REAGENTS IN MINERAL TECHNOLOGY

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Adsorption of Surfactants on Minerals

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I. INTRODUCTION

Adsorption of surface-active agents controls many interfacial processes
such as froth flotation, flocculation, tertiary oil recovery using sur-
factant flooding, detergency, and lubrication. In these processes,
adsorption of surfactants at one or more of the different interfaces is
significant. However, for mineral processing application, adsorption
in the solid/liquid interfacial region is of major importance and will be
the focus of discussion of this chapter. Surfactant adsorption in the
solid/liquid interfacial region is governed by a multitude of interactions
involving a large number of system variables, such as electrochemical
potential and solubility of the solid; solution properties such as pH,
ionic strength, and temperature; and the chemical structure of the ad-
sorbing species itself.
   In general, adsorption of surfactants on minerals is the result
of a number of contributing forces, including covalent bonding, coulom-
bic interaction, ion exchange, desolvation of the polar group of the
collector, desolvation of the surface, hydrogen bonding, and hydro-
phobic and van der Waals interactions. In any particular case, one or
more of the above forces may be responsible for the adsorption. If
forces such as electrostatic attraction and hydrophobic bonding are
the major driving forces for the adsorption, the process is usually
characterized as physical adsorption. If, on the other hand, the col-
lector forms strong covalent or coordinate bonds with surface species,
then the process is characterized as chemisorption. In this chapter
experimental techniques and problems normally encountered in the
study of surfactant adsorption are discussed and followed by an analy-
sis of various contributions to the total energy of interaction between
the surface and the surfactant according to major adsorption models.
Also, the effect of characteristic of the solid surface and the surfactant
on the various interaction forces is discussed.

ADSORPTION MEASUREMENTS—EXPERIMENTAL PROBLEMS

The problems encountered during the study of adsorption mechanisms
can be major and require careful attention if the measurements are to
be of any fundamental value. For completely definitive studies of sur-
face phenomena one needs to obtain detailed information about the sur-
face atomic structure and the chemical composition of a thin surface
layer, ideally no more than two monolayers thick. In 1 cm^3 of a given
solid, for example, there might be 10^{22} atoms with 6×10^{15} on the
surface; i.e., for each atom on the surface there are 10^6 atoms in the
bulk phase. Most experimental techniques either lack sensitivity to
detect such small number of molecules on the surface (about 10^{-8} mole)
or are also sensitive to the large number of bulk atoms.

A. Experimental Techniques

For the study of gas-solid systems a number of experimental techniques exist that employ some form of selective surface excitation such as heat, electric field, electrons, photons, ions, or molecules. As a consequence, the system responds by giving off electrons, photons, ions, or molecules whose energy, mass, or direction can be measured. The key to most of these techniques is the use of electrons that have a high surface sensitivity and are easily generated and detected in vacuum. While electron-spectroscopic techniques have dramatically improved capabilities for surface analysis, these are limited to high vacuum, 10^{-6} to 10^{-9} torr. A cursory list of such methods include: low-energy electron diffraction (LEED), field ion microscopy, electron-impact Auger spectroscopy, X-ray photoelectron spectroscopy, ultraviolet photo-electron spectroscopy, ion neutralization spectroscopy, electron energy-loss spectroscopy, appearance potential spectroscopy, and scanning tunneling microscopy. Unfortunately, these methods, although very useful for the study of gas/solid systems, are not directly useful for the study of adsorption of surfactants on minerals in pulp. This is due partially to the complex structure of both the mineral and the surfactant molecules, which makes interpretation difficult, but mainly it is due to the use of high vacuum, which requires the mineral to be fully dried before the analysis can be performed. Sample manipulation can introduce considerable uncertainty, because there is no assurance that the mineral-collector substrate is not altered during the sample preparation. Nevertheless, attempts have been made to apply some of these techniques [e.g., X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA)] to the study of adsorption of flotation reagents on mineral surfaces.

Infrared technique, often used in the past for adsorption studies, also suffers from the fact that the aqueous solution and the mineral usually adsorb in the infrared region and the elimination of water by drying can alter the nature of surfactant-solid interaction. In a recent publication, however, Neagle and Rochester [1] have shown that the direct determination of infrared spectra in aqueous systems can be achieved. In such cases, infrared methods can provide a substantial amount of information about the adsorbate-solid bond and the adsorbate layer on the surface. Particularly helpful would be the determination of bond shifts and new bonds upon adsorption and the analysis of isotope effects.

B. Surface Heterogeneity

Most solids have heterogenous surfaces, and they are likely to contain a range of high- to low-energy sites. Additionally, in certain cases, both polar and nonpolar sites can coexist in the same solid. It is reasonable to assume that when adsorption occurs, more active sites,

where the interaction forces are stronger, will be covered first. As adsorption proceeds, less active sites, where substrate-surfactant forces are weaker, are occupied. Subsequently, lateral interaction between the adsorbed hydrocarbon chain can also occur. In many cases variations of the heat of adsorption with surface coverage have been reported [2-4]. As a general rule, heats of adsorption tend to decrease as adsorption increases, consistent with the fact that more active sites are preferentially occupied by the surfactant first generating a stronger interaction.

Surface contamination and differences in the surface composition of a given mineral can also affect the adsorption process [5]. For example it has been established that even a simple solid such as silica can show differences in adsorption due to different types and densities of hydroxyl groups on its surface depending on the sample pretreatment [6].

C. Surface Area

In certain cases additional uncertainties may arise from difficulties in establishing the true surface area available for adsorption. Determination of the surface area of solids using gas adsorption (BET method) is a well-established procedure, and reliable information can be obtained on pores of all sizes. However, surfactant molecules are often much larger than the inert gas molecules (usually nitrogen or krypton) used in the BET method, so measurements in many cases, particularly if the solid is highly porous, can grossly overestimate the surface area available for surfactant adsorption. Occasionally, larger molecules such as benzene and stearic acid and water have been used, which yield a more realistic surface area for surfactant adsorption on highly porous solids. Also, it should be noted that in the case of very fine minerals, flocculation of the suspension could reduce the overall surface area available for adsorption.

D. Bulk Precipitation

In many mineral systems dissolved ions can complex with surfactant species, leading to precipitation. For instance, in the adsorption of fatty acids on partially soluble minerals such as dolomite and calcite, calcium and magnesium ions are released into the solution in concentrations high enough to exceed the solubility product of the soap, resulting in precipitation of the surfactant along with molecular adsorption on the surface [7,8]. Under these conditions, the determination of adsorption by conventional solution depletion methods becomes extremely difficult if not altogether impossible. In a recent publication [7], the mechanism of oleic acid adsorption on fluorite, calcite, and barite was investigated by the solution-depletion method. Precipitation of calcium or barium oleate was found to contribute to the amount of oleate abstracted from solution corresponding to several monolayers. It was not clear what fraction of the surfactant was actually adsorbed and what fraction was precipitated, apparently making

the simple task of determining an adsorption isotherm quite difficult. Recently, Morgan et al. [9] have carefully isolated adsorption from precipitation effects for the hematite/oleate system and show the total abstraction of oleate to be markedly different from the adsorption. While abstraction showed no correlation with flotation, adsorption did exhibit a maximum around pH 7 like flotation. In such instances the direct determination of the amount of surfactant attached to the solid surface might be attempted [1,10,11].

III. NONSPECIFIC VERSUS SPECIFIC ADSORPTION

A. Electrostatic Adsorption

In the case of electrostatic adsorption on charged solids, all ions of a given valency might be expected to adsorb with equivalent energy but with some variation due to differences in size of the ionic species. Adsorbed ions may not actually be bound to the surface but will exist in the double-layer region with significant mobility. It may be argued that this type of adsorption is insufficient to induce hydrophobicity to a mineral surface. As a result, therefore, the electrostatic adsorption is of less interest for altering surface wettability and, hence, for flotation purposes.

B. Specifically Adsorbed Ions

In flotation applications one is concerned with the specific adsorption of surfactants in the Stern plane close to the surface and localized to specific surface sites. It is to be noted that experimental adsorption data obtained by the usual depletion methods may include adsorption (or desorption) of surfactant counterions in the diffuse double layer, giving rise to some ambiguity in the amount of surfactant actually adsorbed in the Stern plane. The use of high concentrations of a supporting "inert" electrolyte may help to solve the problem, but extreme care should be taken to demonstrate that the electrolyte used is actually inert. For example, in the system sodium oleate-apatite, both NaCl and KNO_3, two commonly used "inert" electrolytes, were found to influence the systems because chlorine ions apparently are specifically adsorbed on apatite and KNO_3 increases the solubility of calcium from apatite [12], thereby increasing the abstraction of oleate from solution due to calcium oleate precipitation rather than by actual adsorption of oleate on the mineral surface.

The complexity of the adsorption of surfactants at solid/liquid interfaces has made theoretical modeling of the process rather limited. A description of the process based on theoretical concepts and a unified theory that can take into account all the main factors affecting the adsorption process is far from being developed. In the following section some of the theoretical developments on adsorption of surfactants are discussed.

IV   ADSORPTION ISOTHERMS

Adsorption of surfactants at the solid/liquid interface is usually described by the Stern-Grahame equation, which may be written in the form [13,14]

$$\frac{\theta}{1 - \theta} = \frac{C_e}{55.5} \exp - \frac{\Delta G^0_{ads}}{RT} \tag{1}$$

where θ is the fraction of surface sites occupied, C_e is the equilibrium concentration of surfactant, and ΔG^0_{ads} is the standard free energy of adsorption.

Equation (1) could also be written in the form

$$\frac{C_\equiv}{1/\beta + C_e} \tag{2}$$

where

$$\beta = \frac{1}{55.5} \exp - \frac{\Delta G^0_{ads}}{KT}$$

Note that Eq. (2) is similar to a Langmiur-type isotherm. Furthermore, for very low surface coverage, $\beta \ll 1$, Eq. (1) reduces to

$$\theta = \beta C_e \tag{3}$$

which is an expression of Henry's law. It should be noted that the Stern-Graham isotherm, when written in the form of Eq. (4) below, is indeed a Henry's law and therefore valid only at low surface coverages

$$\Gamma = 2rC_e \exp \frac{-\Delta G^0_{ads}}{RT} \tag{4}$$

where Γ_s is adsorption density (surface excess) in the Stern plane, r is the effective radius of the adsorbed species, C_e is the equilibrium bulk concentration of the adsorbate, R is the gas constant, T is the absolute temperature, and ΔG^0_{ads} is the standard free energy of assorption. Modifications of Eq. (4) have been proposed to include elec trostatic interactions as well as lateral interactions between the hydrocarbon chains [15,16]. These modifications yield the equation

$$= 2\gamma C_e \exp \frac{zF\Psi_s - n\phi}{RT} \tag{5}$$

where z is the valency of the surfactant, F is the Faraday constant, Ψ_s is the electrokinetic potential at the adsorption plane, n is the number of CH_2 groups in the surfactant, and ϕ is the cohesive energy per mole of CH_2 groups. This type of modification provides a very useful qualitative description of the complex adsorption mechanism of surfactants. However, it should be kept in mind that the isotherm is valid only for low coverages on homogeneous surfaces.

In more general terms, the contributions to the total free energy of adsorption in Eq. (4) can be divided into several different components as follows:

$$\Delta G^0_{ads} = \Delta G^0_{elec} + \Delta G^0_{h-h} + \Delta G^0_{chem} + \Delta G^0_{c-c} + \Delta G^0_{c-s}$$
$$+ \Delta G^0_{solv/desolv} \tag{6}$$

where ΔG^0_{elec} is the electrostatic contribution to the total standard free energy of adsorption, ΔG^0_{h-h} accounts for the hydrogen bond interaction, and ΔG^0_{chem} represents the possible chemical interactions between the substrate and the surfactant, covalent bond formation, and acid-base interactions. In those particular solid-surfactant systems where ΔG^0_{chem} is small, the adsorption process has been termed physical adsorption. ΔG^0_{c-c} is the contribution derived from the lateral interaction between the adsorbed hydrocarbon chains. ΔG^0_{c-s} accounts for the interaction between hydrocarbon chains and nonpolar solids (hydrophobic bonding). $\Delta G^0_{solv/desolv}$ considers the change in energy derived from the changes in solvation of the surface and surfactant species upon adsorption.

The division of ΔG^0 into various components is somewhat arbitrary because some terms can depend on others; however, it is a convenient schematic way to present the complex interactions that can take place during adsorption.

For a given mineral-surfactant system, as mentioned earlier, one or more of the above forces can be responsible for adsorption depending on the nature and concentration of the surfactant, the chemical composition of the mineral, and medium properties such as ionic strength. Electrostatic and lateral interaction forces are considered to be the major factors determining the adsorption of surfactants on oxides and other nonmetallic minerals. Chemical forces, on the other hand, become more significant for surfactant adsorption on salt-type minerals such as carbonates (calcite) and sulfides (pyrite).

In the following sections a brief discussion of the various factors that determine the adsorption of surfactants on mineral substrates is presented.

V. CONTRIBUTIONS TO THE ADSORPTION ENERGY

A. Electrical Interactions

Most solids in aqueous solution exhibit a surface charge that is dependent on the pH and/or chemical composition of the solution. This charge arises from either preferential dissolution or hydrolysis of surface groups or the preferential adsorption of potential-determining ions [17-21]. The surface charge results in an electrochemical potential in the vicinity of the solid surface that can be determined experimentally, e.g., by electrophoretic mobility measurements. However, even if electrophoresis experiments indicate a neutral surface, it is likely that there are still ions on the surface, only that the number of positive ions is balanced by an equivalent number of negative ions. The electrochemical potential creates a double layer rich in counterions such that the net sum of charges in the surface and the surrounding double layer is zero. Electroneutrality considerations dictate that adsorption of ionic surfactants occurs through either exchange with co-ions in the double layer or with an equivalent co-adsorption of counter-ions.

It is generally agreed that electrical interaction between the adsorbate and the substrate is one of the major factors influencing the adsorption process. In general, the electrostatic interaction may include a coulombic and dipole term [22] such that

$$\Delta G^0_{elec} = \Delta G^0_{coul} + \Delta G^0_{dip} \tag{7}$$

where

$$\Delta G^0_{dip} = \sum \Delta_{nj} \mu_j E \tag{8}$$

and

$$\Delta G^0_{coul} = zF\Psi \tag{9}$$

The dipole term ΔG^0_{dip} arises from the exchange between surfactant and water dipoles upon adsorption according to the following scheme [22]:

$$(\text{Surfactant})_{\text{solution}} + n(H_2O)_{\text{adsorbed}} \rightleftharpoons (\text{surfactant})_{\text{adsorbed}}$$

$$+ \ n(H_2O)_{\text{solution}} \tag{10}$$
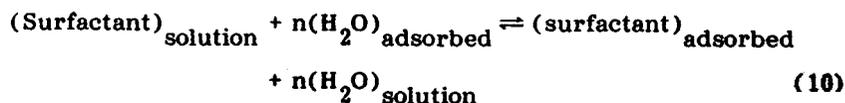
In the dipole term, Δ_{nj} is the change in the number of adsorbed molecules (dipoles) j; μ_j is the dipole moment of j, and E_s is the field strength at the Stern plane (assumed to be the plane of adsorption). In the particular case of an ionic surfactant, only the dipole moment of water needs to be considered. In the original Stern equation and also in several subsequent publications, the ΔG^0_{dip} term has been neglected. However, this term may play an important role when adsorption takes place with the displacement of a large number of dipole molecules from the surface. For example, in the adsorption of tetralkylammonium ions on silver iodide, de Keiser and Lyklema [22] report that at high pH values the displacement of water dipoles outweighs the coulombic interactions between the alkylammonium ions and the surface.

In the coulombic term, z represents the valency of the ionic surfactant, Ψ_s the potential at the Stern plane in the electrical double layer, and F the Faraday constant. It is generally assumed that Ψ_s is similar to the zeta potential and that only a minor error is introduced if experimentally determined zeta potential values are employed to calculate ΔG^0_{coul}. Evidently, under IEP conditions the coulombic term will be negligible. If the surfactant ions and the surface exhibit opposite signs, then the ΔG^0_{coul} is attractive; on the other hand, if they are of the same sign, this term will oppose rather than promote adsorption.

It follows from the above discussion that in the absence of other contributions, coulombic adsorption of surfactant ions is possible only up to the extent that the adsorption reduces the zeta potential of the solid to zero. Further adsorption would not be possible by coulombic attraction alone.

From the experimental evidence of several adsorption systems where ionic surfactants do not adsorb on minerals of the same charge but are shown to adsorb in appreciable amounts on oppositely charged solids, it has been concluded that coulombic interactions play a dominant role in the adsorption process. As seen in Figs. 1 and 2, this seems to be the case in the adsorption of dodecylsulfate on alumina [23] and geothite [24], and also dodecylammonium chloride on goethite. Additionally, the dependence of adsorption on the electrical nature of the interface has been inferred from flotation and electrokinetic measurements on minerals such as calcite [25], apatite [26], corundum [27,28], quartz [24], zircon [29], and magnetite [30] in the presence of various surfactants. In those cases where electrostatic forces play a major role in the adsorption process, the presence of "inert" ions can influence adsorption due to competition between different counterions for the surface. For example, dodecylamine flotation (and by inference amine
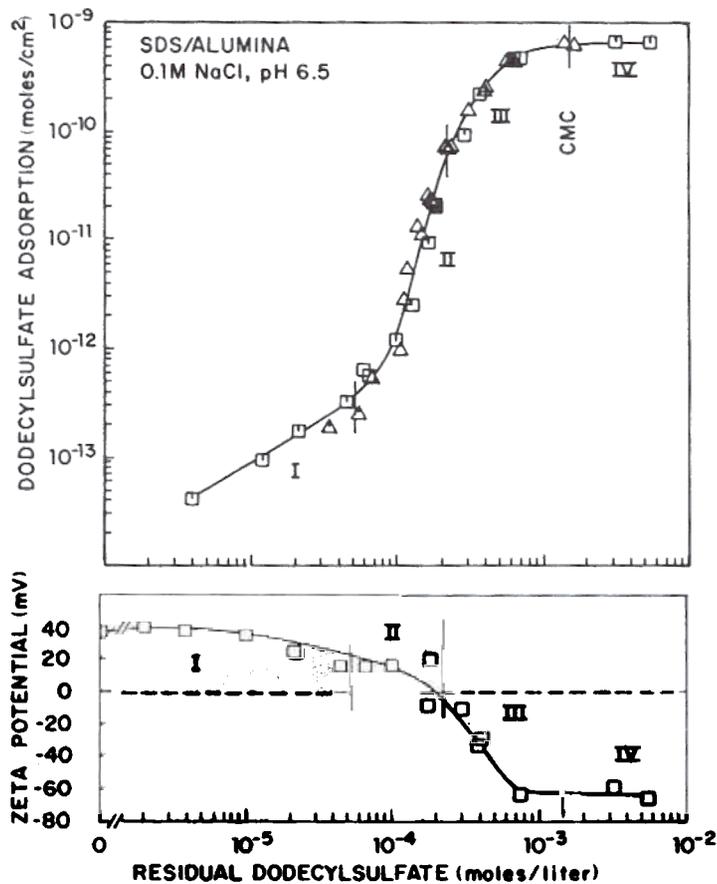
FIG. 1. Adsorption and zeta potential behavior of dodecylsulfate-
alumina system showing various adsorption regimes (Ref. 23).

adsorption on the solid-liquid interface) of quartz is depressed by
KNO_3 [31]. On the other hand, adsorption of ions that exhibit op-
posite charge to the surfactant can induce or enhance adsorption.
For example, fatty acid flotation of quartz in the presence of bivalent
or trivalent cations illustrates this phenomenon [32,33].

1. Case Against the Electrostatic Model of Adsorption

The use of electrokinetic potentials to support adsorption mechanisms
or characterize mineral surfaces has been disputed by M. A. Cook
[34], who instead proposed the hydrolytic adsorption model. Accord-
ing to this author, the net electrokinetic charge is normally less than
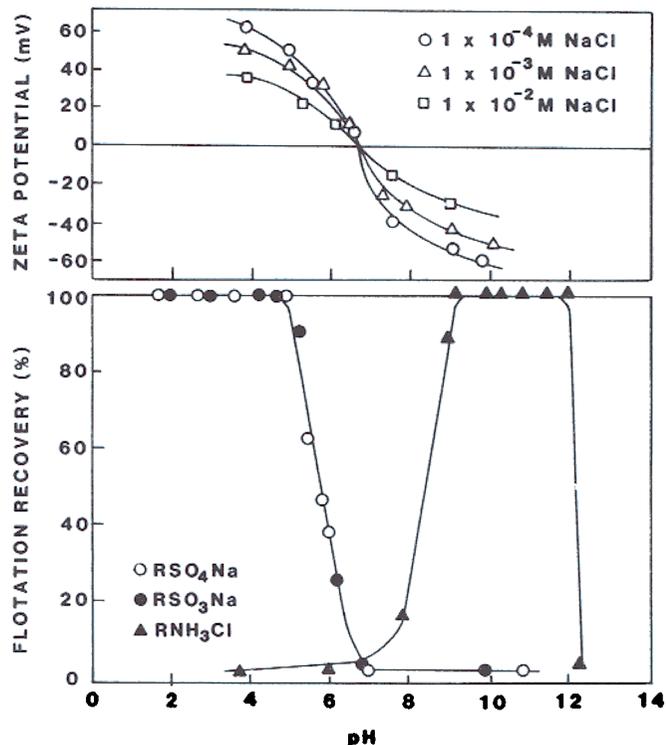
FIG. 2. Zeta potential and flotation recovery of goethite with differen:
C_{12} surfactants as a function of pH (Ref. 24).

about 0.1% of the total charges (sum of positive and negative charges) that can exist at most solid-water interfaces, and therefore the effect of the electrokinetic potential on surfactant adsorption should be very small.

There are many cases in which experimental evidence shows that the electrostatic term in Eq. (6) can be overridden by the other terms. In fact, flotation of most sulfide minerals is accomplished with anionic collectors that are adsorbed in spite of the electrostatic repulsion by the negatively charged mineral surface. Adsorption of fatty acids or alkylsulfonates on oxides or salt-type minerals can take place irrespective of the zeta potential of the minerals. In such cases, evidently, the ΔG^0_{chem} plays a dominant role in the adsorption process.

An example of electrostatic interaction often cited is the ferric oxide/ alkylsulfate system. Even in this case, however, adsorption of the surfactant can take place in spite of (rather than due to) coulombic inter- actions. As seen in Fig. 1, adsorption of dodecylsulfate on alumina
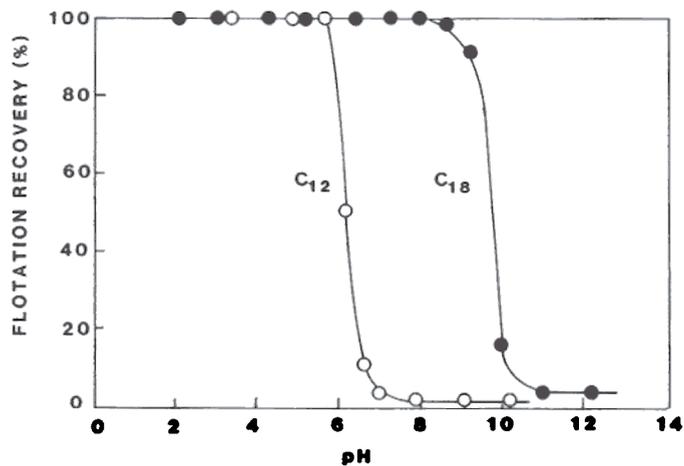
FIG. 3. Flotation of hematite as a function of pH with 1×10^{-4} M dodecyl and octadecylsulfate (Refs. 24,35).

continues well beyond the point where the surface potential becomes negative. Also, Figs. 3 and 4 indicate that octadecylsulfate and octadecylamine (35,36) can adsorb in relatively large amounts on hematite under pH conditions where the electrokinetic potential and the surfactant
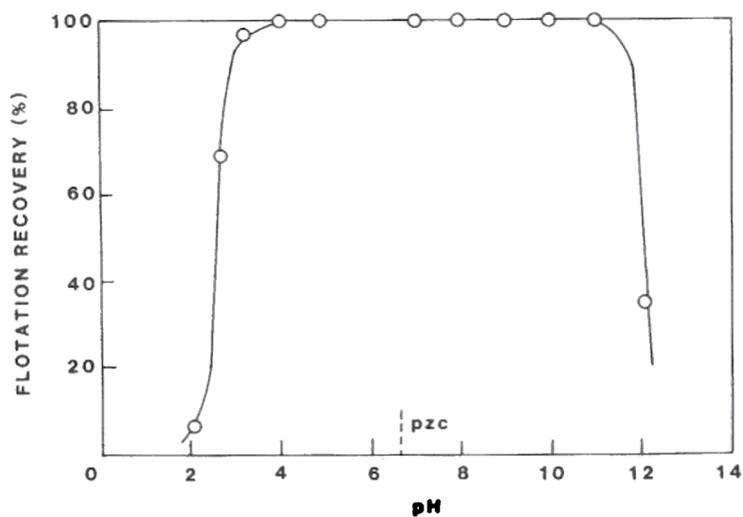
FIG. 4. Flotation recovery of hematite as a function of pH with 1×10^{-4} M octadecylamine (Ref. 35).

exhibit the same polarity. It therefore appears that other forces such as chemical or lateral interactions can easily overcome the electrostatic term, and if the surfactant has a long enough hydrocarbon chain, adsorption can take place almost irrespective of the electrokinetic potential. This concept will be discussed in detail in the next section.

Indeed, the case for electrostatic adsorption seems to be the exception rather than the rule for surfactant adsorption. Only a few systems seem to respond to the theory of electrostatic adsorption; relatively more important contributions to the adsorption energy come from the ΔG^0_{c-c} and ΔG^0_{chem} terms.

If it is assumed that the zeta potential is identical to the Stern potential, one can calculate the ΔG^0_{coul} term by using Eq. (9). Experimentally determined values of zeta potential rarely exceed 50 to 60 mV, so the data in Table 1 can be taken as representative values of the electrostatic contribution to the total free energy of adsorption of an ionic surfactant of unit charge. As seen in Table 1, the energy involved in the coulombic interaction is very small. For zeta potentials in the range 30 to 40 mV, which are common for most minerals, the coulombic energy of adsorption is less than 1 kcal/mole. Therefore, unless Eq. (9) gives a gross underestimation of ΔG^0_{coul}, or zeta potential values computed from electrokinetic measurements are much smaller than the interfacial electrochemical potential, it seems that the importance attached to the role of electrostatic adsorption has been overplayed in the past. As will be shown later, the ΔG^0_{c-c} contribution can be almost an order of magnitude larger than the coulombic term. Also, the relatively small energy of hydrogen bond formation (4 to 8 kcal/mole) would be several times larger than ΔG^0_{coul}, and chemical interac-

TABLE 1. Electrostatic Contribution (ΔG^0_{coul}) Calculated from Eq. (9) for Different Values of Ψ_s

Ψ_s (mV)	ΔG^0_{coul} (kcal/mole)
10	0.23
	0.46
	0.69
40	0.92
50	1.15
60	1.38
70	1.61

tions involve even larger adsorption energies. A probable reason for underestimation of ΔG_{coul}^0 by Eq. (9) lies in the assumption made in the double-layer theory that the surface is uniformly charged, i.e., the charges are assumed not to be localized and an average potential is considered. A more realistic model would be the presence of localized charges and a local potential at the adsorption site, in which case the coloumbic interaction may be larger than that estimated by Eq. (9). Some developments along this line have been presented by Levine et al. [37,38], who consider a double-layer model with discrete acid-base sites on the surface along with ion-ion interaction between counterions and surface sites. This will also be more consistent with the use of Langmuir-type isotherms, which are based on adsorption on a specific site.

B. Lateral Chain-Chain Interactions

Many experimental isotherms for the adsorption of surfactants on solids are of the shape shown in Fig. 1 and are characterized by four regions. At low concentrations adsorption increases with increase in concentration with a slope of about 1. The zeta potential of the particles remains mostly unaffected by the adsorption, and therefore the adsorption in this region has been attributed to ion exchange between surfactant and other ions in the double layer. It is generally assumed that in this region adsorption is electrostatically driven. However, hydrophobic interactions (ΔG_{C-S}^0) can play a role in this region if the surface has hydrophobic sites. Upon increasing the surfactant concentration, a sharp increase in the slope of the adsorption isotherm results at a given concentration that is characteristic of the surfactant for each mineral-solution system. This is a clear indication that increasing surface coverage enhances the affinity of the surfactant for the surface. Adsorption is also accompanied by a sharp increase in the electrokinetic potential, and in some cases a reversal of the zeta potential is observed. These facts have been attributed to lateral association of the surfactant species in the adsorbed layer to form hemimicelles [39], due to the favorable energetics of removal of alkyl chains from the aqueous environment in a process analogous to the formation of micelles in bulk solution [15,16,23,40]. Cases and co-workers [41,42] consider the aggregation phenomenon a two-dimensional condensation of the surfactant on heterogeneous surfaces, which according to them can take place when the alkyl chain of the surfactant contains eight or more CH_2 groups. In order to form surface aggregates, it is necessary that the surfactant reach a certain minimum concentration near the surface; this minimum concentration, known as the hemimicelle con-

REGION I
NO AGGREGATION

REGION II
NUMBER OF
AGGREGATES
INCREASES
~120-130 MOLECULES
PER AGGREGATE

REGION III
SIZE OF AGGREGATES
INCREASES
>160 MOLECULES
PER AGGREGATE
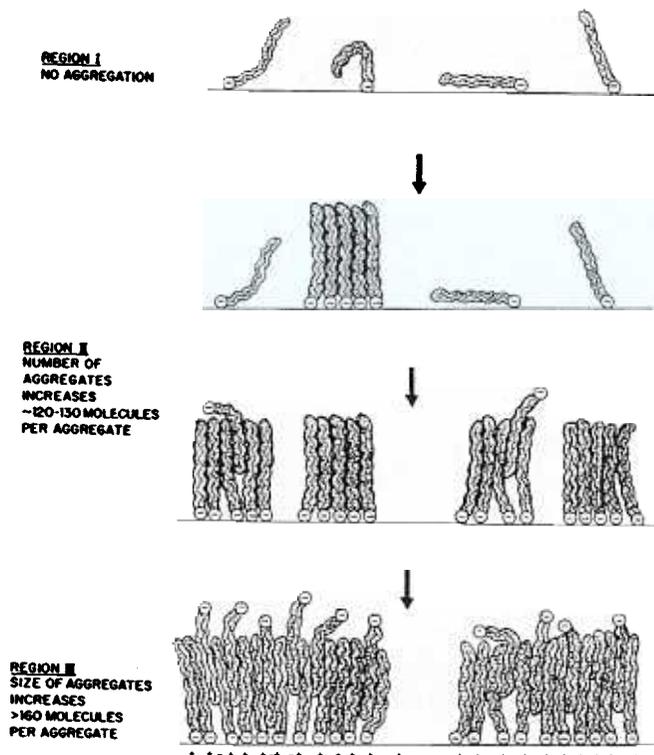
FIG. 5. Evolution and size of surface aggregates determined by pyrene fluorescence decay method in various adsorption regimes (Ref. 23).

centration, depends mainly on the number of CH_2 or aromatic groups and the way they are arranged in the hydrocarbon chain of the surfactant. Other factors, such as pH, temperature, and ionic strength, also influence the hemimicelle concentration. Recently, Chandar et al. [23,43] have obtained direct evidence for such aggregation using fluorescence decay and electron spin resonance techniques. They have obtained information on the number of molecules in the hemimicelle as they grow and merge into each other (see Fig. 5). The energy in-

volved in the lateral chain-chain interactions, ΔG_{c-c}^0, has been proposed (e.g., Ref. 13) to be proportional to the number of CH_2 groups in the surfactant (n) according to the relationship

$$\Delta G_{c-c}^0 = n\phi \tag{11}$$

where ϕ is the cohesive energy per mole of CH_2 group. This factor has been evaluated by different investigators to be about 1 kT/mole, that is, approximately 0.6 kcal/mole CH_2 group [15,44]. Therefore, for surfactants with chain lengths of 12 to 18 carbons, the ΔG_{c-c}^0 contribution to the total energy of adsorption would be 7 to 10 kcal/mole. This is almost an order of magnitude larger than the electrostatic contribution estimated in Table 1. Lateral interactions, therefore, are of primary importance in the adsorption of long-chain surfactants at the solid/liquid interface. This type of interaction is likely to take place between the hydrocarbon chains of ionic and nonionic surfactants as well as nonpolar hydrocarbons when mixtures of these reagents are used in, for example, flotation schemes where frothers or extenders such as fuel oil, kerosene, and other nonpolar oils are added.

It has been shown that nonionic surfactants and nonpolar oils can co-adsorb with ionic surfactants [45,46] at the solid/liquid interface, thereby increasing the hydrophobicity of the minerals. Nonpolar oils do not have a polar head, so whatever their orientation in the adsorbed layer, adsorption of these molecules results in increased hydrophobicity. This is not the case with polar or ionic surfactants, which, by chain-chain interactions, can adsorb with the polar head toward the bulk solution at high concentrations, thus reducing the hydrophobicity of the solid and its flotation (see Fig. 6) [47].

Heats of adsorption of nonpolar hydrocarbons, such as tetradecane, have been reported to be negligible during co-adsorption with surfactants [48]. This is consistent with the generally accepted theory that the chain-chain interaction in the adsorbed layer is mostly entropic and is supported by experimental evidence indicating that heats of micellization of surfactants are very small [49]. The hydrophobic bonding between the adsorbed surfactant chains results from the gain in entropy of the water molecules upon removal of the hydrocarbon chain from the aqueous environment.

C. Chemical Interactions

The chemical contribution term may be the most neglected aspect in the theoretical developments of surfactant adsorption. Although in the earlier development of flotation theory, Taggart and Arbiter [50] proposed that adsorption of collectors corresponds to well-recognized chemical interactions similar to those that occur in bulk, only limited progress has been made to support or dismiss this theory.
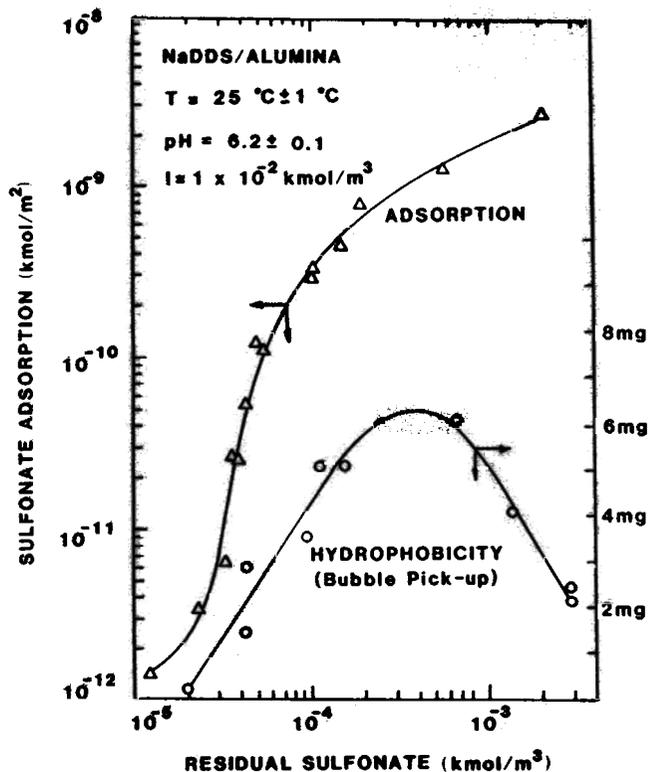
FIG. 6. Change in hydrophobicity determined by bubble pick-up techniques as a function of dodecylsulfonate adsorption (Ref. 47).

The chemical term ΔG^0_{chem} in Eq. (6) accounts for the energy of adsorption derived from possible surfactant-surface site interactions such as covalent or complex bond formation. Surfactants such as fatty acids [51,52], alkylsulfates [53], alkylsulfonates [54], amines [55], and alkylhydroxamate [56] have been proposed to adsorb by means of chemical interactions on a variety of minerals. Also, hydrogen bond formation between mineral surfaces and surfactants containing hydroxyl, phenolic, carboxylic, and amine groups has been proposed [57].

Infrared spectroscopy was first employed by French et al. [51] to support chemisorption of oleate on fluorite. Since then this method has been used to substantiate chemisorption of oleate on calcite, barite [52], and apatite. However, as discussed earlier, infrared methods should be considered cautiously in adsorption studies in aqueous suspensions.
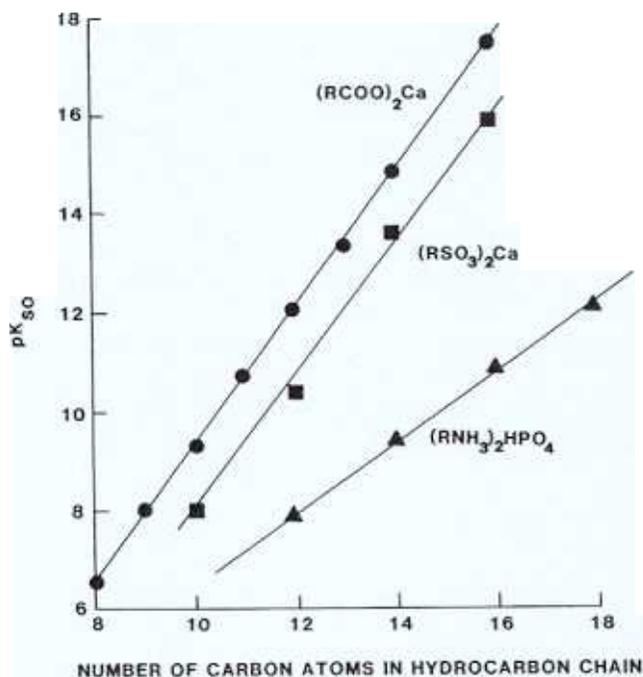
FIG. 7. Solubility as a function of the chain length of fatty acids sulfonic acids, and amine acids salts (Ref. 54,55).

In most of the studies quoted above it has been found that insoluble complexes are formed in the bulk upon reaction of the surfactant with the dissolved ionic species [54,55,58,59]. On the basis of a correlation between solubility of these complexes in the bulk with adsorption and flotation behavior, it has been proposed that adsorption of the surfactant takes place through reaction with ions on the surface or, as suggested by Ananthapadmanabhan and Somasundaran [59], by surface precipitation, under conditions where the corresponding concentration product is exceeded in the interfacial region even though not necessarily in the bulk.

Invariably, the solubility of surfactant-ion complexes such as fatty acid-calcium, alkylsulfonate-calcium, amine-phosphate, and others has been found to be strongly dependent on the number of CH_2 groups in the surfactant chain (see Fig. 7). Also, the heats of reaction of amines with phosphate ions, fatty acids with calcium ions, and heats of adsorption of amines on apatite and dolomite were found to be dependent on the number of CH_2 groups in the hydrophobic moiety of the surfactant. It seems, then, that in certain systems the length of the hydrocarbon chain can influence the chemical term [22,55]. In such

cases the contribution of the CH_2 groups appears to be mostly enthalpic and would be in addition to the entropic contribution due to lateral chain-chain interactions.

VI. NONIONIC SURFACTANTS

Some common flotation collectors such as fatty acid and long-chain aliphatic amines under certain pH conditions are predominantly non-ionic in nature. Also, alcohols and derivatives of polyoxyethylene glycol that are used as frothers are typical examples of nonionic sur-factants (NIS).

Adsorption isotherms of NIS are normally Langmuirean, reversible with little histeresis. It can be reasonably assumed that NIS are adsorbed physically rather than chemically, except for the possible contribution of hydrogen bonding with hydroxyl groups on the sur-face [57]. Most NIS contain polar groups that are likely to form hy-drogen bonds with surface hydroxyls, and therefore a relatively strong adsorption is to be expected. For example, polyethylene glycol adsorption on quartz [60] is very high at low pH. However, adsorp-tion decreases as pH is increased as a result of progressive change of silanol groups, which can form hydrogen bonds, into silicate anions. The maximum adsorption obtained at pH 3.5 was about three times the estimated adsorption observed at pH 9.2.

In general, affinity of NIS for most solids is lower than that of ionic surfactants; i.e., the bonding energy between the hydrophillic moiety and the solid is weak. Microcalorimetric experiments have shown that for low coverages exothermic effects are prevalent, but at higher surface coverages the apparent differential molar heat of ad-sorption is endothermic. At concentrations of importance in flotation practice, the amount adsorbed is in most cases very low, and indeed in many cases absence of adsorption has been reported. This apparent lack of adsorption has been attributed to the low sensitivity of the analytical methods used in the adsorption studies [57]. Since the sur-factant is electrically neutral, the ΔG^0_{elec} is reduced to the dipole-dipole type of interaction, and therefore adsorption is not very sensi-tive to surface potential. Usually, however, the maximum amount ad-sorbed increases with the polar character of the adsorbent because of the larger dipole-dipole interaction. In this case the lateral ΔG^0_{c-c} term plays an important role in the adsorption energy, and therefore adsorption increases with each CH_2 group in a homologous series. But when the reduced adsorption Γ/Γ_{max} is plotted as a function of Ce/CMC, the isotherms obtained in a homologous series can be superim-posed. When the mineral has low polarity, adsorption results mainly from the interaction between the surface and the hydrophobic moiety of the surfactant, that is, ΔG^0_{c-s} in Eq. (6). The shape of the iso-therm and the maximum amount adsorbed (Γ_{max}) depends on the

strength of interaction between the surface and the polar group of the surfactant. Specific contribution of the polar head-surface interaction to the adsorption isotherm [57] is discussed in the following section. In all cases, adsorption of isolated molecules from the solution, and not direct adsorption of micellar aggregates, has been observed. Moreover for concentrations above the CMC, no further adsorption is possible because of stabilization of the chemical potential of the monomer, and a plateau is obtained in the isotherm (region IV in Fig. 1).

A. Weak Polar Head-Surface Interactions

In the case of a weak polar head-surface interaction, the surfactant molecules adsorb lying flat on the solid surface until the surface becomes saturated. This part of the isotherm is concave until a pseudo-plateau is reached. Due to lack of sensitivity, in many cases this plateau has not been observed. If the concentration in solution is increased further, normally near the CMC, additional adsorption occurs with the adsorbed molecules oriented perpendicular to the surface and with the polar head pointing toward the bulk solution. At a complete monolayer of perpendicularly oriented molecules, a plateau is reached and no further adsorption is observed. The overall isotherm corresponds to a L_4-type isotherm according to the Giles et al. classification scheme [61]. According to Cases et al. [41,42], the structure of the adsorbed layer is similar to an oblate ellipsoid micelle of shape and size very similar to those in the bulk, rather than a bidimensional layer.

B. Intermediate Polar Head-Surface Interactions

In intermediate polar head-surface interactions the isotherm resembles a Langmuir isotherm or an L_2 Giles isotherm [61]. In essence, the adsorption is equivalent to the initial part of the isotherm discussed in the previous case. The solid becomes saturated with a monolayer of surfactant lying flat. The interaction of the polar heads with the surface is too strong for them to be reoriented and thus to allow adsorption of additional molecules with the polar head pointing toward the bulk solution. However, the polar head-surface interaction is not strong enough to displace the hydrocarbon chain from the surface and form a monolayer of vertically oriented molecules.

C. Strong Polar Head-Surface Interactions

In strong polar head-surface interactions the isotherm resembles the one described in the first case (L_4 isotherm), with the first plateau corresponding to saturation of the surface with the adsorption of molecules lying flat. Upon increasing concentration, additional adsorption of vertically oriented molecules with the polar heads interacting with the surface occurs.

Additionally, in this case the formation of a double layer of adsorbed molecules is possible, so the Γ_{max} is about twice the Γ_{max} observed in the case of weak solid-surfactant interactions.

VII. ION MOLECULAR COMPLEXES AND MIXTURES OF SURFACTANTS

Normally the CMCs of nonionic surfactants are much lower than those of ionic surfactants. This is explained by the stronger polar head repulsion in the case of ionic surfactants. When a nonionic surfactant such as an aliphatic alcohol is added to a solution of ionic surfactant, it decreases the CMC of the latter, meaning that a smaller amount of surfactant is necessary to obtain a given adsorption density. This effect has been demonstrated by the additoin of long-chain alcohols in the dodecylamine-quartz system [46]. In this case the contant angle of the solid was found to increase significantly in a solution containing a mixture of dodecylalcohol-dodcylamine as compared to dodecylamine alone. A similar effect has been observed with collectors, such as amines and fatty acids, that hydrolyze under basic or acidic conditions. Neutral and ionic forms of these surfactants can coexist in certain pH ranges. It is then likely that the hemimicelle concentration will be reduced under pH conditions where the presence of neutral surfactant molecules reduces the electrostatic repulsion between the ionic surfactant molecules.

Neutral surfactants are probably co-adsorbed with ionic surfactants through hydrophobic interactions between the CH_2 groups of the hydrocarbon chains (i.e., the ΔG^0_{C-C} term discussed earlier). However, unless some affinity between the polar head of the neutral surfactant and the solid surface, or between the hydrophillic moieties or both surfactants, is invoked, it may be argued that the orientation of the nonionic surfactant is likely to be one with the polar head pointing toward the liquid phase, leading to reduced flotation. This is likely to occur particularly when relatively large amounts of either surfactant are present and the most active sites on the surface are already occupied by adsorbed molecules.

Also, amines and fatty acids in aqueous solutions can form ion molecular complexes such as acid-soap dimers [62-65], which show a stronger surface activity than the simple ionic species. Therefore, the existence of these ion molecular complexes as well as the coexistence of ionic and neutral forms of the surfactant can result in a closer packing in an adsorbed layer and hence in increased hydrophobicity of the solid for a given equilibrium concentration of the surfactant. In this case a maximum in collector adsorption and in flotation can be expected under pH conditions where the ion molecular complex concentration is maximum (pH about 8.0 for fatty acids and about 10.5 for amines) or

the ratio of the charged to the neutral species of the surfactant is at an optimum value. This has been substantiated in several cases in which maximum flotation recoveries are obtained at pH values where the ion molecular complexes exhibit a maximum concentration. For example, a maximum in the flotation of hematite [64] and other minerals [63] with oleic acid has been reported at pH 8.0. Also, flotation of quartz [62] and corundum [66] using dodecylamine exhibits a maximum at pH about 10.5. However, a number of cases may be cited where maximum flotation of different minerals with fatty acids or amines is obtained at pH values away from 8.0 or 10.5, respectively. For instance, amine flotation of dolomite [8,67] shows a maximum at pH about 6.0, zircon at 8.5 [41], and apatite at 6.0 [41,67]. Oleic acid flotation of phosphate shows maximum at pH 4.0 and 10.9 [68], and calcite as well as dolomite show maxima at pH 4.0 and 11.0 and rather a minimum in flotation at about pH 8.0 [67,68]. In these systems the effect of co-adsorption of nonionic species and the reported high surface activity of ion molecular complexes appears to be overridden by the other factors that contribute to the adsorption energy, for example, surface and bulk precipitation.

The effect of pH on flotation of most minerals with fatty acids or long-chain amines tends to be minimized when the surfactant concentration is increased, in which case pH optimums are absent and total recovery is normally possible in a broad range of pH values. This shows that due to a major contribution of the ΔG^0_{c-c} term in the overall adsorption process, this type of collector is inherently poorly selective.

VIII CONCLUDING REMARKS

Adsorption of surfactants on minerals is a complex process. Although considerable advances have been made in understanding the isolated role played by various system properties, theoretical developments have not been rigorous and they lag behind experimental and conceptual developments. Some of the experimental difficulties and theoretical complexities that are responsible for the slow development of a unifying adsorption model covering a range of solid-surfactant combinations have been analyzed.

The major individual contributions to the overall energy of adsorption have been identified and discussed. Electrostatic interactions play an important role in many surfactant-solid systems, but other factors such as chemical and lateral chain-chain interactions can be in many cases an overriding factor. It has been argued in this chapter that the coulombic contribution is either poorly described by the theoretical formulations presently available, or the importance assigned in the past to the coulombic interaction has been overestimated.

Most authors agree on the paramount importance of lateral chain-chain interactions during the adsorption of both ionic and nonionic surfactants. However, there is some controversy about the exact mechanism and the correct quantification of this type of interaction. The character of the chain-chain interaction is essentially entropic and is explained by the gain in entropy of the water molecules upon removal of the hydrocarbon chain from the aqueous environment; since the surface of the solid does not play a role in the process, this interaction is inherently independent of the solid surface and therefore nonselective. Chemical interactions, on the other hand, are more specific than either electrostatic or chain-chain interactions and are therefore more significant for flotation purposes. Unfortunately, the understanding of chemical interactions in the adsorption of surfactants is very limited. In certain systems this interaction has been explained in terms of surface precipitation of the surfactant due to reaction with some of the ions that constitute the mineral surface. This has been based on an analogy with the reaction between the same ion and surfactant in the bulk solution.

The role of neutral molecules and ion molecular complexes on the overall adsorption process has also been discussed. Ion molecular complexes appear to be more surface-active than ionic or neutral species and are proposed to be the adsorbing species in certain systems However, this behavior is not necessarily general, since in many systems other factors appear to override the larger surface activity of ion-neutral molecule combinations or ion molecular complexes.

ACKNOWLEDGMENTS

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