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Surfactants in Flotation

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INTRODUCTION

Flotation is an important separation technique today, with its applications ranging from selective separation of minerals to micro-organisms and even ions. The flotation process utilizes the differences in the surface properties of the particulates, normally with the addition of reagents to achieve the separation. Surfactants play a critical role in the flotation process since their interaction with the

TABLE 1 Flotation Techniques Classified on the Basis of Mechanism of Separation and Size of Material Separated

Mechanism	Size range		
	Molecular	Microscopic	Macroscopic
Natural surface activity	Foam fractionation; example: detergents from aqueous solutions	Foam flotation; examples: microorganisms, proteins	Froth flotation of non-polar minerals; example: sulfur
In association with surface-active agents	Ion flotation, molecular flotation, adsorbing colloid flotation; examples: Sr^{2+} , Pb^{2+} , Hg^{2+} , cyanides	Microflotation, colloid flotation, ultraflotation; examples: particulates in wastewater, clay, microorganisms	Froth flotation; example: minerals such as silica Precipitate flotation (first and second kind); example: ferric hydroxide

Source: Ref. 1.

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particle surface essentially determines the hydrophobicity of the particles and their probability of attachment to bubbles during collisions in the flotation cell. A large number of surfactants and auxiliary reagents are used in flotation process depending on the properties of the particles to be processed and the ultimate aim of the process. In this chapter these surfactants are discussed with emphasis on the mechanisms by which they act in various flotation processes. Many types of flotation processes exist today, and these are classified on the basis of size and the mechanism of flotation in Table 1: foam fractionation for the separation of surface-active species such as detergents in aqueous solutions, foam flotation for naturally surface-active organisms and proteins, ion flotation for the separation of ions, micro and ultra flotation for separation of very fine particles, and froth flotation for the separation of minerals. In addition, there are nonfoaming techniques such as bubble fractionation, solvent sublation, and oil flotation [2-4] in which the floated material is collected selectively in a liquid phase that is not compatible with the bulk aqueous media. Among these, froth flotation is the only technique with wide industrial application. Here the role of surfactants in froth flotation of minerals is therefore dealt with in detail.

II. FLOTATION TECHNIQUE

In froth flotation, mineral particles are initially stirred, often intensely with the reagent solution in a mixer, and then transferred into a specifically designed cell for the actual flotation process (Fig. 1). Air is sucked or pushed into the cell and dispersed by a rotating impeller. Hydrophobic particles attach to the air bubbles and levitate to the top of the cell, where they are skimmed off and hydrophilic material is collected at the bottom of the cell. In froth flotation, surfactants have to impart hydrophobicity selectively, to the desired particles, for successful separation. Selective adsorption of the surfactant on the mineral surface itself is a function of a number of parameters such as surface composition of the solid, mineral-solution equilibria and solution chemistry of the surfactant [5-14]. The principles involved in flotation and the complex role of surfactants in different mineral systems are discussed in the following sections.

Mineral particles can be separated by flotation only if hydrophobicity can be selectively imparted to those particles that are to be floated. Since most minerals are naturally hydrophilic (sulfur, talc, molybdenite, graphite, and coal are hydrophobic), they are treated with a surfactant that adsorbs on the mineral surface,

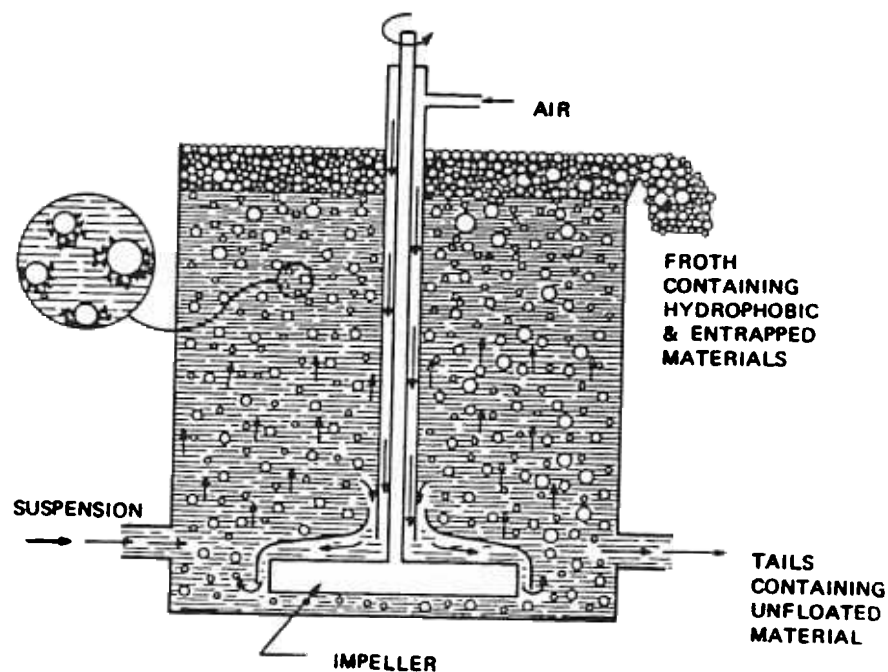


FIG. 1 Schematic representation of a flotation cell

rendering them hydrophobic. These 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.

A. Thermodynamic Aspects

At equilibrium, the forces at the point of contact between an air bubble and a solid in a liquid is defined by the Young-Dupre equation,

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta \quad (1)$$

where γ_{sg} , γ_{sl} , and γ_{lg} are the surface tensions at the solid-gas, solid-liquid, and liquid-gas interface, respectively, and θ is the contact angle. For flotation to occur, $\cos \theta$ has to be a minimum or the contact angle has to be a maximum. This condition is met if

$$\cos \theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \quad (2)$$

is also minimum or if γ_{sg} is as small as possible, keeping γ_{sl} and γ_{lg} at maximum values. It can be seen that the surfactant must adsorb, if possible with maximum effect at the solid-gas interface.

Another way to look at the process of particle-bubble attachment is as a destruction of a solid-liquid and liquid-gas interface and a creation of a solid-gas interface. The free-energy change for this process is given by Dupre's equation,

$$\Delta G = \gamma_{sg} - (\gamma_{sl} + \gamma_{lg}) \quad (3)$$

Combining Eqs. (1) and (2), we get

$$\Delta G = \gamma_{lg} (\cos \theta - 1) \quad (4)$$

It is clear from Eq. (4) that for all finite values of θ there is a net decrease in ΔG upon particle bubble attachment, which leads to the condition that

$$\gamma_{sg} - \gamma_{sl} < \gamma_{lg} \quad (5)$$

for particle bubble attachment. In practice, a minimum contact angle is required for flotation; for example, a 10° angle is reported for the quartz dodecylamine system [15]. The application of Eqs. (1) to (5) to an actual flotation system is limited because these equations are valid only under equilibrium conditions. In an actual system, dynamic conditions prevail and equations based on dynamic factors such as minimum particle-bubble contact time would be more relevant [16-18].

Another approach in this regard is that of Derjaguin [19], who used the concept of disjoining pressure inside the liquid film between the particle and the bubble to examine the attachment process. Disjoining pressure is defined as the derivative of the free energy of the system with respect to the interlayer thickness per unit surface area.

$$P = \frac{\partial G}{\partial A} \quad (6)$$

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As flotation is directly dependent on film rupture, the value of disjoining pressure must be negative for particle-bubble attachment. Three factors contribute to P :

$$P = P_{vw} + P_{edl} + P_s \quad (7)$$

where P_{vw} is the van der Waals contribution, P_{edl} the electrical double-layer contribution, and P_s the surface hydration contribution. The values of these components are directly dependent on the nature and orientation of the adsorbed surfactant species and can be estimated as described in many works [20-25]. It is to be noted that theoretical determination of the values in both Young's and Derjaguin's treatment requires prior knowledge of the orientation of the surfactant at the solid/liquid interface. Recent experiments using fluorescence and electron spin resonance spectroscopy [26] have yielded valuable information on the structure and orientation of adsorbed alkyl sulfates on alumina. Similar data on other mineral-surfactant systems would prove very useful to yield a better insight into the flotation process.

B. Surfactants for Flotation

Surfactants with a large variety of polar and nonpolar groups are available for flotation and they can be classified based on their function and on their chemical composition. A surfactant whose primary role is to render the solid surface hydrophobic is called a collector. Surfactants whose primary role is to provide the required stability to the top froth layer in the flotation cell and to influence the kinetics of particle-bubble attachment are referred to as frothers. These are usually nonionic surfactants such as cresols which can enhance the rate of film thinning and contribute to the stability of the particle-bubble aggregates. The exact mechanism of frothers in flotation is not clearly established. The role of the frothers in particle bubble attachment is supposedly due to the reduction in the repulsion forces between the bubble and the particle by suitable alignment of the surfactant dipoles at the three-phase point of contact. It is the ability of the nonionic surfactants to align their dipoles that make them good frothers. Experimental evidence confirm this theory based on the relaxation time of the frother is, however, lacking. Lekki and Laskowski [27] showed the induction time to decrease markedly in chalcocite flotation using ethyl xanthate in the presence of α -terpineol at pH 9.7. Surface tension, zeta potential, and infrared spectroscopic data in the literature indicate

significant interaction between frothers and collectors in flotation systems. Commercial frothing agents and their utilization have been reviewed comprehensively by Booth and Freyberger [28]. Table 2 shows frother usage in different flotation systems. Surfactants can also be classified on the basis of (1) the charge of the polar group: cationic, anionic, or nonionic; (2) the nature of the hydrocarbon chain: alkyl, aryl and so on; or (3) functionality of the polar group: thio compounds, oximes, amines, carboxylates, and so on. Typical flotation surfactants with their ionization characteristics are listed in Table 3.

III. SURFACTANT ADSORPTION

Adsorption of the surfactant on mineral surfaces is dependent on a number of factors, such as the surface charge and surface chemical composition of the mineral, and the solution chemistry of the mineral and the surfactant. Major forces involved in causing surfactant adsorption are electrostatic attraction, covalent bonding, hydrogen bonding, and nonpolar bonding between the surfactant and the mineral, as well as the lateral attraction between the adsorbed species. In the following sections the various surfactant adsorption mechanisms are discussed with specific examples from the literature.

A. Electrostatic Factors

Electrostatic forces will play a significant role in systems where the surfactant and the mineral are charged. For example, in the system alumina/dodecyl sulfonate, 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 calcite [39,40], apatite [41], corundum [31,32], quartz [47], monazite [34], zircon [35], magnetite [36], and tricalcium phosphate [37].

It is to be noted that the mineral surface charge itself is mainly dependent on the mineral solution equilibria operating in the system under the processing conditions. Several mechanisms [38] have been proposed for the surface charge generation of various systems. Oxides such as hematite, silica, and alumina are considered to acquire their charge due to hydrolysis and pH-dependent dissolution. This process can be represented by the following reactions:

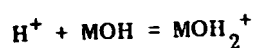


TABLE 2 Frother Usage

Frother	Gold ores, ^a 52 mills	Simple copper ores, ^b 66 mills	Complex copper ores, ^c 35 mills	Lead ores, ^d 95 mills
Pine oil	15	17	23	4
Cresylic acid		11	8	27
Pine oil and cresylic acid		5	3	2
Methylisobutylcarbinol (MIBC)		14	26	29
Other alcohols		3	3	
Polyglycol types		21	8	9
Triethoxybutane (TEB)		8	3	—
None				9
Combinations (other than pine oil and cresylic acid)				
Polyglycols and				
(a) Pine oil		5	8	2
(b) Cresylic acid		1	3	2
(c) Pine oil and cresylic acid				
MIBC and				
(a) Pine oil		5	6	2
(b) Cresylic acid		3	6	12
(c) Pine oil and cresylic acid				
Miscellaneous	2	7	3	2

^aOres from which gold is the only important product recovered by flotation, probably in most cases in pyrite.

^bOres from which copper is the product of major importance. 49 ores classed as containing copper only, 17 ores classed as containing some gold and/or silver.

^cOres from which two important products are obtained, generally by selective flotation. 14 Cu-MoS₂ ores; 13 Cu-Zn ores; 2 Cu-Co ores; 6 Cu-Ni ores.

Complex copper ores, ^c 15 mills	Lead ores, ^d 95 mills
23	4
8	27
3	2
26	29
3	—
8	9
3	—
—	9
8	2
3	2
—	—
6	2
6	12
—	—
3	2

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Percentage of total mills						
Zinc ores, ^e 104 mills	Pyrite ores 14 mills	Bulk sulfide ores, ^f 23 mills	Coal, ^g 15 mills	Amine flotation, 21 mills	Fatty acid, soap, sulfonate flotation, 61 mills	
13	50	17	27	30 (mica; feldspar)	8	
17	22	13	—	—	5	
6	—	9	—	—	—	
33	—	25	53	25 (KC1)	11	
4	7	4	7	5 (KC1)	5	
16	7	9	13	5 (feldspar)	7	
—	7	—	—	—	—	
—	—	—	—	30 (quartz)	64	
2	—	—	—	—	—	
2	—	—	—	—	—	
—	—	—	—	—	—	
1	—	9	—	—	—	
3	—	5	—	—	—	
—	7	—	—	—	—	
3	—	9	—	5	—	

^d4 lead ores; 71 Pb-Zn ores; 15 Pb-Cu-Zn ores. In the last named subgroup it was assumed that a lead, copper float was aimed primarily at recovering the lead.

^e8 zinc ores; 70 Pb-Zn ores, 13 Pb-Cu-Zn ores; 13 Cu-Zn ores. (Zinc frother unidentified in one Pb-Zn ore and two Pb-Cu-Zn ores.)

^fBulk sulfide flotation from ore, not followed by differential flotation.

Eight instances of flotation of sulfides from tungsten ores.

^gSurvey limited to domestic mills in this group.

Source: Ref. 28.

TABLE 3 Characteristics of the Major Types of Collectors

Type	Formula ^a	Ion	Ionization
Fatty acid soap	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-\cdots\text{Na}^+$	RCOO^-	Weak
Alkylphosphate	$\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{P}}(\text{O}^-\cdots\text{Na}^+)(\text{O}^-\cdots\text{Na}^+)$	RPO_4^-	Weak
Alkylsulfate	$\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{S}}(\text{O}^-\cdots\text{Na}^+)(\text{O}^-\cdots\text{Na}^+)$	RSO_4^-	Strong
Alkylsulfonate	$\text{R}-\overset{\text{O}}{\parallel}{\text{S}}(\text{O}^-\cdots\text{Na}^+)(\text{O}^-\cdots\text{Na}^+)$	RSO_3^-	Weak
Primary amine salt	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{N}^+-\text{H} \cdots \text{Cl}^- \\ \\ \text{H} \end{array}$	RNH_3^+	Weak
Secondary amine salt	$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{N}^+-\text{H} \cdots \text{Cl}^- \\ \\ \text{H} \end{array}$	$\text{RNR}'\text{H}_3^+$	Weak
Tertiary amine salt	$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{N}^+-\text{H} \cdots \text{Cl}^- \\ \\ \text{H} \end{array}$	$\text{RN}(\text{R}')_2\text{H}^+$	Weak

Primary amine salt	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{N}-\text{H}^+ \dots \text{Cl}^- \\ \\ \text{H} \end{array}$	RNH_3^+	Weak
Secondary amine salt	$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{N}-\text{H}^+ \dots \text{Cl}^- \\ \\ \text{H} \end{array}$	$\text{RNR}'\text{H}_3^+$	Weak
Tertiary amine salt	$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{N}-\text{H}^+ \dots \text{Cl}^- \\ \\ \text{R}' \end{array}$	$\text{RN(R}')_2\text{H}^+$	Weak
Quaternary amine salt	$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{N}-\text{R}'^+ \dots \text{Cl}^- \\ \\ \text{R}' \end{array}$	$\text{RN(R}')_3^+$	Strong
n-Alkyl xanthates	$\begin{array}{c} \text{S} \\ \\ \text{R}''-\text{O}-\text{C}-\text{S}^- \dots \text{Na}^+ \end{array}$	ROCS_2^-	Strong

aR , long-chain alkyl group containing eight or more carbon atoms; R' , a short alkyl chain, usually a methyl group; R'' , normally ethyl or amyl group.

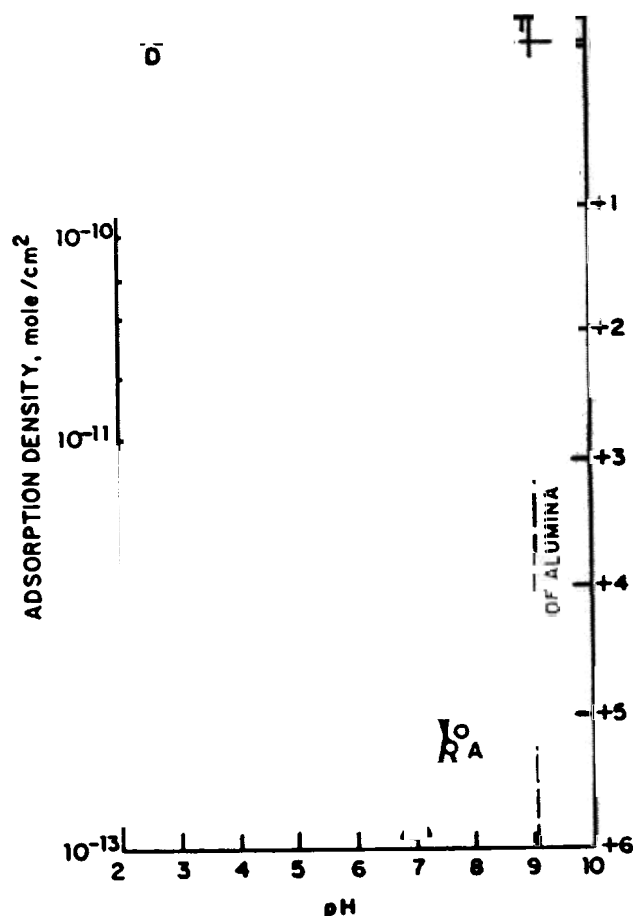


FIG. 2 Adsorption of dodecyl sulfate on alumina as a function of pH.

where M represents the metal atom. It is clear from these equations that the oxide surface will be positive at low pH and negative at high pH values. The pH at which the surface is completely neutral is referred to as the point of zero charge or PZC of the mineral. PZCs of several oxides are listed in Table 4. For salt-type minerals such as calcite, apatite, and dolomite, the preferential dissolution of ions, their reactions with the solution constituents, and subsequent adsorption-precipitation on the surface are mainly responsible for the generation of surface charge. For example, apatite equilibria in water can be represented by the following reactions:

TABLE

Mineral

Anatase

Barite

Calcite

Cassite

Chromite

Corundum

Cuprite

Dolomite

Fluorapatite
(synthetic)

Gibbsite

Hematite

Kaolinite

Quartz

Rutile

Talc

Tenorite

Zircon

Ca₁₀(

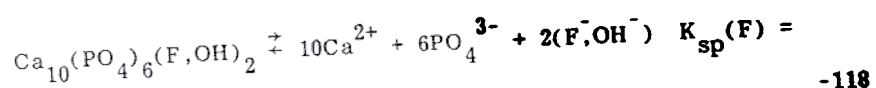
PO₄

HPO₄

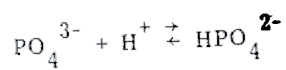
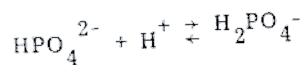
Surfactants in Flotation

TABLE 4 PZCs of Several Oxides

Mineral	PZC	References
Anatase	5.9	5
Barite	9.5	71
Calcite	8 - 10.8	72
Cassiterite	4.5	73
Chromite	5.6 - 7.2	90
Corundum	9 - 9.4	74
Cuprite	7 - 9.5	91
Dolomite	7.0	76
Fluoroapatite	4 - 6	92
Fluoroapatite (syn)	5.2	76
Goethite	6.7	77
Hematite	4.8 - 6.7	90
Kaolinite	5 - 6	88, 89
Quartz	2.3 - 3.7	83
Rutile	6.0	83
Talc	3.5	84
Tenorite	9.5	85
Zircon	5.8	86



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10^{12.3}10^{7.2}

		Surface
$\text{H}_2\text{PO}_4^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{PO}_4$	$10^{2.2}$	4
$\text{Ca}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CaOH}^+ + \text{H}^+$	$10^{-12.9}$	2
$\text{Ca}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2(\text{s}) + 2\text{H}^+$	$10^{-22.8}$	0
$\text{F}^- + \text{H}^+ \rightleftharpoons \text{HF}$	$10^{3.1}$	-2
$\text{Ca}^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{CaHPO}_4(\text{aq})$	$10^{2.7}$	-4
$\text{CaHPO}_4(\text{aq}) \rightleftharpoons \text{CaHPO}_4(\text{s})$	$10^{4.3}$	-6
$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{CaH}_2\text{PO}_4^+$	$10^{1.1}$	-8
$\text{Ca}^{2+} + 2\text{F}^- \rightleftharpoons \text{CaF}_2(\text{s})$	$10^{10.4}$	-10
$\text{Ca}^{2+} + \text{F}^- \rightleftharpoons \text{CaF}^+$	$10^{1.0}$	-12

The distribution of the activities of the dissolved species can be calculated using the information above and is shown in Fig. 3 as a function of pH. It is clear that in the acidic pH range, Ca^{2+} activity governs the behavior of hydroxyapatite, whereas in the alkaline pH range CO_3^{2-} and HCO_3^- activities will predominate. Zeta-potential results on apatite [39,40] support the calculations above (Fig. 4). At pH 7.2, where the zeta potential is zero, the activities of the positive and negative species counteract on another. Similar correlations between zeta-potential and species-distribution diagrams have been obtained for other minerals, such as calcite [41], dolomite [42], and magnesite [43].

Electrostatic adsorption of surfactants can also be influenced by the other charged species present in the system [44-46]. For example, multivalent cations enhance the flotation of quartz using fatty acids due to the uptake of these ions bearing a charge that is opposite to that of the surfactant [45]. In contrast, amine flotation of quartz is depressed by KNO_3 due to the competition between K^+ and the aminium ions for adsorption on the negative sites of the quartz surface (Fig. 5).

FIG. 3

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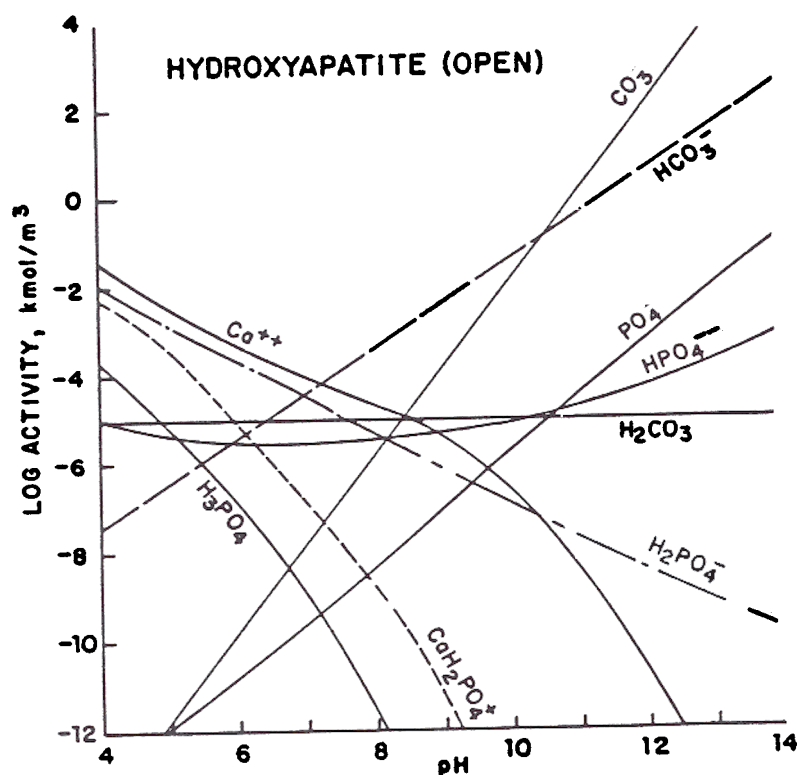


FIG. 3 Species distribution diagram of hydroxyapatite.

B. Chain-Chain Interactions

In the case of flotation of non-sulfide minerals, a major force of collector adsorption results from the association of hydrocarbon chains of adsorbed surfactant at the mineral surface to form two-dimensional aggregates called hemimicelles. Figure 6 illustrates this phenomenon for the alumina dodecylbenzene sulfonate system. Hemimicellization occurs due to the favorable energetics of the partial removal of hydrocarbon chains from the aqueous environment. Recent work by Chandar et al. using fluorescence and electron spin resonance spectroscopy [26] has shown the evolution of two-dimensional aggregates of dodecylsulfate at the alumina surface, supporting the mechanism of associative interactions of the surfactant. These authors further probed the microfluidity of the adsorbed layer and found it to be more viscous than micelles. The evolution of these aggregates

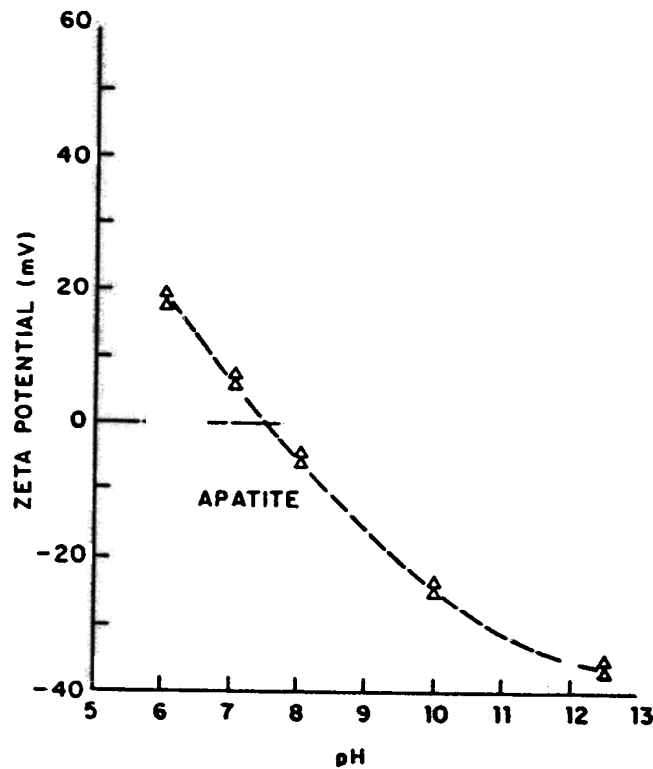


FIG. 4 Zeta potential of apatite as a function of pH.

at the solid-liquid interface is illustrated schematically in Fig. 6b. It is to be noted that the extent of association and hence adsorption will depend on the chain length and branching of the surfactant, the size of the ionic head group, and other features, including the presence of double bonds or perfluoro groups.

C. Chemical Forces

Adsorption of surfactant due to specific covalent bond interaction with the mineral surface is termed chemisorption. The chemical bond between the surfactant and the solid is more system specific than are the other bonds. The chemisorption phenomenon is illustrated here with examples of different mineral-surfactant systems.

Fatty acids adsorption on calcite, barite, and fluorite has been proposed by several investigators to occur by chemisorption [48-51].

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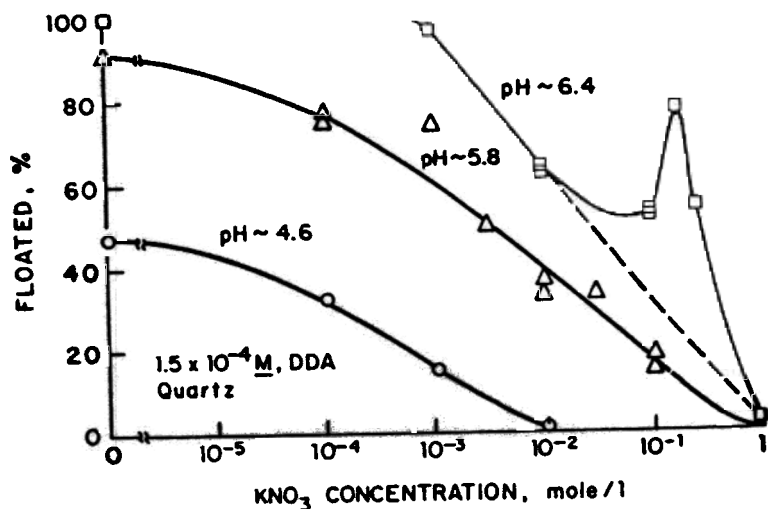


FIG. 5 Flotation recovery of quartz as function of KNO_3 concentration at pH 4.6, 5.8, and 6.4. 1.5×10^{-4} M/liter of dodecylammonium acetate was used as collector. (From Ref. 47.)

Chemisorption in the fluorite-oleate system is thought to take place by an ion-exchange mechanism in which a stoichiometric amount of lattice ions such as F^- is released into the solution during oleate adsorption. Experimental evidence of chemisorption is mainly from infrared spectra of the solid after adsorption. Thus Miller et al. [53] observed that the intensity of the $=\text{CH}$ bond of adsorbed oleate decreased at high temperature in the fluorite-oleate system and attributed this phenomenon to an oxidation-polymerization reaction between the oleyl groups at the fluorite surface. However, the FTIR technique suffers from a major drawback, owing to the possibility of alterations in the chemical state of the adsorbed surfactant during the preparation of the sample for spectroscopic investigation.

In examining the chemical forces involved, a major factor that is often ignored is the change in the active chemical form of the surfactant with change in solution pH. This has often forced researchers to adopt the alternative of chemisorption as the mechanism of adsorption. For example, flotation maximum at pH 8 for the hematite-oleate system has been proposed to be due to covalent bonding between the surfactant species and the mineral surface (Fig. 7). Oleate itself, however, has been found to exhibit maximum surface tension lowering at pH 8, suggesting formation of highly surface

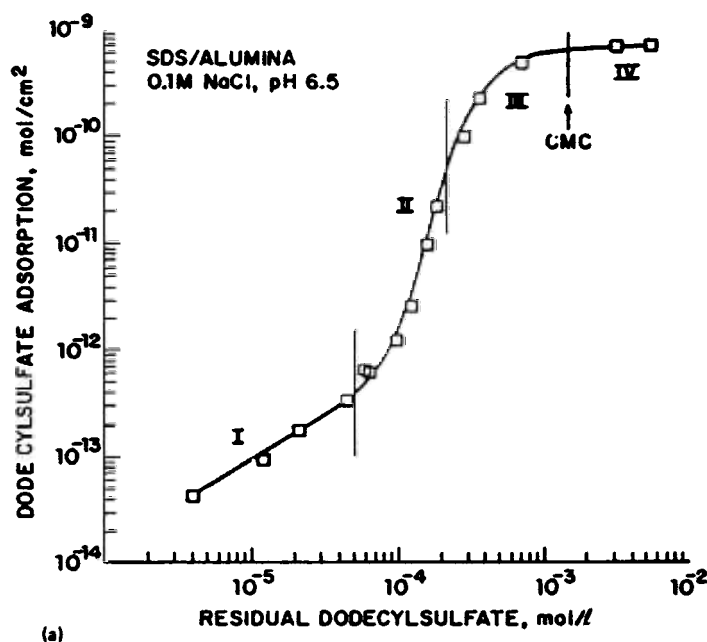


FIG. 6 (a) Adsorption isotherm of dodecyl sulfate on alumina; (b) schematic representation of evolution of surface aggregates at different regions of the adsorption isotherm. (From Ref. 29.)

active complexes in this pH region [54,55]. Ionomolecular complexes that can form between oleic acid and oleate in this pH range can be expected to give rise to a flotation maximum. Indeed, the surface activity of the acid-soap oleate complex hematite flotation exhibit a maximum at the same pH (Fig. 7).

D. Surface Precipitation

An important factor that has to be taken into account in this regard is the possibility of the precipitation of the surfactant on the particle surface. Since the concentration of an ionic surfactant at an oppositely charge surface is higher than that in bulk, precipitation of it can occur at the interface even below concentrations required for precipitation in the bulk. Such surface precipitation can indeed be expected to lead to a sharp dependence of adsorption on solution conditions. Adsorption of multivalent species on oxide surfaces exhibits a sharp pH dependence; in the past this has been attributed

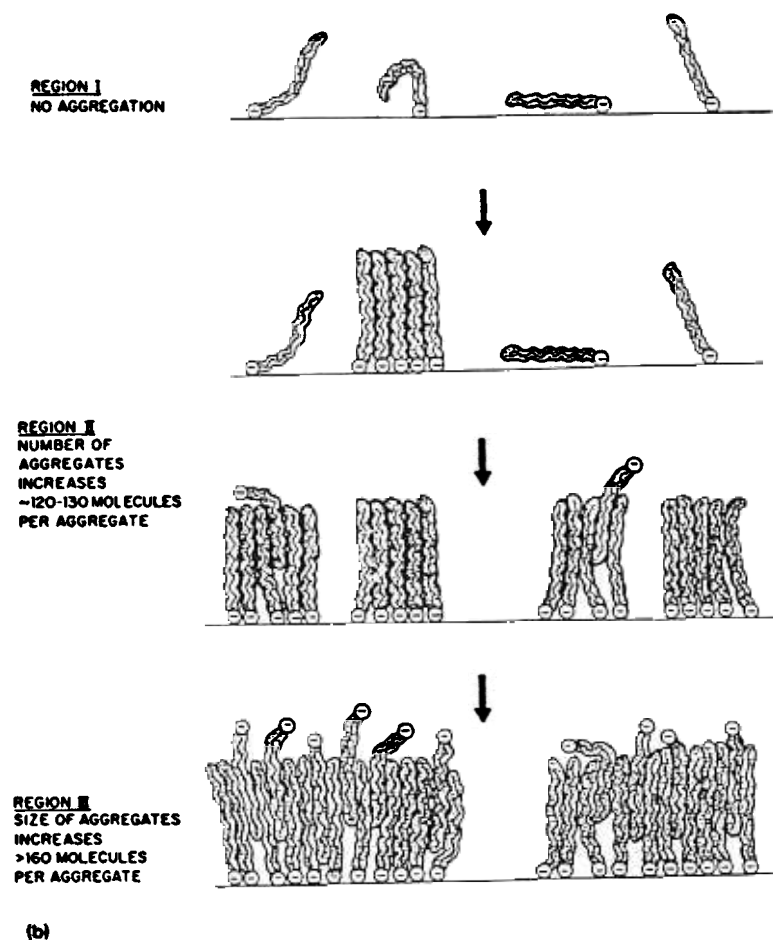


FIG. 6 (Continued)

to chemisorption of the metal hydroxy species. For example, the adsorption of Ca species on silica (Fig. 8) shows a sharp increase around pH 11 which was proposed to be the result of chemisorption of CaOH^+ since Ca(OH)^+ forms in measurable amounts in the bulk around pH 10 to 11. However, if the accumulation of Ca^{2+} ions (as measured by the adsorption) is taken into account, it becomes clear that surface precipitation of Ca(OH)_2 can take place around pH 11. This correlates with the adsorption isotherm, suggesting

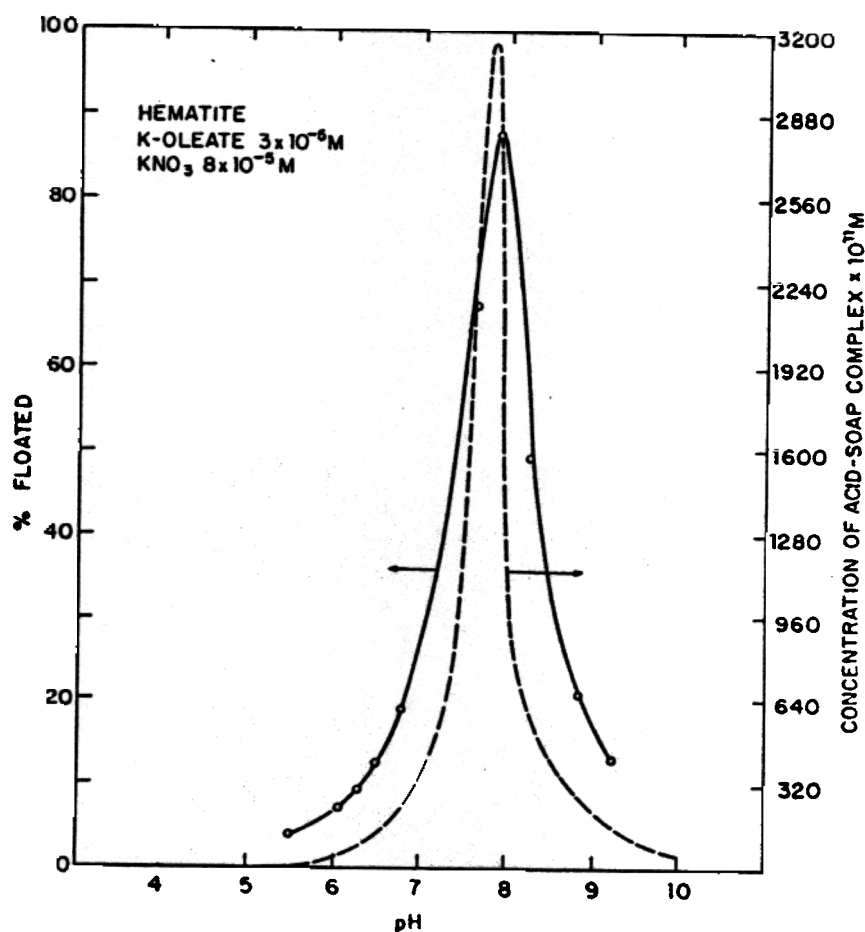


FIG. 7 Correlation of hematite flotation and formation of acid soap complex.

that surface precipitation rather than chemisorption is responsible for the steep rise of the isotherm. Similar correlations have been obtained for the cobalt-silica and the alumina-dodecylsulfonate systems [56].

Adsorption of surfactants on semisoluble minerals has also been considered in the past to be due to chemisorption. Figure 9 shows flotation behavior of dolomite using oleate. By determining the Ca^{2+} activity in equilibrium with the mineral and the surfactant required

ADSORPTION, $\text{mol/cm}^2 \times 10^{10}$

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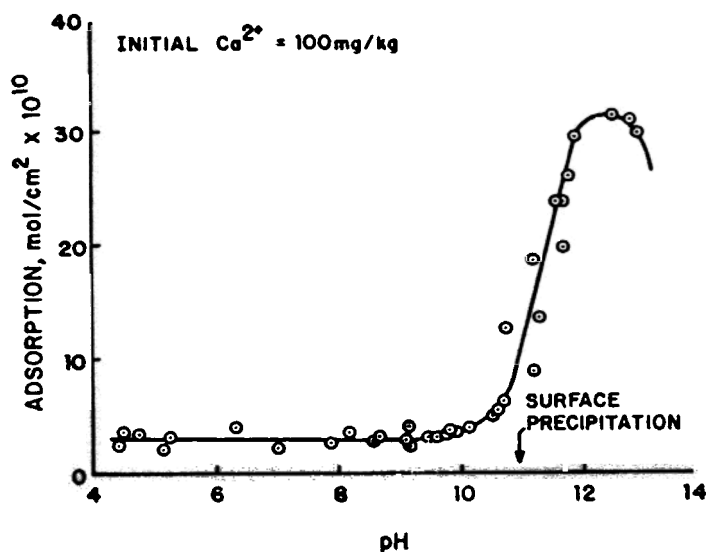


FIG. 8 pH dependence of Ca adsorption on quartz. $K_{sp} \text{Ca(OH)} = 10^{-5.2}$. pH of surface precipitation for different assumed values of adsorbed layer thickness (x): $x=35 \text{ \AA}$, pH 11.4; $x=10 \text{ \AA}$, pH 10.96.

to precipitate the Ca-surfactant salt, Ananthapadmanabhan and Somasundaran [56] clearly showed the flotation maximum in this system to correlate with the onset of surface precipitation of the calcium salt. Evidently, a careful distinction between chemisorption and surface precipitation has to be made based on the chemical equilibria involved in each system.

E. Xanthate Interactions

Sulfide mineral flotation is an important example where chemical interactions between the surfactant and the mineral plays a governing role. The most commonly used collector for sulfides is xanthate, which is essentially a derivative of carbonic acid (H_2CO_3) in which the two oxygens are replaced by sulfurs and one hydrogen by an alkyl or aryl group. Different xanthates used in sulfide flotation are listed in Table 5 along with their solubility products. The exact nature and mechanism of interactions in the xanthate-sulfide system are not established precisely despite many decades of research partly because of the wide and complex variations in the surface properties

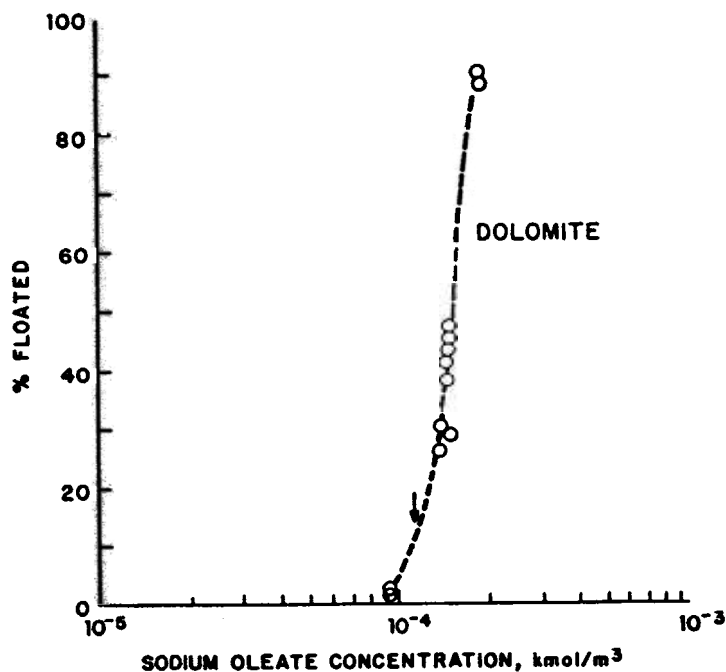
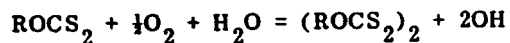
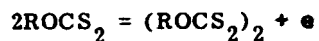


FIG. 9 Flotation of dolomite as a function of oleate concentration. Arrow indicates onset of surface precipitation of Ca oleate (pH 10); Ca^{2+} (dolomite) = $2.8 \times 10^{-3} \text{ kmol m}^{-3}$, K_{sp} (Ca oleate) = 4×10^{-10} (From Ref. 93.)

of sulfides. Thus while it is known that oxygen is necessary for xanthate adsorption [57–65], the role of oxygen in critical reactions involving xanthate oxidation to dioxanthogen,



and consequent hydrophobization of the solid is not clearly established. Finkelstein [59] proposed a two-site electrochemical mechanism involving oxidation of the lattice sulfide ions to explain sulfide flotation. Xanthate adsorption was attributed to ion exchange

TABLE 5 Solubility Products for Metal Xanthates at 20°C^a

		Ag ⁺	Pb ²⁺	Zn ³⁺	Cu ²⁺	Ni ²⁺	Co ²⁺	Fe ²⁺	Mn ²⁺
Ethyl xanthate	C ₂ H ₅ OCSS ⁻	18.6	16.7	8.2	24.2	12.5			
Isopropyl xanthate	C ₃ H ₇ OCSS ⁻	18.6	17.8		24.7	13.4			
Butyl xanthate	C ₄ H ₉ OCSS ⁻	19.5	18.0		26.2				
Butyl (l-) xanthate	C ₄ H ₉ OCSS ⁻	19.2	17.3		26.3				
Amyl (l-) xanthate	C ₅ H ₁₁ OCSS ⁻	19.7	17.6		27.0	14.5			
Hexyl (n-) xanthate	C ₆ H ₁₂ OCSS ⁻	20.8	20.3		29.0	16.5	14.3		
Octyl (l-) xanthate	C ₈ H ₁₇ OCSS ⁻	20.4	21.3			17.7			
Nonyl (n-) xanthate	C ₉ H ₁₉ OCSS ⁻	22.6	24.0	16.2	30.0	22.3	21.3	11.0	9.9
Nonyl (l-) xanthate	C ₉ H ₁₉ OCSS ⁻	21.3				21.7			
Lauryl xanthate	C ₁₂ H ₂₅ OCSS ⁻	23.8	26.3	19.5	37.0	23.0			

^aAll values are given as negative logarithm of the solubility product extrapolated to infinite dilution.

between the oxidation products and the xanthate species. This mechanism was analogous to that of metal corrosion and it was expected that the rest potential of the mineral surface would be between the reversible potentials of the anodic and cathodic reactions. Experimental data on the rest potentials of the galena-xanthate-oxygen system, however, show significant variations possibly due to the mineralogical heterogeneities leading to different extent of oxidation at the interface. Poling [65] reported adjacent localities of the same particulate sample to show variations of several hundred millivolts in potentials with the more anodic areas adsorbing higher amounts of xanthate. The complex nature of xanthate adsorption and hydrophobisation of sulfides is still not adequately explained, mainly because of the surface chemical heterogeneities of different sulfide minerals that result in different mechanisms dominating in different systems.

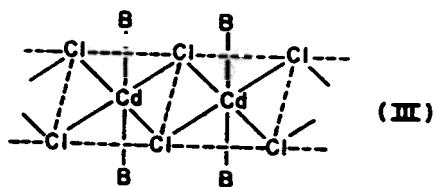
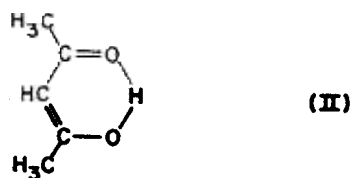
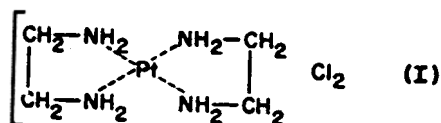


FIG. 10 General structure of chelating agents.

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TABLI

Reage

O-O t

Cup

Salic

α -Ni

Acet

Alky

Pho:

N-O t

β -H

α -H

δ -H

N-N t

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TABLE 6 Examples of Chelating Agents as Collectors

Reagent	Minerals
O-O type	
Cupferron	Cassiterite, uraninite, hematite
Salicylaldehyde	Cassiterite
α -Nitroso β -naphthol	Cobaltite
Acetylacetone	Malachite, chrysocolla
Alkylhydroxamic acid (IM50)	Chrysocolla, hematite and minerals containing Ti, Y, La, Nb, Sn, and W
Phosphonic acids	Cassiterite
N-O type	
β -Hydroxyoximes	Cu oxide minerals
α -Hydroxyoximes	Cu oxide minerals
8-Hydroxyquinoline	Cerussite, pyrochlore, chrysocolla
N-N type	
Diphenylguanidine	Cu minerals
Dimethylglyoxime	Ni minerals
Benzotriazole	Cu minerals
S-S type	
Xanthates	
Dithiophosphates	All sulfide minerals
Dithiocarbamates	
N-S type	
Mercaptobenzothiazole	Sulfide and tarnished sulfides
Dithizone	Sulfides
S-O type	
<i>N</i> -benzoyl- <i>O</i> -alkyl thionocarbamate	Sulfides

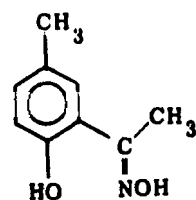
F. Surface Chelation

Another group of collectors used for the flotation of copper, nickel, and other metal sulfides is chelating agents that adsorb by forming metal hydrophobic complexes characterized by ring structures. Figure 10 shows examples of three types of chelating agents: I, where the metal is coordinated to the four nitrogens of two molecules of ethylene diamine; type II, showing an intramolecular hydrogen bridge; and type III, involving polynuclear halogen bridges. The two basic requirements for a molecule to form metal chelates are (1) it should

TABLE 7 Structure and Water Solubility of Various Hydroxyoximes

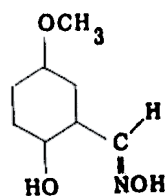
Chemical Structure	Name	Mol. wt.	Water solubility $\underline{\text{M}}$	Stock solution (M)
	SALO (salicylaldehyde oxime)	137.1	2×10^{-1}	10^{-2}
	OHAPO (O-hydroxyacetophenone oxime)	151.2	4.5×10^{-3}	2×10^{-3}
	OHBuPO (O-hydroxybutyrophenone oxime)	179.2	5.0×10^{-4}	3×10^{-4} and 5×10^{-4}
	OHBePO (O-hydroxybenzophenone oxime)	213.2	1.5×10^{-4}	1.5×10^{-4} and 2×10^{-4} (1.2% acetone)





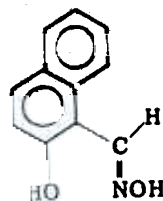
2H5MeApo (2-hydroxy-5-methyl acetophenone oxime)

66.2

 3×10^{-4} 3×10^{-4} 

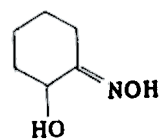
2H5BAO (2-hydroxy-5-methoxy benzaloxime)

168.2

 5×10^{-3} 5×10^{-3} 

2HNAO (2-hydroxy-1-naphthaldoxime)

189.2

 1×10^{-4} $.25 \times 10^{-4}$ 

OHCHO (O-hydroxy cyclohexanone oxime)

129.0

1.0

 5×10^{-1}

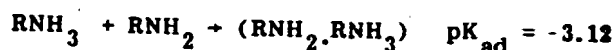
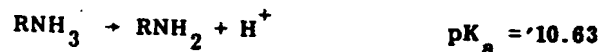
Source: Ref. 19.

have suitable functional groups, and (2) the functional groups must be situated so as to permit ring formation with the metal as the closing member.

In general, it has been observed that a chelate should preferably be neutral if it should function as a collector and be charged to function as a depressant. Selectivity in chelation is achieved by making use of the differences in stability constants of the metal chelates and by optimizing solution properties such as pH and ionic strength [66,67]. Examples of common chelating agents and their structures are given in Tables 6 and 7. It is important to distinguish between the role of surface and bulk chelates in flotation systems. Thus flotation has been shown to correlate with surface chelation rather than bulk chelation in the tenorite-salicylaldoxime system (Fig. 11).

G. Surfactant Solution Chemistry

In addition to the aqueous chemistry of the minerals and the interactions between surfactant and dissolved inorganic species, the solution chemistry of the surfactant itself, plays a significant role in flotation. As mentioned earlier, hydrolyzable surfactants such as fatty acids and amines can undergo associative reactions to form highly surface active ionomolecular complexes leading to enhanced flotation. For example, dodecylamine reactions in aqueous media can be represented by the following reactions [69]:



$$C_T = C_{\text{RNH}_2} + C_{\text{RNH}_3^+} + 2C_{(\text{RNH}_3)_2^{2+}} + 2C_{(\text{RNH}_2\text{RNH}_3)^+} \quad (\text{mass balance})$$

The dimerization constant for dodecylamine hydrochloride is assumed here to be the same as that for dodecylamine thiosulfate [68]. Species distribution diagrams of dodecylamine hydrochloride at two

Surf

12.0

12.0

11.0

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9.0

Cu-SALO CHELATE, mg

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4.0

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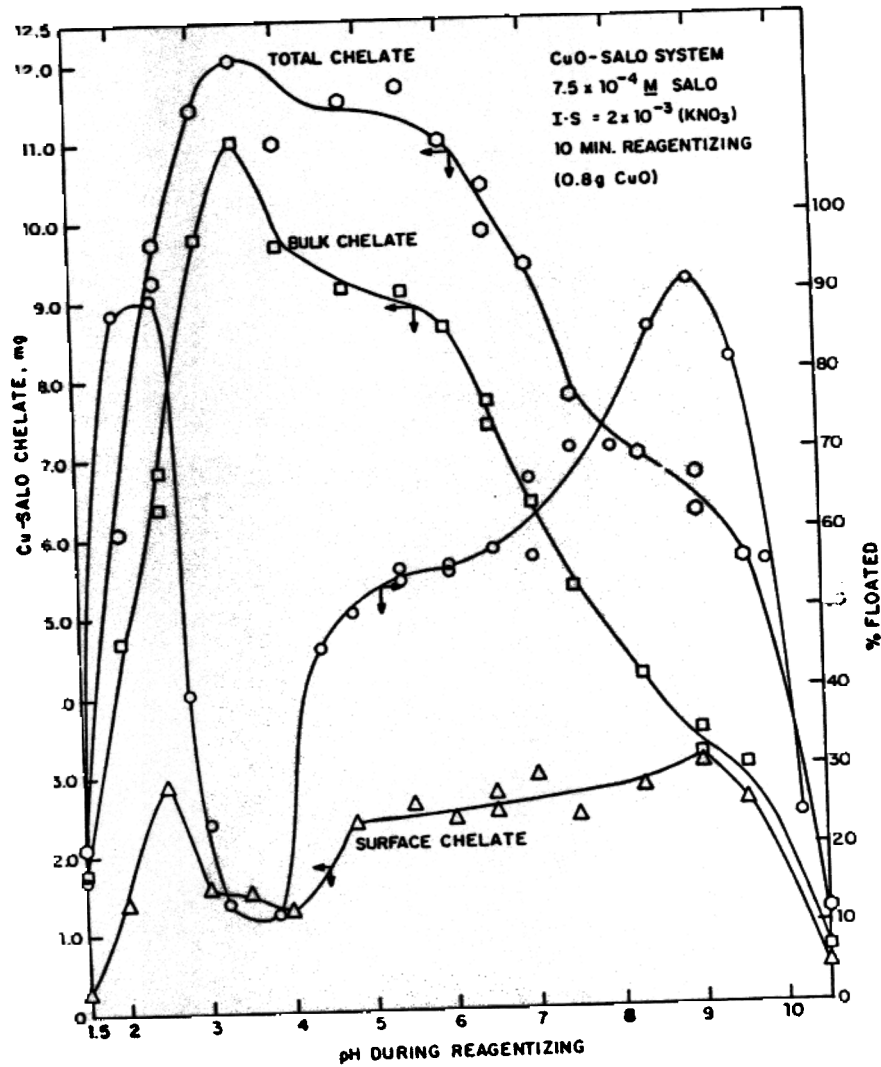


FIG. 11 Correlation of bulk and surface chelation of salicylaldoxime with tenorite and its species with flotation in the tenorite-salicylaldoxime system. (From Ref. 67.)

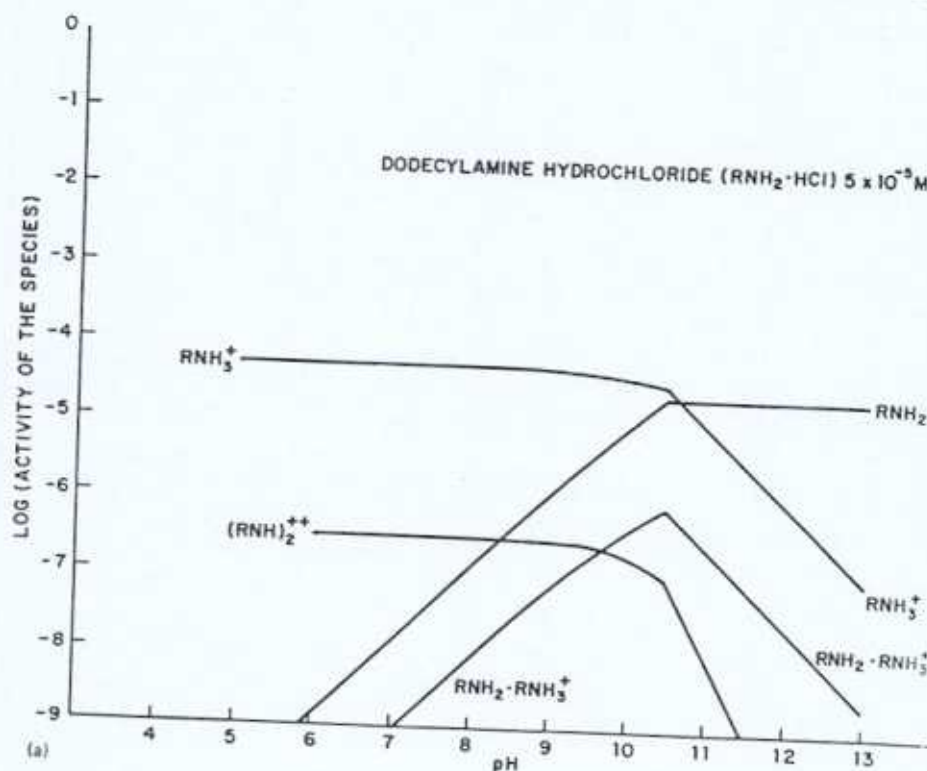


FIG. 12 (a) Species distribution diagram of dodecylamine as a function of pH, total amine = 10^{-5} M, below the solubility limit; (b) species distribution diagram of dodecylamine as a function of pH, total amine = 5×10^{-5} M, above the solubility limit.

different concentrations, 5×10^{-5} M (above the precipitation limit of neutral dodecyl amine) and 10^{-5} M (below the precipitation limit) are shown in Fig. 12. Two important aspects of these calculations are: (1) the pH of maximum amine-aminium complex has shifted to a higher value (10.9) to a lower value (10.4) with increasing total dodecylamine concentration, and (2) the pH of precipitation coincides with the pH of maximum complex formation. Figure 13 shows flotation of quartz using dodecylamine at 10^{-5} M and 5×10^{-5} M concentrations with a maximum at pH 10 to 11. It is to be noted that at 5×10^{-5} M amine concentration, the pH of flotation maximum coincides with the pH of maximum activity of aminium dimer in the

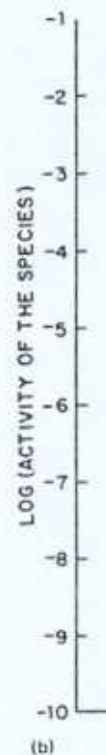


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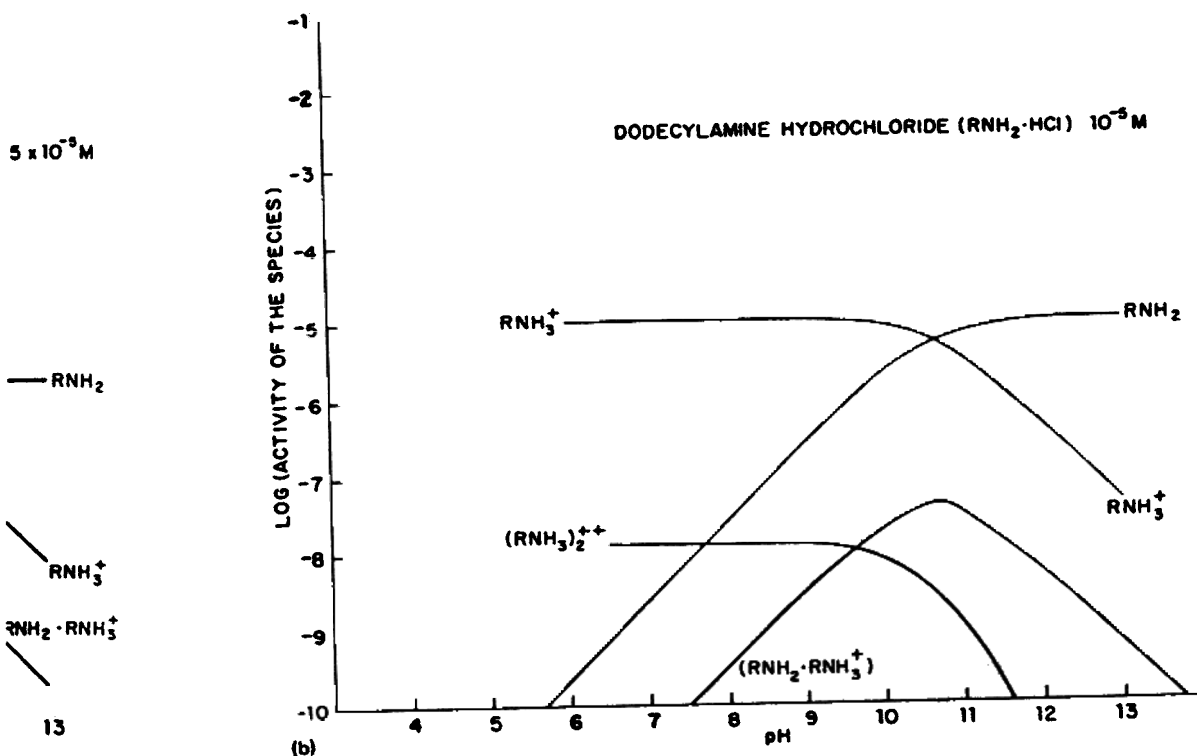


FIG 12 (Continued)

the amine aminium complex and in amine precipitation. However, at 10⁻⁵ M amine concentration, there is no precipitation, and flotation maximum can be correlated solely to the formation of the iono-molecular complex. Similar correlations between collector association and flotation have also been observed for the oleate-hematite system [69].

IV. MODIFYING AGENTS

In addition to surfactants that function primarily as collectors and frothers, other chemicals are added as depressants, deactivators, activators, pH modifiers, and dispersants to most flotation systems. Depressants act by retarding or inhibiting the flotation of the solid selected. Polymers such as starch and tannin are common depressants. Interestingly, depression of flotation does not always take

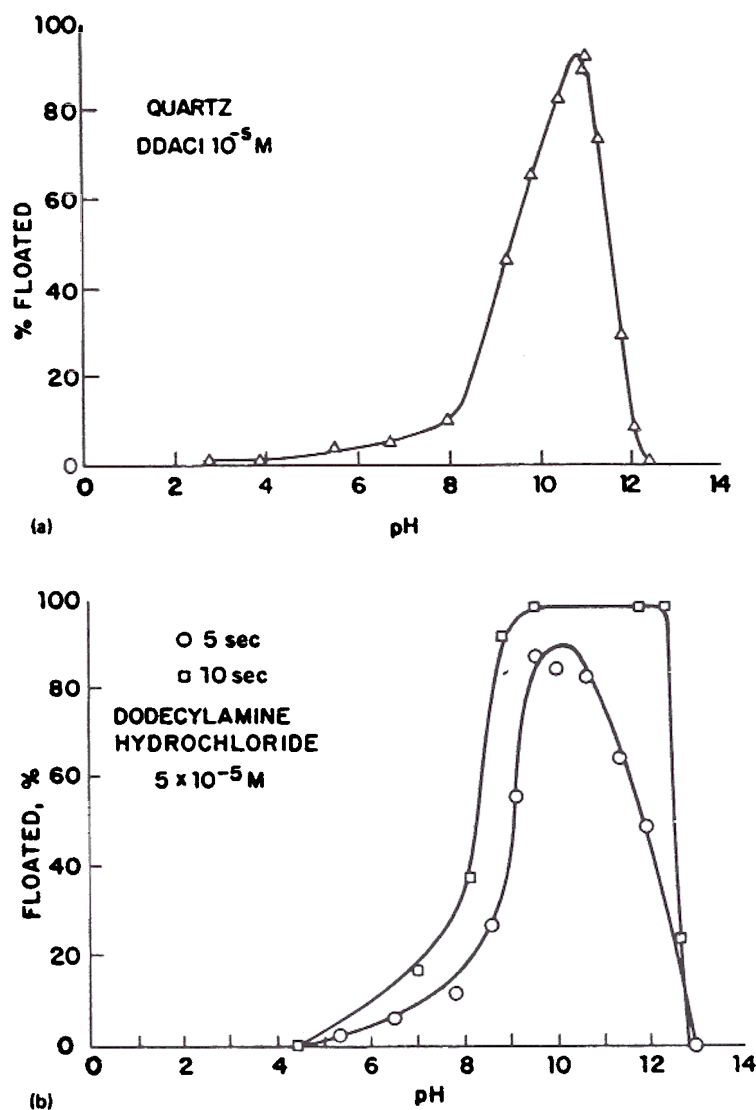


FIG. 13 Hallimond cell flotation of quartz as a function of pH at (a) 5×10^{-5} M amine and (b) 10^{-5} M amine.

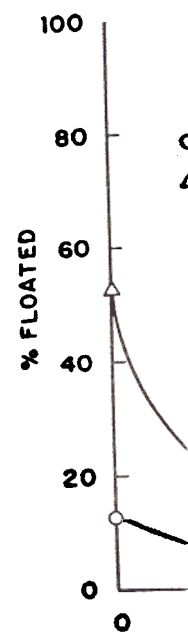


FIG. 14 De cationic pol presence ar

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actants in Flotation

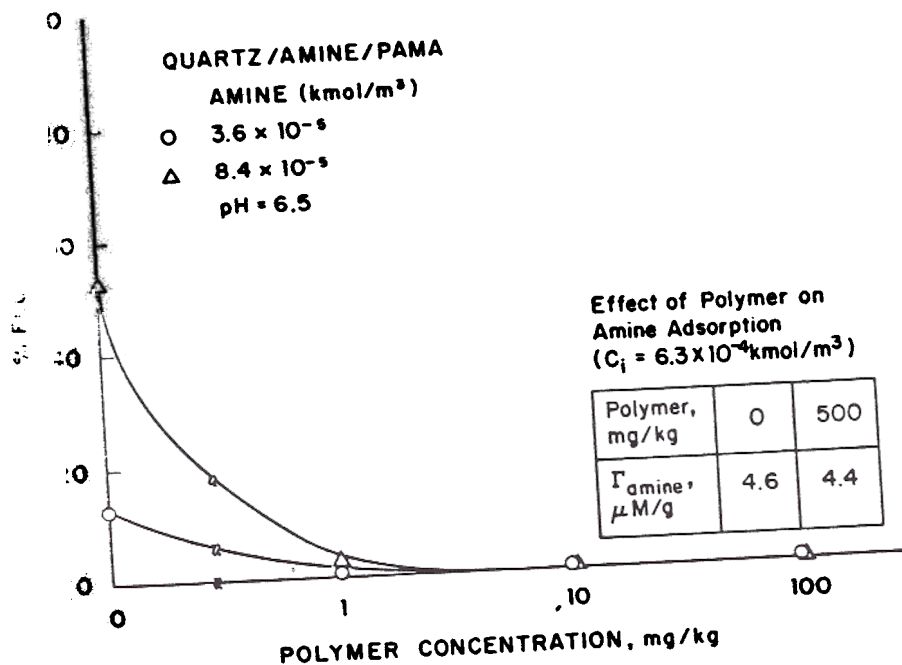


FIG. 14 Depression of flotation of quartz using dodecylamine by the cationic polymer PAMA at natural pH. Adsorption of sulfonate in the presence and absence of polymer is shown in the inset.

place, due to inhibition of collector adsorption. For example, flotation of quartz using amine is depressed by a cationic polymer even though the adsorption is totally unaffected [70] (Fig. 14). Based on information obtained from electrophoretic and surface tension tests, flotation depression has been attributed to masking of the adsorbed amine by the adsorbed massive polymer species. Indeed, such polymers can also be expected to activate flotation: for example, in this case by an anionic surfactant such as alkyl sulfonate (Fig. 15). Figure 16 schematically illustrates the masking phenomenon and the consequent effect on flotation due to variations in surface characteristics after adsorption of polymer and surfactant. Activators thus enhance the adsorption of the surfactant and thereby flotation. Sphalerite activation by copper and quartz activation by multivalent cations are additional examples. Deactivators are reagents that usually react with activators to retard flotation selectively for example,

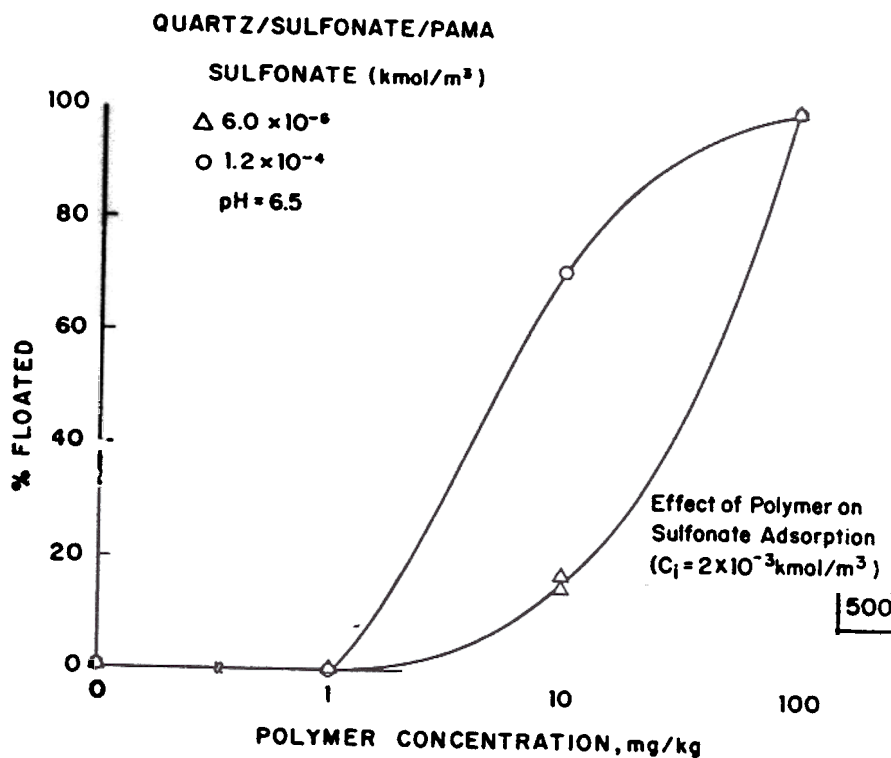
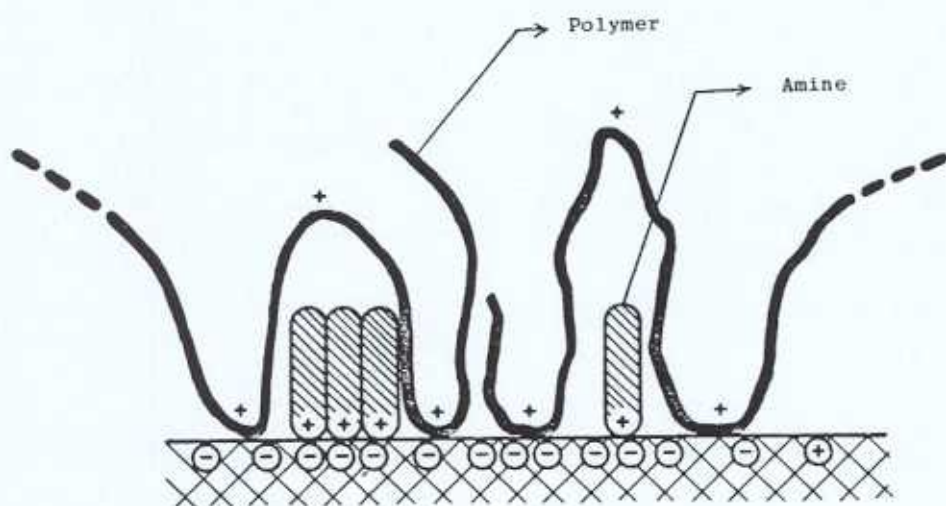
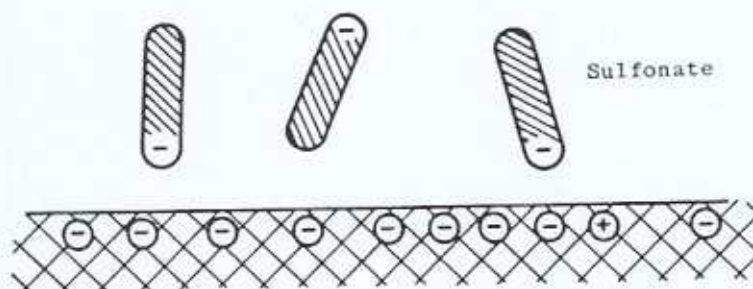


FIG. 15 Activation of flotation of quartz dodecylsulfonate by the cationic polymer PAMA at natural pH. Adsorption of sulfonate in the presence and absence of polymer is shown in the inset.

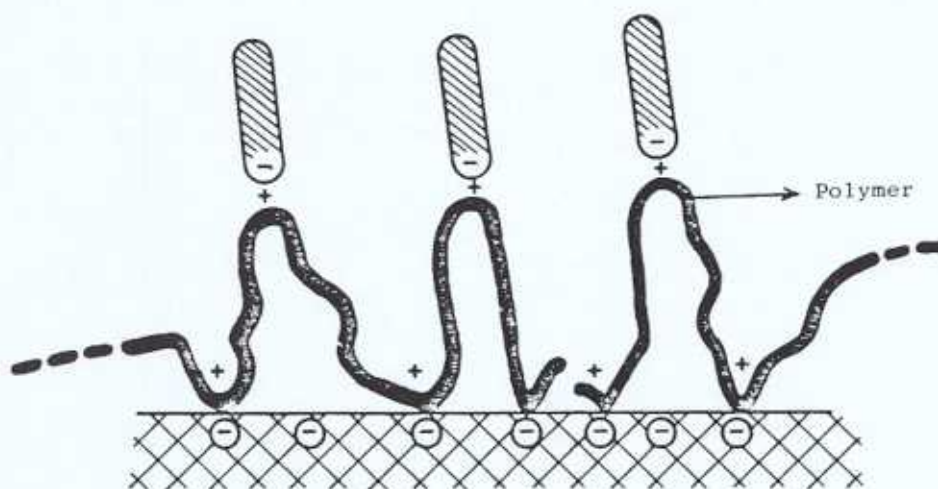
FIG. 16 Schematic representations of (a) cationic polymer PAMA and dodecylamine coadsorption on quartz particles resulting in flotation depression, (b) adsorption in the quartz/dodecylsulfonate system, and (c) cationic polymer PAMA and dodecylsulfonate coadsorption on quartz particles resulting in flotation activation.



(a)



(b)



(c)

FIG. 16

addition of cyanide in xanthate flotation of zinc sulfides causes deactivation of copper flotation. In addition to these chemicals, dispersants such as sodium silicate and modifiers such as oxalic acid, tartaric acid, and ethylenediaminetetraacetic acid (EDTA) are often used in flotation systems either to complex with the deleterious chemical species or colloids that can coat the particles to be floated.

It is clear from the examples above that the role of the surfactant in flotation is influenced by a number of factors. For any flotation system, selection of the best surfactant is dependent on the identification of the relevant interactions between many species that are released into the system on the dissociation of the surfactant as well as the dissolution of the mineral.

ACKNOWLEDGMENTS

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