

CCA-1145

YU ISSN 0011-1643

541.183

*Conference Paper;
Author's Review*

Physico-Chemical Aspects of Adsorption of Surface Active Agents on Minerals*

P. Somasundaran

Henry Krumb School of Mines, Columbia University, New York, New York, 10027, USA

Received December 18, 1978

Basic principles and some special aspects of adsorption on minerals are discussed. Electrostatic forces, lateral interaction between surfactants, chemical and other forces are discussed in more detail as well as the role of the chemical state of surfactants. It is pointed out the importance of pretreatment of mineral systems which can affect their electrokinetic behaviour as well as the presence of other charged particles in solution if electrostatic forces play a major role. The sharp increase in electrophoretic mobility at a given adsorption density for certain conditions and appearance of maximum flotation of certain minerals with hydrolyzable surfactants at the point of zero charge are attributed to micellisation and covalent bonding respectively with possible polymer formation.

Other factors such as hydrogen bonding, solvation or desolvation of species and hydrophobic bonding are mentioned. Special attention is paid to the adsorption in micellar solutions and adsorption kinetics.

INTRODUCTION

Adsorption of surfactants on particulates is a governing parameter in a number of interfacial processes such as flotation, detergency, tertiary oil recovery using surfactant flooding, lubrication, flocculation and clarification for waste treatment, comminution, chromatography etc. Process of adsorption is in turn determined by a large number of system variables such as chemical and structural properties of the particulate including solubility and interfacial electrochemical potential, chemical and physical properties of solution such as salinity, pH and temperature and even the chemical make-up of the adsorbent, particularly in terms of purity. Considerable advance has been made in the past in developing an understanding of the role of various system properties. This has been covered in several recent reviews (Somasundaran and Grieves, 1975; Goddard and Somasundaran, 1976; Somasundaran and Hanna, 1977, Mittal, 1975, Fuerstenau, 1971, Healy, 1974). Here we will examine some special aspects of adsorption on minerals.

* Presented at the 4th Yugoslav Symposium on Surface Active Substances, held in Dubrovnik, Croatia, Yugoslavia, October 17—21, 1977.

BASIC PRINCIPLES

Adsorption of any species in an interfacial region is the result of favorable chemical or physical interaction between the adsorbate species and either the adsorbent surface species or other intermediary species that accumulate in the interfacial region. If ΔG^0_{bi} is the free energy term corresponding to transfer of the adsorbent species from the bulk (b) to the interfacial region (i), concentration in the interfacial region, c_i , can be expressed as

$$c_i = c_b \exp \frac{-\Delta G^0_{bi}}{RT} \quad (1)$$

whereas c_b is the bulk concentration in mol dm⁻³, R is the gas constant and T is the absolute temperature.

To express the adsorption in terms of mol/cm² we simply multiply the right-hand side of equation by the thickness of the adsorbed layer, τ .

$$\Gamma_i = \tau c_b \exp \frac{-\Delta G^0_{ads}}{RT} \quad (2)$$

ΔG^0_{ads} , is equal to ΔG^0_{bi} and can be the result of electrostatic attraction, covalent bonding, hydrogen bonding or non-polar bonding between the adsorbate and adsorbent species, lateral interaction between the adsorbed species etc. In addition, desolvation or solvation of any species due to the adsorption process can also contribute towards determining the extent of adsorption. Another factor that is usually ignored arises from the variations in such physical properties as structure and dielectric constant of the medium from the bulk to interfacial region. Lack of precise information on the above variations makes treatment of adsorption mechanisms difficult. One or more of the above factors can play a governing role in adsorption depending on the mineral-solution system. In fact, some of the factors can even oppose adsorption (positive ΔG), but all that is needed for adsorption to take place is the total sum ΔG^0_{ads} to be negative. One other point to note is that even if ΔG^0_{ads} under equilibrium conditions is positive, species can remain adsorbed on a solid if ΔG^0_{ads} is negative at some point in time prior to attainment of equilibrium and if adsorption is irreversible.

Our work in recent years has been aimed towards establishing the role of some of the major factors in determining adsorption in various systems.

Electrostatic Adsorption

Particulates are often charged in solution either due to preferential dissolution of species, hydrolysis of surface species or even adsorption of various charged ions and complexes. On such particulates, adsorption of species that are charged oppositely can take place with a free energy of adsorption, ΔG^0_{elec} , given by $ZF\psi_i$, Z being valency of the adsorbate species, F the Faraday constant and ψ_i the interfacial potential. The role of electrostatic forces is clearly illustrated in Figure 1 where adsorption of dodecylsulfonate on alumina is plotted as a function of pH at a constant equilibrium bulk sulfonate concentration of 3×10^{-5} mol dm⁻³. The point of zero charge of this alumina is at

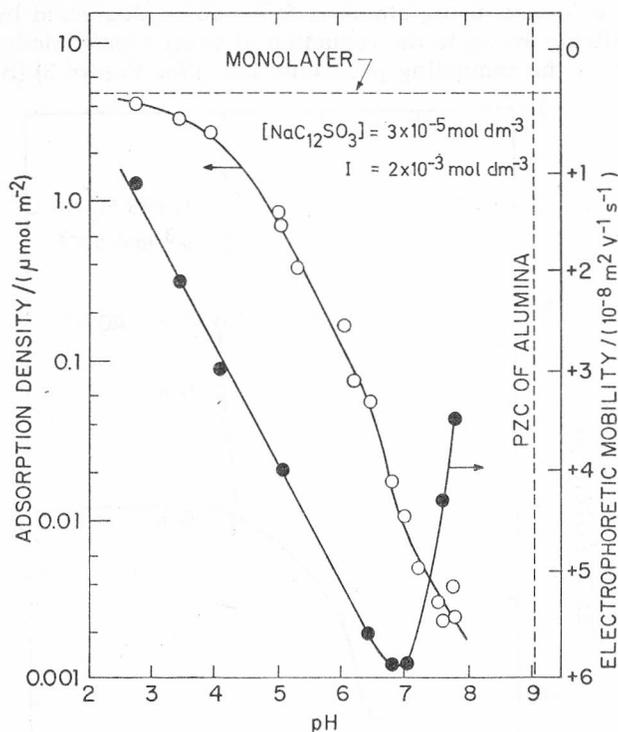


Figure 1. Adsorption of dodecylsulfonate on alumina as function of pH (Somasundaran and Fuerstenau, 1966).

pH = 9.1. It is then to be noted that only below pH = 9.1, when the alumina is positively charged, does the anionic sulfonate adsorb in significant amounts (Somasundaran and Fuerstenau, 1966). We have obtained similar correlation for adsorption of sulfonate and amine on calcite (Somasundaran and Agar, 1967). The results obtained for mineral systems do not however often produce such correlations since the values obtained are affected by the pretreatment procedures used (Somasundaran, 1972, Kulkarni and Somasundaran, 1977, Somasundaran, 1970). We have examined the effects of various commonly used pretreatments such as desliming, ultrasonic scrubbing and leaching with dilute nitric, hydrofluoric and sodium hydroxide solutions on the electrokinetic properties of quartz in aqueous solutions. It was found that these treatments can affect, sometimes severely, the electrokinetic properties of quartz. The changes in these properties even during subsequent aging is found to be governed by the type of treatment used. For example, the isoelectric point of quartz can be raised from below 2 to as high as 6 by leaching it in hydrofluoric solution (See Figure 2). Upon ageing the hydrofluoric acid leached quartz in water, the isoelectric point slowly shifts to lower values over a period of several days.

In systems where electrostatic forces play a major role, presence of other charged species in solution can influence adsorption owing to competition for adsorption sites by ions that are charged similarly to the adsorbate species.

Thus flotation of quartz using amine is found to be depressed by the addition of potassium nitrate owing to the reduction of adsorption of dodecylammonium ions on quartz by the competing potassium ions (See Figure 3) (Somasundaran,

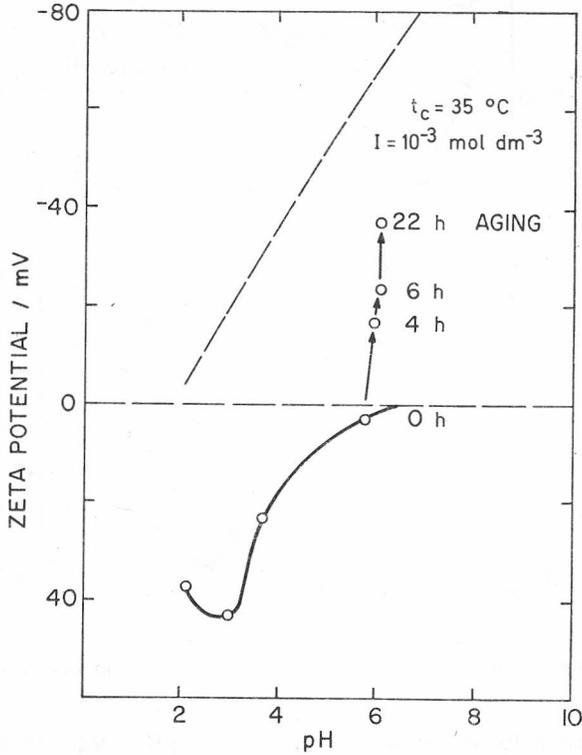


Figure 2. Zeta potential of quartz treated with HF and then with hot NaOH solutions as a function of pH without aging, and at pH = 6 after 4, 6, and 22 hours of aging; dotted curve is for equilibrium values obtained for HNO₃-treated quartz for comparison (Kulkarni and Somasundaran, 1977).

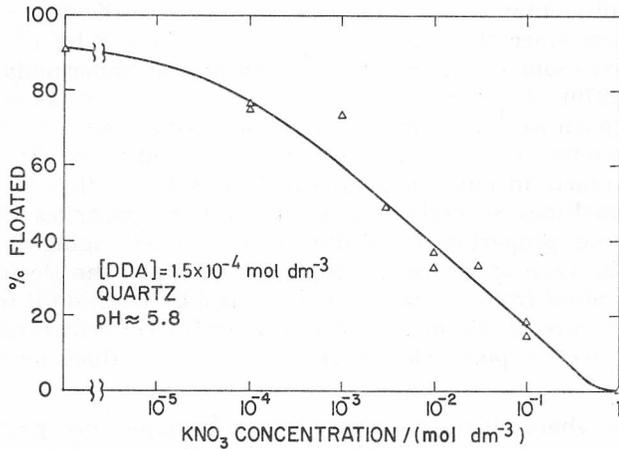


Figure 3. Flotation of quartz as a function of KNO₃ concentration at natural pH of 5.8 in 1.5 × 10⁻⁴ mol dm⁻³ dodecyl-ammonium acetate solutions (Somasundaran, 1974).

1974). Effectively, addition of the potassium ions causes a compression of the electrical double layer and reduces interfacial potential that is responsible for the adsorption of the dodecylammonium ions. In contrast to the above, uptake of ions that are charged oppositely to the surfactant can produce an increase on adsorption of it provided the surface is not already fully charged. It is interesting to note in this regard the observation of Saleeb and Hanna (Saleeb and Hanna, 1969; Hanna, 1976) that the introduction of SO_4^{2-} ions increased the adsorption of a cationic surfactant, cetyltrimethylammonium bromide, on CaCO_3 , but not on $\text{Ca}_3(\text{PO}_4)_2$. This was attributed to the possible increase in the number of negative sites on the CaCO_3 surface owing to the sorption of the bi-valent sulfate ions. Such increase could not be obtained on $\text{Ca}_3(\text{PO}_4)_2$ since this mineral is apparently saturated with negative sites even in the absence of sulfonate. This postulate is supported by the observation that introduction of Mg^{++} into the solution reduced the adsorption of the cationic surfactant on both CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$.

Lateral Interaction Between Surfactants

An examination of the data given in Figure 1 for the dependence on pH of electrophoretic mobility of alumina in sulfonate solutions suggests that there must be another force responsible for this adsorption in addition to electrostatic attraction below about $\text{pH} = 7$. Adsorption isotherms as well as settling data obtained for the alumina/sulfonate systems also suggest such a possibility (See Figure 4). Both the above properties are found to undergo a sharp increase

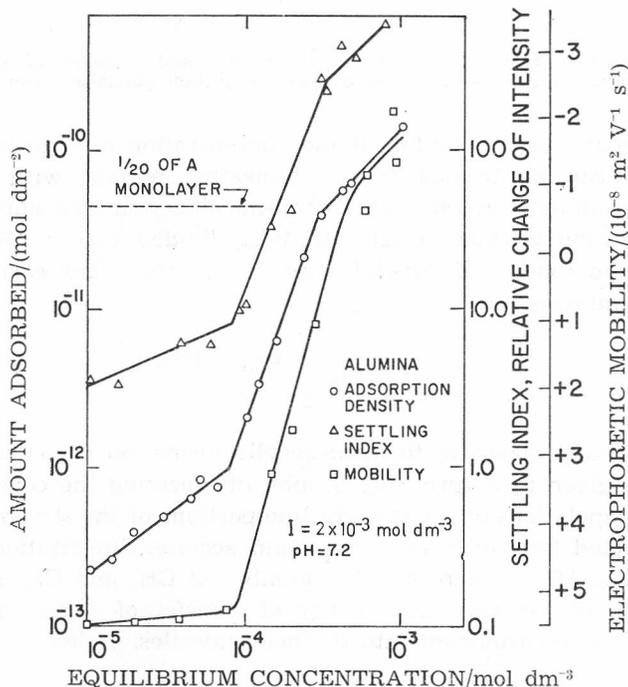


Figure 4. Adsorption density of dodecylsulfonate, electrophoretic mobility, and settling rate of alumina-sodium dodecylsulfonate system as a function of the concentration of sodium dodecylsulfonate (Somasundaran, 1964).

at a given adsorption density. This was attributed to lateral association of the surfactant species in the interfacial region above a critical adsorption density. Such association to form two-dimensional aggregates called hemi-micelles is analogous to micelle formation and results from the favorable energetics of removal of the alkyl chains partially from the aqueous environment. The energy gained due to the process of hemi-micellization has been estimated in a number of ways. For example, the data given in Figure 5 for the zeta

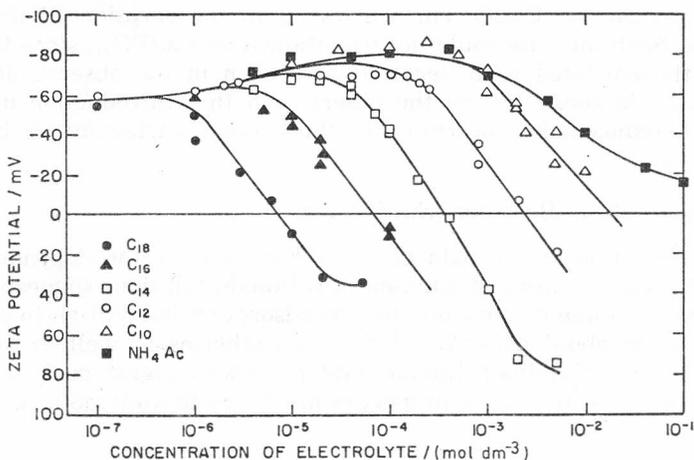


Figure 5. Effect of hydrocarbon chain length on the ζ -potential of quartz in solution of alkyl-ammonium acetate and in solutions of ammonium acetate (Somasundaran et al., 1964).

potential of quartz as a function of the concentration of amines of different chain lengths can be treated in the following manner with the help of equation (2) to obtain free energy of hemi-micellization (Lin and Somasundaran, 1971). We rewrite equation (2) with ΔG_{ads} divided into the two terms, one corresponding to that of electrostatic forces and the other corresponding to that of the hemi-micellization.

$$\Gamma_i = \tau c_b \exp \frac{-\Delta G_{\text{el}} - \Delta G_{\text{hm}}}{RT} \quad (3)$$

Concentrations corresponding to hemi-micelle formation (c_{HMC}) were obtained from the data given in Figure 5 by graphically locating the concentrations at which the extrapolations of the straight line portions of the streaming potential curves intersected the curve for ammonium acetate. Substitution of c_{HMC} for c_b and $n\varphi_{\text{h(s)}}$ for ΔG_{hm} , where n is the number of CH_2 and CH_3 groups in the chain and $\varphi_{\text{h(s)}}$ the average free energy of transfer of 1 mol of CH_2 groups from the aqueous environment into the hemi-micelles, yields

$$\Gamma_i = \tau c_{\text{HMC}} \exp \frac{-\Delta G_{\text{el}} - n\varphi_{\text{h(s)}}}{RT} \quad (4)$$

The arrangement of equation 4 yields

$$\lg \text{HMC} = \frac{n\varphi_{h(\text{sl})}}{RT} + \Delta G_{\text{elec}} + \log \frac{\Gamma_i}{\tau} \quad (5)$$

A least square plot of $\log \text{HMC}$ as a function of number of carbon atoms in the alkyl chain is given in Figure 6. $\varphi_{h(\text{sl})}$ obtained from this line is $-0.95 kT$ comparable to that obtained for free energy of micellization (see Figure 7). Heat and entropy of adsorption calculated for alkyl chains adsorbed on mineral particles (Somasundaran and Fuerstenau, 1972) show marked changes at given concentrations that are in agreement with the postulate of interaction of surfactant ions to form two dimensional aggregates.

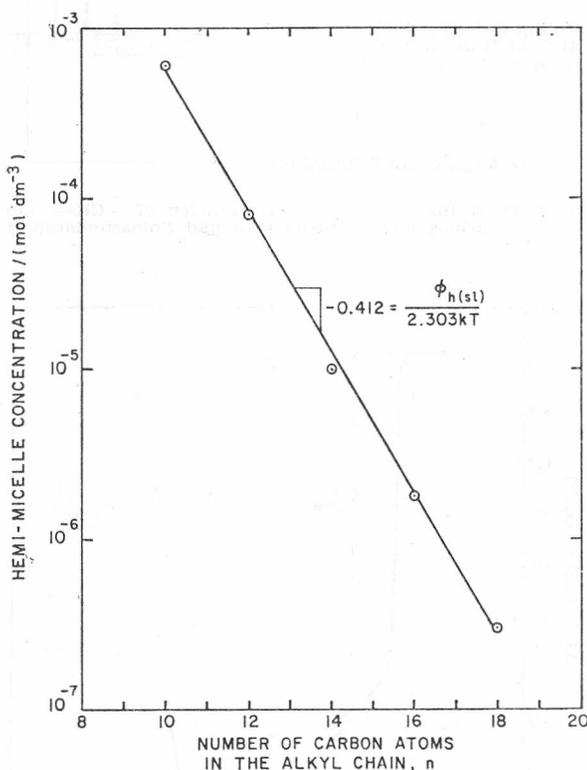


Figure 6. Least-square plot of $\log \text{HMC}$ of alkyl-ammonium acetates from streaming potential data as a function of the number of carbon atoms in the chain (Lin and Somasundaran, 1971).

Most interestingly, the association was found to produce a net increase in the entropy of the system suggesting a decrease upon aggregation in the ordering the water molecules that were originally around isolated surfactant chains (See Figure 8). Because of the necessity to initiate the surfactant adsorption on solid by some primary adsorption force such as electrostatic attraction and of the requirement to pack the molecules in an orderly manner, the extent of aggregation and the concentration at which the aggregation

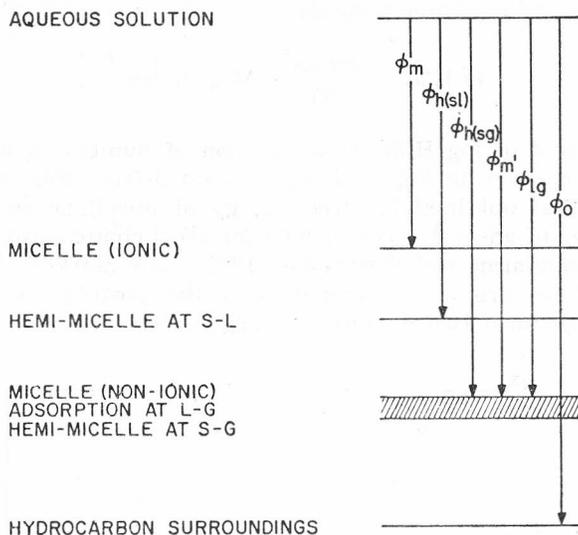


Figure 7. Schematic diagram for free energy of transfer of $-\text{CH}_2-$ groups from aqueous solution to various environments (Lin and Somasundaran, 1971).

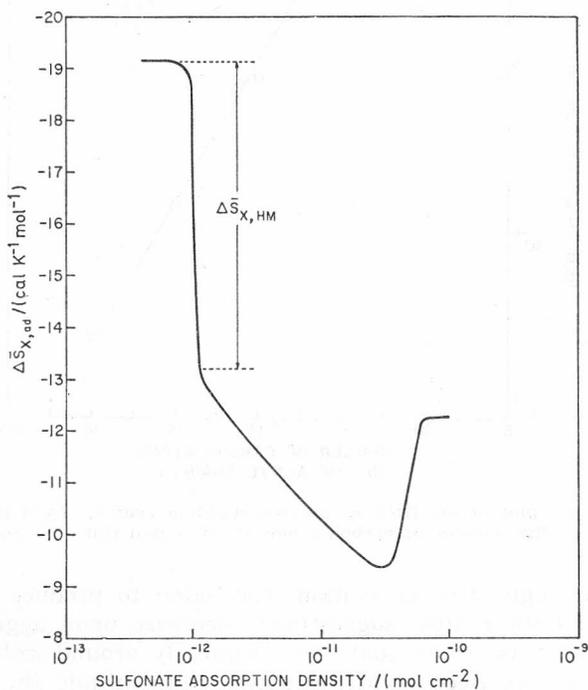


Figure 8. Partial molar entropy of adsorption of sulfonate as a function of its adsorption density (Somasundaran and Fuerstenau, 1972).

becomes significant are dependent, among other things, on such system properties as pH, temperature, ionic strength, and the chemical structure of the surfactant.

Chemical Forces

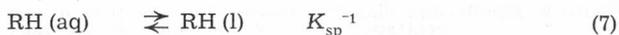
Mainly on the basis of infra-red results obtained for adsorbed surfactant layers on certain minerals, it has been proposed, for example, that fatty acids and sulfonates can also adsorb due to covalent bonding (French, et al., 1954, Peck and Wadsworth, 1965). Also the observation that maximum flotation of certain minerals with fatty acids is obtained at the point of zero charge (where the electrostatic attraction should be minimum) has led to dependence on mechanisms based on covalent bonding between the surfactant species and the mineral surface species.

Both of the above observations cannot however be considered to provide sufficient evidence for chemisorption. Identification of a bonding type in an IR spectrum does not necessarily suggest existence of such bonding on minerals in surfactant solution because of the possible alterations in chemical state of the adsorbed surfactant during the preparation of the sample for the spectroscopic examination. Dependence of flotation maximum on pH, on the other hand, can be attributed for a number of systems such as that of hematite/oleate to the change in chemical state of the oleate species in solution with pH. This is further described in the next section. Chemisorption has been proposed to take place also by means of ion exchange. Thus in the case of adsorption of oleate on fluorite, the surfactant ions are found to release an equivalent amount of fluoride ions to form a surface layer of calcium oleate (Bahr, et al., 1968; Bilsing, 1969). Hanna (1975, 1976) also observed salt formation to be the mechanism of adsorption for the first layer of Aerosol OT, dodecylbenzenesulfonate and dodecylsulfonate on CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$. A second layer with the ionic heads exposed to the bulk solution was considered to be formed in these cases owing to interchain cohesion. Such a mechanism is supported by the observation that the contact angle and flotation response obtained were maximum at concentrations corresponding to the completion of the first layer.

Chemical State of the Surfactant

In addition to micellization and precipitation, hydrolyzable surfactants such as fatty acids and amines can undergo various associative interactions in aqueous solutions giving rise to dimers, acid-soaps, trimers etc. (Mukerjee, 1967). The role of these species in determining adsorption has largely been ignored in the past. Depending upon solution properties such as pH, ionic strength, temperature, etc., some of these species can be present in significant amounts to play a governing role in adsorption. Due to the possibility of marked differences in surface activities of these species, one can obtain considerable variation in adsorption with changes, for example, in solution pH.

The major chemical equilibria in a system consisting of an anionic surfactant (R^-Na^+) are





Among the various species listed above, the acid-soap complex may be more surface active than other forms of the surfactant complexes because of its higher effective molecular size and lower solubility. These species formed between various ionic and molecular forms of the surfactant are termed ionomolecular complexes or IM complexes (Somasundaran, 1976).

Associate interactions to form IM complexes have been considered to be the reason for the deviations in behavior of surfactant solutions in terms of their conductivity, transport number, partial molar volume, osmosis etc. It is reasonable to expect such interactions to affect adsorption at different interfaces also. As an example, a most widely used hydrolyzable surfactant, namely oleic acid is considered in detail here. Various equilibria in oleate system to be considered here are (Somasundaran et al., 1977, Jung, 1976):



The equilibrium diagram showing the activities of various species at 3×10^{-5} mol/dm³ oleate is shown in Figure 9. The precipitation of oleic acid takes place

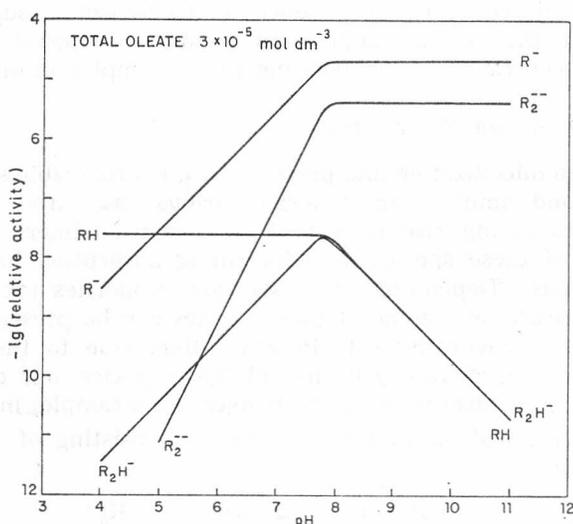


Figure 9. Equilibrium diagram showing the activities of various species of oleate at a concentration of 3×10^{-5} mol dm⁻³ (Somasundaran et al., 1977).

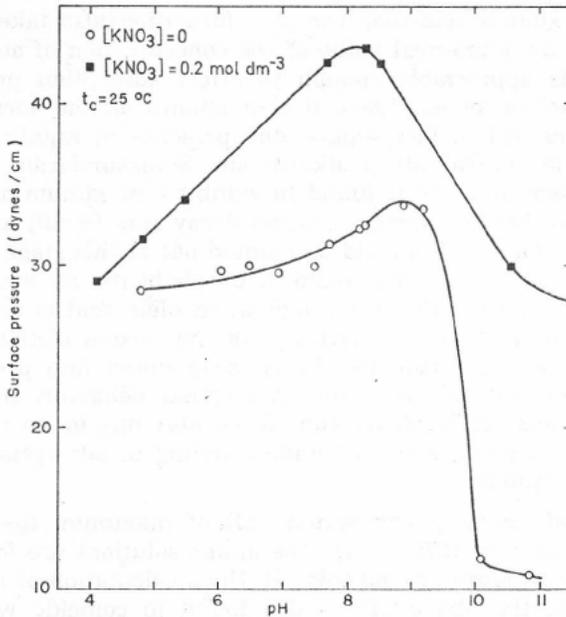


Figure 10. Equilibrium surface pressure of $3 \times 10^{-5} \text{ mol dm}^{-3}$ potassium oleate solution in water and 2×10^{-1} molar KNO_3 (Kulkarni and Somasundaran, 1975).

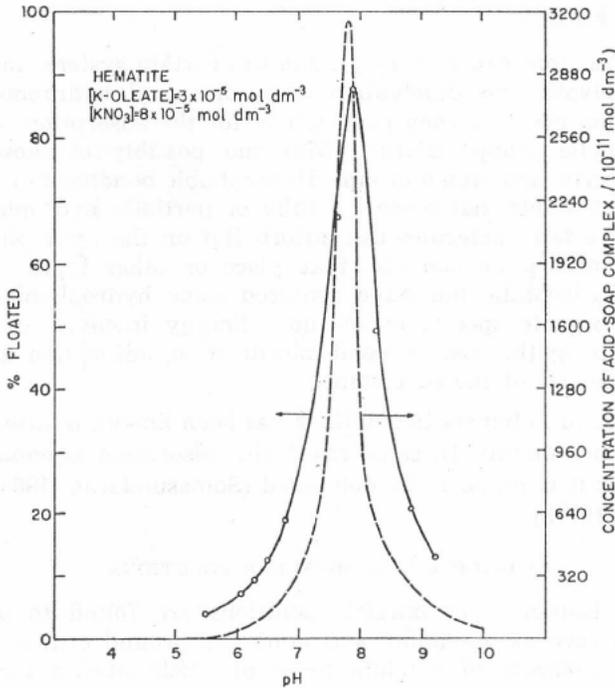


Figure 11. Hematite flotation and acid-soap concentration as a function of pH for $3 \times 10^{-5} \text{ mol dm}^{-3}$ oleate solution at an ionic strength of $8 \times 10^{-5} \text{ mol dm}^{-3}$ KNO_3 (Somasundaran et al., 1977).

at $\text{pH} = 7.78$. Maximum acid-soap complex formation also takes place at this pH . Even though the numerical value of the concentration of acid-soap species may be low, it is appreciable enough to affect adsorption processes at the interfaces (Fuerstenau, et al., 1964). Recent studies on the surface tension of oleic acid solutions did in fact suggest the presence of highly surface active species around the neutral pH (Kulkarni and Somasundaran, 1975). As seen in Figure 10 surface pressure is found to exhibit a maximum at this pH . It is of interest to note that the surface tension decay rate ($d\gamma/dt$) also exhibited a peak around the same pH . It should be pointed out at this stage that a number of minerals have exhibited maximum hydrophobicity as measured by the flotation technique around this pH range when oleic acid is used as collector (see Figure 11). Correlation of flotation with the species distribution diagram suggests that the role of acid-soap dimer, soap dimer and precipitated oleic acid can be significant in controlling adsorption behavior. In addition, the formation of various ferric oleate complexes also has to be certainly taken into account in developing a proper understanding of adsorption phenomenon in these complex systems.

In the case of amine/quartz system, pH of maximum flotation is above about 10 (Somasundaran, 1976). Again the amine solutions are found to exhibit maximum surface pressure around this pH . Upon calculation of the distribution of various species, the above pH is also found to coincide with the pH of maximum in ionomolecular complex concentrations and the pH of precipitation of amine.

Miscellaneous Forces

Other factors that can play major roles in certain systems include hydrogen bonding, solvation or desolvation of species, and hydrophobic bonding. Hydrogen bonding can be strong particularly for the adsorption of surfactants containing phenolic groups (Parks, 1975) and possibly of those containing hydroxyl, carboxylic and amine groups. Hydrophobic bonding can be important for adsorption on solids that possess a fully or partially hydrophobic surface. In this case surfactant molecules can adsorb flat on the hydrophobic sites on the solid. Such adsorption can also take place on other types of solids that are originally hydrophilic but have acquired some hydrophobicity owing to reactions with organic species in solution. Energy involved in this case is additive and, like in the case of hemi-micellization, adsorption due to it will increase with the size of the surfactant.

The presence of polymers in solutions has been known to affect adsorption of surfactants on minerals. In some cases, the adsorption is enhanced, but in some other cases it is found to be depressed (Somasundaran, 1969; Hanna and Somasundaran, 1977b).

ADSORPTION IN MICELLAR SOLUTIONS

Adsorption isotherms in micellar solutions are found to often exhibit special features such as maximum and minimum around critical micelle concentration. The presence of a minimum is of much interest for tertiary oil recovery using surfactant flooding since operation under conditions corresponding to the minimum would lead to minimum surfactant loss during flooding.

Our recent studies on Berea sandstone/Mahogany sulfonate, limestone/Mahogany sulfonate and kaolinite/dodecylbenzenesulfonate have shown presence of adsorption maximum under certain conditions of salinity (Hanna and Somasundaran, 1977a). The nature of the adsorption isotherm obtained is also dependent to a great extent on the type of sulfonate used.

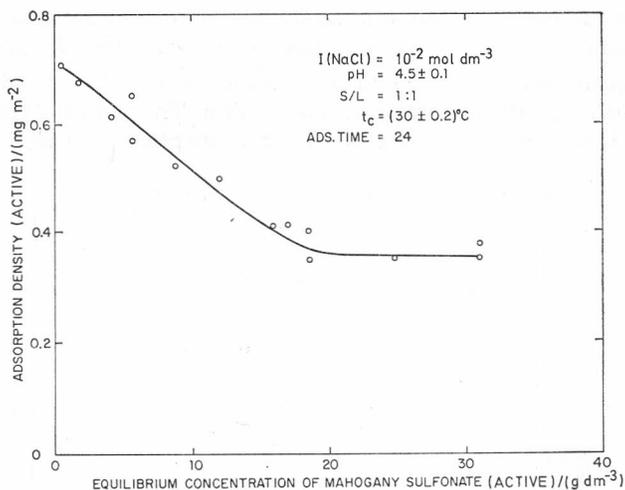


Figure 12. Adsorption isotherms of Mahogany sulfonate-AA (a petroleum sulfonate) on kaolinite (Hanna and Somasundaran, 1977).

While adsorption maxima were obtained for Mahogany sulfonate-AA (a petroleum sulfonate) on previously unwetted kaolinite, isotherms of dodecylsulfonate exhibited only positive slopes but concentrations studied in this case were restricted to premicellar range due to solubility problems (see Figures 12 and 13). Increase in ionic strength due to the addition of NaCl

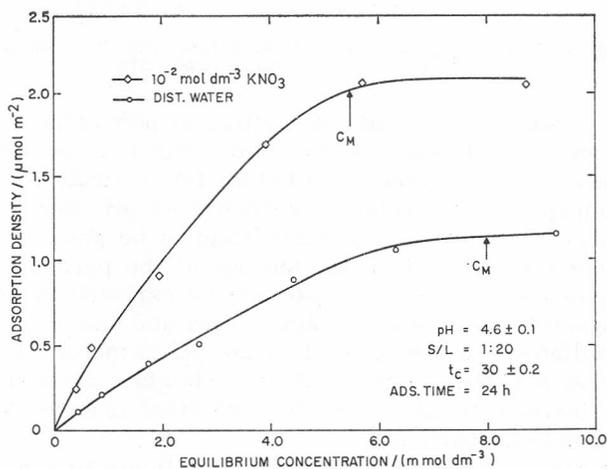


Figure 13. Adsorption isotherms of dodecylsulfonate on kaolinite (Hanna and Somasundaran, 1977).

pH conditions, possibly due to the non-wetting of pores and the effect of the presence of pores on interfacial volume from which micelles that are charged similarly to the solid are excluded (see Figure 14). Agricultural limestone also increased the adsorption in all cases. Adsorption maximum was sensitive to the amount of NaCl added. At lower NaCl concentrations, the maximum existed for Mahogany sulfonate/Berea sandstone system; at intermediate concentrations the isotherm exhibited a maximum followed by a shallow minimum; at still high concentrations the adsorption maximum was not present.

Mineralogical and morphological characteristics of the adsorbent were found to produce significant effect on adsorption. The porous type of limestone (Agricultural limestone) possessed a lower adsorption density under natural

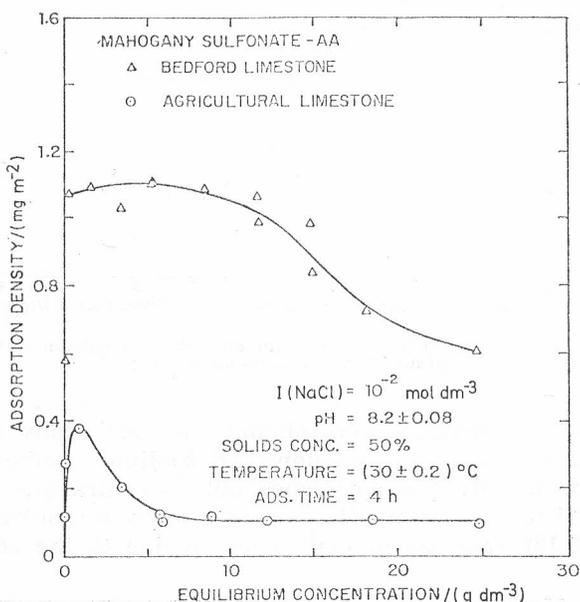


Figure 14. Adsorption of Mahogany sulfonate-AA on Agricultural limestone and Bedford limestone (Hanna and Somasundaran, 1976).

pH conditions, possibly due to the non-wetting of pores and the effect of the presence of pores on interfacial volume from which micelles that are charged similarly to the solid are excluded (see Figure 14). Agricultural limestone also exhibited an unexpected adsorption dependence on pH. (see Figure 15). This was attributed to the silicates that were found to be present in the sample. Silicates that are concentrated on the surface of the particles following dissolution of exposed calcite or magnesite can be expected to be activated by calcium or magnesium species above neutral pH and thereby cause increased adsorption of sulfonate on the mineral as the pH is increased. Bedford limestone which does not contain such silicate exhibits decreased adsorption of sulfonate with increase in pH owing to concurrent decrease in the positive potential of the mineral particles.

Adsorption studies using clay yielded some interesting new information that proved helpful in understanding the mechanisms involved (Hanna and

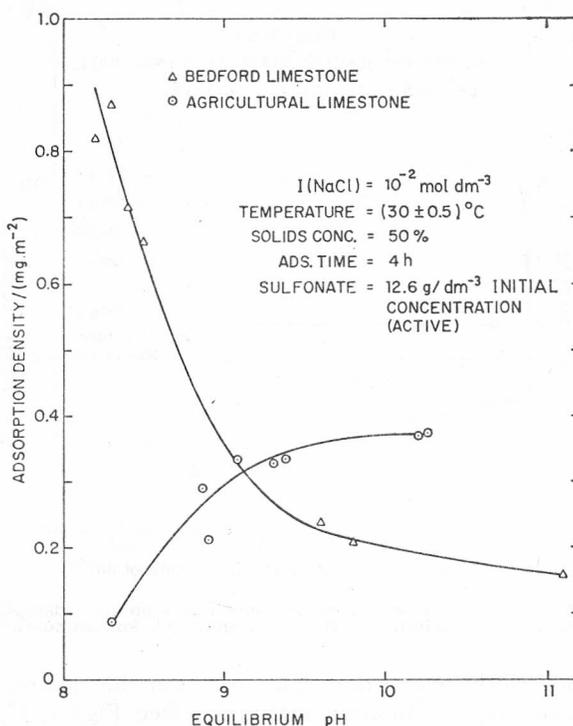


Figure 15. Data for adsorption of Mahogany sulfonate-AA on Agricultural limestone and Bedford limestone as a function of pH (Hanna and Somasundaran, 1976).

Somasundaran, 1977b). Both equilibration of dry kaolinite with water and adsorption of sulfonate on it were found to involve a fast and a slow step, the latter possibly due to slow dissolution of aluminum species from kaolinite during prolonged contact of it with water and consequent activation of sulfonate adsorption. Past studies using kaolinite appear not to have considered the possibility of an intermediate metastable condition. The effect of increase in salinity was in general to increase the adsorption of sulfonate mainly due to the less energetically favorable environment for the surfactant chains in a saline solution. The effect of the inorganic electrolytes' addition was most interesting in that the shape of the isotherm was dependent on both the cation and anion used (see Figure 16). The adsorption capacity was found to increase in the order $\text{NaCl} < \text{NH}_4\text{COOCH}_3 < \text{NH}_4\text{Cl} < \text{NH}_4\text{NO}_3 < \text{KCl}$ in agreement with the order of increasing cationic size and hydration capacity of cations. Most importantly, it was observed that an adsorption maximum is obtained in inorganic electrolyte solutions made up of »structure-making« ions. No such maximum is obtained when there is a predominance of »structure-breaking« ions.

The existence of maximum is attributed to the exclusion of surfactant aggregates from the structured interfacial region around the particles owing essentially to their incompatibility with this region. Structure-breaking ions facilitate transport and accommodation of the surfactant aggregates eliminating the possibility for such exclusion.

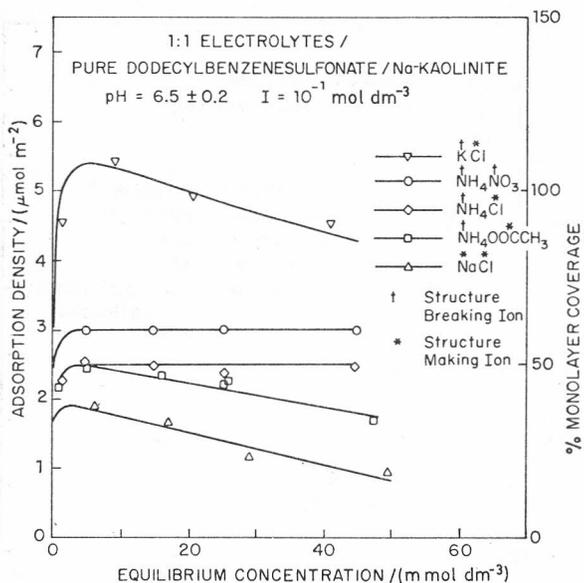


Figure 16. Effect of certain 1:1 electrolytes (10⁻¹ mol dm⁻³) on the adsorption of dodecylbenzenesulfonate on kaolinite at pH = 6.5 (Hanna and Somasundaran, 1977).

The adsorption isotherms of dodecylammonium chloride on kaolinites were of simple Langmuir type without a maximum (see Figure 17). Absence of a maximum can be attributed to lack of micellar exclusion owing to both the favorable electrostatic attractive forces between the surfactant species (Mukerjee and Anavil, 1975) and the mineral and the structure breaking properties of the ammonium head groups.

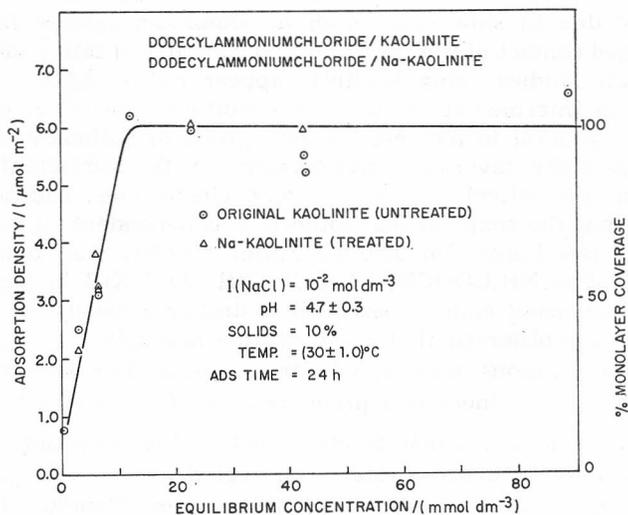


Figure 17. Adsorption isotherms of dodecylammonium chloride on pretreated kaolinites (untreated and NaCl treated) under natural pH conditions (Hanna and Somasundaran, 1977).

THE ADSORPTION KINETICS

The nature of adsorption kinetics and reversability are dependent to a large extent on the mechanisms involved. In Figure 18, adsorption density of sodium dodecylsulfonate is given as a function of time (Somasundaran, 1964). Adsorption takes place relatively fast as expected for a case of physical adsorption. Oleate adsorption on hematite is also found to occur rapidly at pH = 8 (Kulkarni and Somasundaran, 1976) (Figure 19). However, the same system is found to exhibit a markedly different type of kinetics at a pH of 4.8 (Figure

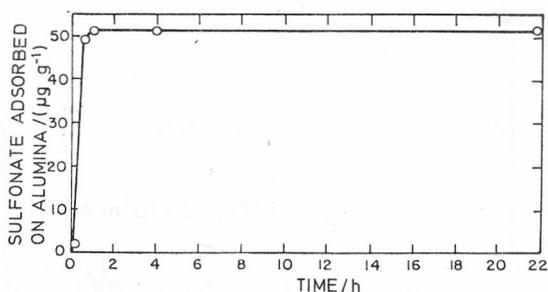


Figure 18. Adsorption of sodium dodecylsulfonate on alumina as a function of time (Somasundaran, 1964).

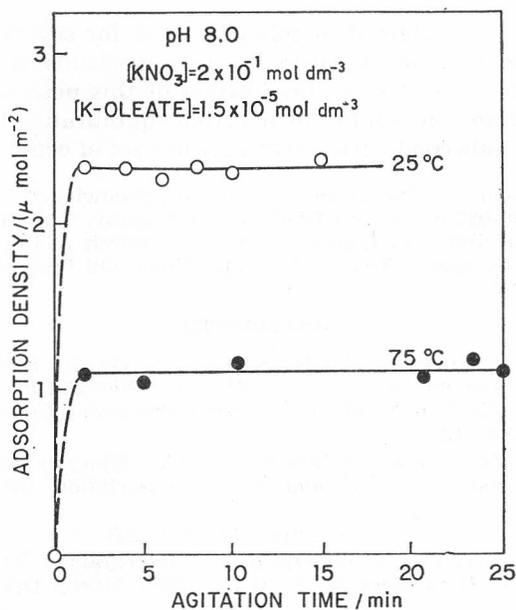


Figure 19. Adsorption of oleate on hematite as a function of time at pH = 8 (Kulkarni and Somasundaran, 1975).

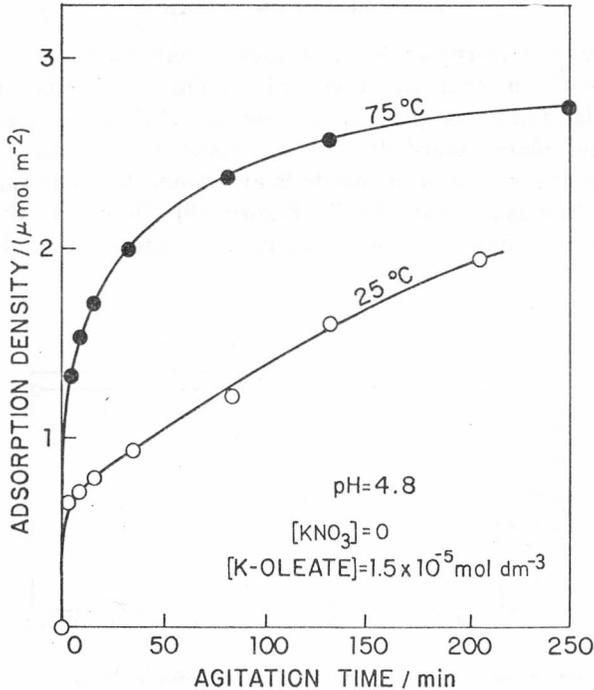


Figure 20. Adsorption of oleate on hematite as a function of time at pH = 4.8 (Kulkarni and Somasundaran, 1975).

20). Equilibrium is not attained in this case even for several hours. Evidently adsorption of oleic acid on hematite involves mechanisms that are different than that of oleate or acid soap. Implication of this observation in regard to the danger of the common practice of selecting equilibration time for adsorption experiments from tests conducted under only one set of conditions is to be noted.

Acknowledgement. — The author wishes to acknowledge the National Science Foundation (ENG-76-08756), Amoco Production Company, Gulf Research & Development Company, Marathon Oil Company, Mobil Research & Development Company, Shell Development Company, Texaco, Inc., and Union Oil Company of California for support of this work.

REFERENCES

1. A. Bahr, M. Clement, and H. Surmatz, *On the Effect of Inorganic and Organic Substances on the Flotation of Some Non-Sulfide Minerals by Using Fatty Acid-Type Collectors*, 8th Int'l Mineral Processing Congress, Leningrad, paper S-11, pp. 1968, 12.
2. U. Bilsing, *The Mutual Interaction of the Minerals During Flotation For Example the Flotation of CaF₂ and BaSO₄*, Dissertation, Bergakademie Freiberg (1969).
3. R. O. French *et al.*, *J. Phys. Chem.* **58** (1954) 805.
4. D. W. Fuerstenau, *The Adsorption of Surfactants at Solid/Water Interfaces, The Chemistry of Biosurfaces*, M. L. Hair (Ed.), Marcel Dekker, Inc., New York, **1** (1971) 143.
5. D. W. Fuerstenau, T. W. Healy, and P. Somasundaran, *Trans. AIME* **229** (1964) 321.

6. E. D. Goddard and P. Somasundaran, *Croat. Chem. Acta* **48** (1976) 451.
7. H. S. Hanna, *Adsorption of Anionic Surfactants on Precipitated CaCO₃ and Calcite*, Paper presented at 4th Arab Chem. Conference, National Research Center, Cairo (1975).
8. H. S. Hanna, *Relation Between Crystal Lattice Structure and the Adsorption Behavior of Some Salt-Type Minerals*, Paper presented at the 7th Int'l Congr. Surf. Active Sub. (1976).
9. H. S. Hana, A. Goyal, and P. Somasundaran, *Surface Active Properties of Certain Micellar Systems for Tertiary Oil Recovery*, VIIth International Congress on Surface Active Substances, Moscow, 1976.
10. H. S. Hanna and P. Somasundaran, *Physico-Chemical Aspects of Adsorption at Solid/Liquid Interfaces, II. Mahogany Sulfonate/Berea Sandstone, Kaolinite*, in: D. O. Shah and R. S. Schechter (Ed.) *Improved Oil Recovery by Surfactant and Salt Flooding*, Academic Press, 1977a.
11. H. S. Hanna and P. Somasundaran, Unpublished Results, 1977b.
12. T. W. Healy, *J. Macromol. Sci. Chem.* **8** (1974) 603.
13. R. F. Jung, *Oleic Acid Adsorption at the Geothite-Water Interface*, M. S. Thesis, Univ. of Melbourne, Australia (1976).
14. R. D. Kulkarni and P. Somasundaran, *Am. Electrochem. Soc.* (1972) 31—44.
15. R. D. Kulkarni and P. Somasundaran, *Oleate Adsorption at Hematite/Solution Interface and its Role in Flotation*, AIME Annual Meeting, New York (February, 1975).
16. R. D. Kulkarni and P. Somasundaran, *Kineticse of Oleate Adsorption at the Liquid/Air Interface and its Role in Hematite Flotation*, in P. Somasundaran and R. B. Grieves (Eds.) *Advances in Interfacial Phenomena*, AIChE Symp. Ser. **150** (1975) 124.
17. R. D. Kulkarni and P. Somasundaran, *Int. J. of Mineral Processing* **4** (1977) 89.
18. I. J. Lin and P. Somasundaran, *J. Colloid Interface Sci.* **37** (1971) 731.
19. K. L. Mittal (Ed.), *Adsorption at Interfaces*, Amer. Chem. Soc., Symp. Ser. **8** (1975).
20. P. Mukerjee, *Advan. Colloid. Interface Sci.* **1** (1967) 241.
21. P. Mukerjee and A. Anavil, *Adsorption of Ionic Surfactants to Porous Glass: The Exclusion of Micelles and Other Solutes from Adsorbed Layers and the Problem of Adsorption Maxima*, in: K. L. Mittal (Ed.), *Adsorption at Interfaces ACS. Symp. Ser.* **8** 1975, pp. 107—128.
22. G. A. Parks, *Adsorption in the Marine Environment*, *Chemical Oceanography*, 2nd Ed., Riley and Skirrow (Eds.), Academic Press 1975, pp. 241—308.
23. A. S. Peck and M. E. Wadsworth, *Infrared Studies of the Effect of Fluoride, Sulfate and Chloride on Chemisorption of Oleate on Fluorite and Barite*, *Proc. 7th Int'l Mineral Processing Congress*, N. Arbiter (Ed.), Gordon and Beach, 1965, pp. 259—267.
24. F. Z. Saleeb and H. S. Hanna, *J. Chem. U.A.R. (Egypt)* **12** (1969a) 229.
25. P. Somasundaran, *The Effect of van der Waals Interaction between Hydrocarbon Chains on Solid-Liquid Interfacial Properties*, Ph. D. Thesis, University of California, Berkeley (1964).
26. P. Somasundaran, *J. Coll. Interface Sci.* New York **31** (1969) 557.
27. 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, 1972, pp. 285—306.
28. P. Somasundaran, *Trans. AIME* **255** (1974) 64.
29. P. Somasundaran, *Int. J. Mineral Processing* **3** (1976) 35.
30. P. Somasundaran and G. E. Agar, *J. Coll. Interface Sci.* **24** (1967) 433.
31. P. Somasundaran and D. W. Fuerstenau, *J. Phys. Chem.* **70** (1966) 90.
32. P. Somasundaran and D. W. Fuerstenau, *Trans. AIME* **252** (1972) 275.
33. P. Somasundaran and R. B. Grieves (Ed.), *Advances in Interfacial Phenomena of Particulate Solution/Gas Systems*, AIChE Symp. Ser. **71** (1975).
34. P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *J. Phys. Chem.* **68** (1964) 3562.

35. P. Somasundaran and H. S. Hanna, *Physico-Chemical Aspects of Adsorption at Solid/Liquid Interfaces I. Basic Principles*, in: D. O. Shah and R. S. Schechter (Eds.) *Improved Oil Recovery by Surfactant and Polymer Flooding*, Academic Press, 1977.
36. P. Somasundaran, K. P. Ananthapadmanabhan, and R. D. Kul-karni, *Flotation Mechanism Based on Ionomolecular Complexes*, *XIIth International Mineral Processing Congress* (Sao Paulo), *Iron* 2 (1977) 80.

SAŽETAK

Fizičko-kemijski aspekti adsorpcije površinski aktivnih tvari na mineralima

P. Somasundaran

Diskutirani su osnovni principi i neki posebni aspekti adsorpcije na mineralima. Detaljnije su razrađene uloge elektrostatskih sila, lateralnih interakcija između surfaktanata, kemijskih i ostalih sila kao i uloga kemijskog stanja surfaktanata. Istaknuta je važnost prethodne obradbe mineralnih sistema koja utječe na njihovo elektrokinetičko ponašanje kao i prisutnost ostalih nabijenih čestica u otopini ako elektrostatske sile imaju znatniju ulogu. Nagli porast u elektroforetskoj pokretljivosti za određenu gustoću adsorpcije i stanovite uvjete objašnjava se stvaranjem micela, a pojava maksimalne flotacije nekih minerala, sa surfaktantima podložnim hidrolizi, u području nultog naboja pripisuje se stvaranju kovalentnih veza uz moguće stvaranje polimera. Ostali faktori kao što su vodikova veza, solvatacija, desolvatacija specija i hidrofobno vezanje također su spomenuti. Posebna pažnja posvećena je adsorpciji u micelarnim otopinama i adsorpcijskoj kinetici.

HENRY KRUMB SCHOOL OF MINES,
COLUMBIA UNIVERSITY,
NEW YORK, NEW YORK 10072, USA

Prispjelo 18. prosinca 1978.