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# Reagent Adsorption on Phosphates

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## Introduction

Adsorption of surfactants on minerals is the basic process governing flotation. It is controlled by various physicochemical processes in the pulp involving interactions among the mineral particles, surfactants, dissolved inorganics, solvent species and other additives such as polymers. Adsorption can be considered as selective partitioning of the surfactant adsorbate into the interfacial region, resulting from the more energetically favourable interactions between the adsorbate and the solid than those between the former and the species in the bulk solution. The interactions leading to adsorption include chemical bonding, electrostatic interaction, desolvation of the surfactant polar group and the mineral surface species, hydrogen bonding, van der Waals interactions, etc.

Water chemistry plays an important role in the adsorption process by affecting the surfactant–solution equilibria, the mineral–solution equilibria and subsequently the interactions between the surfactants and the mineral particles. The interactions in mineral–solution system include dissociation, micellization and precipitation of the surfactant, dissolution of a small amount of solids followed by hydrolysis, complexation and precipitation of the dissolved species, and the interactions between dissolved mineral species with surfactant in the bulk in various forms. The dissolved species, including those introduced due to dissolution from all the minerals present in the ore and those from the water source, fresh and recycled, are the major elements that affect the water chemistry. While impurities introduced from water can be controlled to some extent, the chemical species released into the system due to dissolution from the minerals cannot be avoided. In systems containing soluble or sparingly soluble minerals where the extent of dissolution is markedly higher than that in most oxide/silicate systems, the effect of dissolved mineral species can be drastic. Understanding the mineral–solution–surfactant chemical equilibrium under different physicochemical conditions is critical for developing reagent and processing schemes for separation.

Phosphate is one of the most important minerals processed by flotation techniques. Flotation is efficient for the beneficiation of phosphate ores with silicate gangues, but those with carbonaceous gangues are difficult to separate by flotation techniques. The low selectivity has been attributed to the similarities in the surface chemical properties of the constituent minerals. These properties, in turn, are influenced by the water chemistry of the surfactant–mineral systems. In this section the effects of water chemistry on the surfactant–solution equilibrium, the mineral–solution equilibrium, the surfactant–mineral interactions in the separation of phosphate and associated minerals are discussed. Methods to manipulate and control the solution chemistry to achieve selectivity in flotation are also examined.

## Water Chemistry of Flotation Reagents

Long chain fatty acids such as oleic acid are among the commonly used reagents for the flotation of oxides, silicates and salt-type minerals. Flotation of these minerals using fatty acids is affected greatly by solution properties such as pH, since weakly acidic fatty acids undergo association interactions that can influence their adsorption and flotation properties. For example, oleic acid species will undergo dissociation to form ions ($Ol^-$) at high pH values and exist as neutral molecules (HOl) at low pH value. In the intermediate region, the ionic and the neutral molecular species can associate to form ion–molecule complexes ($(Ol)_2H^-$). As the surfactant concentration is increased, micellization or precipitation of the surfactant can occur in the solution. In addition, surfactant species can associate to form other aggregates such as the dimer ($Ol_2^{2-}$) in premicellar solutions. Also, long chain fatty acids such as oleic acid have very limited solubility, which is a sensitive function of pH. The pH of precipitation of oleic acid calculated as a function of total oleate is shown in **Figure 1**.

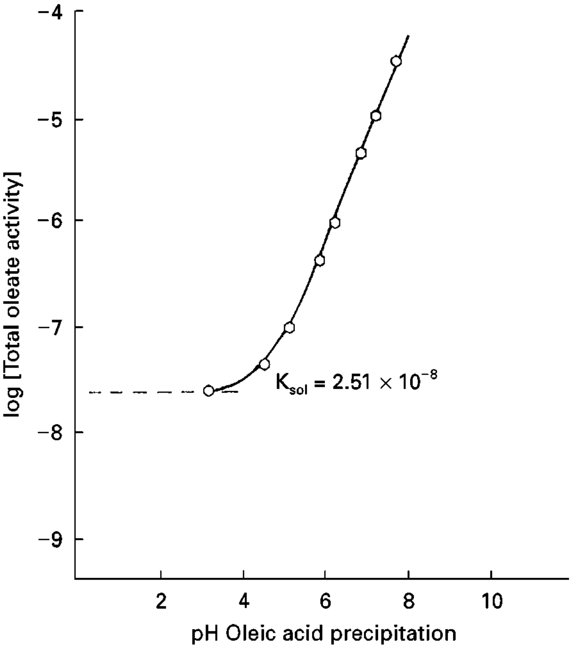

**Figure 1** pH of oleic acid precipitation. (From Morgan LJ, Ananthapadmanabhan KP and Somasundaran P (1986) Oleate adsorption on hematite: problem and methods. *International Journal of Mineral Processing* 18: 39. Copyright: Elsevier Science.)

The solution equilibria of oleic acid (HOl) are expressed as below:

$HOl(\mathit{liquid}) = HOl(\mathit{aq})$
$pK_{sol} = 7.6 \quad (K_{sol}\text{: solubility product})$

$HOl(aq) = H^+ + Ol^-$
$pK_a = 4.95 \quad (K_a\text{: acid dissociation constant})$

$2Ol^- = (Ol)_2^{2-}$
$pK_d = -3.7 \quad (K_d\text{: dimerization constant})$

$HOl + Ol^- = (Ol)_2H^-$
$pK_{ad} = -5.25 \quad (K_{ad}\text{: acid–soap formation constant})$

The species distribution of oleic acid as a function of pH based on the above equilibria at a given concentration is shown in **Figure 2**. It can be seen from this figure that:

1. The pH of the precipitation of oleic acid at the given concentration is 7.45.
2. The activities of oleic monomer and dimer remain almost constant above the precipitation pH and decrease sharply below it.
3. The activity of the acid–soap $(Ol)_2H^-$ exhibits a maximum in the neutral pH range.

The surface activities of the various surfactant species can be markedly different from each other. It has been estimated that the surface activity of the acid–soap $(Ol)_2H^-$ is five orders of magnitude higher than that of the neutral molecule (HOl) and about seven orders of magnitude higher than that of the neutral molecule (HOl) and about seven orders of magnitude higher than that of the oleate monomer $Ol^-$.

The existence of salt will also affect the surfactant–solution equilibria by changing the surface activities of the various surfactant species, the critical micelle concentration and the solubility of the surfactant, and the solvent properties of the solution.

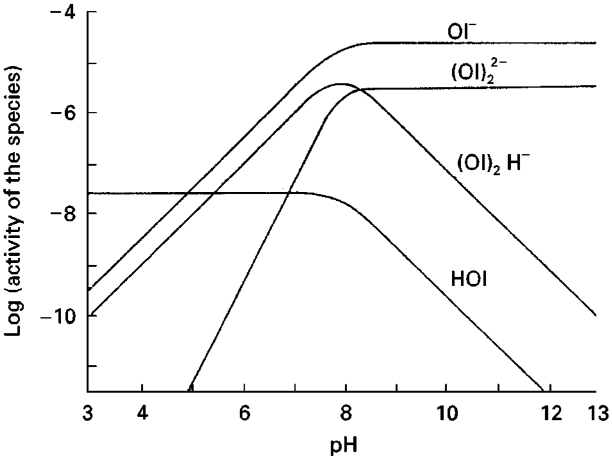

**Figure 2** Oleate species distribution as a function of pH. Total oleate concentration $= 3 \times 10^{-5}$ mol $L^{-1}$. (From Ananthapadmanabhan KP and Somasundaran P (1980) Oleate chemistry and hematite flotation. In: Yarar B and Spottiswood DJ (eds) *Interfacial Phenomena in Mineral Processing*, p. 207. New York: Engineering Foundation.)

It is clear that, to understand the adsorption of reagents on solids, the effects of concentration, pH, ionic strength and activities of the various possible reagent species on the adsorption process need to be taken into account.

## The Effect of Water Chemistry on Mineral–Solution Equilibrium

When mineral particles are in contact with water, they undergo dissolution, the extent of which is dependent on the type and concentration of chemicals in solution. The dissolved mineral species can undergo further reactions such as hydrolysis, complexation, adsorption and precipitation. The complex equilibria involving all such reactions can be expected to determine the interfacial properties of the minerals and their flotation behaviour. The equilibria that control the dissolution of calcite and apatite in water are given in **Table 1**.

In the case of carbonaceous phosphate minerals, apatite, calcite and dolomite will dissolve in water, followed by pH-dependent hydrolysis and complexation of the dissolved species. Since these minerals are sparing soluble, the dissolved species have a marked effect on their interfacial properties.

It should be noted that, from theoretical considerations, depending on the solution conditions, the surface of apatite can be converted to calcite and vice versa through surface reactions or bulk precipitation of the more stable phase. The stoichiometry of the equilibrium governing the conversion of apatite to calcite can be written as:

$$\begin{aligned} &Ca_{10}(PO_4)_6(OH)_2(S) + 10CO_3^{2-} \\ &= 10CaCO_3(S) + 6PO_4^{2-} + 2OH^- \end{aligned}$$

It can be seen from this equation that, depending on the pH of the solution, apatite can be converted to calcite if the total carbonate in solution exceeds a certain value. In fact, the amount of dissolved carbonate from atmospheric $CO_2$ does exceed that required to convert apatite to calcite under high pH conditions.

Surface conversion due to the reaction of the dissolved species with the mineral surface can be predicted using stability diagrams for heterogeneous mineral systems. This is illustrated in **Figure 3** for the calcite–apatite system. The activity of $Ca^{2+}$ in equilibrium with various solid phases shows that the point of interception for calcite and apatite is pH 9.3. Above this pH, apatite is less stable than calcite and hence conversion of apatite to that of calcite can be expected in the calcite–apatite system. Similarly, apatite is more stable than calcite below pH 9.3. It is to be noted that $Ca^{2+}$ in equilibrium with calcite in an open system (open to atmospheric $CO_2$) is significantly different from that in a closed system. Also,

**Table 1** Equilibria controlling the dissolution of calcite and apatite in water

| | | $K_{sp}$ | | | $K_{sp}$ |
|---|---|---|---|---|---|
| *Calcite* | | | | | |
| $CaCO_3$ (S) | $\rightleftarrows Ca^{2+} + CO_3^{2-}$ | $10^{-8.4}$ | $Ca^{2+} + HCO_3^-$ | $\rightleftarrows CaHCO_3^+$ | $10^{0.8}$ |
| $CO_3^{2-} + H^+$ | $\rightleftarrows HCO_3^-$ | $10^{10.3}$ | $Ca^{2+} + CO_3^{2-}$ | $\rightleftarrows CaCO_3(aq)$ | $10^{3.3}$ |
| $HCO_3^- + H^+$ | $\rightleftarrows H_2CO_3$ | $10^{6.3}$ | $Ca^{2+} + H_2O$ | $\rightleftarrows CaOH^+ + H^+$ | $10^{-12.9}$ |
| $CO_2(g) + H_2O$ | $\rightleftarrows H_2CO_3$ | $10^{-1.5}$ | $Ca^{2+} + 2H_2O$ | $\rightleftarrows Ca(OH)_2 + 2H^+$ | $10^{-22.8}$ |
| *Apatite* | | | | | |
| $Ca_{10}(PO_4)_6(F,OH)_2(S)$ | $\rightleftarrows 10\ Ca^{2+} + 6\ PO_4^{3-} + 2\ (F, OH)^-$ | | | | $10^{-118}$ |
| $PO_4^{3-} + H^+$ | $\rightleftarrows HPO_4^{2-}$ | $10^{12.3}$ | $Ca^{2+} + HPO_4^{2-}$ | $\rightleftarrows CaHPO_4(aq)$ | $10^{2.7}$ |
| $HPO_4^{2-} + H^+$ | $\rightleftarrows H_2PO_4^-$ | $10^{7.2}$ | $CaHPO_4(aq)$ | $\rightleftarrows CaHPO_4(s)$ | $10^{4.3}$ |
| $HPO_4^- + H^+$ | $\rightleftarrows H_3PO_4$ | $10^{2.2}$ | $Ca^{2+} + H_2PO_4^-$ | $\rightleftarrows CaH^2PO_4^+$ | $10^{1.1}$ |
| $Ca^{2+} + H_2O$ | $\rightleftarrows CaOH^+ + H^+$ | $10^{-12.9}$ | $Ca^{2+} + 2F^-$ | $\rightleftarrows CaF_2(s)$ | $10^{10.4}$ |
| $Ca^{2+} + 2H_2O$ | $\rightleftarrows Ca(OH)_2 + 2H^+$ | $10^{-22.8}$ | $Ca^{2+} + F^-$ | $\rightleftarrows CaF^+$ | $10^{1.0}$ |
| $F^- + H^+$ | $\rightleftarrows HF$ | $10^{3.1}$ | | | |

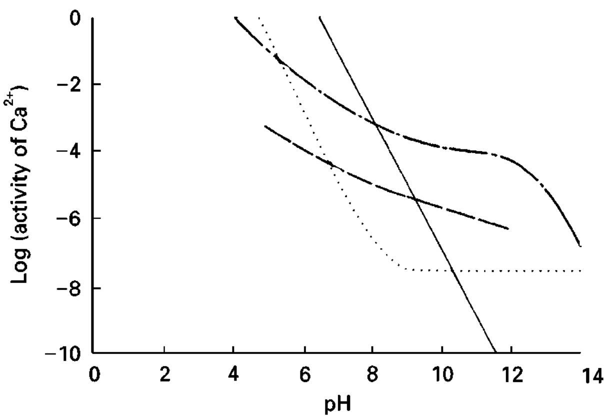

**Figure 3** pH dependence of activity of $Ca^{2+}$ in equilibrium with calcium oleate (dotted line: $Ol_T = 10^{-4}$ kmol $m^{-3}$), calcite (open (closed lines) and closed (dots and dashes) systems) and apatite (dashed lines). (From Ananthapadmanabhan KP and Somasundaran P (1984) The role of dissolved mineral species in calcite-apatite flotation. *Mineral and Metallurgical Processing* 1: 36.)

in the absence of atmospheric $CO_2$, apatite has a wider stability region than in the open system. Atmospheric $CO_2$ can thus be expected to play an important role in these types of mineral–solution equilibria and in operations dependent on interfacial properties.

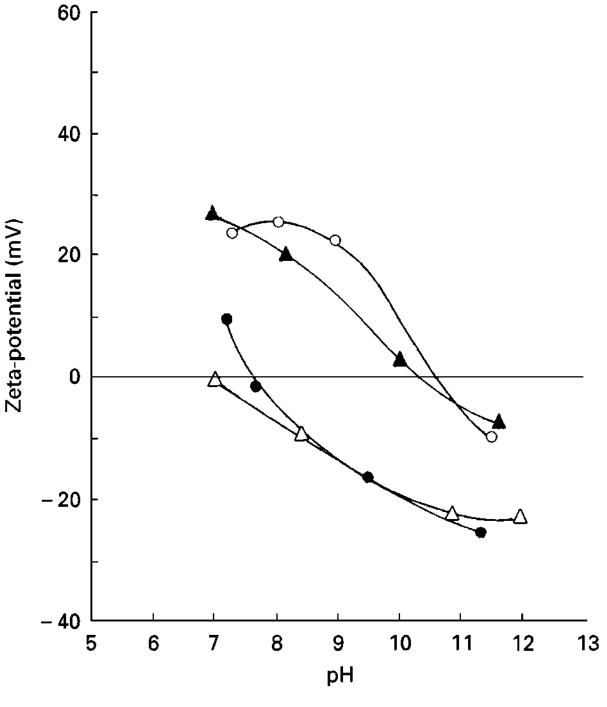

**Figure 4** Illustration of the effect of supernatants on the zeta potential and isoelectric point of calcite and apatite: $2 \times 10^{-3}$ kmol $m^{-3}$ $KNO_3$. Open circles, calcite in water; open triangles, apatite in water; filled triangles, apatite in calcite supernatant; filled circles, calcite in apatite supernatant. (From Ananthapadmanabhan KP and Somasundaran P (1984) The role of dissolved mineral species in calcite-apatite flotation. *Mineral and Metallurgical Processing* 1: 36.)

The surface conversions in the calcite–apatite system have been proved experimentally; electrokinetic data obtained for the calcite–apatite system in water and in the supernatant of each other are shown in **Figure 4**. When apatite is in contact with calcite supernatant, its zeta potential is seen to shift to that of calcite and vice versa, suggesting surface conversion of apatite to calcite and calcite to apatite, respectively.

The zeta potential data obtained in mixed supernatants of calcite and apatite also show the effect of dissolved mineral species. If supernatants of calcite and apatite are combined as a 1 : 1 mixture, the two minerals have almost identical surface charge characteristics in the basic pH range (**Figure 5**).

The surface conversion of apatite and calcite is further supported by the result of electron spectroscopy for chemical analysis (ESCA) measurements. The results in **Figure 6** show that, when apatite is conditioned in the supernatant of calcite at pH ~ 12, its surface exhibits spectroscopic properties characteristic of both calcite and apatite. This behaviour is attributed to the precipitation of calcite on the apatite.

Dissolution equilibria of sparingly soluble minerals play a major role in determining the surface properties of these minerals and in turn, adsorption of reagents on them.

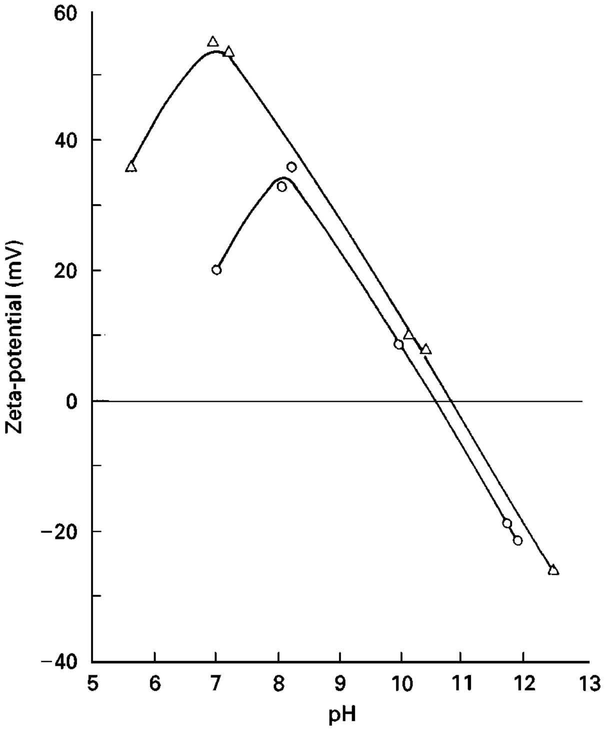

**Figure 5** Illustration of the similarity in zeta potentials of calcite (circles) and apatite (triangles) in mixed supernatants. (From Ananthapadmanabhan KP and Somasundaran P (1984) The role of dissolved mineral species in calcite-apatite flotation. *Mineral and Metallurgical Processing* 1: 36.)

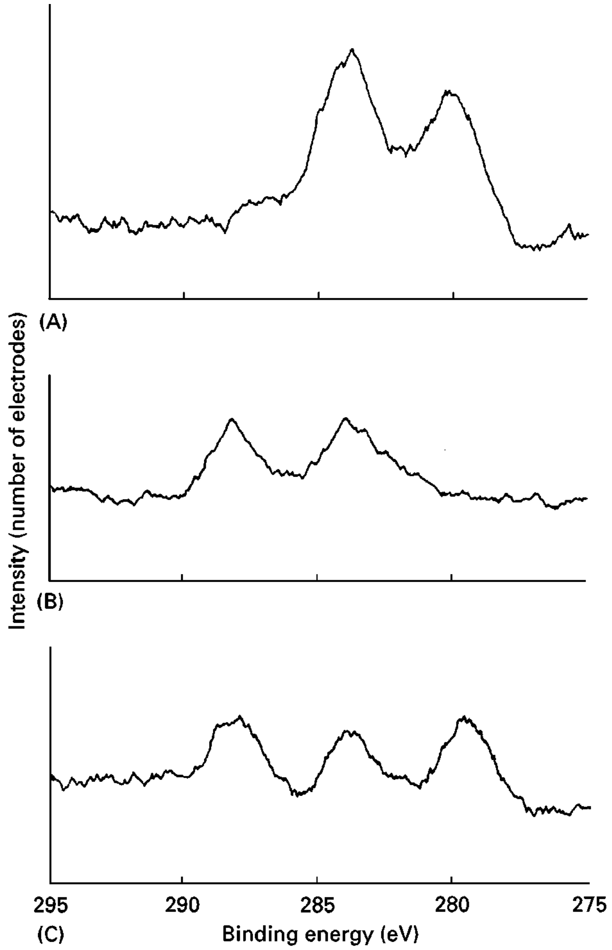

**Figure 6** ESCA spectra of C(1s) peak of apatite conditioned in calcite supernatant at pH ~ 12. (A) Apatite in water; (B) calcite in water; (C) apatite in calcite supernatant. (From Ananthapadmanabhan KP and Somasundaran P (1984) The role of dissolved mineral species in calcite-apatite flotation. *Mineral and Metallurgical Processing* 1: 36.)

## The Effect of Water Chemistry on Adsorption of Reagents on Minerals

Chemical equilibria in aqueous solutions containing both the minerals and the surfactants can be expected to be much more complex than in either of the individual systems discussed above. In addition to surfactant adsorption at the solid–liquid interface, interactions between dissolved mineral species with various surfactant species can be expected. All these interactions can affect the surfactant adsorption and the subsequent flotation.

As indicated earlier, oleic acid has a very low solubility and adsorption of oleate, in some cases, is in fact precipitation of the surfactant in the interfacial region. In Figure 3, the activity of $Ca^{2+}$ in equilibrium with various solid phases is plotted. If, at any stage, activity of $Ca^{2+}$ in solution is greater than that in equilibrium with $Ca^{2+}$-oleate, $Ca^{2+}$-oleate can be expected to precipitate.

Depletion isotherms of oleic acid on both francolite and dolomite has been observed to be a two-region linear isotherm with a change of slope at about $10^{-4}$ kmol m$^{-3}$ (**Figure** 7). Simultaneous analysis of the dissolved mineral species in the supernatants of the samples used in the adsorption experiments (**Figure** 8) shows a sharp decrease in the concentrations of both Mg and Ca species when oleate concentration exceeds $1.0 \times 10^{-5}$ kmol m$^{-3}$ in the case of francolite and $3.0 \times 10^{-5}$ kmol m$^{-3}$ in the case of dolomite. This suggests that bulk precipitation of calcium and magnesium species can occur under such conditions.

Major chemical equilibria for the precipitation of Ca and Mg species by oleate can be given as follows:

$$\mathrm{Ca}^{2+} + 2\,\mathrm{Ol}^- = \mathrm{Ca(Ol)_2} \qquad K_{\mathrm{Ca(Ol)2}} = 3.81 \times 10^{-13}$$

$$\mathrm{Mg}^{2+} + 2\,\mathrm{Ol}^- = \mathrm{Mg(Ol)_2} \qquad K_{\mathrm{Mg(Ol)2}} = 1.58 \times 10^{-11}$$

The onset of the precipitation of $Ca(Ol)_2$ and $Mg(Ol)_2$ is calculated from the solubility products given above and marked in Figure 8. The calculated oleate concentrations at the onset of precipitation are in good agreement with experimental observations.

It is postulated that, in the case of oleate adsorption on dolomite and francolite, different mechanisms govern the adsorption process. In the low concentration range ($<10^{-4}$ kmol m$^{-3}$), the adsorption

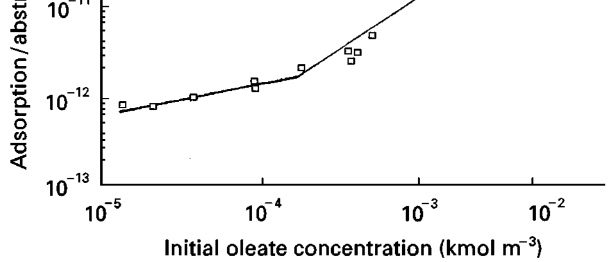

**Figure 7** Depletion isotherms of $^{14}$C-labelled oleic acid on francolite (squares: pH = 8.2) and dolomite (circles: pH = 9.2). Temperature, 25°C; S/L = 0.3; I = $3 \times 10^{-2}$ kmol m$^{-3}$ $KNO_3$. (From Somasundaran P, Xiao L and Wang D (1991) Solution chemistry of flotation of sparingly soluble minerals. *Mineral and Metallurgical Processing* 8: 115–121.)

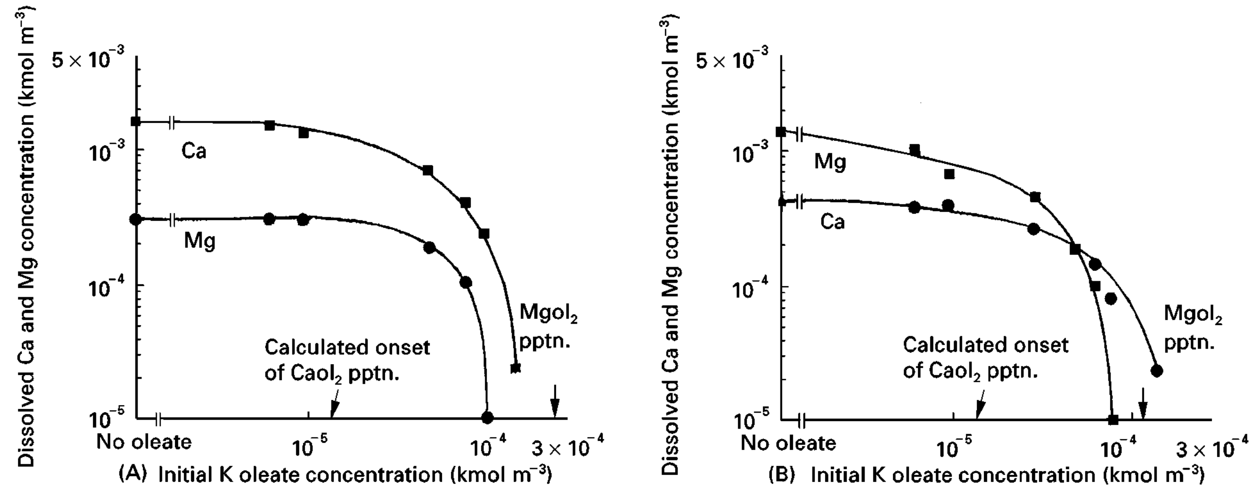

**Figure 8** Dissolved Ca (squares) and Mg (circles) levels from (A) francolite (pH = 8.2) and (B) dolomite (pH = 9.2) suspensions as a function of oleate concentration. (From Somasundaran P, Xiao L and Wang D (1991) Solution chemistry of flotation of sparingly soluble minerals. *Mineral and Metallurgical Processing* 8: 115.)

of oleate on both minerals occurs mainly due to chemical bonding on surfaces without any precipitation. At an intermediate concentration of about $10^{-4}$ kmol m$^{-3}$, the solubility limit of Ca and Mg oleate can be reached in the interfacial region but not in the bulk solution, suggesting surface precipitation of oleate on both minerals. In the high concentration range ($>5 \times 10^{-4}$ kmol m$^{-3}$), oleate depletion may be dominated in the case of both minerals by the precipitation of Ca and Mg species with oleate, on the mineral surface and in the bulk solution.

From the above discussion on apatite–calcite conversion, it is clear that a flotation separation scheme designed on the basis of the surface properties of a single mineral is not likely to perform satisfactorily. The effect of dissolved species of calcite and apatite on fatty acid flotation of both minerals has in fact been studied using mineral supernatant solutions containing various dissolved species. The flotation results are shown in **Figure 9**. Both supernatants of calcite and apatite are found to depress the calcite flotation by oleic acid in the tested pH range, with apatite supernatant exhibiting a greater depressing effect. Similar results have also been obtained for apatite flotation. The supernatants of calcite and apatite depress the apatite flotation under all tested pH conditions.

Studies on the dissolved species responsible for the observed effect revealed that, for calcite flotation, the depression role of apatite supernatant results from the combined effects of calcium species and the phosphate species in solution, while the depression role of calcite supernatant is mostly that of the calcium ion and possibly some carbonate ions. The depression due to calcium ion is caused by the depletion of oleate owing to the precipitation of calcium oleate. In the case of apatite flotation, the depression is due to phosphate and carbonate species in solution. The adsorption of these ions on the surface calcium sites reduces the sites available for oleate adsorption which, in turn, lowers the hydrophobicity of the surface and so depresses the apatite flotation. Calcium oleate precipitation, in this case, does not occur to a significant extent due to the low concentration of oleic acid used in flotation. The above observations clearly show that water chemistry plays a crucial role in the flotation of apatite–calcite systems.

In addition to reagent complexation and precipitation, other reactions that occur in the bulk solution can take place in the interfacial region. For example, hemimicellization at a solid–liquid interface is a phenomenon that drastically affects the adsorption of collector reagents on solids.

Flotation is a dynamic process. In addition to the equilibrium effects associated with the water chemistry, it can also influence the adsorption kinetics of surfactants on the solid surfaces. Anionic conditioning is a unit operation that precedes rougher flotation and skin flotation of phosphates in Florida flotation plants. The effect of water chemistry on oleic acid adsorption on francolite during anionic conditioning has recently been studied in detail. In order to identify the effect of process variables on the adsorption, the experiment was carried out under both laboratory and plant conditions (**Table 2**).

The kinetics of oleic acid adsorption on francolite under both laboratory and plant conditions, using distilled water and plant water, is shown in **Figure 10**. The adsorption density and kinetics are quite different depending on the conditions and the

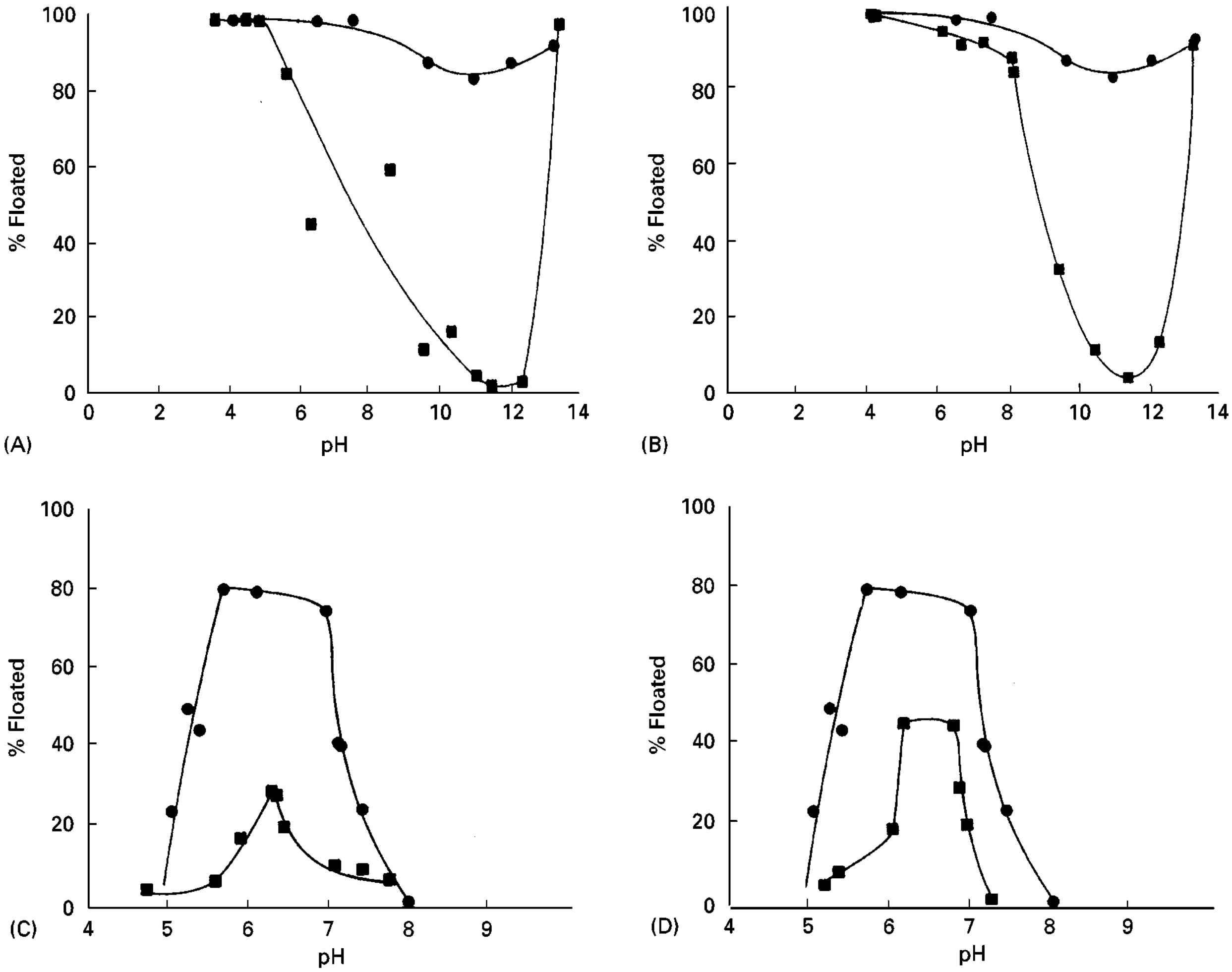

**Figure 9** (A) Effect of apatite supernatant (squares) on calcite flotation. K oleate $10^{-4}$ kmol m$^{-3}$; I = $3 \times 10^{-2}$ kmol m$^{-3}$ KNO$_3$. Circles, water. (B) Effect of calcite supernatant (squares) on calcite flotation. K oleate $10^{-4}$ kmol m$^{-3}$; I = $3 \times 10^{-2}$ kmol m$^{-3}$ KNO$_3$. Circles, water. (C) Effect of calcite supernatant (squares) on apatite flotation. K oleate = $2 \times 10^{-6}$ kmol m$^{-3}$; I = $3 \times 10^{-2}$ kmol m$^{-3}$ KNO$_3$. Circles, water. (D) Effect of apatite supernatant (squares) on apatite flotation. K oleate = $2 \times 10^{-6}$ kmol m$^{-3}$; I = $3 \times 10^{-2}$ kmol m$^{-3}$ KNO$_3$. Circles, water. (From Ananthapadmanabhan KP and Somasundaran P (1984) The role of dissolved mineral species in calcite-apatite flotation. *Mineral and Metallurgical Processing* 1: 36.)

water. Under laboratory conditions, the adsorption in plant water is significantly lower than that in the distilled water. It is proposed that this is due to reagent loss resulting from the dissolved species in plant water precipitating the oleic acid. In contrast, under plant conditions, the adsorption behaviour of oleic acid in plant water and distilled water is similar and adsorption densities are lower than those under laboratory conditions. The high solid/liquid ratio under plant conditions will reduce the adsorption density on the solids because of the much greater solid surface on to which the reduced total amount of

**Table 2** Comparison of laboratory and plant conditions

| | *Laboratory conditions* | *Plant conditions* |
|---|---|---|
| Conditioner | Wrist-action shaker | Lightnin Labmaster L1U08, four-bladed cruciform propeller operating at 350 rpm |
| pH | 9.1–9.5 | 9.1–9.5 |
| Water | Distilled and plant water | Plant water |
| Solid (%) | 10 (2 g sample) | 72 (1000 g sample) |
| Time (min) | 120 (except for kinetics) | 3 (except for kinetics) |

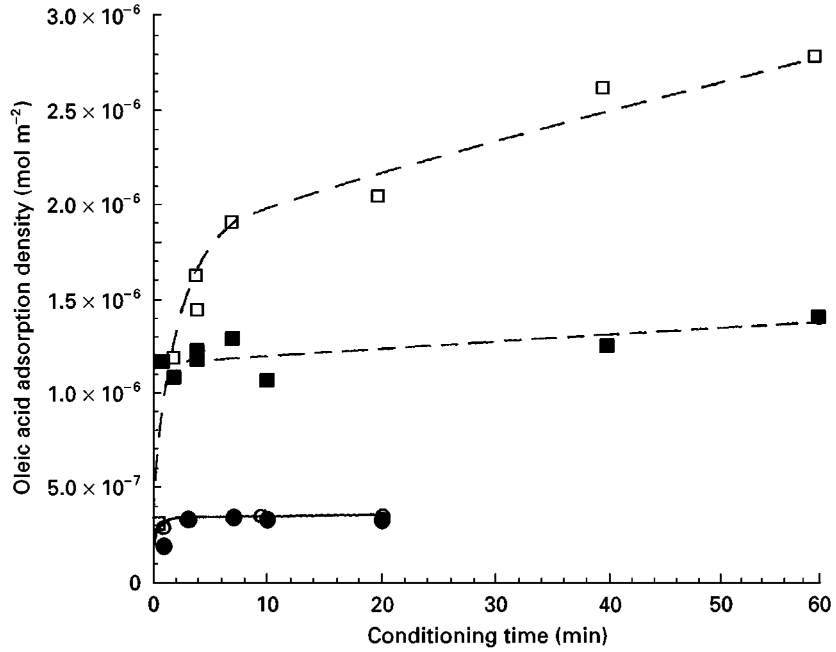

**Figure 10** Kinetics of oleic acid adsorption on francolite in distilled water and plant water under laboratory and plant conditions. Open squares, distilled water in laboratory conditions; filled squares, plant water in laboratory conditions; open circles, distilled water in plant conditions; filled circles, plant water in plant conditions. Oleic acid concentration: $8.1 \times 10^{-3}$ mol L$^{-1}$; pH 9.1–9.5. (From Maltesh C, Somasundaran P and Gruber GA (1996) Fundamentals of oleic acid adsorption on phosphate flotation feed during anionic conditioning. *Mineral and Metallurgical Processing* 13: 157.)

reagent in the water adsorbs. This will also result in a lower reagent concentration in solution reducing the precipitation eject. The intense agitation in the plant conditioner may also remove some of the bound reagent from the surface.

The adsorption isotherms of oleic acid on francolite under laboratory and plant conditions are compared in **Figure 11**. Adsorption is markedly higher under laboratory conditions than under plant conditions. On the other hand, under plant conditions the adsorption is similar in distilled water and plant water. This suggests that the effect of dissolved species is reduced under plant conditions.

From the above discussion, it can be seen that the adsorption of surfactant on a mineral is a complicated process involving interactions such as surfactant self-association, mineral dissolution, bulk precipitation, adsorption and surface precipitation. The interactions are further complicated by the kinetic effects of the various reactions.

Understanding the effect of the water chemistry on reagent adsorption offers opportunities to manipulate such processes by optimizing the contributing factors such as alteration of the surface properties, complexation of ions which cause precipitation of the surfactant, prevention or enhancement of collector adsorption and changes in the adsorption kinetics to achieve the desired selectivity in flotation.

In the anionic flotation of phosphate, $Ca^{2+}$ affects the grade of phosphate by activating the quartz through formation of calcium-bearing precipitates at high pH. This detrimental effect can be prevented by adding sodium silicate, which can interact with $Ca^{2+}$ and form calcium silicate. Since calcium silicate and quartz are negatively charged, detachment of calcium silicate from quartz can occur and thus quartz flotation can be depressed.

It has been found that in carbonate/phosphate systems, with fatty acid as collector, apatite is depressed in the acid medium (pH 5.5–6.0) while carbonate is floated. The depression of phosphate at this pH is possibly due to the adsorption (or formation) of aqueous $CaHPO_4$ on its surface, preventing surfactant ions from approaching the surface of the phosphate particles. Free $Ca^{2+}$ in solution can affect the formation of aqueous $CaHPO_4$. From thermodynamic considerations it can be predicted that the selective flotation of carbonates from phosphates in acid media can be enhanced by minimizing free $Ca^{2+}$ in solution and by increasing $HPO_4^{2-}$ in the system. This can be done by (1) decreasing free $Ca^{2+}$ concentration in the system to low values by adding suitable chemical reagents such as sulfuric acid or chelating agents such as oxalic acid, and (2) adding soluble phosphate salts to enhance the depression of the phosphate minerals. Results from experiments with

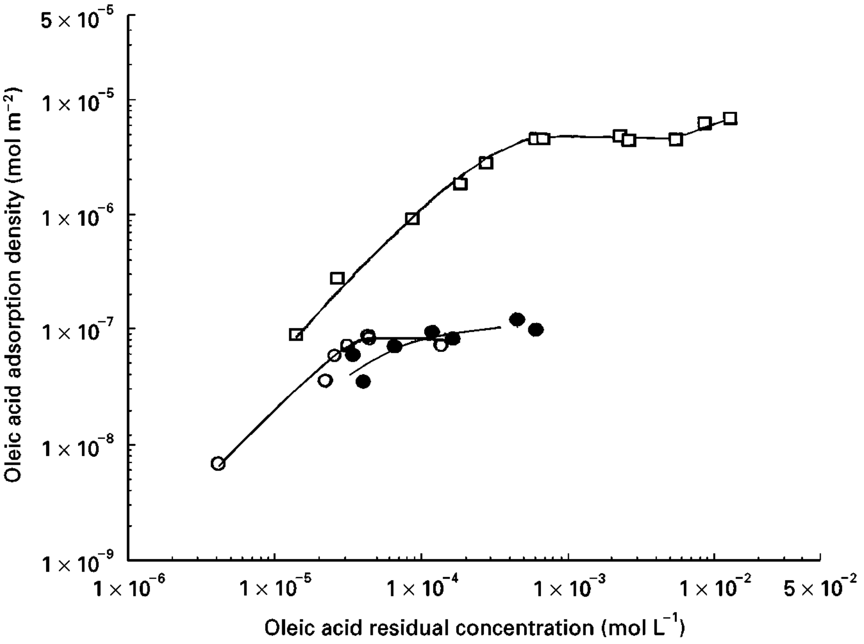

**Figure 11** Adsorption isotherms of oleic acid adsorption on francolite in distilled water and plant water under laboratory and plant conditions. Squares, distilled water in laboratory conditions; open circles, distilled water in plant conditions; filled circles, plant water in plant conditions. (From Maltesh C, Somasundaran P and Gruber GA (1996) Fundamentals of oleic acid adsorption on phosphate flotation feed during anionic conditioning. *Mineral and Metallurgical Processing* 13: 157.)

natural phosphate ores are in agreement with the theoretical predictions.

Based on the oleic acid solution chemistry, a two-stage conditioning process for the flotation of dolomite from apatite has been proposed. The mixed minerals are first conditioned at pH 10 with oleic acid collector. The system is then reconditioned below pH 4.5 where dolomite is floated. The selectivity of dolomite from apatite is attributed to two factors in this process.

1. High adsorption of oleate on dolomite during the first stage at pH 10, which is maintained after reconditioning at lower pH.
2. Oleate to oleic acid transformation upon reconditioning, reducing its efficiency, and this reduction being more severe for apatite than for dolomite.

In the high pH range, oleate adsorbs on to apatite and calcite through specific interactions, while at low pH, when oleic acid is the major species, the adsorption is through weaker physical interaction. Thus, oleic acid is a poor collector compared to oleate.

Modification of collector adsorption on minerals can be used to control their flotation response. In one study, Alizarin Red S, a dye that stains calcite, was tested as a modifying agent in calcite–apatite system due to its preferential adsorption on these minerals. Even though Alizarin Red S adsorbs more on apatite than on calcite, it depresses the flotation of apatite using oleate as collector more than that of calcite (**Figure 12**). In the absence of the dye, both calcite and apatite float with oleate at pH 10.5. When the dye concentration increases to $5 \times 10^{-6}$ mol m$^{-3}$, the flotation of calcite is very little affected with a recovery of about 90%, while apatite flotation is depressed to 5–10%. Calcite flotation is only affected at higher concentrations of dye. Alizarin Red S or its derivatives are hence promising reagents for the beneficiation of phosphate with carbonaceous gangues.

## Summary

Mineral–solution equilibria, surfactant–solution chemistry, as well as interactions among dissolved species, surfactant and solids, can have a drastic effect on surfactant adsorption and flotation separation of sparing soluble minerals. Studies on the effects of water chemistry on adsorption of surfactant on phosphate minerals such as apatite and francolite and associated minerals such as calcite and dolomite show that these interactions have marked effects on the reagent adsorption as well as flotation. Surfactant can exist in different forms in solution depending on the solution pH and the surfactant concentration. Minerals can undergo dissolution, with the extent of

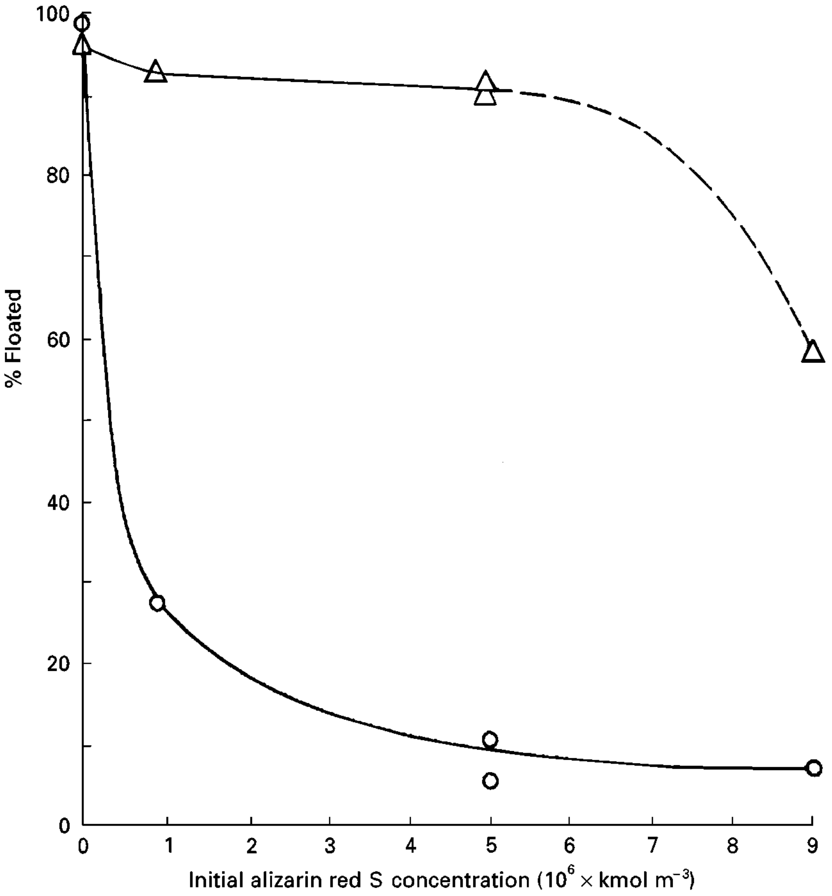

**Figure 12** Flotation of calcite (triangles) and apatite (circles) from their mixture (1 : 1) at pH 10.5 as a function of Alizarin red S concentration. Alizarin red S conditioning time = 1 min; K oleate = $9 \times 10^{-5}$ kmol m$^{-3}$; KCl = $3 \times 10^{-2}$ kmol m$^{-3}$; pH = 10.5 ± 0.2. (From Fu E and Somasundaran P (1986) *International Journal of Mineral Processing* 18: 287, with permission from Elsevier Science.)

dissolution depending upon solution conditions such as pH, ionic strength and concentration of constituent ions. The dissolved mineral species can further interact with mineral solids, leading to surface conversion of the minerals. They can also interact with surfactant, leading to surface and bulk precipitation. All these processes can significantly affect the adsorption of surfactant on minerals. A full understanding of the various interactions in surfactant–solid–solution system is essential for developing efficient separation schemes. Indeed, desired selectivity can be achieved by using appropriate additives to control dissolved species or modifying collector adsorption and by optimizing solution conditions as well as the kinetics involved.

## Acknowledgement

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# ION EXCHANGE

## Catalysis: Organic Ion Exchangers

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### Introduction

The ion exchange polymers most often used in catalysis are insoluble materials that can be constructed from inorganic or organic monomer units. This article will present only catalysis performed by the organic ion exchangers that are insoluble solids. There are commercial ion exchangers that are liquids, but to date they have been used very little in catalysis and, therefore, will not be included in this discussion.

Insoluble ion exchangers carry out their catalytic work in a heterogeneous rather than a homogeneous fashion and are, therefore, part of the group called heterogeneous catalysts. Heterogeneous catalysts have three very significant advantages over homogeneous catalysts: first, they are not corrosive; second, they are very readily separated from the reaction mixture by a simple filtration; and third, they are most often recyclable from one run to the next without any added treatment. Potentially, they suffer one major disadvantage over homogeneous catalysts. Intimate contact between reactants and the catalytic site is not achieved simply by mixing the heterogeneous catalyst with the reactants. In a stirred reactor, intimate contact between reactants and the homogeneous catalyst is very easily achieved and mass transport of reactants to catalyst is very rapid and almost never rate-limiting. With heterogeneous catalysis, mass transport of reactants to the catalytic site may often be the rate-limiting element, especially if the activation energy for the reaction is small and the chemical reaction is rapid. There are excellent texts and monographs on the issues surrounding heterogeneous catalysis, and the reader is referred to these for the development of a fuller understanding (see Further Reading).

### Nature of Organic Ion Exchange Polymers

#### Chemical Composition

Organic ion exchangers are made by polymerization of organic monomers into large molecules which are made insoluble by crosslinking with a polyfunctional monomer. The nature and the level (concentration) of