Advances in characterization of adsorbed layers and surface compounds by spectroscopic techniques

P. Somasundaran and J. T. Kunjappu

Abstract — Spectroscopic techniques are becoming increasingly popular for characterizing the interior of adsorbed layers of surfactants and polymers at solid-liquid interface as well as in the identification of compounds on mineral surfaces. This review encompasses the application of fluorescence and ESR spectroscopic techniques to reveal the microscopic environment of the adsorbed layers of surfactants and polymers on minerals with a special reference to the adsorption of anionic surfactants (e.g., sodium dodecyl sulfate) and polyelectrolytes (e.g., polyacrylic acid) at positively charged mineral (e.g., alumina) - water interfaces. Finally, the utility of XPS and auger techniques to identify the surface elemental composition of different mineral species has been related to their flotation efficiency.

Introduction

Ever since Langmuir laid the foundation of adsorption phenomenon of gases on solids (Langmuir, 1918), a great number of theories and experimental methodologies have revolutionized the domain of surface science, expanding the scope of Langmuir's discovery to the solid/liquid adsorption process, which plays a major role in industrial processes. For example, many processes such as flotation (Somasundaran, 1975) derive their efficacy from the modification of surface properties of solids owing to the adsorption of surfactants or polymers.

A molecular understanding of the structure of the adsorbed layer at the solid/liquid interface is essential for adsorption to the resultant processes. Such an understanding is considered necessary for improving these processes by manipulating the adsorbed layers for optimum configurational characteristics. However, until recently, methods of surface characterization were limited to measurement of macroscopic properties like adsorption density, zeta potential, flotation efficiency, etc. (Somasundaran et al., 1964; Hough and Rendall, 1983). Such studies, while helpful for developing insight into the adsorption mechanisms, could not provide any direct information on the microscopic characteristics of the adsorbed species. With the advent of spectroscopic and other allied techniques, the interior of the adsorbed layer has become accessible. These techniques answered many of the questions, on atomic and molecular levels, concerning the bonding of adsorbates onto surface sites of solid particles.

A variety of spectroscopic techniques are currently practiced in the area of surface science. To cite a few, the elemental nature of the surface could be characterized by X-ray photoelectron spectroscopy (Roberts, 1981) and auger spectroscopy (Czanderna, 1975), and its chemical state could be inferred from valence-level
In addition to *T. ferroxidans* and *T. thiooxidans*, many other bacteria have been reported to play a role in the leaching process although their activities are not significant from the point of metal solubilization. However, moderately thermophilic thiobacilli (Brierly and Lockwood, 1977) and sulfur-oxidizing *Sulfolobus* species (Marsh et al., 1983) have been successfully used in the leaching process.

The thermophilic thiobacilli can be isolated by enrichment in the conventional media described previously, the incubation temperature being 55°C and above.

The *Sulfolobus* species can be enriched on a sulfur-containing basal salts medium supplemented with 0.01% yeast extract. The medium pH is acidic (pH 2.0) and the incubation is at 100°C for several days.

Using the methods described, potentially useful iron- and sulfur-oxidizing bacteria were isolated from different ecosystems including ores, wastes, soils, acid-mine waters, etc., collected from various copper mining areas in India (Table 1). The major organisms isolated by enrichment techniques belonged to *T. ferroxidans* and *T. thiooxidans* species. In addition, a few thermophilic species like *Sulfolobus* species and thermophilic thiobacilli were also isolated. Starting from flask-level experiments, the process of copper leaching was systematically scaled up to a 300-kg level in PVC columns (Fig. 1).

<table>
<thead>
<tr>
<th>Table 1 — Microorganisms Isolated from Indian Copper Mines</th>
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<tbody>
<tr>
<td>Culture</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Thiobacillus ferroxidans</td>
</tr>
<tr>
<td>Thiobacillus thiooxidans</td>
</tr>
<tr>
<td>Thermophilic Thiobacillus sp.</td>
</tr>
<tr>
<td>Sulfolobus sp.</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

Preservation of cultures used in copper leaching

In laboratories around the world, cultures of *T. ferroxidans* and *T. thiooxidans* have been routinely maintained by serial transfers in their respective media every two months or so. This method has two limitations for long-term culture preservation. First, monthly transfer of cultures into fresh media is a laborious and time-consuming task, and, second, it is not possible to maintain the genetic uniformity of these cultures since thiobacilli presumably have mobile genetic elements (D.H. Holmes, personal communication).

Lyophilization or storage in liquid nitrogen are effective methods for preserving many types of microorganisms. However, thiobacilli cannot be stored effectively by these conventional methods. Hence, we have developed a novel method for their storage in which *T. ferroxidans* and *T. thiooxidans* cultures are mixed with sterile chalcopyrite ore and stored at 8°C (Gupta and Agate, 1986). This method has resulted in retention of the viability of these bacteria for prolonged periods (Table 2). In addition, we observed that such preserved cultures retained their copper extraction ability after one year's storage (Table 3) when the leaching experiments were carried out on an expanded scale in PVC columns (Gupta and Agate, 1986a).

<table>
<thead>
<tr>
<th>Table 2 — Activity check on selected cultures preserved by different methods and using different suspending media/carriers after storage for 12 months. Activity is expressed in percent loss in iron oxidation rate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacteria</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td><em>T. ferroxidans</em></td>
</tr>
<tr>
<td>MCM B-8</td>
</tr>
<tr>
<td>MCM B-185</td>
</tr>
<tr>
<td>MCM B-191</td>
</tr>
<tr>
<td>MCM B-231</td>
</tr>
<tr>
<td>MCM B-175</td>
</tr>
</tbody>
</table>

*Not possible to revive after storage for 4 months.*

<table>
<thead>
<tr>
<th>Table 3 — Leaching of Copper from Rakha Chalcopyrite Ore Using <em>T. ferroxidans</em> MCM B-231 in PVC Columns (75 kg Ore)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set</td>
</tr>
<tr>
<td>Fresh culture inoculum</td>
</tr>
<tr>
<td>Preserved culture inoculum</td>
</tr>
<tr>
<td>Unsterilized (positive) ore control</td>
</tr>
<tr>
<td>Chemically sterilized (negative) ore control</td>
</tr>
</tbody>
</table>
photoemission spectra and molecular vibrational spectra. Similarly, the local order or geometry could also be probed with vibrational spectroscopy, while the long-range order could be investigated by diffraction methods. Many of these techniques needed ultra-high vacuum and, hence, failed to yield in situ information on the adsorbed layer. But, some of the vibrational spectroscopic methods, e.g., IR (Hayden, 1987), Raman (Takenaka, 1979), etc., have been found to be particularly useful for elucidating the structure of the adsorbed layer under equilibrium conditions. Luminescence and electron spin resonance spectroscopic techniques with proven capabilities in the biological sciences (Weber, 1972; Ohnishi and McConnell, 1965) also find interesting applications in understanding the microstructure of adsorbed surfactants and polymers on solids.

Scope of the review

This review addresses the application of certain spectroscopic techniques for in situ characterization of adsorbed layers at solid/liquid interfaces. Most of the examples, viz., application of fluorescence, electron spin resonance (ESR), and X-ray photoelectron spectroscopies (XPS) are selected from authors' publications. Adsorption of two classes of materials — surfactants and polymers — is detailed to exemplify the validity of these spectroscopic methods. Sodium dodecyl sulfate (SDS) and polyacrylic acid (PAA) are selected as the adsorbates and alumina (Linde-Union Carbide, 0.3 μm, 15 m²/g) as the adsorbent.

While the fluorescence technique demonstrates the estimation of micropolarity, microviscosity, and aggregation number of the adsorbed layers, based on the fluorescence intensity and lifetime of pyrene and dinaphthyl propane probes, the ESR studies estimate the variation of microviscosities in the adsorbed layer as reported by 5-, 12-, and 16-doxylstearic acid spin labels. The conformational changes of polyacrylic acid in the adsorbed state with change in pH are monitored by making use of the excimer-forming ability of a pyrene-labeled polyacrylic acid. Finally, the importance of XPS (ESCA) in mineral engineering processes has been brought forth with reference to the surface characterization of some carbonate, phosphate, and sulfide minerals.

Adsorption of sodium dodecyl sulfate on alumina

As most of the spectroscopic applications cited in this review make use of the adsorbed layer of sodium dodecyl sulfate on alumina as a working model, it is expedient to be familiar with the features of the adsorption isotherm of SDS on alumina. Fig. 1a represents a typical isotherm of SDS on alumina at pH 6.5 and a salt concentration of 10⁻¹ kmol/m³. This isotherm is characterized by four regions, which are attributed to the different stages of adsorption. Results of zeta potential studies corresponding to these regions are depicted in Fig. 1b. Mechanically, these regions may be viewed as follows.

- Region I with a slope of unity under constant ionic strength conditions is indicative of the existence of electrostatic interaction between the anionic surfactant and the positively charged mineral.

- The conspicuous increase in adsorption in region II marks the onset of surfactant association at the surface through lateral interaction between hydrocarbon chains (this phenomenon is referred to as hemimicellization (Somasundaran and Fuerstenau, 1966)).

- Region III is marked by a decrease in the slope that is ascribed to the increasing electrostatic hindrance to the surfactant association process following interfacial charge reversal (see Fig. 1b).

- The plateau adsorption in region IV corresponds to the maximum surface coverage as determined by micelle formation in bulk or monolayer coverage, whichever is attained at the lowest surfactant concentration; further increase in surfactant concentration does not alter the adsorption density.

The surfactant aggregation process on the surface of a solid as described above has been generally accepted as a working hypothesis to explain the general pattern of the adsorption isotherm, though some modification of this treatment has appeared in literature (Harwell et al., 1985).

The exact nature of these aggregates, referred to as hemimicelles, could not be ascertained until spectroscopic techniques were applied to inquire into the details of the adsorbed layers. The succeeding sections delineate the utility of spectroscopic techniques to investigate the structure and, in some cases, evolution of adsorbed layers.
Fluorescence spectroscopic studies

Subsequent to absorption of light by a molecule, a part of the light may be emitted radiatively from its first singlet excited state. This phenomenon, called fluorescence emission, bears a wealth of information regarding the environment of the light-absorbing species. Parameters of fundamental importance in fluorescence emission are (1) emission maximum (wavelength of maximum emission intensity), (2) quantum yield of fluorescence (emission efficiency as measured by the intensity of fluorescence), and (3) fluorescence lifetime (time taken by the excited state to decay to 1/e of its initial value, e being the base of natural logarithm).

They are quantitatively related to various experimental parameters by the following expressions.

\[ I_f = I_o (1 - 10^{-c t}) \frac{\Phi_f}{e} \]

where \( I_f \) is the fluorescence intensity, \( I_o \) the intensity of the incident light, \( c \) the molar absorptivity, \( e \) the molar concentration of the solute, \( t \) the path length of the sample, and \( \Phi_f \) the quantum yield of fluorescence.

\[ I_{f(t)} = I_{f(0)} \exp^{-t/\tau} \]

where \( I_{f(0)} \) is the initial fluorescence intensity at time \( t = 0 \), \( I_{f(t)} \) the fluorescence intensity at a given time \( t \), and \( \tau \) the average lifetime of the excited singlet state.

The fluorescence measurements are generally carried out by a steady-state fluorescence spectrofluorometer and lifetime of fluorescence by a time resolved fluorescence lifetime instrument (Lakowicz, 1983). The dependence of fluorescence intensity and lifetime on the physicochemical environment of the fluorescing molecule has been well documented (Thomas, 1984). Such data have been applied to micellar photophysics and photochemistry to study the properties of micelles and also to understand micellar catalysis (Turro et al., 1985). Application of the foregoing technique to the adsorbed layer of surfactants on solids can provide information on the interior of the adsorbed surfactant layers on solids at the solid/liquid interface under in situ conditions. We now proceed to describe the application of the foregoing solution phase methodology to probe the micropolarity, microfluidity, and aggregation number of adsorbed surfactant layers.

**Micropolarity**

Here, advantage is taken of the fact that the polyaromatic hydrocarbon, pyrene, possesses a highly structured fluorescence spectrum whose vibrational lines are susceptible to intensity fluctuations brought on by the polarity changes of the medium. A properly resolved fluorescence spectrum of pyrene in fluids has five vibrational fine structures in the region from 370 to 400 nm. The intensities of first (\( I_1 \)) and third (\( I_3 \)) vibrational bands are found to be particularly dependent on the polarity of the environment. Thus, \( I_1/I_3 \) value for pyrene changes from -0.6 in water to a value of greater than unity in hydrocarbon media.

\( I_1/I_3 \) values for pyrene were determined for alumina/SDS/water systems for various regions of the adsorption isotherm. The data are shown in Fig. 2, which is marked by an abrupt change in the local polarity of the probe from an aqueous environment to a relatively nonpolar micelle-type environment. This abrupt change occurs in a region that is well below the CMC and approximately coincides with the transition in the adsorption isotherm from region I to II. At the plateau region, the \( I_1/I_3 \) value coincides with the maximum \( I_1/I_3 \) value for SDS solutions (Fig. 2a), indicating the completion of aggregation on the surface. It may be observed that the \( I_1/I_3 \) values of pyrene are relatively constant (-1) throughout most of region II and above and, hence, seem to be independent of surface coverage. Thus, fluorescence studies provide a means to measure the micropolarity of the adsorbed layers.

The fact that pyrene in small concentrations does not perturb hemimicelle formation can be seen from the adsorption isotherms in Fig. 1a.

**Microviscosity**

To obtain the microfluidity changes, the excimer-forming ability of 1,3-dinaphthyl propane (DNP) is utilized. The intramolecular excimer formation of DNP is a sensitive function of the microviscosity of its neighborhood. This property, expressed as the ratio of the yields of monomer and excimer (\( I_m/I_e \)), is determined in solution and in the adsorbed layer (Somasundaran et al., 1986) for various regions of the adsorption...
This model yields the following relation for the time dependence of monomer emission.

\[
I_{m(t)} = I_{m(0)} \exp\left[\frac{k_0}{n} t + \bar{n} \left(\exp\left(-k_e t\right) - 1\right)\right]
\]

where \(k_0\) is the reciprocal lifetime of excited pyrene in the absence of excimer formation, \(k_e\) is the intramicellar encounter frequency of pyrene in excited and ground states, and \(I_{m(0)}\) and \(I_{m(t)}\) represent the intensity of monomer emission at zero time and time \(t\).

Knowledge of \(\bar{n}\) leads to the aggregation number \(N\) for the adsorbed layer as given by the expression

\[
\bar{n} = \frac{[P]/[A_{gg}]}{([S] - [S_{eq}])}
\]

where \([P]\) is the total pyrene concentration, \([A_{gg}]\) is the concentration of aggregates, and \(([S] - [S_{eq}])\) is the concentration of adsorbed surfactant.

A kinetic analysis based on this relation was carried out from the decay profiles of pyrene in the adsorbed layer (Chandar et al., 1987) for different regions of the Al\(_2\)O\(_3\)/SDS adsorption isotherm. Figure 4a represents typical decay curves for monomer (curves A and B) at two pyrene levels and excimer (curve C) corresponding to curve B. The fluorescence spectra of these two cases are represented in Fig. 4b.

The aggregation number was calculated from \(\bar{n}\) using the foregoing equation. The SDS aggregation numbers thus obtained are marked on the adsorption isotherm in Fig. 5. The aggregates in region II appear to be relatively of uniform size (121 to 128). But in region III, there is a marked growth in the aggregate size (166 to 356). These results are of special significance with respect to the evolution and structure of the adsorbed layer. Region II and above seem to be characterized by surfactant aggregates of limited size. Here, the surface is still not fully occupied and enough positive sites are available (Fig. 1b). Further adsorption occurs mainly by increasing the number of aggregates as
revealed by a near constant aggregation number. The transition from region II to III corresponds to the isoelectric point of the mineral, and adsorption in region III is likely to occur through the growth of existing aggregates rather than the formation of new ones. This is possible by the hydrophobic interaction between the hydrocarbon tails of the already adsorbed surfactant molecule and the unadsorbed ones. Such a situation can be expected to result in a reverse orientation of the surfactant molecules as illustrated in Fig. 6, where the whole process of adsorption has been portrayed schematically.

The fact that the aggregation number in region II essentially remains the same suggests that adsorption in this region occurs by increasing the number of aggregates on the positive sites of the particle. When the positive charge on the mineral is neutralized, the energetics favors the growth of existing aggregates rather than the formation of new aggregates. Thus, in region III, the size of aggregates increases significantly with adsorption density ($N > 166$).

**Fig. 4a** — Pyrene monomer and excimer decay profiles in SDS micellar solution, [SDS] = $8.2 \times 10^{-2}$ kmol/m$^3$; [NaCl] = $1 \times 10^{-2}$ kmol/m$^3$; CMC = $1.5 \times 10^{-3}$ kmol/m$^3$; pyrene levels are indicated as the ratio of micellized SDS to added pyrene (emission monitored at 383 nm for monomer and 480 nm for excimer); (A) monomer emission for SDS/PY = 2160, (B) monomer emission for SDS/PY = 108, (C) excimer emission for SDS/PY = 108.

**Fig. 5** — Surfactant aggregation numbers determined at various adsorption densities (average numbers at each adsorption density shown along isotherm).

In summary, these studies on the adsorbed layer of SDS on alumina establish the earlier concepts of hemimicellization. Surfactant aggregation occurs above a critical concentration referred to as hemimicellar concentration, which is marked by a sharp increase in the adsorption isotherm, eventually leading to the formation of highly organized and finite size assembles even at relatively low surface coverages.

**Fig. 6** — Schematic representation of the correlation of surface charge and the growth of aggregates for various regions of the adsorption isotherm depicted in Fig. 5.
Polymer conformation in the adsorbed state

The adsorption of polymeric materials onto solid surface is quite different from the adsorption of small molecules (Morawetz, 1975). This difference stems from the existence of polymers in different sizes and conformations. In addition, macromolecules possess multifunctional groups, each having the potential to adsorb on a surface.

Of the polymeric materials finding a variety of applications, polyelectrolytes stand out because of their participation in many biological processes (Lipatov and Sergeeva, 1974) involving globular proteins and other biopolymers. Polyelectrolytes, e.g., polyacrylic acid, also have importance in understanding and controlling the processes of colloidal stabilization and flocculation, which have immediate application in energy-related areas like enhanced oil recovery and in other fields such as paint formulation and solid-liquid separation processes.

Polyacrylic acid can exist in different conformations depending on the solvent, pH, and ionic strength conditions (Arora and Turro, 1987). Such a flexibility would influence the adsorption of macromolecules from solution onto solids and, in turn, would affect the dispersion behavior of suspensions. We have used a pyrene-labeled fluorescent polyacrylic acid to investigate the adsorbed polymer conformations at the solid-liquid interface of alumina in water (Chandar et al., 1987a) (1.5 mole% of pyrene-bearing moiety; molecular wt 40,000; degree of polymerization ~510).

The rationale behind the implementation of this technique is the observation that the extent of excimer formation, which depends on the interaction of an excited state pyrene of polymer pendant group with another pyrene group in the ground state, has a direct bearing with the polymer conformation. This may be understood with reference to Fig. 7a, which shows that, at low pH, there is a better probability for intramolecular excimer formation between pyrene groups resulting from a favorable coiled conformation. Similarly, a low probability for the excimer formation at high pH may be understood as a consequence of repulsion between highly ionized carboxylate groups in the polymer and the subsequent stretching of the polymer chain. This difference is discernible in their fluorescence spectra (Fig. 7b).

The foregoing methodology was applied to the adsorbed layer of pyrene-labeled polyacrylic acid (PPAA) to investigate the polymer conformations in the adsorbed layers on alumina. It was observed that adsorption of PPAA from aqueous solution onto positively charged alumina was rapid enough so that the adsorbed polymer adopted a conformation that reflected its state in solution prior to adsorption. This is represented in Fig. 8, which shows similar monomer/excimer ratio curves as a function of pH for the solution and the adsorbed cases. Further, it was observed that the polymer adsorption at high pH is an irreversible process with respect to the conformation, as the efficiency of excimer formation remained unaffected by the change of pH to acidic values. At the same time, the polymer adsorbed at low pH could be stretched to some extent by increasing the pH. These processes are represented mechanistically in Fig. 9.

Fig. 7b — Fluorescence emission spectra of adsorbed polymer at two pH values.

Fig. 8 — Monomer to excimer ratio as a function of pH for aqueous solution of polymer and adsorbed polymer on alumina.

Electron spin resonance studies (ESR)

ESR studies as applied to micellar systems rely on the sensitivity of a free radical probe to respond to its microenvironment. Molecular species with a free electron possess intrinsic angular momentum (spins), which in an external magnetic field undergoes the Zeeman splitting. For a system with \( S = \frac{1}{2} \), two Zeeman energy levels are possible whose energy gap \( \Delta E \) is given by the equation:

\[
E = h\nu = gBH
\]

where \( g \) is a proportionality constant, \( B \) is the Bohr magneton (natural unit for the magnetic moment of the electron), \( H \) is the applied magnetic field, and \( \nu \) is the frequency of electromagnetic radiation corresponding to \( \Delta E \), which causes resonance absorption. The position of an absorption line is generally specified by the \( g \) value.
The magnetic moment of the free electron is susceptible to secondary magnetic moments of neighboring nuclei. Thus, the Zeeman splitting will be superimposed by the effect called hyperfine splitting, which brings further splitting of the absorption signal. The separation between the hyperfine line is an indicator of the nuclear neighborhood about the free electron. The hyperfine splitting pattern depends on the spins and actual number of the neighboring nuclei with spins. If the electron is in the field of a proton \( (S = 1/2) \), then the ESR spectrum would yield two lines of equal intensity. Similar interaction by a nucleus with \( S = 1 \), as in nitrogen, would produce a triplet of equal intensity.

The line shape of ESR signals is subject to various relaxation processes (Wertz and Bolton, 1986) occurring within the spin system (spin-lattice and spin-spin relaxations) as well as anisotropic effects (due to the differently oriented paramagnetic centers being acted upon by an external magnetic field). These effects result in broadening of the spectral lines.

Three types of ESR studies may be applied to the micellar systems (Raney, 1977). They are spin-probing, spin-labeling, and spin-trapping techniques. In the spin-probing technique, a molecule with a spin is externally added to the system, whereas in the spin-labeling technique, a spin-bearing moiety through covalent bonding forms a part of the molecule. The spin-trapping technique is mainly applied in the identification of radicals produced thermally, photo-chemically, or radiolytically by trapping the radical through chemical reactions with a spin-trap (a molecule like t-butyl nitroxide) and converting the radical into a stable free radical to be examined by ESR technique.

In the study under review, stable free radical nitroxide spin labels were chosen for use of electron spin resonance spectroscopy. They were the three isomeric doxylstearic acids bearing the doxyl groups at positions 5, 12, and 16 of the stearic acid chain. Their molecular structures may be represented as follows:

\[
\begin{align*}
&\text{16-doxyistearic acid (16-D)} \\
&\text{12-doxyistearic acid (12-D)} \\
&\text{5-doxyistearic acid (5-D)}
\end{align*}
\]

These spin labels (in micromole levels) were co-adsorbed individually on alumina along with the main adsorbate, viz., sodium dodecyl sulfate, and the main regions of the adsorption isotherm were studied.

Information on micropolarity and microviscosity of the environment was obtained by measuring the hyperfine splitting constant \( A_H \) and rotational correlation time \( \tau_r \). For this, the ESR spectra of 5-D, 12-D, and 16-D were recorded in water, ethanol, and ethanol-glycerol mixtures. Ethanol-glycerol mixtures served as calibration standards to monitor the viscosity changes within the matrices of interest, viz., micelles and hemimicelles. Figure 10 represents the ESR spectra of 16-D in different ethanol-glycerol mixtures. The three-line isotropic spectrum of 16-D in pure ethanol \((n = 1 \text{ Cp})\) considerably broadens as the glycerol content of the ethanol-glycerol mixture is increased, imparting anisotropic features to the system due to the decreasing mobility of the spin label.

The rotational correlation time for the three spin labels are depicted in Fig. 11 for different solvent viscosities. It may be seen that although the \( \tau_r \) values increase with increasing solvent viscosity, their magnitude is different for different probes. This is attributed to the difference in the entropy of internal rotation of the probes.

Before applying the methodology to \( \text{Al}_2\text{O}_3/\text{SDS} \) adsorbed layers, it is beneficial to examine the ESR spectral changes observed in SDS solution (Fig. 12). The nitrogen hyperfine splitting constants \( (A_H) \) and rotational correlation times in these cases are listed in Table 1. It is obvious that all the probes experience a waterlike atmosphere as could be seen from \( A_H \) values, comparable to the value of 16.0G in pure water. Microviscosities could be evaluated by comparing the ESR spectra in micelles and in ethanol-glycerol mixtures. The fact that the spectral features of these probes matched well with the ESR spectra of these probes in an ethanol-glycerol mixture \((40:60 \text{ v/v}; \ n = 40 \text{ Cp})\) shows that the nitroxide groups of the probes feel the same environment as indicated earlier by the polarity parameter \( A_H \).

Figure 13 gives a comparative picture of the ESR spectra of 16-D in \( \text{Al}_2\text{O}_3/\text{SDS} \) hemimicelles, SDS micelles, and various ethanol-glycerol mixtures with respect to their estimated rotational correlation time \( \tau_r \). The hemimicellar case reported a nitrogen hyper-
fine splitting value of 15.0 G, indicating a less polar environment in hemimicelles (\(A_N\) in water = 18.0 G, \(A_N\) in ethanol = 14.6 G, and \(A_N\) in SDS micelles = 15.6 G). Three different microviscosities were obtained for the probes in hemimicelles, indicating that the nitroxide group in each case felt a different viscosity within the hemimicelle. Figure 14 depicts the ESR spectra of the three probes in hemimicelles and the corresponding ESR spectra simulated in ethanol-glycerol mixtures of appropriate viscosities. The estimated values of viscosities were 120, 180, and >800 Cp for 16-, 12-, and 5-D, respectively.

![Fig. 10 - ESR spectra of 16-doxylstearic acid (16-D) in ethanol-glycerol mixtures.](image)

Fig. 10 - ESR spectra of 16-doxylstearic acid (16-D) in ethanol-glycerol mixtures.

![Fig. 11 - Rotational correlation times of 5-, 12-, and 16-doxylstearic acid as a function of viscosity of ethanol-glycerol mixtures.](image)

Fig. 11 - Rotational correlation times of 5-, 12-, and 16-doxylstearic acid as a function of viscosity of ethanol-glycerol mixtures.

![Fig. 12 - ESR spectra of 5-, 12-, and 16-doxylstearic acid in SDS solutions below (A) and above CMC (B).](image)

Table 1 - Nitrogen Hyperfine Splitting Constant and Rotational Correlation Times of 5-, 12-, and 16-Doxylstearic Acid in SDS Solutions Below and Above CMC

<table>
<thead>
<tr>
<th>Probe</th>
<th>(A_N), gauss</th>
<th>(T_{\text{corr}}), sec</th>
<th>(A_N), gauss</th>
<th>(T_{\text{corr}}), sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>16-D</td>
<td>16.0</td>
<td>1.5 x 10^{-10}</td>
<td>15.6</td>
<td>4 x 10^{-10}</td>
</tr>
<tr>
<td>12-D</td>
<td>15.8</td>
<td>1.7 x 10^{-10}</td>
<td>15.4</td>
<td>18 x 10^{-10}</td>
</tr>
<tr>
<td>5-D</td>
<td>15.8</td>
<td>2.0 x 10^{-10}</td>
<td>15.4</td>
<td>15 x 10^{-10}</td>
</tr>
</tbody>
</table>

![Fig. 13 - Comparison of ESR spectra of 16-doxylstearic acid in hemimicelles, micelles, and ethanol-glycerol mixtures and corresponding rotational correlation times and corresponding viscosity.](image)

Fig. 13 - Comparison of ESR spectra of 16-doxylstearic acid in hemimicelles, micelles, and ethanol-glycerol mixtures and corresponding rotational correlation times and corresponding viscosity.
nitrone spin probes demonstrated to be a facile method for probing microenvironments within hemimicelles.

**X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), and auger electron spectroscopy (AES)**

XPS (ESCA) and AES are two complementary spectroscopic techniques proven to be effective in establishing surface elemental composition. ESCA can even distinguish the electronic structure, the oxidation state, and bonding of atoms of the element (Selbahn, 1967). Characterization of surfaces by these techniques has found beneficial use in mineral engineering processes involving the complex phenomena of flotation, selective flocculation, etc., as well as in semiconductor technology to characterize the dopants.

Briefly, XPS takes advantage of the fact that monoenergetic X-rays [Mg(Kα), Al(Kα); >1000 eV], on impinging a surface, dislodge the inner electrons of surface elements producing photoelectrons. These electrons are sorted out in an electric field according to their kinetic energies. The kinetic energy of the photoelectrons depends on the binding energy of the shell electrons, which is discreet and easy to associate with an element. XPS can view a surface region of up to 100 Å in depth. The peak position and the peak intensity provide qualitative and semiquantitative information about the identity of the element.

In AES, high energy electrons form the irradiation source, and the emitted secondary electrons (auger electrons) are analyzed as in XPS. But in AES, the chemical shift effect (the change in the peak position of an element due to change in chemical environment) is not as pronounced as in XPS. Another advantage of XPS over AES is that the high energy electron beam used in AES can cause more surface damage than X-rays used in XPS. However, both the methods, being high vacuum techniques, can give information only under ex-situ conditions.

We have applied these techniques for characterizing some mineral surfaces. Information gathered from these, coupled with that from morphological studies with scanning electron microscopy (SEM), has been helpful in revealing surface chemical composition (Roussev and Somasundaran, 1986; Somasundaran and Moudgil, 1979; Kulkarni and Somasundaran, 1976). For instance, grinding of litharge with sulfur can change the morphology of the particles as shown by SEM. This is attributed to the formation of galena on the litharge surface (Roussev and Somasundaran, 1986). Direct proof for the latter hypothesis is obtained from XPS, which can identity sulfur on the surface in the sulfide form.

Application of XPS in a surface science laboratory may commence with the examination of solids for purity prior to experimentation. This may be illustrated with the calcite-apatite system. Since the binding of one mineral on the other can be expected to have detrimental effects on the selective flotation of these minerals, they were studied individually after treatment in the supernatant of the other. Figure 16 shows the XPS spectra of pure calcite and apatite. The absence of any extraneous peaks is an indication of the purity of these minerals.

The effect of calcite supernatant on apatite at pH 11 may be understood with reference to Fig. 17, where its XPS spectrum is compared with the XPS spectra of individual minerals in water under identical conditions. The former spectrum contains the features of

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**Fig. 14** — ESR spectra of 5-, 12-, and 16-doxylstearic acid in SDS adsorbed layer and equivalent spectra obtained in ethanol-glycerol mixtures of indicated composition.

**Fig. 15** — Schematic representation of hemimicelle structure showing flexibility of chain segments as reported by nitroxide of doxylstearic acid in 16th position (a) and 5th position (b).

This work is the first reported indication of variations in microviscosity within a hemimicelle as estimated by any known technique (Waterman et al., 1986; Chandar et al., 1987b). Thus, ESR spectroscopy with nitroxide spin probes is demonstrated to be a facile method for probing microenvironments within hemimicelles.
the latter, suggesting the formation of a layer of CaCO₃ on the surface of the apatite. But the CaCO₃ layer may be less than 100 Å since features of apatite also are obvious in the XPS spectrum and since XPS cannot see through more than the 100 Å thick layer of the surface. This observation is reinforced by the fact that the phosphorous peak in apatite is reduced in intensity as a result of its surface coverage by CaCO₃. This is represented in Fig. 18. The effect of carbonate species alone in the supernatant of the foregoing system makes an interesting case study. Earlier experiments (Amankonah, 1985) based on electrokinetics, dissolution behavior, and equilibrium pH of the system indicated that the effect of carbonate addition to the aqueous supernatant was to convert the apatite surface into calcite under high pH conditions. XPS results shown at different K₂CO₃ concentrations reveal that carbon 1s peak of apatite, due to K₂CO₃ addition, is transformed into carbonate as if it were in a calcite environment. This is shown in Fig. 19.
XPS spectrum of chalcopyrite conditioned in pentlandite supernatant and rinsed with water showed that nickel ions can be found on the surface of chalcopyrite. This is shown in Figs. 20 and 21, which show XPS spectra of pure chalcopyrite and chalcopyrite conditioned in pentlandite supernatant. On the other hand, spectrum of pentlandite conditioned in chalcopyrite supernatant and rinsed with water also showed that copper is present on the pentlandite surface (Figs. 22 and 23).

Treatment of millerite with FeCl₂ solution shows that ferrous ions are electrostatically adsorbed onto the millerite surface. These are depicted in Figs. 24 and 25. Similarly, millerite conditioned with CuCl₂ solution gives evidence for the adsorption of copper on millerite. Other minerals also showed comparable behavior: covellite treated with FeCl₂ showed iron in covellite spectrum; covellite conditioned with NiCl₂...
gave evidence for nickel in covellite spectrum; pyrrhotite spectra after conditioning with CuCl₂ and NiCl₂ solutions and rinsing gave evidence, respectively, for copper and iron on the surface of pyrrhotite.

These observations have direct bearing on the flocculation behavior of minerals. This may be elaborated for the case of millerite. Flocculation of millerite with polyethylene oxide is enhanced by CuCl₂. On the basis of the foregoing discussion, one can understand this behavior as due to the formation of the partly hydrophobic covellite on the surface of millerite.

In conclusion, XPS studies along with other measurements show that dissolved mineral species can interact with the mineral surface, causing surface conversions and thereby drastic alteration of their behavior in processing systems. Moreover, such studies can assist in controlling and regulating the reagents used in mineral processing.

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Fig. 24 — XPS spectrum of millerite.

Fig. 25 — XPS spectrum of millerite conditioned in 10⁻² kmol/m³ FeCl₂ · 4H₂O.
Applications of chelating agents in mineral processing

Pradip

Abstract Chelating agents, because of their metal specificity, can function as effective mineral processing reagents. A brief review of the work carried out in this area is presented. Some of the salient features of mineral flotation and flocculation with chelating-type reagents, such as bulk vs. surface chelation, the role of pH, mineral solubility, solution chemistry of reagents, and temperature, are illustrated with appropriate examples. The problems associated with the commercialization of chelating reagents for ore beneficiation and the research efforts required in this area are also discussed.

Introduction

Froth flotation is one of the most widely used separation processes for beneficiating low-grade ores. The key element responsible for the success of a flotation separation flowsheet is the choice of the reagent combination (collector-activator-depressant) used for achieving the desired selectivity. With steady depletion of rich and medium-grade ores, the exploitation of more complex and disseminated ore reserves has become essential. This calls for innovative means of concentrating desired minerals at relatively finer sizes and/or separating them from a number of associated minerals having similar surface properties. Flocculation separation in such complex ore systems is possible only with highly selective collectors.

A promising technology for achieving mineral separation at a substeve size range of particles has recently been developed. The process, known as selective flocculation, is based on the preferential adsorption of a polymeric flocculant on the desired mineral surface causing its aggregation while leaving the remainder in suspension. The success of a selective flocculation scheme largely depends on a judicious choice of a flocculant-dispersant combination. Except for the successful use of starches in beneficiating low-grade taconites at Cleveland Cliffs, the work carried out thus far with commonly available reagents has not shown encouraging results (Yu and Attia, 1987). Efforts are underway to design, synthesize, and test new or modified polymers having desired functional groups for specific applications.

The basic surface chemical principles underlying both these processes, namely flotation and selective flocculation, are very similar. The selectivity of separation in either case is primarily controlled by the selective adsorption of reagents at the mineral/water interface. It is essentially a function of the affinity of the reagent functional groups for the adsorption sites on the mineral surface. Chelating-type functional groups, because of their high specificity toward certain metal ions, thus appear to be ideal constituents of mineral processing reagents.

A number of successful attempts have been reported on developing tailor-made reagents with chelating functional groups for specific applications. In this paper, the published work on the application of chelating reagents in mineral processing has been reviewed, with special emphasis on identifying certain common trends observed in such systems. The ultimate objective of researchers in this area still remains to be the development of a comprehensive theory that can help practicing engineers to a priori select the appropriate reagent combinations for the particular separation problem at hand.

Chelating agents and chelation

A chelate-forming reagent must have at least two atoms that can be coordinated by the metal at the same time. Such atoms are usually oxygen, nitrogen, sulfur, and phosphorus. The "coordinating" species providing these donor atoms is known as the "ligand." When more than one atom of a single ligand molecule or ion interacts with the metal ion, it may be presumed to bend itself pincerlike around the central atom to form a complex ring structure called a "chelate" (from the Greek for claw). The ligands are referred to as bidentate, tridentate, tetradentate, pentadentate, or hexadentate according to their respective attachments in two, three, four, five, or six positions in the sphere of coordination around a positively charged metal ion. An example of (1:2) chelation of a bidentate S-S type ligand of the diethyl dithio carbamate reagent with nickel is shown below. Here, all the four Ni-S bonds are equivalent, and, therefore, the chelate ring has a flat, square-shaped configuration (Zolotov, 1970).

![Chelate Structure](image)

Chelating agents can be classified on the basis of donor atoms involved (O-O, N-O, N-N, S-S, N-N) or ring size (4-, 5-, or 6-membered) or charge on the complex (anionic, cationic, or neutral) or the number of bonds to the metal for every chelating molecule (Somasundaran and Nagaraj, 1984). To form chelate compounds, the reagent must have at least one active group with a mobile hydrogen atom (acid group) that is substituted by the metal during compound formations. Examples of such groups are -OH, -COOH, -SO$_3$H, -AsO$_3$H$_2$, -PO$_4$H$_2$, -NH, -NH$_3$, -NOH, and -SH. The other groups may be acidic or, more often, basic, usually groupings like =O, =OH, =O-, =N, =NH$_2$, =NOH, =S, =S-. The locations of these groups in the chelate molecule should allow formation of at least one closed ring (Zolotov, 1970).

Selectivity of chemical groups in chelation

There have been a number of monographs published on the stability of chelate compounds and the factors governing the specificity of certain chemical groups for cations (Martell and Calvin, 1952; Ballar and...