is not necessary to invoke chemisorption of hydrolyzed metallic species, to account for the above pH dependence. Furthermore, a detailed analysis of the Co^{2+} -silica system suggests that the solubility product which governs the precipitation in the bulk solution, controls also the surface precipitation. It is noted that the reactions that occur in the interfacial region are determined by the activities of the species in the interfacial region and that the latter can be significantly different from the activities in the bulk solution. It is seen that the reactions that occur in the interfacial region can be predicted from a knowledge of the mineral-solution equilibria and surface chemical and electrokinetic properties of the solid.

ACKNOWLEDGEMENT

The authors acknowledge the support of the Minerals and Primary Materials Program of the National Science Foundation (CPE-83-04059).

REFERENCES

- 1 D.W. Fuerstenau and S. Raghavan, Some Aspects of the Thermodynamics of Flotation, in M.C. Fuerstenau (Ed.), Flotation, A.M. Gaudin Memorial Vol. I, AIME, New York, NY, 1976, pp. 21-65.

- 2 M.C. Fuerstenau and B.R. Palmer, Anionic Flotation of Oxides and Silicates, in M.C. Fuerstenau (Ed.), Flotation, A.M. Gaudin Memorial Vol. I, AIME, New York, NY, 1976, pp. 148—196.
- 3 S.W. Clark and S.R.B. Cooke, Trans AIME, 241 (1968) 334.
- 4 R.O. James and T.W. Healy, J. Colloid Interface Sci., 40 (1972) 53.
- 5 R.O. James and T.W. Healy, J. Colloid Interface Sci., 40 (1972) 42.
- 6 W. Stumm and J.J. Morgan, Aquatic Chemistry, Wiley Interscience, New York, NY, 1981, pp. 241—247; 749—756.
- 7 D.W. Fuerstenau, The Adsorption of Surfactants at the Solid—Water Interfaces, in M.L. Hair (Ed.), The Chemistry of Biosurfaces, Dekker, New York, NY, 1971, pp. 143—176.
- 8 K. Mishra, S. Chander and D.W. Fuerstenau, Colloids Surfaces, 1 (1980) 105.
- 9 K.P. Ananthapadmanabhan and P. Somasundaran, The Role of Dissolved Mineral Species in Calcite—Apatite Flotation, Minerals and Metallurgical Processing, May, 1984, pp. 36—42.
- 10 Y.H. Wang and P. Somasundaran, Trans AIME, 272 (1981) 1970—1974.
- 11 S. Raghavan and D.W. Fuerstenau, J. Colloid Interface Sci., 50 (1975) 319—330.
- 12 M.C. Fuerstenau, J.D. Miller and G. Gutierrez, Trans. AIME, 238 (1967) 200—203.
- 13 D.R. Nagaraj and P. Somasundaran, Trans. AIME, 270 (1981) 1351.
- 14 D.R. Nagaraj and P. Somasundaran, Trans. AIME, 266 (1979) 1892.
- 15 D.R. Nagaraj, Chelating Agents as Flotoids: Hydroxyoximes—Copper Minerals Systems, D. Eng. Science Thesis, Columbia University, New York, NY, 1979.
- 16 K. Burger and I. Egyed, J. Inorg. Nucl. Chem., 27 (1965) 2361—2370, quoted in Ref. [15].
- 17 L.G. Sillen and A.E. Martell, Stability Constants of Metal-Ion Complexes, The Chemical Society of London, Publ. No. 17, 1964 and No. 25, 1971.
- 18 M.C. Fuerstenau and J.D. Miller, Trans. AIME, 238 (1967) 153—160.
- 19 B.M. Moudgil and R. Chanchani, Flotation of Apatite and Dolomite Using Sodium Oleate as the Collector, SME-AIME preprint No. 83-160, 1984.
- 20 P. Somasundaran, J.O. Amankonah and K.P. Ananthapadmanabhan, Mineral—Solution Equilibria in Sparingly Soluble Mineral Systems, Colloids Surfaces, submitted.
- 21 C. DuRietz, Chemisorption of Collectors in Flotation, XIth International Mineral Processing Congress, Cagliari, Paper No. 13, 1975, Istituto di Arte Mineraria, University Cagliari.
- 22 H.S. Hanna, A. Goyal and P. Somasundaran, Surface-Active Properties of Certain Micellar Systems for Tertiary Oil Recovery, 7th International Congress on Surface-Active Substances, Vol. 3, VTE, Moscow, 1976, p. 892.
- 23 K.P. Ananthapadmanabhan and P. Somasundaran, Colloids Surfaces, 7 (1983) 105—114.
- 24 P. Somasundaran and D.W. Fuerstenau, J. Phys. Chem., 70 (1966) 90.
- 25 P. Somasundaran, T.W. Healy and D.W. Fuerstenau, J. Phys. Chem., 68 (1964) 3562.
- 26 P. Siracusa and P. Somasundaran, unpublished results, Columbia University, New York, NY, 1984.
- 27 T. Wakamatsu and D.W. Fuerstenau, Adv. Chem. Ser., 79 (1968) 161.

