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# Adsorption of Surfactants on Mineral Solids

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Factors influencing the adsorption of ionic surfactants on solids are outlined. Emphasis is placed on the role of electrostatic forces and of lateral association within adsorbed layers. Mechanisms leading to charge generation on solids are described, and the dependence of adsorption on charge effects is illustrated by reference to published data on a number of different solid surfactant systems. It is shown how the electrostatic factor can be strongly modified by the presence of inorganic salts. The importance of chain-chain interactions is illustrated by the influence of chains length and composition on adsorption, and also by the pH dependence of the adsorption of long chain, weak electrolytes. This leads to a discussion of the possible role of highly surface active long chain complexes. Lastly, the influence of polymers on the adsorption of surfactants is discussed.

## INTRODUCTION

Adsorption on solids in contact with aqueous solutions (or the absence of it) is important in controlling a variety of interfacial processes such as mineral flotation and other solid-liquid separations, blood clotting, micellar flooding of oil wells, *etc.* Adsorption, which is essentially selective partitioning of the adsorbate into the interfacial region, must result from the more energetically favorable interaction between the adsorbate species and the chemical species in the interfacial region than between the former and those in the bulk solution. Several factors, such as electrostatic attraction, covalent bonding, hydrogen bonding or non-polar interaction between the adsorbate and interfacial species, lateral interaction among the adsorbed species and desolvation effects, can contribute to the adsorption process.

Density of adsorption of the organic species or the inorganic species, adsorption of which can in turn control adsorption of the former, is commonly interpreted using the Stern-Grahame equation:

$$\Gamma_{\delta} = 2r\ C\ exp\left(\frac{-\overline{\Delta G^{0}}_{\text{ads}}}{RT}\right) \tag{1}$$

where $\Gamma_{\delta}$ is the adsorption density in the plane $\delta$, which is at the distance of closest approach of counter ions to the surface, $r$ is the effective radius of the adsorbed ion, C is the bulk concentration of the adsorbate in mole/m. l., R is the gas constant, T is the absolute temperature and $\overline{\Delta G^{0}}_{\text{ads}}$ is the standard free energy of adsorption. $\overline{\Delta G^{0}}_{\text{ads}}$, the driving force for adsorption will be the sum of a number of contributing forces mentioned above and can be writen as[1,2]

$$\overline{\Delta G}^{o}_{ads} = \Delta G^{o}_{elec} + \Delta G^{o}_{chem} + \Delta G^{o}_{c\text{-}c} + \Delta G^{o}_{c\text{-}s} + \Delta G^{o}_{H} + \Delta G^{o}_{H_2O} \ \ldots \tag{2}$$

$\Delta G^{o}_{elec}$ is the electrostatic interaction term and is equal to z $F\Psi_{\delta}$ where z is the valency of the adsorbate species, F the Faraday constant and $\Psi_{\delta}$ the potential in the $\delta$ plane, $\Delta G^{o}_{chem}$ is the chemical term due to covalent bonding, $\Delta G^{o}_{c-c}$ is the lateral interaction term owing to the cohesive chain-chain interaction among adsorbed long chain surfactant species, $\Delta G^{o}_{c-s}$ is similar interaction between the hydrocarbon chains and hydrophobic sites on the solid, $\Delta G^{o}_{H}$ is the hydrogen bonding term and $\Delta G^{o}_{H_2O}$ is the desolvation term owing to hydration of the adsorbate species or any species displaced from the interface due to adsorption. For each surfactant-mineral system several of the above terms can be contributing depending on the mineral and surfactant type, surfactant concentration, temperature, etc. For non-metallic minerals, electrostatic attraction and lateral interaction effects are considered to be the major factors determining adsorption of surfactants and will receive emphasis in this paper. On the other hand, for salt-type minerals such as calcite and sulfides such as galena, the chemical term can become significant.

Adsorption, as mentioned earlier, is also dependent on the type of surfactant. Even for the same surfactant, its adsorptive power can change as a function of pH owing to its tendency to form complexes between its own various forms. This effect is recognized to be a major one for certain systems and will also receive particular emphasis here.

## *Electrostatic Factor*

The generation of the electrical field at the interface that is responsible for the electrostatic interaction can be brought about by preferential dissolution of lattice ions, which is often accompanied by reactions with the solution constituents, and possible uptake of the complexes by the solid, as in the case of calcite[3] and apatite[4] or by hydrolysis of surface species followed by pH and potential[5] dependent dissociation of the surface hydroxyls, as in the case of silica and alumina[6,7]. Alternate mechanisms, which involve dissolution of lattice ions followed by hydrolysis in the bulk and subsequent adsorption of the complexes proposed for the surface charge generation on oxides[8], or that involve preferential hydrolysis of the surface species proposed for surface charge generation on salt-type minerals[3,4], yield thermodynamically identical final results. The sign and magnitude of the electrical field is indeed determined by the relative concentration of the positive and negative (surface) potential determining ions; $H^+$ and $OH^-$ are considered to be such ions for oxide minerals and, in addition, dissolved species such as calcium and phosphate for salt-type minerals like apatite. For minerals such as silica, only $H^+$ and $OH^-$ are considered as potential determining. However, as these minerals will have a finite solubility, it will be more accurate to consider dissolved hydrolyzed species such as $Si(OH)^{+++}$ as determining surface potential. The point of zero charge (pzc) is an important, experimentally accessible parameter that is characteristic of the interfacial potential of the particle. It reflects the solution concentration conditions under which the surface charge of the particle is zero. For oxide and several salt-type minerals, the particles will carry a positive charge in solutions that are more acidic than the pzc and a negative charge in solutions that are more alkaline. The influence of the pzc is important in the sense that adsorption of charged species will be controlled by the conditions of the solution with respect to the pzc. One must, however, note that the magnitude as well as the sign of the interfacial potential, frequently obtained by zeta potential measurements, can be significantly affected by pretreatment[9,10] of the solid and, in turn, by its degree of hydroxylation. The latter has been shown to be strongly influenced by aging time in contact with the aqueous solution and possibly by pH and ionic strength of it[11]. Common cleaning procedures such as leaching in acidic[12] and hot solutions[10] can also drastically alter the interfacial electrical properties.

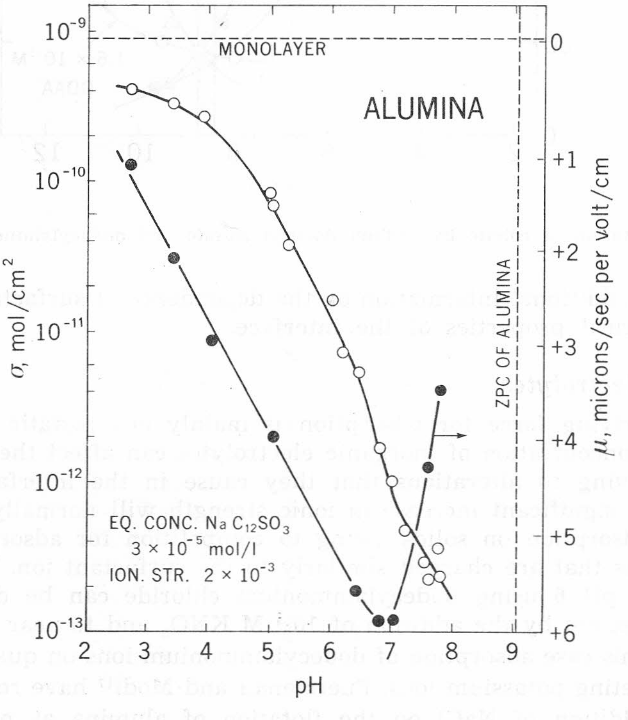

Figure 1. Adsorption density ($\sigma$) of Na dodecane sulfonate on alumina and the electrophoretic mobility ($\mu$) of alumina, as a function of pH. Reference 13.

The dependence of adsorption on the electrical nature of the interface has been clearly shown in the case of alkylsulfonate adsorption on alumina[13]. See Figure 1. Only below the point of zero charge, when the alumina is positively charge does the sulfonate adsorb to any measurable extent. Results obtained for the flotation[3] of calcite with anionic dodecylsulfate below the pzc, and with cationic dodecylammonium ion above the pzc, have confirmed the strong dependence of adsorption on the electrical condition of the interface. This correlation is given in Figure 2. Similarly good correlation has been found for adsorption of surfactants and flotation of monazite[14], zircon[15], apatite[4], corundum[17], quartz[16] and magnetite[18]. Froth flotation experiments have yielded

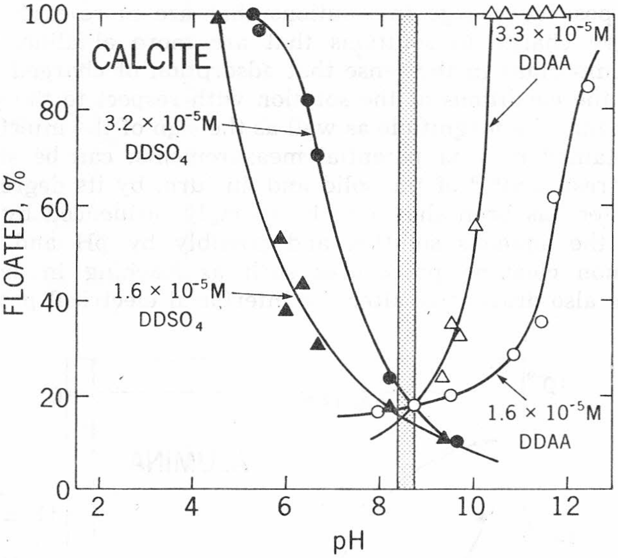

Figure 2. Flotation of calcite by sodium dodecyl sulfate and dodecylamine. Reference 3.

considerable additional information on the dependence of surfactant adsorption on the electrical properties of the interface.

### *Inorganic Electrolytes*

If the driving force for adsorption is mainly electrostatic attraction, an increase in concentration of inorganic electrolytes can affect the adsorption of surfactant owing to alterations that they cause in the interfacial electrical properties. A significant increase in ionic strength will normally decrease the surfactant adsorption on solids owing to competition for adsorption sites by inorganic ions that are charged similarly to the surfactant ion. Thus flotation of quartz at pH 6 using dodecylammonium chloride can be depressed to a measurable extent by the addition of $10^{-4}$ M $KNO_3$ and to near zero by 0.1 M $KNO_3$[19]. In this case adsorption of dodecylammonium ions on quartz is reduced by the competing potassium ions. Fuerstenau and Modi[17] have reported similar effects of addition of NaCl on the flotation of alumina at pH 6 using an anionic surfactant, sodium dodecylsulfonate. These can be viewed as resulting from a reduction in electrical potential but specific counter ion[20] effects can be encountered. Electrokinetic experiments[17] have shown that if the added salt contains multivalent ions the inorganic adsorption can, in some cases, be sufficiently strong to produce a reversal of the zeta potential. More marked depression, that has been obtained for quartz flotation using calcium nitrate[19], results from the stronger tendency of bivalent over monovalent ions to adsorb and compete with the collector ions. It is of interest that, if the bivalent ions are of opposite charge to that of the particle and the collector ions, then activation of flotation can occur due to charge reversal of the particle caused by the adsorbed bivalent ions[17]. In this connection it might be mentioned that alkaline earth ions such as calcium have been reported to function most effectively in the pH range where they are in hydrolyzed soluble form[21–24].

### *Lateral Chain-Chain Interactions*

Figure 1 includes zeta potential values of alumina in the presence of surfactant. The reversal of slope of the zeta potential *versus* pH curve for alumina below pH 7 suggests that increased adsorption below this pH involves forces in addition to electrical attraction. The adsorption isotherm given in Figure 3, which shows a marked increase in slope at a particular surfactant concentration, supports this interpretation. It can be seen from the same figure that below this surfactant concentration, the zeta potential, as indicated by particle mobility, changes very little, while above it, it decreases and then reverses the sign as adsorption density of the surfactant increases. The ionic strength was kept constant in these experiments and the observations are consistent with a mechanism involving ion exchange at lower surfactant concentrations and lateral associative interactions of the adsorbed surfactant species at higher concentrations[13] in a process termed »hemimicelle« formation. This can occur at concentrations considerably less than the CMC. The concentration at which the two dimensional association of the surfactant begins has been shown by adsorption, electrokinetic and froth flotation experiments to depend

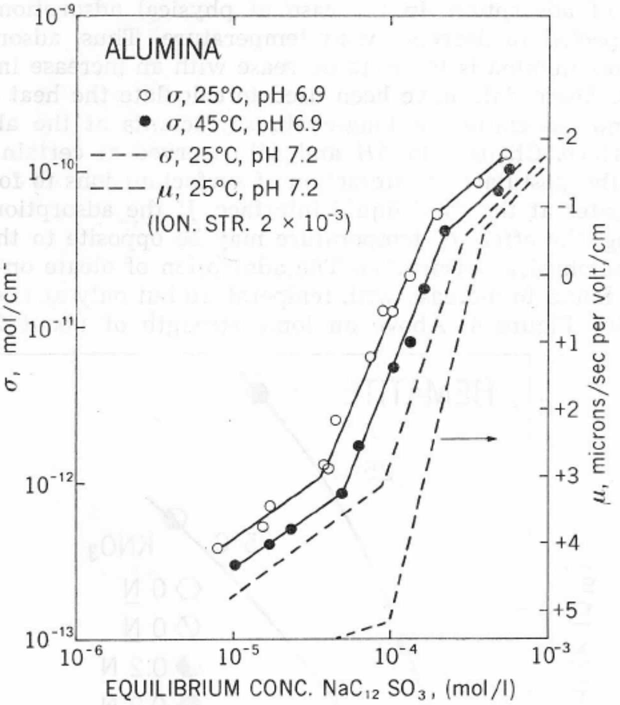

Figure 3. Adsorption density (σ) of dodecane sulfonate ($NaC_{12}SO_3$) on alumina, and the electrophoretic mobility (μ) of alumina, as a function of $NaC_{12}SO_3$ concentration. References 13, 25.

upon pH and hence surface potential[5] of oxide particles[13], temperature[25], and the chemical state and structure of the surfactant[27].

The sensitive effect of solution pH is also clearly seen in Figure 3, which includes adsorption data for sodium dodecylsulfonate on alumina at two pH values[13]. At lower pH the critical adsorption density required for lateral interaction is attained at a lower surfactant concentration owing to higher electrostatic attractive forces resulting from a larger surface potential. It must be noted that pH can also influence adsorption through its control of the hydrolysis of certain surfactants. This important effect will be discussed elsewhere.

The effect of solution temperature on adsorption in general is determined by the type of adsorption. In the case of physical adsorption of surfactant, it can be expected to decrease with temperature. Thus, adsorption of dodecylsulfonate on alumina is found to decrease with an increase in temperature[25]. See Figure 3. These data have been used to calculate the heat and entropy of adsorption and association of long-chain surfactants at the alumina-aqueous solution interface. Changes in $\Delta H$ and $\Delta S$ observed at certain concentrations agreed with the postulate of interaction of surfactant ions to form two dimensional aggregates at the solid-liquid interface. If the adsorption involves chemical bonding, the effect of temperature may be opposite to that encountered in the case of physical adsorption. The adsorption of oleate on hematite[28] has, in fact, been found to increase with temperature but only at low ionic strength conditions. See Figure 4. Above an ionic strength of about $2 \times 10^{-3}$ $N$, ad-

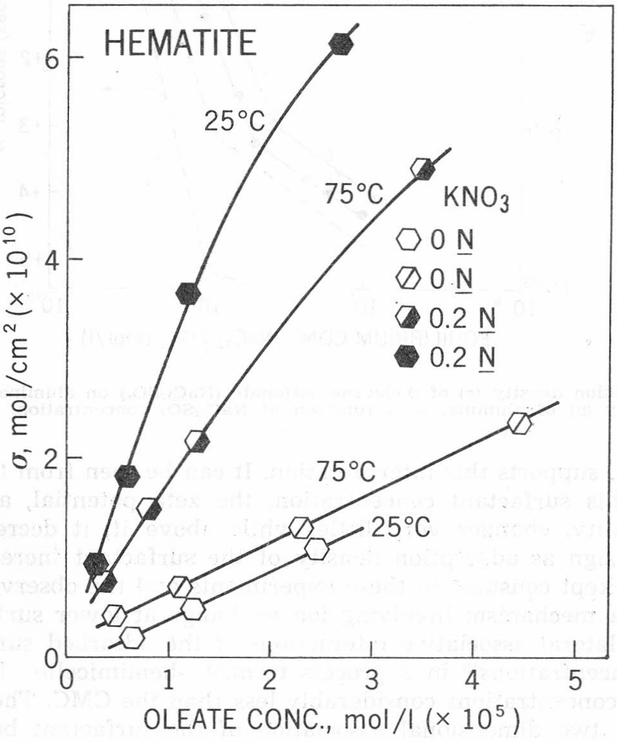

Figure 4. Effect of KNO$_3$ and temperature on the adsorption of oleate on hematite. Reference 28.

sorption was found to decrease markedly with increase of temperature. This interesting observation is under further study.

Increase in length of the non-polar part of a surfactant is expected to cause an increase in its adsorption owing to increased surface activity and increased lateral interaction between chains. The generation of an effectively lower di-electric constant of the interface would also promote adsorption of a long chain material there. Results in Fifure 5 for the flotation of quartz at natural pH using alkylammonium acetates of varying chain length clearly signify an increase in adsorption with increase in chain length[29]. Direct measurements of adsorption of sulfonates of varying chain length by Wakamatsu and Fuerstenau[26] also show the dependence of adsorption and lateral chain--chain interaction on the length of the hydrocarbon chain.

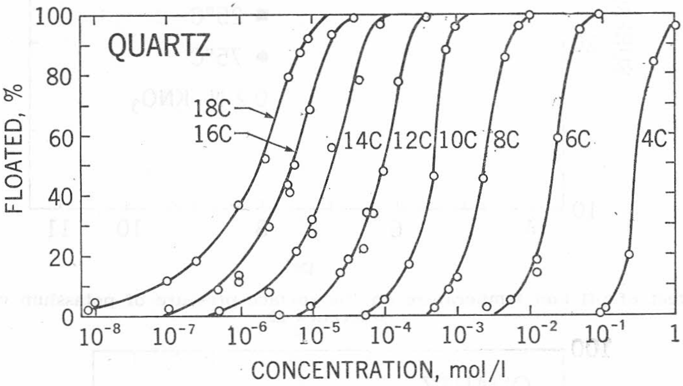

**Figure 5. Effect of alkyl chain length on the flotation of quartz by alkyl ammonium acetate. Reference 29.**

Differences in chemical structure of the surfactant, such as polar substitution or chain branching that retard lateral interaction, can indeed be expected to decrease the adsorption. On the other hand, substituting fluorine for hydrogen in an alkyl chain increases the surface activity and adsorption. Flotation of alumina using perfluorocarboxylic acid was found to be significantly higher than that obtained using the corresponding alkyl acid[27].

## *Surfactant Complex Formation*

The effect of the chemical state of the surfactant on adsorption is particularly significant. For example, the formation of long chain ion/long chain polar complexes has to be considered as a potentionally important factor in the pH dependence of the surface activity of various soap and amines. Flotation of haematite by oleic acid was found to be highest in the pH range where acid soap complex formation[30-32] is expected[28,33]. Evidence of high surface activity of mixed acid, soap was obtained by surface tension measurements of oleate solutions[33] shown in Figure 6. Similarly, maximum flotation of quartz with alkylamine observed around pH 10.2 very likely involves the formation of ion/dipole complexes[34-36]. The pH of maximum flotation of quartz using amine, in fact, coincides with the pH at which maximum lowering of

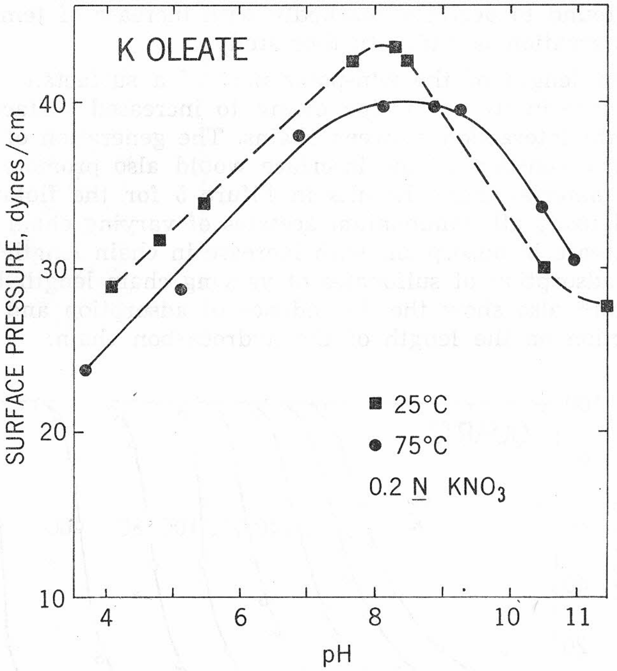

Figure 6. Effect of pH and temperature on the surface pressure of potassium oleate solutions. Reference 33.

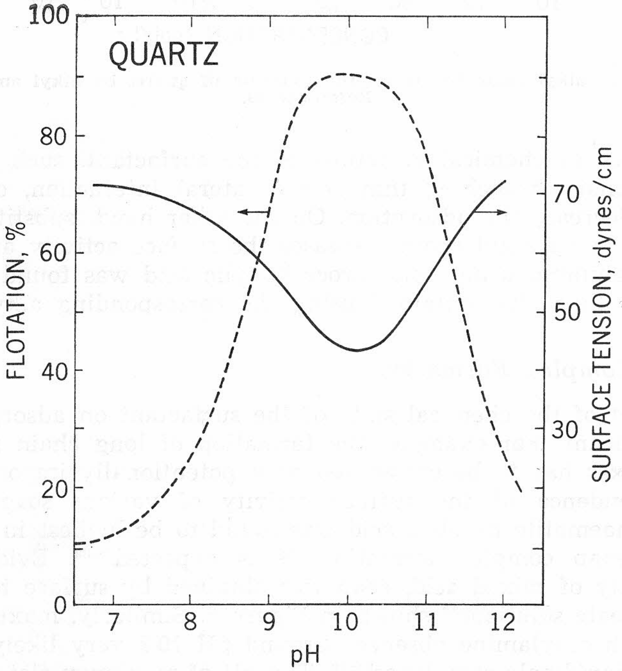

Figure 7. Flotation of quartz and surface tension lowering of water by dodecylamine ($4 \times 10^{-5}$ M) as a function of pH. Reference 36.

the adhesion tension of this system and of the surface tension of amine solutions occurs[35,36]. See Figure 7. This is also the pH region in which stable amine-aminium ion complexes can be expected. Kung and Goddard[37] have recently examined association reactions of amine/ammonium hydrochloride systems in bulk phase. By using differential thermal analysis measurements, they demonstrated the formation of a 1 : 1 amine-aminium complex. The thermogram of the $C_{12}$ 1 : 1 mixture was characterized by the complete disappearance of endotherms at 26 °C and 67 °C, which characterize the free amine and the hydrochloride, respectively, and the presence of a single new peak at 56 °C. These results indicate conversion of the two components into a single new species. Similar results were obtained for the octadecylamine-octadecylamine hydrochloride system.

Thus, from results of surface tension, thermal analysis and flotation experiments, formation of complexes between neutral ionizable surfactant molecules and their ionized counterparts appears to be implicated in enhanced adsorption observed at certain pH values at both the air/water and mineral//water interfaces. Despite apparent correlation between bulk phase complex formation and adsorption phenomena, discordant information does exist. For example, work in one of the authors' laboratories has shown that maxima in surface pressure, adsorption and quartz flotation occur at a well defined pH (9.5) for the tertiary amine, dodecyldimethylamine. While these data suggest interfacial complex formation other studies did not reveal such formation in bulk phase between the tertiary amine and its hydrochloride salt. While the mechanism of adsorption of the complexes requires further study, one important factor will clearly be electrostatic attraction: since the complex retains a charge, affinity to an oppositely charged mineral surface will remain high, as in the case of amine adsorbing on quartz. Secondly, it is known that fatty acid/soap complexes have very low solubility which helps to explain their unusual surface activity. A similar situation is expected for amine/aminium complexes, and in fact Finch and Smith[36] have reported the appearance of visible scum on the surface of dodecylamine solution at the pH of maximum surface activity.

### *Polymeric Reagents*

Other than the previously discussed inorganic species, reagents that affect surfactant adsorption are polymers such as starch. For example, adsorption of oleate on calcite was found to be enhanced by the addition of starch and vice versa[38]. The former effect and flotation results are shown in Figure 8. It is of interest that even though the particles adsorbed more surfactant in the presence of starch, they became less hydrophobic according to the flotation results given in Figure 8. This interesting effect was ascribed to the helical structure[39] that starch assumes in the presence of hydrophobic species under alkaline conditions, *i. e.*, a hydrophilic exterior and hydrophobic interior. Mutual enhancement of adsorption is possible owing to the formation of a helical starch-oleate clathrate with the hydrophobic oleate held inside the hydrophobic starch interior.

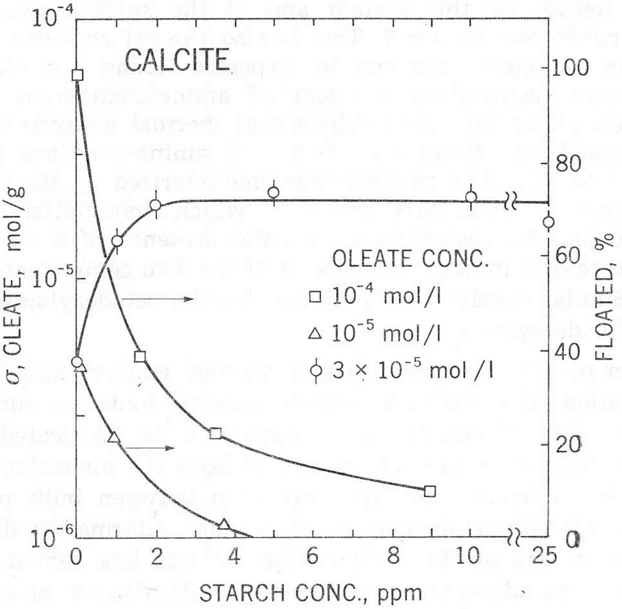

Figure 8. Flotation of calcite and adsorption of oleate as a function of starch concentration. Reference 38.

## REFERENCES

1. D. A. Haydon and F. H. Taylor, *Prod. 3rd Int. Cong. of Surface Activity,* Vol. **1**, 1960, p. 157.
2. D. W. Fuerstenau, »*The Adsorption of Surfactants at Solid-Water Interfaces*«, in *The Chemistry of Biosurfaces, HAIR, M. ed.,* Vol. **1**, 1971, p. 143.
3. P. Somasundaran and G. E. Agar, *J. Colloid Interface Sci.,* **24** (1967) 433.
4. P. Somasundaran, *J. Colloid Interface Sci.,* **27** (1968) 659.
5. E. D. Goddard, *Croat. Chem. Acta* **45** (1973) 16.
6. P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *J. Phys. Chem.,* **68** (1964) 3562.
7. J. Yopps and D. W. Fuerstenau, *J. Colloid Sci.,* **19** (1964) 61.
8. G. A. Parks, *Chem. Rev.,* **65** (1965) 177.
9. P. Somasundaran, »*Pretreatment of Mineral Surfaces and its Effect on Their Properties*« in *Clean surfaces: Their Preparation and Characterization for Interfacial Studies,* Marcel Dekker, New York (1970) 285—306.
10. P. Somasundaran and R. D. Kulkarni, *J. Colloid Interface Sci.,* **45** (1973) 591.
11. R. D. Kulkarni and P. Somasundaran, »*The Effect of Aging on the Electrokinetic Properties of Quartz in Aqueous Solutions*« in *Oxide-Electrolyte Interfaces,* American Electrochemical Society (1972) 31—44.
12. R. D. Kulkarni and P. Somasundaran, »*Pretreatment Effects on the Electrokinetic Properties of Quartz*«, 164th ACS Meeting, New York, August 1972.
13. P. Somasundaran and D. W. Fuerstenau, *J. Phys. Chem.,* **70** (1966) 90.
14. H. S. Choi and K. U. Whang, *Korean Chem. Soc.,* **7** (1963) 91.
15. H. S. Choi and K. U. Whang, *Trans. Can. Inst. Min. Met.,* **66** (1963) 242.
16. I. Iwasaki, S. R. B. Cooke, and A. F. Colombo, *U. S. Bureau Mines Rep. Inv.* (1960) 5593.
17. H. J. Modi and D. W. Fuerstenau, *Trans AIME* **217**, 381 (1960); *J. Phys. Chem.* **61** (1957) 640.
18. I. Iwasaki, S. R. B. Cooke, and Y. S. Kim, *Trans. AIME,* **223** (1962) 113.
19. P. Somasundaran, *Trans. AIME,* **255** (1974) 64.

20. E. D. Goddard, *Croat. Chem. Acta* **42** (1970) 413.
21. T. W. Healy, R. O. James, and R. Cooper, *The Adsorption of Aqueous Co(II) at the Silica/Water Interface*, in *Adsorption from Aqueous Solution, Advances in Chemistry Series, American Chemical Society,* Washington, D. C., no. **79**, (1968), p. 62—81.
22. M. C. Fuerstenau, C. C. Martin, and R. B. Bhappu, *Trans. AIME,* **226** (1963) 449.
23. M. C. Fuerstenau, D. A. Rice, P. Somasundaran, and D. W. Fuerstenau, *Trans. IMM (London),* **73** (1965) 381.
24. J. M. MacKenzie and T. T. O'Brien, *Trans. AIME,* **244** (1969) 168.
25. P. Somasundaran and D. W. Fuerstenau, *Trans. AIME,* **252** (1972) 275.
26. T. Wakamatsu and D. W. Fuerstenau, »*The Effect of Hydrocarbon Chain Length on the Adsorption of Sulfonate at the Solid/Water Interface*« in *Adsorption from Aqueous Solution, Advances in Chemistry Series,* No. 79 **(1968)** 161—172.
27. P. Somasundaran and R. D. Kulkarni, *Trans. IMM (London),* **82** (1973) C163.
28. R. D. Kulkarni and P. Somasundaran, to be published.
29. D. W. Fuerstenau, T. W. Healy and P. Somasundaran, *Trans. AIME,* **229**, (1964) 321.
30. H. C. Kung and E. D. Goddard, *J. Colloid and Interface Sci.,* **29** (1969) 242.
31. E. D. Goddard and J. A. Ackilli, *J. Colloid Sci.,* **18** (1963) 585.
32. E. D. Goddard, S. R. Smith, and O. Kao, *J. Colloid Interface Sci.,* **21** (1966) 320.
33. R. D. Kulkarni and P. Somasundaran, *Amer. Inst. Chem. Eng. Symposium Series,* No. 150 **71** (1975) 124.
34. P. Somasundaran and D. W. Fuerstenau, *Trans. AIME,* **241** (1968) 102.
35. P. Somasundaran, to be published in *International Journal of Mineral Processing.*
36. J. A. Finch and G. W. Smith, *J. Colloid Interface Sci.,* **45** (1973) 81.
37. H. C. Kung and E. D. Goddard, *Koll-Z-Z-Polymere,* **232** (1969) 812.
38. P. Somasundaran, *J. Colloid Interface Sci.,* **31** (1969) 557.
39. K. Freudenberg, E. Schaaf, G. Dumpfert, and T. Poletz, *Naturwiss,* **27** (1939) 850.

## SAŽETAK

### Adsorpcija površinski aktivnih tvari na mineralnim krutinama

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Opisani su faktori, koji utječu na adsorpciju ionskih, površinski aktivnih tvari na krutine. Naglašena je uloga elektrostatskih sila i opisani su mehanizmi, koji dovode do stvaranja naboja na krutinama. Ovisnost adsorpcije o djelovanju naboja pokazana je na mnogim sistemima, krutih, površinski aktivnih tvari. Elektrostatski faktor može biti bitno izmijenjen u prisustvu anorganskih soli. Unutar adsorbiranih slojeva dolazi do asocijacije, a interakcija između lanaca površinski aktivnih tvari je značajna, jer duljina i struktura lanaca utječe na adsorpciju. Pokazana je ovisnost pH o adsorpciji dugih lanaca slabih elektrolita, kao i utjecaj polimera na adsorpciju površinski aktivnih tvari.

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