Advances in understanding flotation mechanisms

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Abstract – *Flotation of minerals is governed by many processes at the solid/liquid/gas interface, such as adsorption and precipitation of surfactants. In this paper, the basic principles governing these processes and hence flotation are discussed. Also, recent techniques such as fluorescence and ESR spectroscopy which have been used to study in situ surfactant adsorption and to obtain information on the structure of adsorbed layer are discussed.*

Introduction

Flotation processes are used to separate or concentrate minerals and other chemical species. Separation by flotation is the result of many complex physicochemical processes occurring at the solid/liquid, liquid/gas, and the solid/gas interfaces. Flotation depends on the probability of attachment of the particles to the bubbles in the flotation cell, which in turn is determined by the hydrophobicity of the particle surface. In most flotation systems, the particle surface is rendered hydrophobic by the selective adsorption of surfactants called collectors.

Many types of flotation processes such as froth flotation for the separation of minerals, foam flotation for proteins, bubble fractionation, and oil flotation exist today (Somasundaran, 1972; Lai and Fuerstenau, 1968; Shah and Lemlich, 1970; Sheiham and Pinfold, 1972). Among these, froth flotation is the only technique with wide industrial applications. In this review, various mechanisms governing the effect of surfactants and other auxiliary reagents on froth flotation are examined.

Method

In froth flotation, mineral particles are initially conditioned with appropriate reagents, followed by agitation in a cell. Air bubbles are introduced into the cell and are dispersed by an impeller. The particles that are hydrophobic rise to the cell top on collision with the air bubbles and are skimmed off.

As mentioned earlier, the particles are made hydrophobic by the adsorption of surfactants. This adsorption depends on a number of parameters such as surface composition of the solid, structure of the surfactant, mineral-solution equilibria and the surfactant solution chemistry (Gaudin, 1957; Fuerstenau, 1962; Sutherland and Wark, 1955; Glemblotskii et al., 1972; Fuerstenau, 1976; Somasundaran and Grieves, 1975; Joy and Robinson, 1964; Somasundaran, 1972a; Somasundaran, 1975; Somasundaran, 1968). Under flotation conditions, the surfactants adsorb with their polar head oriented toward the mineral surface and the hydrophobic tail pointing toward the solution, thus making the mineral surface hydrophobic.

Basic principles

For efficient flotation, the contact angle between an air bubble and a solid in a liquid has to be greater than zero. The contact angle, in terms of the forces at the solid/liquid/gas interface is given by the Young-Dupre equation,

$$\mathrm{Cos}\Theta = (\gamma_{sg} - \gamma_{sl}) / \gamma_{lg}$$

where γ_{sl}, γ_{sg}, and γ_{lg} are the surface tensions at the solid-liquid, solid-gas, and the liquid-gas interface, respectively. A maximum contact angle is obtained when γ_{sg} is minimum, indicating that the surfactant adsorption must take place with maximum effect at the solid-gas interface. The driving force for the process of particle-bubble attachment in terms of the free energy change for this process is

$$\Delta G = \gamma_{sg} - (\gamma_{sl} + \gamma_{lg})$$

From these two equations,

$$\Delta G = \gamma_{lg}(\mathrm{Cos}\Theta -$$

which indicates that for any finite value of Θ, ΔG is negative. However, in practice, a minimum contact angle is required for flotation to occur and this minimum depends on the hydrated nature of the mineral and the solvent. In practical systems, often dynamic conditions rather than equilibrium conditions prevail and hence the use of these equations is limited (Reay and Ratcliff, 1973; Anfruns and Kitchner, 1976; Jameson et al., 1977).

Derjaguin (1960) examined the attachment process in terms of the disjoining pressure, which is defined as

$$P = \partial G / \partial A$$

where G is the free energy of the system and A is the surface area. P, which has contributions from the van der Waal forces, the electrical double layer forces, and the surface hydration forces, must have a negative value for the particle-bubble attachment.

A prior knowledge of the orientation of the surfactant at the solid/liquid interface is needed to determine certain key parameters in both these treatments. In addition to adsorption of collectors, interactions of other reagents that act as frothers, activators, and depressants have to be also considered for analyzing flotation systems. The role of these reagents and the mechanisms involved in flotation are discussed in a later section.

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Surfactant adsorption

With the exception of a few minerals, hydrophobicity has to be imparted to most of the minerals in order to float them. This is achieved by adding a surfactant that will selectively adsorb on the material to be floated. In the following section, the major forces involved in surfactant adsorption are discussed with selected examples from the literature.

Electrostatic forces

In systems where the surfactant and the mineral are charged, electrostatic forces play an important role. Because electrostatic forces are the basic cause for the selective adsorption in these cases, it is helpful to understand the mechanism of charge generation on the mineral surface.

The predominating mechanism of surface charge generation in the case of oxides is the hydrolysis of the surface species followed by the pH dependent dissociation of surface hydroxyl groups.

$$MOH = MO^- + H^+$$

$$H^+ + MOH = MOH_2^+$$

where *M* represents the metal atom. The pH at which the surface charge is zero is referred to as the point of zero charge (PZC). The oxides carry a positive charge in solutions that are more acidic than PZC and a negative charge in solutions that are more alkaline. For minerals such as calcite and apatite, the charge generation could be due to dissolution of lattice ions or dissolution, followed by hydrolysis in the bulk and subsequent adsorption of the resulting complexes. For example, from the species distribution diagram shown in Fig. 1, it is clear that in the acidic pH range, Ca^{2+} activity governs the behavior of hydroxyapatite, whereas in the alkaline pH range, for an open system (open to the atmosphere), CO_3^{2-} and HCO_3^- activities will predominate. Zeta potential measurements on apatite (Amankonah et al., 1985a; Amankonah and Somasundaran, 1985) support the previous calculations. Similar correlations have been obtained for other minerals such as calcite, dolomite, and magnesite (Amankonah et al., 1985; Somasundaran et al., 1985; Amankonah, 1985). Interestingly, when calcite is contacted with the supernatant of apatite, the zeta potential shifts to that of apatite in water, suggesting surface conversion (Amankonah and Somasundaran, 1985). In contrast to these minerals, clay minerals are controlled by a dual mechanism: they are negatively charged on the face, due to substitutions, for example, Al^{3+} for Si^{4+} in the silica tetrahedra, but on the edges the charge generation mechanism is similar to that of oxides. PZCs of several minerals are listed in Table 1.

The role of electrostatic forces is best illustrated by the adsorption of the anionic surfactant dodecylsulfate on alumina. In this system, significant adsorption was observed only below pH 9, where the mineral is positively charged (Fig. 2). Similar correlations on the electrostatic dependence of surfactant adsorption have been observed for many other minerals (Modi and Fuerstenau, 1960, 1957; Choi and Whang, 1963, 1963a; Iwasaki et al., 1962; Hanna, 1968; Amankonah et al., 1985, 1985a; Amankonah and Somasundaran, 1985; Somasundaran, 1974). Adsorption of other charged species that are present in the system or impurities can also give rise to a charge on the surface. Fuerstenau et al. (1965, 1963) studied the role of iron, aluminum, lead, manganese, and calcium in the anionic flotation of quartz and found that the multivalent cations enhanced the flotation of quartz due to the uptake of these ions bearing a charge that is opposite to that of the surfactant.

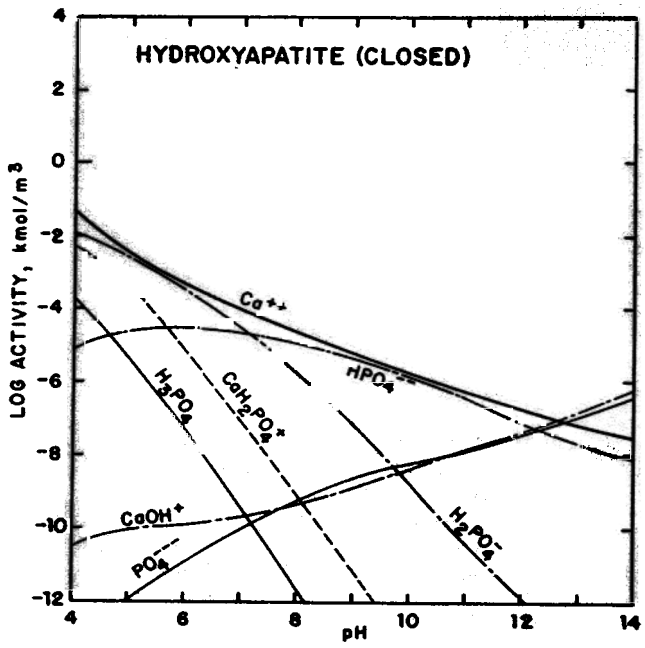

Fig. 1 — Species distribution diagram of hydroxyapatite (Amankonah, 1985).

Table 1 — PZCs of Several Oxides

Mineral	PZC	References
Anatase	5.9	Gaudin, 1957
Barite	9.5	Johansen and Buchanan, 1957
Calcite	8 - 10.8	Somasundaran and Agar, 1967
Cassiterite	4.5	Laskowski and Sobieraj, 1969
Chromite	5.6 - 7.2	Fuerstenau, et al., 1970
Corundum	9 - 9.4	Parks, 1965
Cuprite	7 - 9.5	Fuerstenau, 1970
Dolomite	7.0	Stumm and Morgan, 1970
Fluoroapatite	4 - 6	Berube and de Bruyn, 1972
Fluoroapatite (syn)	5.2	Stumm and Morgan, 1970
Goethite	6.7	Parks, 1967
Hematite	4.8 - 6.7	Fuerstenau, et al., 1970
Kaolinite	5 - 6	Lorenz, 1969
Quartz	2.3 - 3.7	Gaudin and Fuerstenau, 1955
Rutile	6.0	Gaudin and Fuerstenau, 1955
Talc	3.5	Iwasaki, et al., 1961
Tenorite	9.5	Huber and Weigl, 1964
Zircon	5.8	Cases, 1970

Associative interactions

Fig. 3 shows the adsorption of sodium dodecylsulfate on alumina. At a certain residual concentration, there is a sharp increase in the adsorption density. This phenomenon is also observed in other oxide systems. This is due to the association of the hydrocarbon chains of the adsorbed surfactant at the mineral surface, forming two-dimensional aggregates, similar to the formation of micelles in the bulk solution. This aggregation occurs due to the favorable energetics of the partial removal of the hydrocarbon chains from the aqueous environment. Fluorescence and ESR spectroscopic work (Chandar, 1986) support the mechanism of aggregation. A schematic illustration of the evolution of these aggregates is shown in Fig. 4.

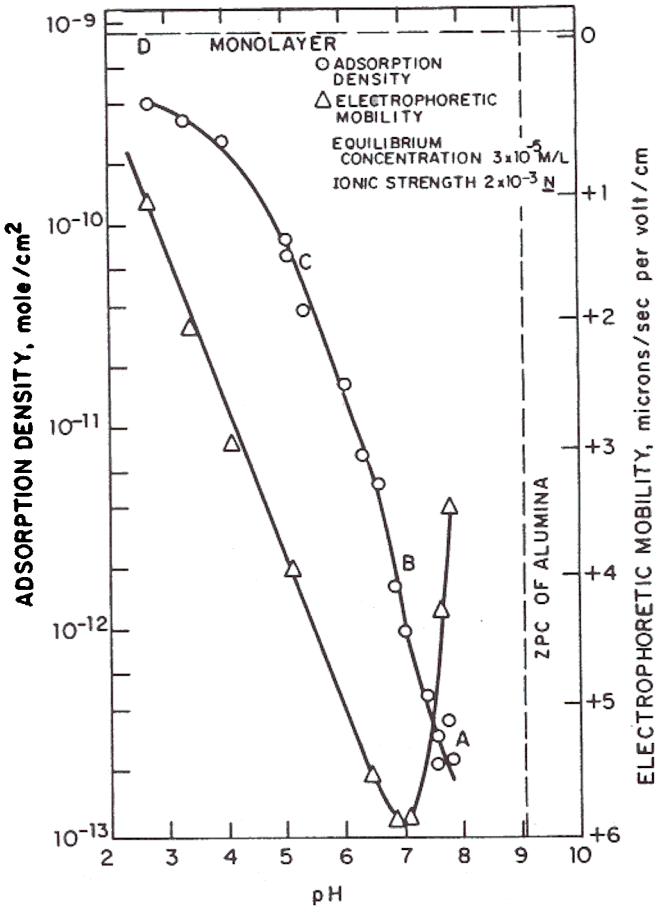

Fig. 2 — Adsorption of dodecylsulfate on alumina as a function of pH (Somasundaran and Fuerstenau, 1966).

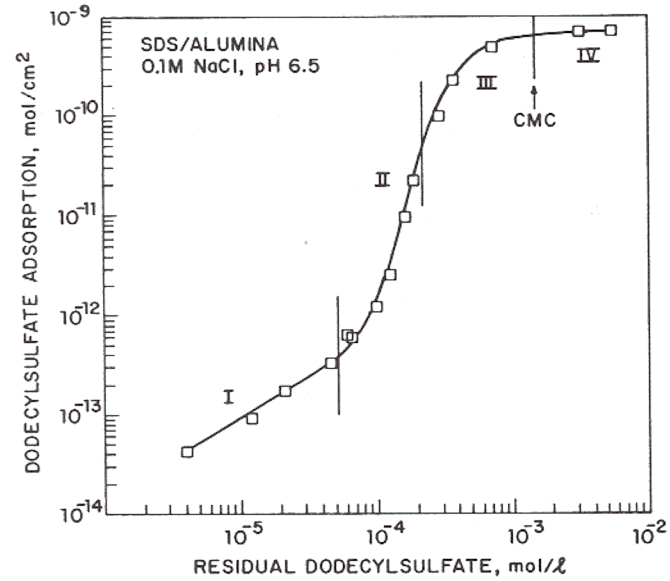

Fig. 3 — Adsorption isotherm of dodecylsulfate on alumina (Somasundaran and Fuerstenau, 1966).

Chemical forces

One of the major driving forces for adsorption of surfactant is covalent bond interactions with the mineral surface species. This interaction between the surfactant and the solid is more system specific than other interactions. Adsorption of fatty acids on fluorite, calcite, and barite has been attributed in neutral and alkaline solutions to chemical bonding between the surfactant and the mineral surface (French, 1954; Bhar et al., 1968; Peck and Wadsworth, 1965; Blissing, 1969; Shergold, 1972). Infrared studies have been reported to provide evidence for the formation of chemical bonds between oleate and fluorite and oleate and hematite (Peck and Wadsworth, 1965; Peck et al., 1966). However, the problem with such spectroscopic techniques is the possible alteration of the species on the mineral surface during sample preparation. The analyzed surface might not correspond to the surface in the flotation cell.

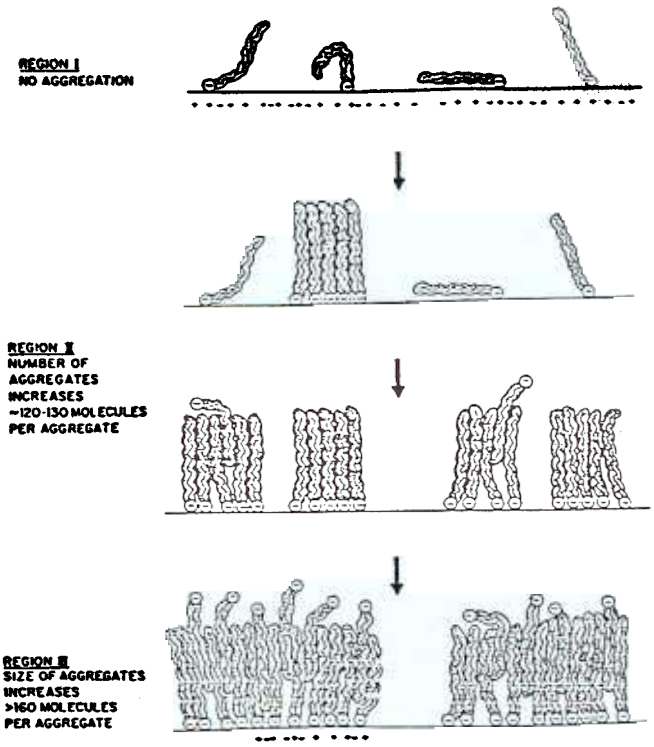

Fig. 4 — Schematic representation of evolution of surface aggregates at different regions of the isotherm.

Sulfide mineral flotation is the important example where chemical interactions between the surfactant and the mineral plays a governing role. The most commonly used collectors for sulfides are xanthates. The exact nature and mechanism of interactions in the xanthate-sulfide system have been debated for decades and still not clearly established because of the complex variations in the surface properties of sulfides and multitude of possible reactions.

Often changes in solution conditions such as pH can change the chemical form of the surfactant and these changes are not often considered when examining considering the chemical interactions between the surfactant and the mineral. For example, covalent bonding has been proposed as the mechanism for the flotation maximum in the hematite-oleate system at pH 8 (Fig. 5). Work done by Somasundaran et al. (1984) and Ananthapadmanabhan (1980) shows that iono-molecular complexes between oleic acid and oleate can form in this pH range and these complexes can be expected to give rise to the flotation maximum (Fig. 5).

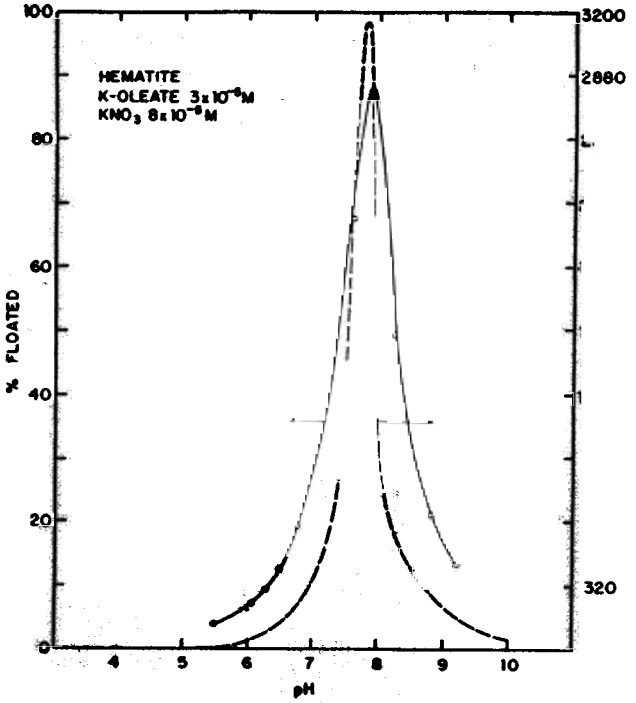

Fig. 5 — Correlation of hematite flotation and formation of acid-soap complex (Ananthapadmanabhan, 1980).

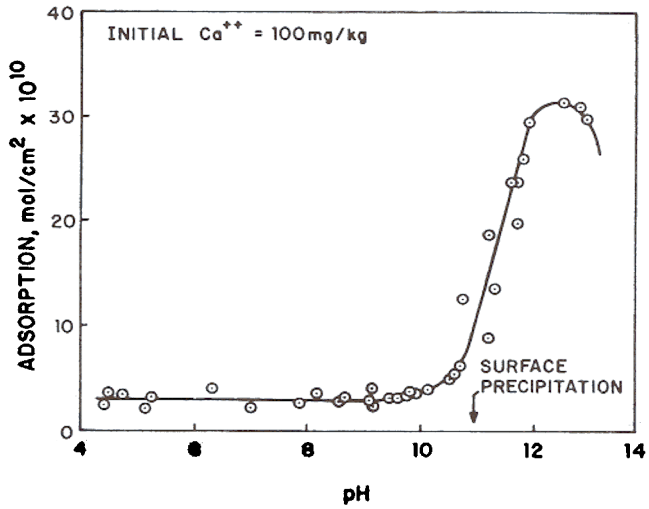

Fig. 6 — pH dependence of calcium adsorption on quartz. $K_{sp}(Ca(OH)_2)$ is $10^{-5.2}$. pH of surface precipitation for different assumed values of adsorbed layer thickness(x): x = 10 Å, pH = 10.96; x = 35 Å, pH = 11.4 (Ananthapadmanabhan and Somasundaran, 1985).

Surface precipitation

In many mineral-reagent systems, surface precipitation has been proposed as an alternate mechanism for chemisorption. The solubility product for precipitation and the activities of the species at the solid-liquid interface determine the surface precipitation process. Under appropriate electrochemical conditions the activity of the species can be higher in the interfacial region than in the bulk solution. For example, a charged mineral surface would attract oppositely charged species, resulting in the increased activity of the latter at the interface. Such a redistribution of the species could lead to many reactions. For example, chemisorption of hydrolyzed calcium ions was thought to be the reason for the sharp increase in the adsorption of the calcium species on silica around pH 11 (Fig. 6). However, calculation of the concentration of Ca^{2+} ions at the interface shows that surface precipitation of $Ca(OH)_2$ is possible at pH 11 (Ananthapadmanabhan and Somasundaran, 1985). Similar correlations have been obtained for the cobalt-silica, alumina-dodecylsulfonate, calcite/apatite/dolomite-fatty acid, and tenorite-salicylaldoxime systems (Ananthapadmanabhan and Somasundaran, 1985).

Solution chemistry of surfactants

Apart from interactions of the surfactant with the dissolved mineral species, the surfactant solution chemistry itself plays an important role in the adsorption and the flotation processes. Hydrolyzable surfactants, such as weakly acidic fatty acids, dissociate to form ions (R^-) at high pH values and exist as neutral molecules (RH) at low pH values. The surfactant species can also associate to form ionomolecular complexes and other aggregates such as dimers, R_2^{2-} (Somasundaran et al., 1984; Ananthapadmanabhan, 1980). Solution conditions such as pH affect the activities of the species and hence the flotation of minerals in their presence.

From the species distribution diagram of oleic acid as a function of pH, Fig. 7 (Ananthapadmanabhan, 1980), it can be seen that (1) pH of precipitation of oleic acid at the given concentration is 7.45, (2) activities of oleate monomer and dimer remain almost constant above the pH of precipitation and decrease sharply below it, and (3) in the neutral pH range the activity of the acid-soap (R_2H^-) is maximum. Depending on the monomer size and charge, the surface activities of the different oleate species could be different from that of each other. The surface activity of acid-soap is estimated to be higher than that of the neutral molecule and the oleate monomer (Ananthapadmanabhan, 1980). The pH range, in which a maximum in flotation of hematite and other minerals by oleate is observed, corresponds to the range where oleate is most surface active. Similar correlations between collector association and flotation of minerals have also been observed for the dodecylamine-quartz system (Somasundaran and Ananthapadmanabhan, 1979).

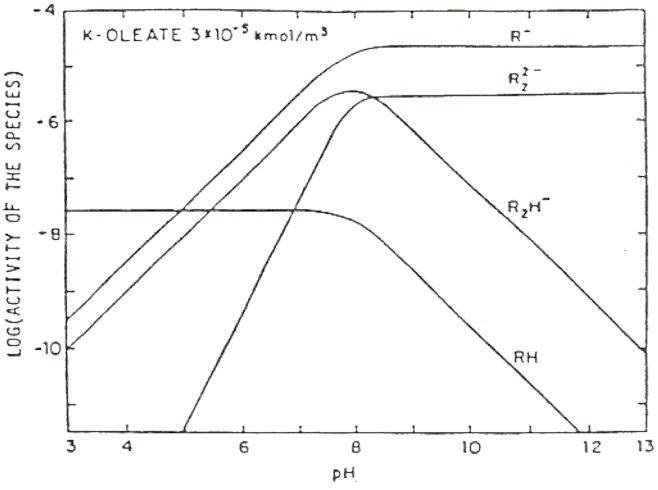

Fig. 7 — Oleate species distribution diagram as a function of pH. Total oleate concentration = 3 × 10^{-5} M (Ananthapadmanabhan and Somasundaran, 1981).

Surface chelation

Surfactants that adsorb by forming metal hydrophobic complexes that are characterized by ring structures are called chelating agents. The two basic requirements for a molecule to form metal chelates are it should have suitable functional groups and the functional groups must be situated so as to permit ring formation with the metal as the closing member. Usually, differences in stability constants of the metal chelates and variation in the solution properties such as ionic strength and pH are utilized to get selective chelation (Somasundaran and Nagraj; Schulman and Leja, 1958). In many systems, flotation correlates with surface chelation rather than bulk chelation, as shown in Fig. 8 for the tenorite-salicylaldoxime system. Recently, Aliaga and Somasundaran (to be published) have examined the differences in the efficiency of various aromatic hydroxy-oximes using UV-Vis spectroscopy and extended Huckel molecular orbital calculations and have correlated the energies at which the electronic transitions appear in the UV-Vis spectra of the hydroxy-oximes with their flotation efficiency. It was observed that electron density of the nitrogen of the oxime plays a major role in determining chelation and flotation and that the electron density can be easily manipulated by introducing substituent groups for the hydrogen attached to the nitrogen. For example, introduction of the methyl group, an electron releasing group, will enhance the chelation and flotation. The flotation effectiveness has been explained by determining the fraction of the surfactant adsorbed and the nonpolar nature on the surfactant.

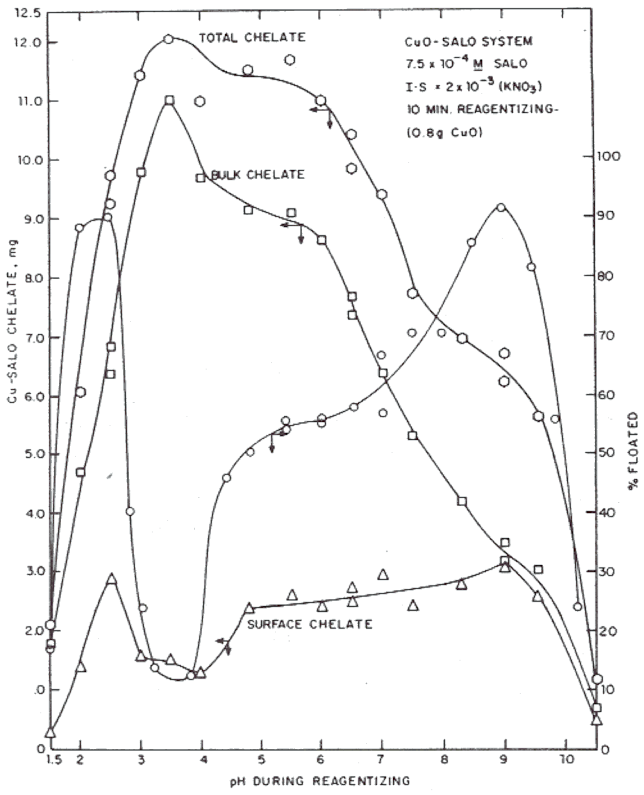

Fig. 8 — Correlation of bulk and surface chelation of salicylaldoxime with tenorite and its species with flotation in the tenorite-salicylaldoxime system (Nagraj and Somasundaran, 1981).

Auxiliary reagents

In addition to collectors, other reagents are used as frothers, activators, and depressants in the flotation cell.

Frothers are added to induce the desired froth stability during flotation. Generally monohydroxylated nonionic compounds such as cresol are used as frothers. Many interactions take place between the frother and the collector. The frother species coadsorb with the collector species and this can favor flotation by the reduction in the repulsion of the ionic collector species (Schulman and Leja, 1954, 1958; Leja, 1967; Fuerstenau and Yamada, 1962). Recently, using isomerically pure surfactants, Fu and Somasundaran (unpublished) observed an increase in the adsorption of octylbenzenesulfonate on alumina in the presence of ethoxylated alcohol. Further, the sulfonate, which did not adsorb on silica, adsorbed in the presence of the alcohol.

Activators enhance the flotation of minerals by collectors. Activators normally adsorb at the mineral-solution interface and provide sites for the adsorption of the collector species. A major driving force for the adsorption of many activators on the mineral surface is the electrostatic attraction between the two. In some cases, activators react with the collectors to form compounds of low solubility, thereby increasing the adsorption of the collector (Fuerstenau, 1973).

Depressants act by retarding the flotation of the solid. Polymers such as starch depress flotation, but in this case the collector adsorption is found to be enhanced by the depressant, at least in some systems (Somasundaran, 1969). The decrease in flotation in spite of the increased collector adsorption is attributed to the collector-starch complex, which has a hydrophilic exterior. Flotation of quartz using amine was depressed by cationic polyacrylamide (Fig. 9) though the adsorption was unaffected (Somasundaran and Cleverdon, 1985). This has been attributed to the masking of the adsorbed amine species by the adsorbed polymer. However, the same polymer activated the flotation of quartz when alkylsulfonate was used as the collector as seen in Fig. 10. A schematic representation of the masking phenomenon is shown in Fig. 11.

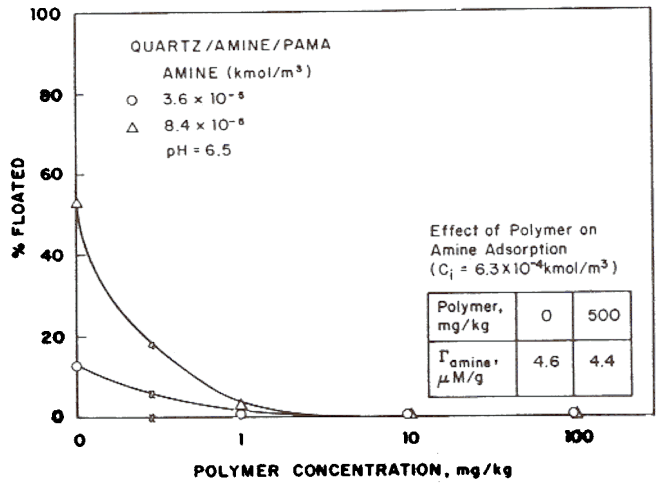

Fig. 9 — Depression of flotation of quartz using dodecylamine by the cationic polymer PAMA at natural pH. Adsorption of amine in the presence and absence of polymer is shown in the inset (Somasundaran and Cleverdon, 1985).

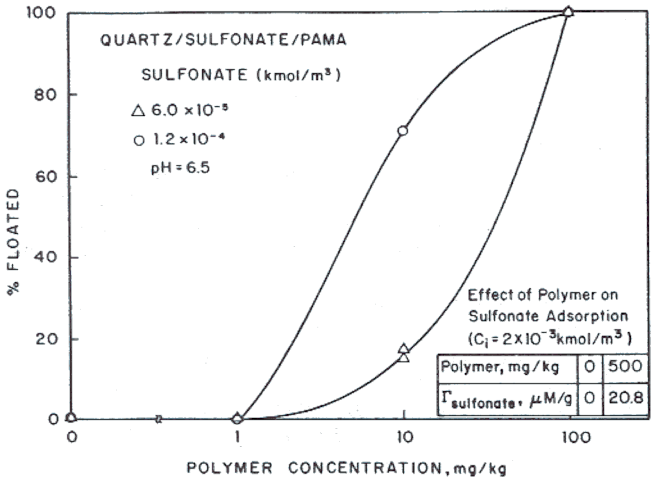

Fig. 10 — Activation of flotation of quartz using dodecylsulfonate by the cationic polymer PAMA at natural pH. Adsorption of sulfonate in the presence and absence of polymer is shown in the inset (Somasundaran and Cleverdon, 1985).

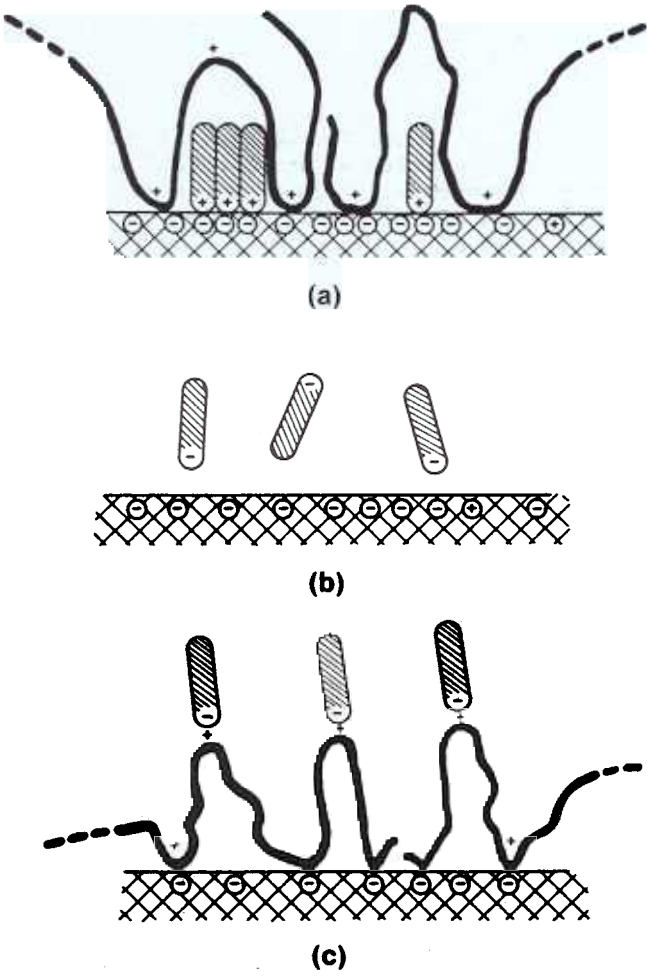

Fig. 11 — (a) Schematic representation of the cationic polymer PAMA and dodecylamine coadsorption on quartz, resulting in its flotation depression. (b) Schematic representation of quartz-dodecylsulfonate system. (c) Schematic representation of the cationic polymer PAMA and dodecylsulfonate coadsorption on quartz, resulting in its flotation activation (Somasundaran and Cleverdon, 1985).

Calorimetric studies

Thermodynamic data are of paramount importance toward understanding the mechanism of surfactant interactions, whether it is enthalpically or entropically driven. Calorimetry is used to directly measure the thermodynamic quantities. Differential heats of adsorption in the system heptylbenzenesulfonate-alumina showed a maximum at a surface coverage of about 0.7, which was attributed to surfactant rearrangement in the surface layer (Partyka et al., 1986; Arnaud, 1984). Calorimetric measurements indicated two distinct mechanisms of adsorption in the system galena-ethyl xanthate (Arnaud et al., 1985). At low surface coverage, a highly exothermic interaction, −80kJ/mole, suggested an initial chemisorption reaction while at plateau coverage, heat of −40kJ/mole, suggested multilayer precipitation of lead-xanthate. At low surface coverage, the adsorption of triton-type nonionic surfactants on silica was found to be exothermic, while at higher surface coverage, it was endothermic, the latter being attributed to the formation of surface micelles (Arnaud 1985). Adsorption of oleate on hematite was found to be an endothermic process (Morgan, 1986). Recently, fundamental information on the heats of mixed micellization and mixed hemimicellization have been obtained for the octylbenzenesulfonate/etholyxated alcohol-alumina system by Fu and Somasundaran (unpublished). In the case of sulfonate, a marked decrease in adsorption enthalpy in the hemimicellar region showed hemimicellization to be an entropy-driven process like micellization. However, such a trend was not observed for the adsorption enthalpy of 1:1 mixture of sulfonate and alcohol. Adsorption enthalpy in this system remained constant throughout the hemimicellar region and this has been attributed to the changes in the electrostatic conditions for adsorption created by the presence of the nonionic surfactant. This effect of charge density reduction was also observed for the mixed micellization case.

Spectroscopic studies

Spectroscopic techniques are extremely useful in characterizing the solid surfaces and in understanding the reactions at the solid/liquid interface. Using ESCA, Somasundaran et al. (unpublished) showed the surface conversion of calcite to apatite in the presence of apatite supernatant and vice-versa. Infrared spectroscopy has been used to study the chemical interactions of surfactant with the mineral surface in the oleate-fluorite and oleate-hematite systems (Peck and Wadsworth, 1965; Peck et al., 1966). However, as mentioned before, in the spectroscopic techniques, the possibility of surface alteration during sample preparation exists. Also, these methods have limited applicability for studying in situ surfactant adsorption in aqueous media.

Recently, Chandar, Somasundaran, Turro, and Waterman (Somasundaran et al., 1986; Chandar et al., 1987, 1987a; Waterman et al., 1986) have used fluorescence and ESR spectroscopy to obtain information on the adsorbed layer of dodecylsulfate on alumina. Measurements of the microviscosity and polarity of the environment experienced by the fluorescent probes, pyrene, and dinaphthylpropane, indicated the presence of surfactant aggregates at the alumina/water interface. Further, they determined the size of the aggregates and their evolution as a function of surface coverage, leading to fundamental information on the orientation and structure of the surfactant. The

fluidity of the ESR spin probes in different regions of hemimicelles showed that the chain segments near the alumina surface are packed tighter than those away from it. These results have direct implication to strength of attachment of aggregates to the interface and desorption.

Summary

Froth flotation is a complex physicochemical phenomena, governed by the properties of the various interfaces formed between the solid, liquid, and gas phases. Adsorption and flotation are influenced by mineral-solution equilibria, surfactant solution chemistry, and interactions between the dissolved mineral species, surfactants, and modifying reagents. In many systems, the marked increase in adsorption and flotation can be explained in terms of surface precipitation of the species instead of chemisorption of the species. Spectroscopic techniques can be used to understand the mechanism of adsorption and flotation at the molecular level. ■

Acknowledgments

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Electrochemistry of sulfide mineral flotation

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Abstract – *The use of various electrochemical techniques to study mechanisms of sulfide mineral-flotation reagent interactions is briefly reviewed in this paper. Prior to such studies it is desirable to thermodynamically determine solution conditions favorable for formation of hydrophobic species deemed to be responsible for flotation. The thermodynamic equilibrium involving both the stable and metastable species can be conveniently represented by an Eh-pH diagram. Thermodynamics can also be used to predict conditions where a mineral might not float if depressants are present. Under favorable conditions of flotation there is competition between reactions leading to formation of hydrophobic species with reactions that lead to formation of hydrophilic species. Due to the sluggish nature of the reactions involving sulfide minerals, a knowledge of the kinetic behavior of the system is necessary. Electrochemical methods of investigation are used in laboratory studies to (1) control the state of oxidation, (2) determine the type and amount of electroactive species present at the mineral surface, and (3) study kinetics of electrode processes. By combining electrochemical techniques and wetting measurements the identification of hydrophobic species that might be present at the mineral surface could be achieved. Both contact angle measurements at mineral electrodes or flotation in a cell equipped with a particulate bed electrode can be used for the wetting measurements.*

Introduction

The flotation of sulfide minerals continues to dominate the flotation industry as it has for the past 80 years or so. Today, very lean ores are processed using relatively small quantities of reagents. The total quantities of reagents used are quite substantial considering the high tonnage of ore processed, however. It is estimated that in the year 1980, approximately 500 Mt of sulfide ores were processed worldwide using 12 Gg collectors (nonfuel oil), 16 Gg depressants, 10 Gg activators, and 300 Gg pH regulators. However in the United States since 1980, the number, capacity, throughput, and reagent consumption of sulfide ore processing plants have declined. Of particular significance is the decline in the concentration ratio from 38:1 in 1980 to 28:5 in 1985 (Anon, 1986). Many factors have contributed to improvements in separation and recovery of valuable minerals, namely, selective mining, ore blending, more efficient flotation machines, more effective reagents, etc. Since several sulfide mineral flotation reagents undergo electrochemical reactions, this paper is written with the objective to review various electrochemical techniques that have been used to study sulfide mineral-flotation reagent interactions. In order to relate electrochemistry to the flotation behavior, a brief review of the floatability of sulfides is presented in the next section.

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Floatability of sulfides

It is generally recognized that most sulfide minerals are readily floated though the reasons may differ considerably. Some sulfide minerals can be floated without collectors whereas others require a small quantity of a collector.

Native floatability of sulfide minerals in the absence of oxygen

Some sulfides, such as molybdenite, are naturally floatable under most conditions whereas others are considered to have intrinsic hydrophobic character in the absence of oxidation (Ravitz and Porter, 1933; Fuerstenau and Sabacky, 1981). The basis for native floatability rests on the assumption that sulfide lattice ions are expected to be weakly hydrated and do not interact strongly with water molecules. The critics of this hypothesis argue that sulfide minerals are thermodynamically unstable and sufficient oxygen remains in the system to cause oxidation (Miller, 1988), presumably leading to the formation of elemental sulfur (a hypothesis originally proposed by Wark, 1938, and later suggested by several others. More recently, a metal-deficient sulfur layer has been postulated by Woods (1987). The minimum quantity of the hydrophobic entity (elemental sulfur or metal-deficient layer) needed for complete flotation is yet to be established.

Other reasons for native floatability of sulfides have been postulated in the past. Gaudin (1932) considered that surfaces formed by rupture of van der Waals bonds are naturally hydrophobic. Chander and Fuerstenau (1972) postulated that molybdenite retains its hydrophilic character because the product of oxidation of the lattice metal ion is a soluble anion, which does not have the same hydration characteristics as other metal cations. In other words, many sulfides may acquire surface hydrophilic character through dissolution and readsorption of hydroxylated cations. These arguments suggest that the reasons for the floatability of sulfide minerals observed in the absence of collectors may vary from mineral to mineral. In most cases, the flotation behavior depends upon the nature of the surface which might be readily altered by electrochemical reactions.

Collectorless flotation of sulfide minerals under modest oxidizing conditions

Several investigators have suggested that sulfide minerals can be floated under mild to modest oxidizing conditions although the reasons vary considerably. As early as 1949, Plaksin (1949) proposed that adsorbed