



# A Century of Research Leading to Understanding the Scientific Basis of Selective Mineral Flotation and Design of Flotation Collectors

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Received: 10 December 2018 / Accepted: 18 December 2018 / Published online: 15 January 2019  
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## Abstract

The design and development of selective flotation collectors has been the key to the remarkable success of flotation in beneficiating complex, difficult-to-process ores. Sustained research efforts in the field over the past hundred years have led to delineating the scientific basis of selective mineral flotation in terms of the crystal chemistry and the surface and colloid chemistry of minerals including their solubility, and the aqueous solution chemistry of added reagents. It is now well-established that the electrical double layer theory (EDL) is the most powerful means of quantifying the relative strength of mineral-reagent interactions in the case of nonsulfide minerals. We illustrate the utility and the power of the EDL in delineating the science underlying selective mineral flotation with the help of a few examples taken from our own work, in particular on the selective flotation of rare-earth minerals (bastnaesite) from associated semisoluble minerals (barite and calcite) using alkyl hydroxamate collectors and the flotation separation of lithium-containing minerals (spodumene) from associated alumino-silicate minerals with oleate (fatty acids). Both of these mineral separation systems are of contemporary research interest and of immense value to the industry today. Recent advances in utilizing molecular modeling computations, particularly in the context of quantifying the effect of crystal chemistry and the relative distribution of adsorption sites available on mineral cleavage planes, are also reviewed.

**Keywords** Molecular modeling · Flotation reagents design · Surfactants · Electric double layer · Spodumene flotation · Bastnaesite flotation · Hydroxamate · Oleate · Zeta potential

## 1 Introduction

Froth flotation is the single most important unit operation in mineral processing. One can selectively float any mineral from associated minerals in an ore provided an appropriate reagent is designed to make the given mineral surface, selectively and sufficiently hydrophobic so that it can attach to bubbles in the flotation cell and thus be collected in the froth layer. The advent of flotation separation, more than a century ago, revolutionized the mining industry since it led to the

possibility of a beneficiating complex, difficult-to-process ores, which were not amenable to successful separation by other known techniques such as gravity separation. Today about two billion tons of ore are concentrated successfully by flotation. In this communication, we briefly review the major advances made in the surface/colloid chemistry of flotation in the context of challenges confronting the industry today.

We are living in an exciting digital era. With the advent of cloud computing and social media on the one hand and rapid advances being made in several research areas of interest to us in the minerals and metals industry, such as artificial intelligence (AI) and machine learning, robotics, unmanned vehicles, including drones, big data analytics, 3D printing, sensor technologies, electricity based on renewable energy sources, and internet of things (IoT), many disruptive transformations in our industry are on the horizon. Recent advances in information technology (IT) and knowledge engineering, in combination with appropriate domain expertise, that is, our enhanced understanding of the underlying science of mining and mineral processing operations and the availability of a

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variety of powerful modeling/simulation tools make it possible to address the challenging problems facing the mining and mineral processing industry in an integrated manner. But that is not the topic of our discussion in this paper. It is important to emphasize that these phenomenal developments in the digital technologies are possible only if we possess the ability to produce the critical minerals, metals, and materials required for the electronic and computing hardware needed to sustain information technology. That is where the mineral engineers will have to innovate and meet the emerging challenges in the coming decades.

Another revolution in the making is the availability and affordability of electricity based on renewable sources of energy. Even though more work needs to be done to develop appropriate energy storage solutions including large batteries, the anticipated disruptive transformation of electricity based on non-fossil fuel sources must be recognized. The mining and mineral processing industry will play a crucial role in the impending transition of our society from fossil fuels as a source of energy to that of electricity based on renewables, such as solar, wind, and biomass. This transition will result in a remarkable increase in demand for some metals, for example, aluminum, copper, lithium, manganese, nickel, silver, steel, zinc, cobalt, molybdenum, rare-earths, and graphite [1]. As an illustration, lithium-ion batteries (requiring lithium, nickel, cobalt, manganese and graphite) are currently being used on a commercial scale, for all kinds of applications including batteries for electric vehicles. The commercialization of vanadium flow batteries for large-scale energy storage is on the horizon. Rare-earth magnets (requiring neodymium, dysprosium, and praseodymium) are needed for the production of modern wind turbines as well as all-electric transportation vehicles [2, 3].

The global race for exploration, acquisition, and development of new resources for meeting the projected demand for such elements is already on. New ways of beneficiation, extraction, and processing will have to be invented to produce these elements at an affordable cost. Furthermore, with electricity becoming available at a more affordable price, the extraction of various elements from minerals (reduction of oxides, for example, to produce corresponding metals—rare-earths, iron, titanium, etc.) will increasingly be based on molten salt electrolysis [4–6]. Novel recycling technologies will have to be invented to meet the needs of the industries in the coming decade [7, 8]. Innovative research to find substitutes for many of these elements has also accelerated.

Another interesting development relevant in this context is the investment being made in asteroid mining (companies like Planetary Resources and Luxembourg Space agency are pursuing it vigorously), mining on the moon (Naveen Jain's Moon Express founded in 2010) and deep-sea mining (companies like Neptune Minerals). Nautilus Minerals has already obtained necessary licenses to mine and process sea-floor

massive sulfide deposits, so-called manganese nodules, and rare earths [9–11].

Considering the complexity of these potential deposits, mineral engineers will have to innovate on all fronts, take advantage of our past knowledge, and meet these new challenges. We present a brief review of some of our work on the beneficiation of spodumene (an important source of lithium) and bastnaesite (an important source of rare earths), in order to illustrate the scientific principles underlying adsorption of surfactants at mineral-water interfaces and its utility in designing novel reagents, tailor-made for a given mineral separation problem. Since the interaction of flotation reagents with minerals in water is controlled by the electrical double layer, we will first review double layer phenomena in these systems.

## 2 Electrical Double Layer and Electrokinetics of the Mineral-Water Interface

When brought into contact with aqueous solutions, minerals develop an electric charge on their surface. This excess surface charge (either positive or negative) is exactly balanced by a region of equal but opposite charge (termed counterions) on the solution side of the interface. Counterions that have no affinity for the surface other than electrostatic are called indifferent ions. Because of thermal or Brownian motion, counterions extend in a diffuse layer out into the solution. The surface charge and diffuse layer of counterions are known as the electrical double layer (EDL).

Figure 1 presents a schematic representation of the EDL. The closest distance of approach of hydrated counterions to the surface is in a plane at a distance  $\delta$ , called the Stern plane. The total double layer potential, or surface potential, is  $\psi_0$  and the potential at the Stern plane is  $\psi_\delta$ . The potential across the double layer from the Stern plane to the bulk drops exponentially to zero, as described by the Gouy-Chapman theory [12]. Those ions which determine the surface charge are defined as potential-determining. On the other hand, specifically adsorbing ions that interact with surface sites, either chemically or by some other strong specific adsorption mechanisms, the adsorbed ion may lie even closer to the surface at the plane  $\beta$ . These two planes are known in the literature as inner and outer Stern planes. As a simple approximation, one often simply refers to adsorption in the Stern plane—that is,  $\delta$  and  $\beta$  planes coincide, as would be the case if specifically adsorbed counterions were the only ions present. In the case of large organic ions such as surfactants, plane  $\beta$  could lie even outside plane  $\delta$ . The adsorption of indifferent as well as specifically adsorbing ions at the mineral-water interface is discussed in the following sections.

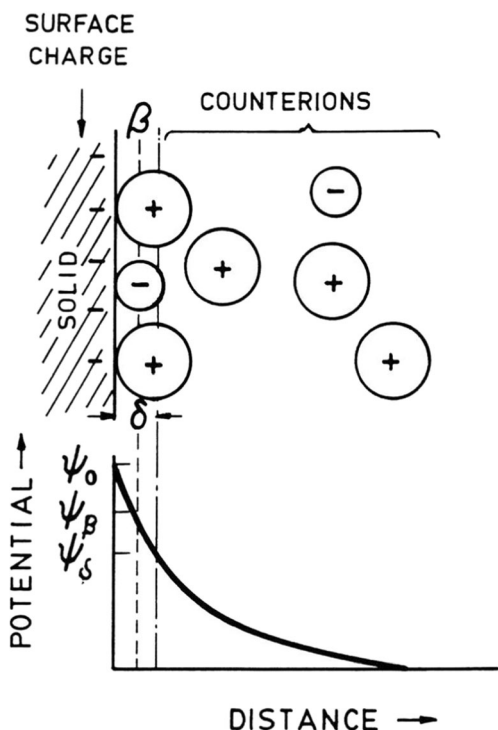


Fig. 1 Schematic representation of the electrical double layer and potential drop through the double layer at a mineral-water interface. The planes  $\beta$  and  $\delta$  represent the inner and outer Stern planes

### 2.1 Potential-Determining Ions

The surface charge in systems of importance to mineral processing may arise from a variety of different sources. In the case of ionic solids, such as  $\text{BaSO}_4$ ,  $\text{CaF}_2$ ,  $\text{CaCO}_3$ , and  $\text{AgI}$ , the surface charge arises from a preference of one of the lattice ions for sites at the solid surface in comparison to the aqueous phase. These are ions that are free to pass between both phases and therefore establish the EDL are called potential-determining ions. In the case of semisoluble minerals like calcite and bastnaesite, the lattice constituent ions, as well as the  $\text{H}^+$  and  $\text{OH}^-$  ions are potential-determining ions because of the equilibria between the ions and their hydrolysis products. In some instances, isomorphous substitution in the lattice (replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  in sheet silicates) gives rise to a permanent charge on the surface.

For oxide minerals, hydrogen and hydroxyl ions are known to be potential-determining. When an oxide mineral such as hematite or quartz is crushed, the broken O-M bonds react with water to form surface hydroxyl sites that undergo adsorption/dissociation reactions:



In general, for a mineral consisting of  $\text{M}^{+z}$  and  $\text{A}^{-z}$  as the potential-determining ions, the surface charge is defined as follows:

$$\sigma_0 = zF(\Gamma_{\text{M}^{+z}} - \Gamma_{\text{A}^{-z}}) \quad (3)$$

where  $z$  is the valence and  $F$  is the Faraday constant. The adsorption density  $\Gamma_{\text{M}^{+z}} - \Gamma_{\text{A}^{-z}}$  in mole per  $\text{cm}^2$  can be measured by titration of a suspension of the mineral in water [12].

One of the most important parameters that describe the EDL characteristics of the mineral/water interface is the point of zero charge (pzc). The pzc is the activity (concentration) of potential-determining ions in the aqueous solution at which  $\sigma_0$  is zero, and also the surface potential is zero. The value of surface potential at any activity of potential-determining electrolyte  $a_{\text{M}^{+z}}$  is given by the following:

$$\psi_0 = \frac{RT}{zF} \ln \frac{a_{\text{M}^{+z}}}{a_{\text{M}^{+z}}^{\text{pzc}}} \quad (4)$$

where  $R$  is the gas constant and  $T$  the absolute temperature.

As a first approximation, considering the activity coefficient to be unity and assuming that  $\text{H}^+$  and  $\text{OH}^-$  ions are primarily the potential-determining ions, the change of  $\psi_0$  with pH can be represented by an equation of the form as follows:

$$\psi_0 = 2.3 (RT/F) [\text{pH}_{\text{pzc}} - \text{pH}] = 0.059 [\text{pH}_{\text{pzc}} - \text{pH}] \text{ Volts} \quad (5)$$

The above Nernstian equation is strictly valid for a reversible electrode. In actual practice, we find that the slope of potential vs. pH is 59 mV only close to the pzc. The pzc of the different oxides ranges widely:  $\text{SiO}_2$  pH 1–2,  $\text{TiO}_2$  pH 6,  $\text{Fe}_2\text{O}_3$  (synthetic) pH 8.6, and natural hematite pH 4.8 to 6.7,  $\text{Al}_2\text{O}_3$  pH 9, and  $\text{MgO}$  pH 12. Trace elements in natural minerals have a marked effect on observed pzc values [13].

### 2.2 Indifferent Electrolytes

It is important to note that in contrast to potential-determining ions which are specific to that mineral, any ions present in the solution can act as counterions that make up the diffuse layer. Counterions that interact with the mineral surface by electrostatic forces only are called indifferent ions (or electrolytes).

The charge in the diffuse layer  $\sigma_d$  given by the Gouy-Chapman equation as modified by Stern (for a symmetrical electrolyte) is as follows:

$$\sigma_d = -\sigma_0 = -(2\epsilon RTC/\pi)^{1/2} \sinh [zF \psi_\delta / (2RT)] \quad (6)$$

when there is no specific adsorption at the Stern plane.  $C$  is the equilibrium concentration of the indifferent electrolyte in

solution and  $\varepsilon$  is the dielectric constant of the solution.

Another important property of the electrical double layer is its “thickness” which is given by  $1/\kappa$  and depends on the ionic strength of the solution. For a symmetrical electrolyte  $\kappa$  is given by the Debye-Hückel equation as follows:

$$\kappa^2 = [8\pi z^2 F^2 C / (\varepsilon RT)] \quad (7)$$

where  $C$  is the concentration of electrolyte in solution. In  $10^{-5}$  M solutions,  $1/\kappa$  is 100 and 10 nm in  $10^{-3}$  M solutions [12].

The concentration profile of counterions of type  $i$  in the double layer at a position where the electrical potential is  $\psi$  is given by a Boltzmann type distribution:

$$C_i = C_{io} \exp\left(-\frac{zF\psi}{RT}\right) \quad (8)$$

where  $C_{io}$  is the concentration in the bulk solution,  $C_i$  is the concentration of the ion  $i$  at the point where potential is  $\psi$ ,  $z$  is the valence (including sign) of ions of type  $i$ . As the surface is approached, the local concentration of ions charged oppositely to the surface increases and that of ions charged similarly decreases. This equation is of particular importance in the adsorption of ions that are flotation reagents. This can be used to calculate the adsorption of indifferent ions in the Stern plane, after defining their concentration in the Stern plane as  $C_\delta = \Gamma_\delta / 2r$  where  $2r$  is the diameter of the adsorbing ions, by rewriting Eq. 8:

$$C_\delta = \Gamma_\delta / 2r = C \exp\left(-\frac{zF\psi_\delta}{RT}\right) \quad (9)$$

### 2.3 Specific Adsorption at the Stern Plane

In some cases, counterions in the Stern plane adsorb by forces in addition to simple electrostatics. Such counterions are considered to be specifically adsorbed, and in flotation, these are the ions that function as collectors. Based on the concepts developed by Stern and modified by Graham, one can describe the adsorption density of specifically adsorbing ions at the Stern plane as a function of equilibrium concentration in solution,  $C$ , and the standard free energy of adsorption,  $\Delta G_{\text{ads}}^0$ , by the well-known Stern-Langmuir adsorption isotherm as follows [14]:

$$[\theta / (1-\theta)] = (C/55.5) \exp[-\Delta G_{\text{ads}}^0 / (RT)] \quad (10)$$

where  $\theta$  ( $=\Gamma_\delta/\Gamma_m$ ) is the fractional surface coverage of the adsorbing species at the equilibrium concentration  $C$  in solution and  $\Gamma_m$  is the adsorption density equivalent to monolayer coverage.

At low surface coverage (less than about 30% of a monolayer), Graham simplified this equation (or its equivalent) for adsorption in the Stern plane as follows:

$$\Gamma_\delta = 2rC \exp(-\Delta G_{\text{ads}}^0 / RT) \quad (11)$$

where  $2r$  is the effective diameter of the adsorbing ion (usually estimated from its cross-sectional area). Grahame’s derivation was for adsorption in the inner Stern plane, but we are approximating the system for the inner and outer Stern planes coinciding. Eq. 11, which is essentially Eq. 9, has been extensively used in the mineral processing literature to estimate  $\Delta G_{\text{ads}}^0$  from adsorption isotherms of surfactants at mineral-water interfaces.

For systems where specific adsorption phenomena occur, the standard free energy of adsorption includes an additional term:

$$\Delta G_{\text{ads}}^o = \Delta G_{\text{elec}}^o + \Delta G_{\text{spec}}^o = zF\psi_\delta + \Delta G_{\text{spec}}^o \quad (12)$$

If the specific adsorption free energy is great enough, the charge due to adsorption in the Stern plane can exceed the surface charge.

Surfactants used in mineral separation belong to the category of specifically adsorbing ions. Unlike indifferent electrolytes, specifically adsorbing counterions can adsorb at the Stern plane in concentrations greater than what is needed to neutralize the charged surface. A positively charged surface can thus be transformed into a negatively charged surface through super-equivalent adsorption of specifically adsorbing anions or vice versa. The means to distinguish between these two kinds of interactions, namely chemisorbing and electrostatic interactions is discussed in the following section.

### 2.4 Zeta Potentials

If the liquid moves tangentially across a solid surface (or even another fluid phase), ions in the diffuse part of the double layer are stripped off, giving rise to an electrical potential, the so-called electrokinetic phenomena. Just where the slipping plane occurs is not known but it is assumed to be just outside the Stern plane. The potential at the slipping plane is called the zeta potential and is generally equated to the potential at the Stern plane [15]. Two electrokinetic methods have been used quite extensively in flotation chemistry research: electrophoresis and streaming potentials. In electrophoresis, if an electric potential is applied to a suspension of fine particles, the particles migrate and, from their mobility, the zeta potential can be calculated [12, 15]. If an aqueous solution is forced through a bed of particles or a capillary, an electric potential is set up across the ends of the bed or capillary, from which the zeta potential can be calculated [16]. Indifferent electrolytes can

only reduce the magnitude of the zeta potential and cannot reverse its sign. Potential-determining ions can reverse the surface charge and hence the sign of the zeta potential at the pzc. Specifically, adsorbing ions can adsorb so strongly in the Stern layer that their charge exceeds that of the surface charge and thereby reverse the sign of the zeta potential. The point where the zeta potential is zero under these conditions is called the isoelectric point IEP or the point of zeta potential reversal PZR [15]. How electrokinetic phenomena can be used to understand adsorption behavior is discussed in sections that follow.

### 3 Adsorption of Surfactants at the Mineral/Water Interface

One of the important advances in flotation research was the introduction of electrical double layer theory to understanding and delineating the mechanisms of adsorption of surfactants at mineral-water interfaces [17–20]. Flotation collector molecules (and surfactants in general) consist of a polar functional group and a nonpolar hydrocarbon chain (aliphatic or aromatic) or a polymeric backbone. This discussion will not include sulfide minerals and sulfhydryl collectors since the chemistry of these systems is of a completely different nature. In designing selective collectors, we must look for factors that determine the adsorption of a surfactant on one mineral and not on the other. It is now a well-established that the selectivity of adsorption of a surfactant is determined by the following:

- (a) The chemical nature of the surfactant/reagent, that is,
  - Character of its functional group (cationic/anionic/nonionic, diameter, ionization, hydrolysis, solubility, stability constants)
  - Nature of its hydrocarbon/polymer chain (chain length and the degree of branching, double bonds, critical micelle concentration)
  - Conformation in solution in the case of polymers (expanded or not)
  - Associative complexes of surfactants in solution (acid-soap complexes in case of fatty acids and aminium ion-neutral amine complexes, micelle formation)
- (b) The nature of the mineral surface onto which the surfactant is adsorbed, that is,
  - Surface charge (the point of zero charge, pzc, potential-determining ions)
  - Natural hydrophobicity (talc, graphite, molybdenite are naturally hydrophobic)
  - Nature of available adsorption sites (determined by the crystal structure of the mineral, metal sites available on its cleavage plane)

- (c) The nature of the solution environment—for example, the presence of soluble ions that can complex with surfactants, pH, temperature, ionic strength (electrolyte concentration) determining the EDL, Eh (the pulp potential in some cases)

Several excellent reviews are available in the literature elucidating the precise nature of these interactions and the mechanisms through which the selectivity of surfactant adsorption is determined [15, 18–20]. We illustrate our scientific understanding of the selective adsorption of surfactants at mineral-water interfaces through a couple of case studies based on some of the work carried out at our laboratories in Berkeley.

#### 3.1 Physisorption vs. Chemisorption

The adsorption of surfactants at mineral-water interfaces may result from or be influenced by one or more of the following:

- Electrostatic interactions
- Covalent-coordinate bonding
- Hydrogen bonding
- Hydrophobic forces
- Solvation effects
- Steric effects

In those systems where there is no special affinity between the polar functional group of the surfactant and the mineral surface, adsorption occurs because the surfactant ions are charged oppositely to the surface. Since there is no chemical bond with surface sites, this is called *physisorption*. The very first application of this concept to flotation was the flotation of corundum (alumina), which floats well with anionic collectors (alkyl sulfonates and sulfates) at pHs below its pzc (pH 9) and with cationic collectors (amines) above its pzc. On the other hand, potassium octyl hydroxamate (anionic collector) adsorbs strongly on hematite at pH 9 (at a pH above its pzc), even though the mineral surface is negatively charged. This is possible since hydroxamates have a special affinity for the hematite surface and it forms coordinate-covalent bonds with iron metal ion sites on the surface. Such specific interaction is called *chemisorption*.

Several investigations showed that oleate acts as a flotation collector by chemisorption at pHs above the pzc and by physisorption at pH's below the pzc: manganese dioxide, hematite, chromite [13].

At low concentrations, collectors (surfactants) that like to bind with metal ions chemisorb on oxides and sparingly soluble salt minerals, but at higher concentrations, they may undergo *surface reaction*. Examples are the chelating hydroxamates on oxides such as hematite and such salt minerals as barite and bastnaesite, and oleate on calcite, fluorite, etc. If the metal-surfactant compound is more stable than the

metal in the mineral, the reaction can proceed until the reagent is consumed.

One of the most elegant ways to quantify the specific interactions (chemisorption) using the electrical double layer theory was proposed and established by Fuerstenau and coworkers [15–17, 20–26]. As discussed in Section 2, the standard free energy of adsorption,  $\Delta G_{\text{ads}}^0$ , can be estimated using either the Stern-Grahame (Eq. 11) or the Stern-Langmuir adsorption isotherm (Eqs. 8 and 9).

Furthermore, since  $\Delta G_{\text{ads}}^0$  is a thermodynamic quantity, one can write it in terms of the contributions due to specific interactions and the contribution to the energy due to electrostatic interactions:

$$\Delta G_{\text{ads}}^0 = \Delta G_{\text{elec}}^0 + \Delta G_{\text{spec}}^0 \quad (13)$$

If adsorption occurs by electrostatic interactions only, the standard free energy of adsorption is given by the following:

$$\Delta G_{\text{ads}}^0 = \Delta G_{\text{elec}}^0 = zF\psi_{\delta} \quad (14)$$

In case the adsorbing ion is surface-active, that is, there is a specific interaction contribution to the standard free energy of adsorption, one can write as follows:

$$\Delta G_{\text{ads}}^0 = \Delta G_{\text{elec}}^0 + \Delta G_{\text{spec}}^0 = zF\psi_{\delta} + \Delta G_{\text{spec}}^0 \quad (15)$$

Various kinds of possible specific interactions including chemical bonding, hydrogen bonding, hydrophobic association, solvation, and steric effects can be accounted for in  $\Delta G_{\text{spec}}^0$  as follows:

$$\Delta G_{\text{spec}}^0 = \Delta G_{\text{chem}}^0 + \Delta G_{\text{h}}^0 + \Delta G_{\text{hyphb}}^0 + \Delta G_{\text{solv}}^0 + \Delta G_{\text{steric}}^0 + \dots \quad (16)$$

### 3.2 Electrokinetics of Surfactant Adsorption

One of the most sensitive techniques to delineate the mechanisms of adsorption in mineral processing systems where electric double layer effects predominate is the electrokinetic measurement. Often small changes in adsorption of ions and surfactants at the interface result in pronounced changes in electrokinetic potentials. The phenomenon of hemi-micelle formation, that is the adsorbed surfactant ions associating at the interface was proposed by Fuerstenau [16] based on the observation that at a critical concentration, dodecyl ammonium ions caused the zeta potential of quartz to deviate from that of indifferent sodium ions. With the help of Eq. 8 and the value of zeta potential measured during the experiments, it was possible to show that the concentration of dodecyl ammonium

ions in the Stern plane was the same as the critical micelle concentration (CMC) for bulk solutions. It was thus clear that hydrophobic forces that gave rise to the formation of micelles in the bulk solution are the same for adsorbed surfactants in the Stern layer. The removal of water from the associating hydrocarbon chains thus leads to free energy reduction—leading to the formation of micelles in the bulk and hemimicelles at the interface. It was further demonstrated that as in the case of micelle formation in bulk solution, the magnitude of  $\Delta G_{\text{hyphb}}^0$  is directly related to the number of carbon atoms in the hydrocarbon chain of the adsorbing reagent. The displacement of water adjacent to the mineral surface by the chains of surfactants adsorbing at the surface of a hydrophobic mineral can also lead to specific adsorption.

Fuerstenau and coworkers [15] established that one of the easiest techniques to distinguish between physisorption and chemisorption is to conduct electrokinetic experiments. The experimental results plotted as the zeta potential versus pH (or as a function of pPD) for systems at the constant concentration of electrolyte with and without added surfactant provide the means to identify and/or confirm if there is chemisorption. The effect of different possible interactions on the zeta potential versus pH characteristics, as measured through electrokinetic measurements, is schematically illustrated in Fig. 2. The solid line in the figure represents the results of zeta potential measurements carried out as a function of the concentration of potential-determining ions at a fixed concentration of the indifferent electrolyte, with the reversal of the zeta potential at A being the pzc. At the pzc (point A), the surface charge (and the surface potential) is zero under these conditions.

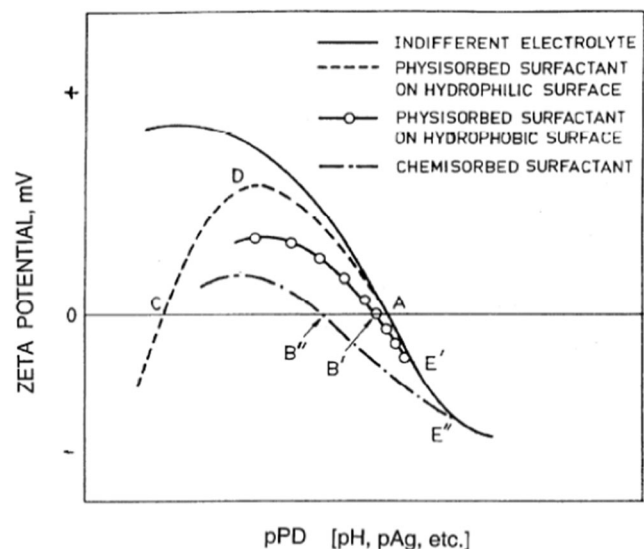


Fig. 2 Schematic illustration of the effect of potential-determining ions (pH for example) on the zeta potential of an indifferent electrolyte, a physisorbing surfactant on a hydrophilic mineral surface, a physisorbing collector on a hydrophobic mineral and a chemisorbed anionic collector

In the presence of *physisorbing* surfactants, for instance, an anionic surfactant such as alkyl sulfate on alumina surface, with the ionic strength controlled by the same indifferent electrolyte, the zeta potential vs. pH curve is typified by the dotted line in Fig. 2. Starting at high pPD, there is no adsorption of surfactant above the pzc since the surfactant and the surface are charged similarly. Below the pzc when the surface and surfactant are oppositely charged, the surfactant is functioning as an indifferent ion and adsorption essentially through electrostatic forces only until point D is reached where the adsorption density of the anionic surfactant reaches the hemi-micelle concentration and the chains of the adsorbed surfactant begin to associate on the positively charged surface. (Numerous investigations have found the break between the curves with and without the surfactant to be quite sharp). At D,  $\Delta G_{\text{hyphb}}^0$  becomes effective, increasing specific adsorption of the surfactant until at point C the zeta potential becomes zero and the double layer becomes a molecular condenser, the charge on one plate being the surface charge on the mineral and the other being a layer of identically opposite charge of adsorbed surfactant in the Stern plane. At this condition, flotation rates should be maximal. Due to  $\Delta G_{\text{hyphb}}^0$ , surfactant adsorption continues as the pH is lowered, causing the zeta potential to become negative. Point C is called the point of zero zeta potential (PZR) or the isoelectric point (IEP) but it is not a pzc.

In the case of a hydrophobic mineral (such as graphite, or talc, etc.), one observes the zeta potential behavior shown as the curve with open circles. Below the pzc, alkyl sulfate ions adsorb not only because of the opposite charge but also because of the alkyl chain displacing water from the surface. This leads to zeta potential reversal at point B', somewhat lower than point A. This is an IEP and not the pzc. There is adsorption of an anionic surfactant even above the pzc due to interaction between the hydrophobic surface and the hydrophobic surfactant chain. Point E' represents the pH where  $\Delta G_{\text{spec}}^0$  (due to specific hydrophobic interactions) is equal and opposite to  $\Delta G_{\text{elec}}^0$  (repulsive free energy of adsorption between the surface and surfactant which are now similarly charged).

For surfactants that chemisorb at the surface of a mineral, one observes a distinct shift in the IEP in the presence of surfactant as compared to indifferent electrolyte only (compare the point A, pzc of the mineral and point B'' in the presence of surfactant). The adsorption, in this case, an anionic collector adsorbing on a mineral surface above its pzc, is possible since there is a sufficiently strong chemical affinity (specific energy of adsorption is sufficiently high). The adsorption ceases at a pH (point E'') when  $\Delta G_{\text{spec}}^0$  is exactly equal and opposite to  $\Delta G_{\text{elec}}^0$ . Point B'' is again an IEP and not the pzc; it can be considered the point of zero adsorption. Therefore, above this pH, the flotation of the mineral ceases.

### 3.3 Shift in IEP in Chemisorbing Surfactant Systems is a Measure of $\Delta G_{\text{spec}}^0$

Specific interactions during adsorption of a surfactant on the mineral surface thus result in a shift of isoelectric point (IEP) of the system. Pradip [27] has shown that this shift in IEP, ( $\Delta\text{pH} = \text{PZR} - \text{pzc}$ ) is related to the following equation based on the EDL theory:

$$\Delta\text{pH} = 1.040 C_0 \exp \left[ -\Delta G_{\text{spec}}^0 / RT \right] \quad (17)$$

where  $C_0$  is the concentration of the surfactant corresponding to the shift in IEP.

$\Delta\text{pH}$  vs.  $C_0$  plotted on a log-log scale will thus represent a straight line relationship and the slope of this plot provides an estimate of  $\Delta G_{\text{spec}}^0$ .

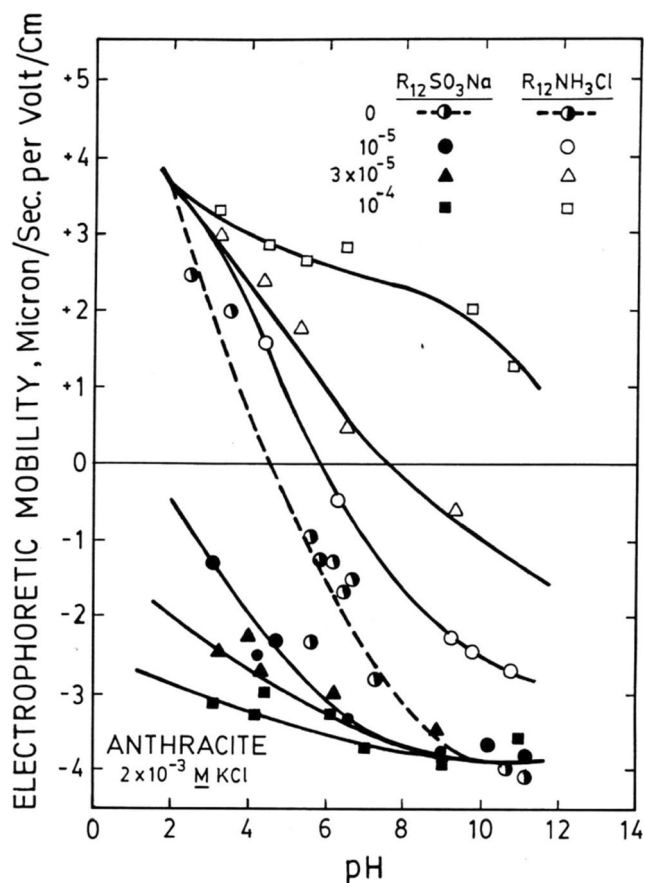
Based on the analysis of a wide variety of mineral-surfactant systems, Pradip [27] showed that  $\Delta G_{\text{spec}}^0$  calculated using the measurement of the shift in IEP in the presence of chemisorbing surfactants through electrokinetic experiments compare very well with the values of  $\Delta G_{\text{spec}}^0$  estimated through adsorption experiments on the same system.

### 3.4 Adsorption of Surfactants on Hydrophobic Anthracite Coal

One of the most illustrative examples of specific interactions of surfactants with a hydrophobic surface was reported by You and Fuerstenau [28].

As discussed in Section 3.2, the adsorption of surfactants on hydrophobic surfaces (for example anthracite coal) involves hydrophobic interactions between the long-chain surfactants (nonpolar part) and the hydrophobic surface. The results of electrokinetic experiments on anthracite coal in the presence of sodium dodecylamine (cationic collector) and sodium dodecyl sulfonate (anionic collector) reported by You and Fuerstenau [28] are plotted in Fig. 3. Please note that both are C12 chains and one expects similar hydrophobic interactions with the surface. It is interesting to note that the results summarized in Fig. 3 clearly demonstrate that the shift in IEP in both cases are similar, and the electrokinetics with dodecylamine hydrochloride and dodecyl sulfonate is a mirror image of each other as one would expect since the nonpolar chains are primarily responsible for the adsorption on the anthracite coal surface.

The direction of the shift in IEP (to the left of the pzc in case of an anionic sulfonate collector and to the right of pzc in case of cationic amine collector) of coal in presence of long-chain surfactants is determined by the polar functional group but the magnitude of that shift as a function of surfactant concentration is a measure of the  $\Delta G_{\text{spec}}^0$ , that is, the specific



**Fig. 3** Electrokinetics of surfactant adsorption on anthracite coal (PZC pH 4.5)

free energy of hydrophobic interaction of the C12 chain with the anthracite surface.

Using Eq. 16, we have computed the specific free energy of interaction for both C12 amine and C12 sulfonate adsorbing on anthracite coal. The results are summarized in Table 1.

As one would expect, since both chains are C12 and the adsorption is primarily due to the hydrophobic interactions between the surfactant chain and the hydrophobic coal surface (the conformation of chains will be horizontal with chains lying down on the surface), the specific interaction energy of adsorption,  $\Delta G_{\text{spec}}^0$ , will be similar and that is indeed the case, as illustrated by the results presented in Table 1.

**Table 1** Computation of  $\Delta G_{\text{spec}}^0$  from electrokinetic data for surfactant adsorption on anthracite coal (PZC pH 4.5)

Surfactant	$C_0$ in mole per liter	$\text{pH}_{\text{IEP}}$	$\Delta\text{pH}_{\text{IEP}}$	$\Delta G_{\text{spec}}^0$ (in RT units)
Dodecyl sulfonate	$10^{-5}$	2.0	2.5	-12.4
Dodecyl ammonium chloride	$5 \times 10^{-6}$	5.2	0.7	-11.8
	$10^{-5}$	5.6	1.1	-11.6
	$3 \times 10^{-5}$	7.9	3.4	-11.6

## 4 Selective Flotation of Spodumene with Oleate Collector

One of the sources of lithium, a critical element for the manufacture of energy storage batteries is lithium-rich pegmatites containing spodumene  $\text{Li Al} [\text{SiO}_3]_2$ . Spodumene containing 8%  $\text{Li}_2\text{O}$ , 27.4%  $\text{Al}_2\text{O}_3$  with the rest being  $\text{SiO}_2$  occurs in nature along with mica, feldspar, and quartz. Moon and Fuerstenau [29, 30] conducted a detailed study of the mechanisms of adsorption of oleate on all of the constituent minerals of pegmatitic spodumene ore and the basis of flotation selectivity between these silicate minerals. The study established that the characteristic crystal chemistry of spodumene is responsible for the selectivity observed in spodumene-muscovite-feldspar-quartz flotation separation with oleate collector. Crystallographically, the surface Al sites available on the cleavage plane of spodumene were found to be the most favorable site for the adsorption of Oleate. Such sites are not available on the other associated silicate minerals in the ore because the Al ions are inside the silica tetrahedra due to isomorphous substitution for Si ions, leading to selective adsorption and flotation of spodumene with oleate collector. The results for the measurement of Hallimond tube flotation response, contact angles, adsorption densities, and electrokinetics in the oleate-spodumene system are summarized in Fig. 4.

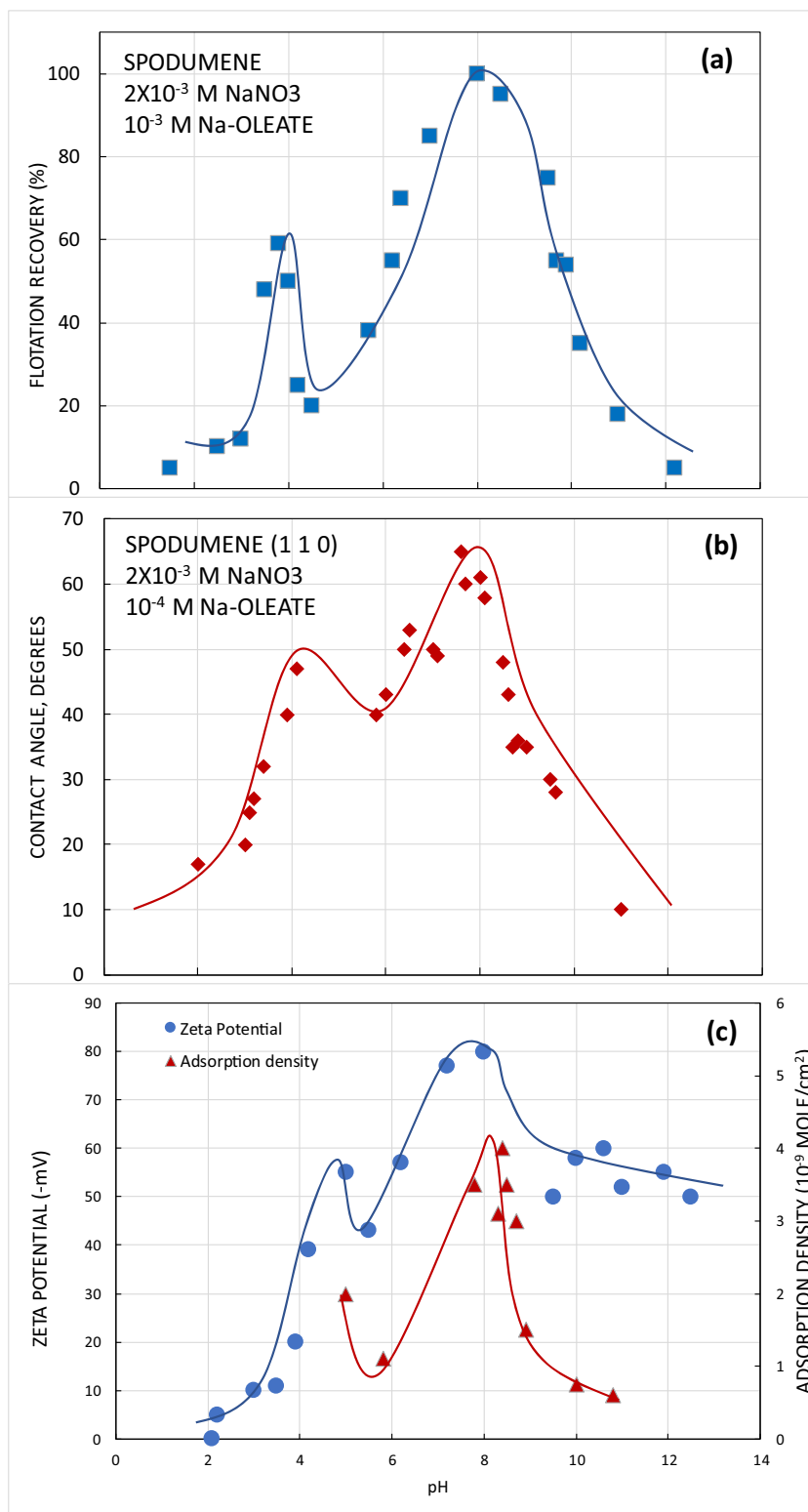
As might be expected, there is excellent correlation between the adsorption, electrokinetics, contact angles, and flotation recovery in the spodumene-oleate system. Two peaks which are observed in all experiments are attributed to the interesting surface chemistry of this system. The primary flotation (and corresponding peaks observed in electrokinetic, contact angle, and adsorption experiments) that is maximum at pH 8 is related to the surface aluminum sites (available on the cleavage plane of spodumene) where oleate chemisorption takes place. The secondary flotation peak at around pH 4 appears to be related to ferric iron impurities present in the spodumene samples.

Subsequently, a detailed molecular modeling study was conducted by Rai et al. [31] on this system and their results are summarized in Fig. 5.

It is possible to cleave the spodumene crystal computationally and study various planes of interest. Moon and Fuerstenau [29, 30] had measured contact angles of physically cleaved



**Fig. 4** The effect of pH and oleate collector on **a** the flotation of spodumene, **b** contact angles on the cleavage plane of spodumene, and **c** zeta potentials of spodumene and oleate adsorption density of oleate (data taken Ref [29, 30])



spodumene in the laboratory in order to expose two different planes namely the common cleavage plane (110) and also (001). They measured contact angles of spodumene in the presence of physisorbing dodecylamine collector on both of the planes as well as in the presence of chemisorbing oleate

collector. Unlike physisorption, since chemisorption involves interaction of the collector with specific surface sites (Al sites in this case), it is expected that one would observe differences in the contact angles with oleate depending on which plane is exposed for adsorption and this was observed in actual

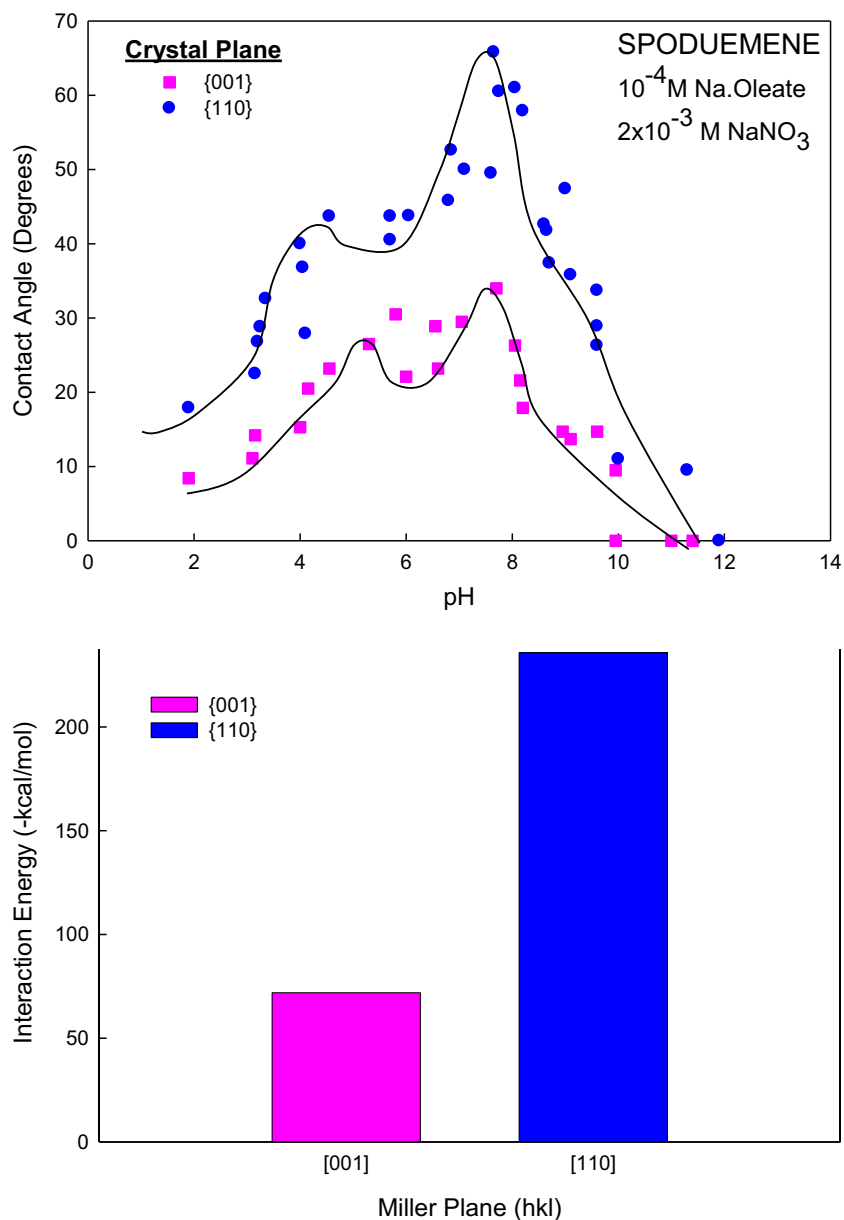
experiments. It was therefore of interest to simulate the same through molecular modeling computations. As illustrated in Fig. 5 (oleate adsorption on spodumene) and in Fig. 6 (amine adsorption on spodumene), the results of molecular modeling computations match well with the experimental observations. These computations further lend support to the hypothesis of Moon and Fuerstenau that not only chemisorption of oleate is necessary for selective adsorption but also the crystallography of spodumene (having cleavage on plane 110) determines the availability of Al sites for chemisorption. The same sites are not available on other associated silicate minerals, leading to the possibility of selective flotation.

A more recent study on flotation as well as molecular dynamic (MD) simulation of oleate adsorption on the spodumene surface confirms the abovementioned findings [32,

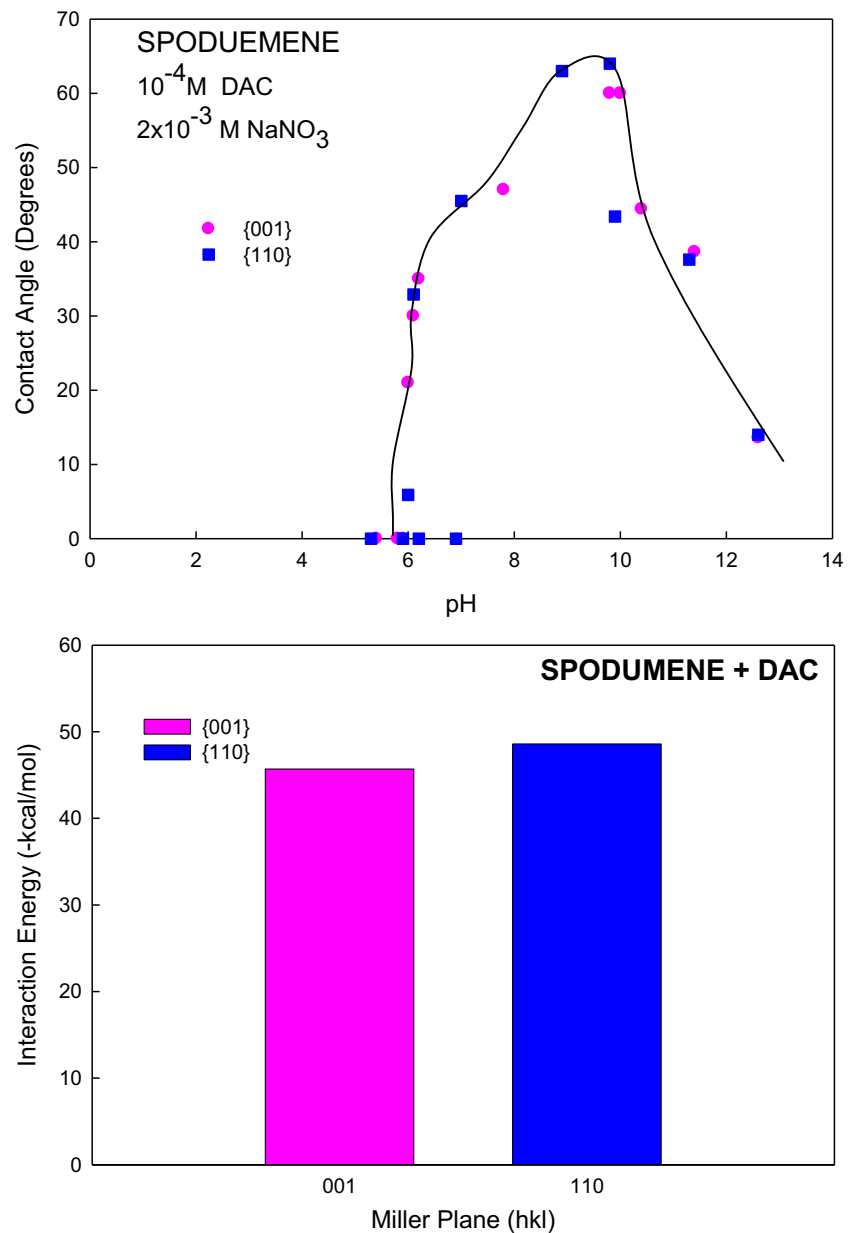
33]. Based on a detailed MD simulation study, Xu et al. [33] suggested that oleate prefers to chemisorb on the [110] plane with two broken Al-O bonds in a mono-dentate chelating complex configuration (two oxygen atoms chelating with one Al atom on the surface). On the other hand, on the [001] plane of spodumene, oleate binds in a mono-dentate mononuclear configuration (single oxygen atom binding the Al atom on the surface). The latest study reported by Zhu et al. [34] on spodumene flotation with oleate and dodecyl ammonium chloride, which included a detailed MD simulation study on the interfacial water structure as well as collector adsorption on four different planes of spodumene, also confirm the main findings of Moon and Fuerstenau [29, 30] and Rai et al. [31]

Another interesting effort that is to develop a mixed anionic-cationic collector (sodium oleate-dodecyl ammonium

**Fig. 5** A comparison of theoretically computed interaction energies of oleate molecules on spodumene {110} and {001} planes with experimentally measured contact angles (after Ref [31])



**Fig. 6** Comparison of theoretically computed interaction energies of dodecyl ammonium chloride molecules on spodumene {110} and {001} planes with experimentally measured contact angles (after Ref [31])



chloride in the ratio of 9:1) for the separation of spodumene from feldspar is worth citing in this context [35]. The authors found that the oleate chemisorbs first on the Al sites on spodumene, followed by co-adsorption of dodecyl ammonium chloride and appears to exhibit higher selectivity against feldspar.

## 5 Selective Flotation of Bastnaesite with Hydroxamate Collectors

Pradip, Fuerstenau, and coworkers [36–41] studied the flotation separation of bastnaesite [(Ce, La)  $\text{FCO}_3$ ] from the associated barite [ $\text{BaSO}_4$ ] and calcite [ $\text{CaCO}_3$ ] minerals, the

constituent minerals of a carbonatite ore from Mountain Pass, California, using chemisorbing oleate and alkyl hydroxamate collectors. Alkyl hydroxamates were demonstrated to be more selective collectors for the beneficiation of Mountain Pass ore [36–40, 42]. Through their detailed studies on this system including the synthesis and electrokinetic studies on the pure mineral bastnaesite [36, 43–45], they delineated the scientific basis of selective separation of bastnaesite from calcite and barite in the industrial Mountain Pass flotation plant with fatty acid collectors using high temperature (steam) conditioning of the ore with lignin sulfonate and soda ash as the selective depressants [36, 46, 47]. Two important aspects of this detailed study have been selected for discussion in this paper.

## 5.1 Selective Adsorption of Hydroxamate Collectors on Bastnaesite

It is now a well-established fact that selective chemisorption of flotation collectors at the mineral-water interface is the single most important criterion for the design of highly selective flotation collectors. The crystal structure and cleavage characteristics of the mineral to be floated must be taken into account in the design of selective flotation collectors. Flotation chemistry research may involve Hallimond tube flotation test work both on individual minerals and their synthetic mixtures and detailed studies applying the full range of experimental methods available. As illustrated in the previous section on spodumene, the results of all these different measurements do correlate well suggesting that adsorption phenomena at the mineral-water interface is the key to understanding the basis of selectivity observed in commercial flotation separation of ores.

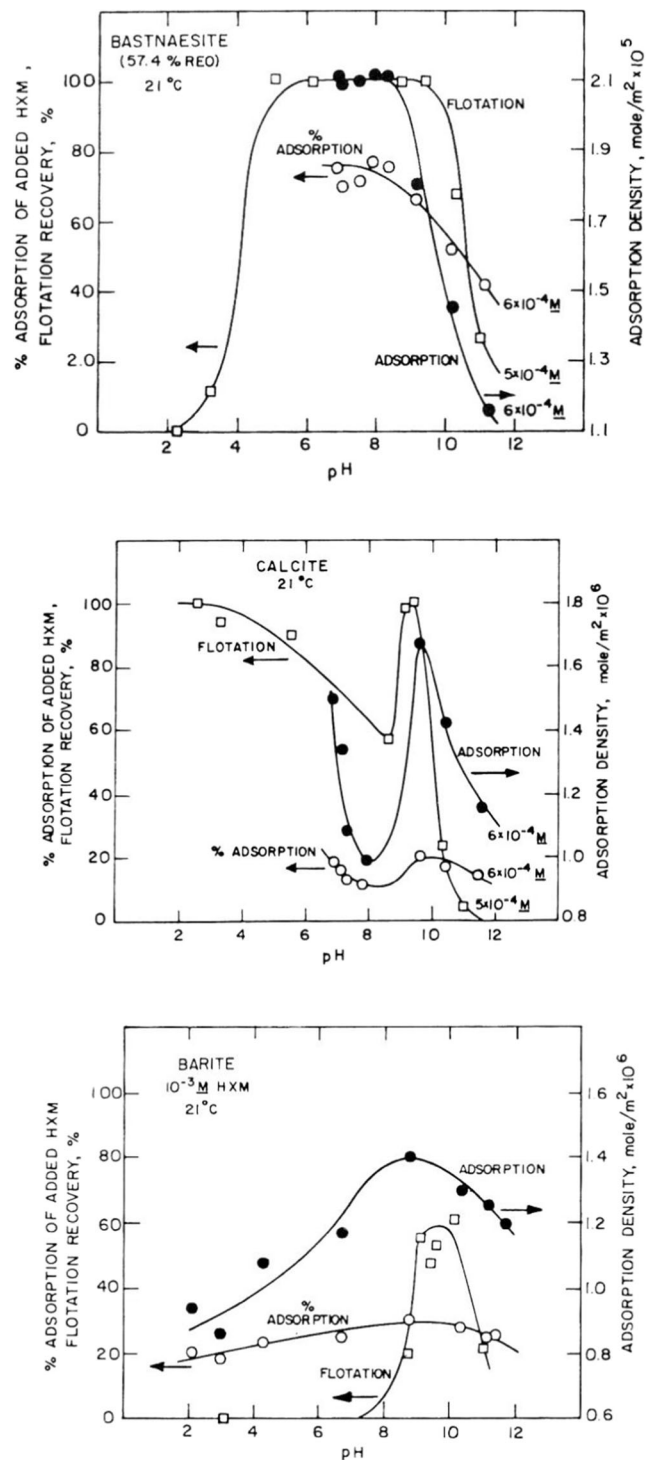
Results are presented here on the adsorption and flotation on bastnaesite, calcite, and barite as a function of pH in Fig. 7. All three minerals exhibit a peak in flotation around  $\text{pH } 9 \pm 0.5$ . This value also happens to be the range of  $\text{pK}_a$  reported for hydroxamic acids [36, 38]. Fuerstenau and Pradip [38] proposed that the maximum in flotation recovery and adsorption of hydroxamates at mineral-water interface was due to the co-adsorption of neutral hydroxamate species together with the chemisorbed hydroxamate anions. The maximum observed in flotation and adsorption tests is thus a consequence of the ion/molecule adsorption, both of which can form stable metal chelates. Surface reaction leading to the formation of the stable metal chelate may well be the final surface coating in this system.

Fuerstenau and Pradip [38] further proposed the following possible mechanisms by which a chelating collector like hydroxamate adsorbs at a mineral surface.

The collector ion (molecule) specifically adsorbs by chemically interacting with surface lattice ions of the mineral. Monolayer coverage would be the limiting adsorption density.

Systems involving surface reaction are two types. One would be that involving hydroxamate where the adsorbing species are hydroxamic acid molecules, clearly shown by Raghavan and Fuerstenau for hematite [24]. The  $\text{pK}_a$  of hydroxamic acid is 9 and maximal adsorption occurs below that pH and ceases above pH 9. Hematite changes color, indicating a thick coating. The hydroxamic acid reacts with the metal ion (iron in this case) so strongly that a new phase is formed at the surface (ferric hydroxamate in this case). The second type involves the collectors (oleate or hydroxamate for example) and the slightly soluble salt minerals (calcite, etc.). In this case, the more insoluble soap would continue to form by an exchange reaction until the available reagent is used up if given enough time.

The chemical interaction of hydroxamate at the mineral-water interface, for example, could take place by



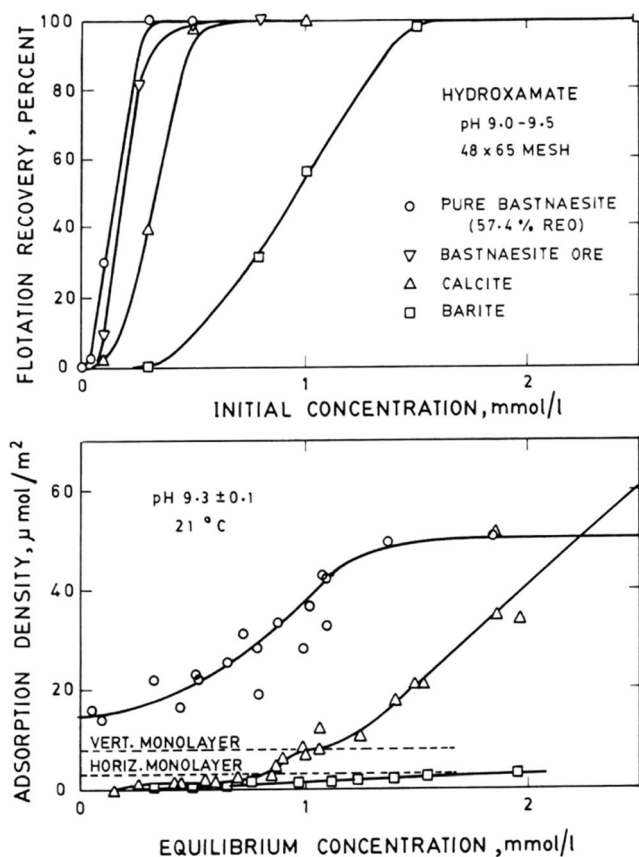
**Fig. 7** Correlation of flotation recovery with adsorption results as a function of pH for bastnaesite (top), calcite (middle), and barite (bottom) (after Ref. [47])

chemisorption where the reagent covalently bonds with metal cations that do not move from their lattice positions. Adsorption could also take place by surface reaction, where the reagent bonds with the metal cations that move away from

their lattice positions to a region adjacent to the surface in the region of EDL.

In sparingly soluble mineral systems, metal ion hydrolysis may also play an important role in the adsorption of hydroxamate on the mineral surface. Many authors have shown that the peak in flotation and adsorption with hydroxamate coincides with the pH at which the metal hydroxy species are present [38]. In case of bastnaesite, the pH at which maximum concentration of constituent metal hydroxy species, that is, cerium [Ce OH<sup>+</sup> and Ce (OH)<sup>+2</sup>] and lanthanum [La OH<sup>+</sup>, La (OH)<sup>+2</sup>] hydroxy species is achieved also is in the same range, that is between pH 8–9 [38]. In those cases where the metal hydrolyzes at a pH away from pH 9, two peaks may be observed. For example, chrysocolla [CuSiO<sub>3</sub>.2H<sub>2</sub>O] exhibits two peaks—one at around pH 6 which coincides with the pH at which the copper hydroxy species are present and the other at around pH 9 which coincides with the pK<sub>a</sub> of hydroxamic acid.

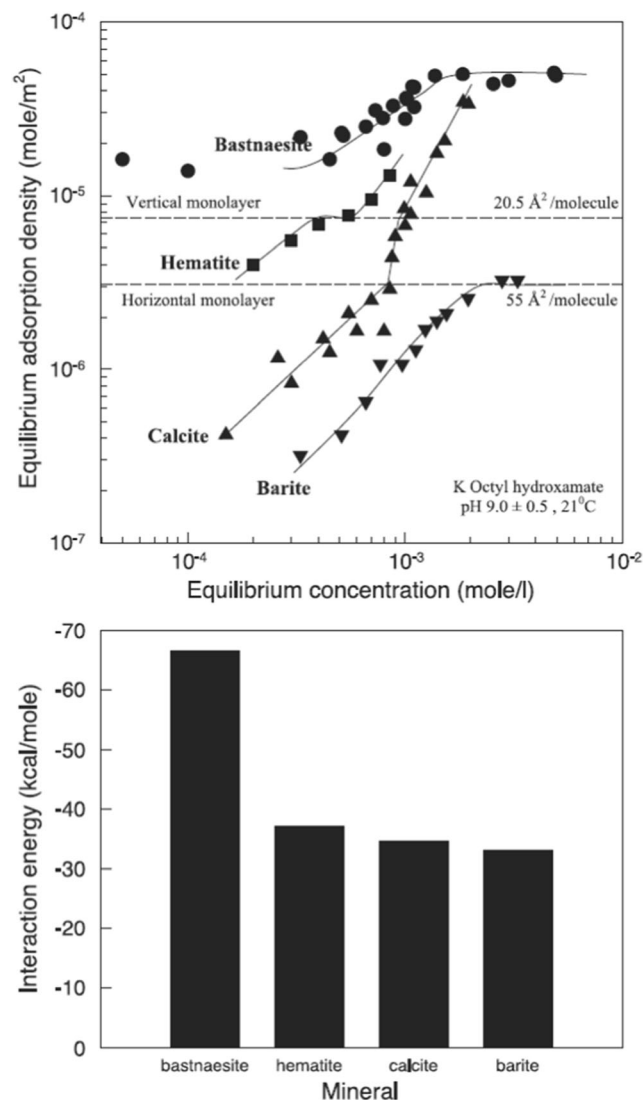
The adsorption isotherms of potassium octyl hydroxamate on bastnaesite, barite, and calcite are shown in Fig. 8. It is interesting to note that hydroxamate does not adsorb strongly on barite, but on both calcite and bastnaesite, multilayers are



**Fig. 8** Hallimond tube flotation recoveries of bastnaesite, barite, and calcite as a function of the initial concentration of hydroxamate collector (a) and adsorption isotherms of hydroxamates as a function of the equilibrium concentration in solution at room temperature (b) (after Ref. [46])

formed. The precipitous increase in the disappearance of hydroxamate from solution (expressed here as adsorption) in the presence of calcite suggests the onset of surface reaction leading to the formation of calcium hydroxamate. These results correlate well with flotation experiments since bastnaesite responds well to hydroxamate, whereas flotation of barite requires much higher concentration, of reagent.

Pradip and Rai [48] also carried out molecular modeling computations on the interaction of the same three minerals and hematite with hydroxamate. The computed interaction energy values plotted in Fig. 9 indicate that the adsorption of hydroxamate on bastnaesite will be considerably higher than on the other three minerals. The equilibrium adsorption isotherms for potassium octyl hydroxamate adsorbing on these



**Fig. 9** Adsorption isotherms for octyl hydroxamate adsorption on bastnaesite, hematite, calcite, and barite (top) and the corresponding interaction energies computed used universal force field (UFF) for potassium octyl hydroxamate adsorption on the cleavage planes of bastnaesite (100), hematite (001), calcite (104), and barite (001). (after Ref. [48])

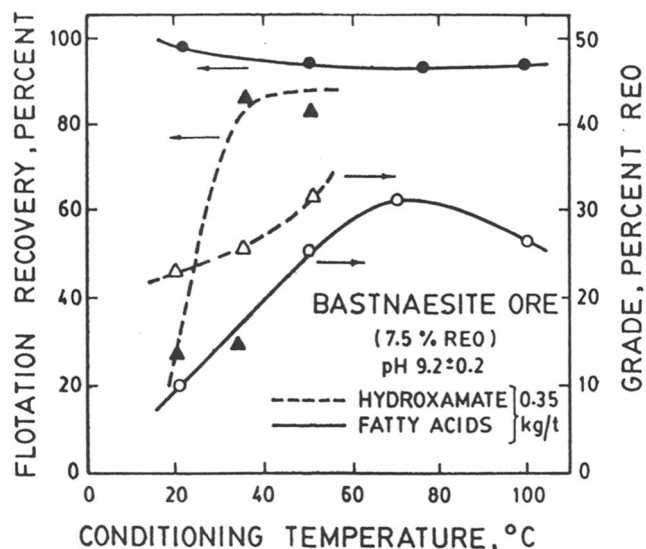
minerals confirm these trends. Hematite data is also included in the figure for comparison since hydroxamate is known to strongly complex with iron metal ions.

As expected, the design and development of new reagents for the flotation separation of rare-earth ores is an area of intense research activity currently. A critical review of the recent publications [49–55] indicates that various research groups are focusing their efforts on conventional fatty acids (oleate) and alkyl hydroxamate collectors along with such known selective depressants such as ammonium lignin sulfonate and sodium silicate for separation of rare-earth minerals, such as bastnaesite, monazite [(Ce, La, Nd, Th) PO<sub>4</sub>], and xenotime [YPO<sub>4</sub>] from the associated gangue minerals (calcite, barite). It is heartening to note that several research groups are banking on molecular modeling computations to provide valuable clues to help design more selective collectors for rare-earth minerals separation [56–58].

Interestingly, Miller and coworkers [59, 60] explored potassium lauryl phosphate as an alternate flotation collector for bastnaesite.

## 5.2 Effect of Temperature in Enhancing Selectivity of Separation

Pradip and Fuerstenau [36, 40, 42, 46] made considerable efforts to delineate the role of temperature in enhancing the selectivity of flotation both with conventional fatty acids (oleate) and alkyl hydroxamate collectors. As illustrated in Fig. 10, both oleate and hydroxamate collector respond well to high-temperature flotation.



**Fig. 10** The effect of temperature on bench-scale tests of rougher flotation of Mountain Pass ore. Recovery and grade of the rougher concentrate of the bastnaesite ore sample using fatty acid (solid line) and hydroxamate (dashed line) as the collector are compared in the figure (after Ref. 42)

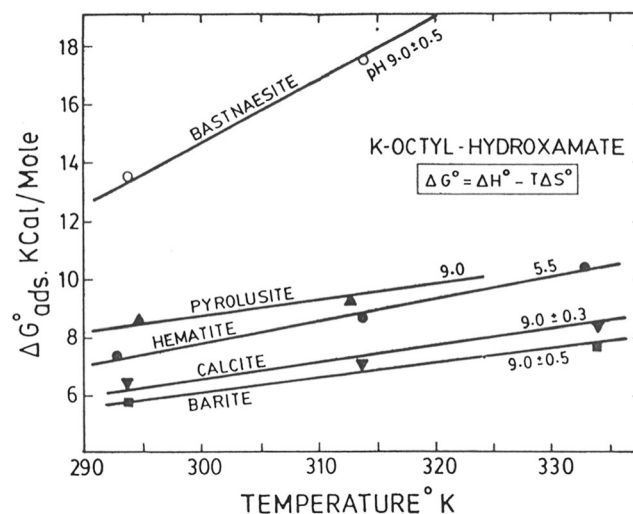
While the hydroxamate collector is more selective (as compared to fatty acids) to start within the flotation separation of Mountain Pass bastnaesite ore (even at room temperature), the selectivity is further enhanced at a relatively higher temperature. The primary reason why high temperature helps enhance selectivity of flotation is because the chemisorption of hydroxamate on bastnaesite is an endothermic reaction with a large entropy of adsorption.

Pradip and Fuerstenau [40] determined the adsorption isotherms of alkyl hydroxamate on bastnaesite, barite, and calcite at three different temperatures namely at 21 °C, 41 °C, and 61 °C. The standard free energies of adsorption for these three minerals were computed from the adsorption isotherms using the Stern equation of adsorption (Eq. 10, Section 2.1). Knowing the free energies of adsorption as a function of temperature, the corresponding enthalpies  $\Delta H^0_{\text{ads}}$  and entropies  $\Delta S^0_{\text{ads}}$  for the adsorption reaction can be estimated using the following equation (assuming that both  $\Delta H^0_{\text{ads}}$  and  $\Delta S^0_{\text{ads}}$  are independent of temperature in the limited range of temperature used during the investigation):

$$\Delta G^0_{\text{ads}} = \Delta H^0_{\text{ads}} - T \Delta S^0_{\text{ads}} \quad (18)$$

$\Delta G^0_{\text{ads}}$  as a function of temperature is plotted in Fig. 11 and the corresponding enthalpies and entropies of adsorption are summarized in Table 2.

The relatively large entropies of adsorption for bastnaesite as compared to calcite and barite in the case of Mountain Pass ore are responsible for the enhanced selectivity of adsorption of hydroxamate on bastnaesite at relatively elevated temperatures. The large entropies associated with adsorption of alkyl hydroxamate on bastnaesite can be attributed to the relative loosening of water structure at the bastnaesite-water interface and also due to hydrophobic chain association effects.



**Fig. 11** Standard Stern-Graham free energy of adsorption of potassium octyl hydroxamate on barite, calcite, hematite, pyrolusite, and bastnaesite as a function of temperature (data taken from Ref. [40, 41])

**Table 2** Standard enthalpies and entropies of adsorption of potassium octyl hydroxamate on bastnaesite, calcite, and barite (computed from standard free energies of adsorption as a function of temperature for the three minerals)

Mineral	$\Delta H_{\text{ads}}^0$ (in Kcal per mole)	$\Delta S_{\text{ads}}^0$ (in cal/per mole per $^{\circ}\text{K}$ )
Pyrolusite	4.4	44
Barite	4.8	37.5
Calcite	10.8	60
Hematite	15	76
Bastnaesite	44.8	198.5

## 6 Reagent Design Based on Molecular Modeling Computations

During the past two decades, theoretical molecular modeling computational methodologies have matured to a level that the results of such computations, can be gainfully employed to significantly reduce the experimental effort needed in the design, development, and even selection of reagents for mineral processing applications. Molecular modeling computations (based on the knowledge of the molecular structure of the reagent and the crystal structure of the mineral only) have been demonstrated to provide reliable estimates of the relative affinity of different reagents for the same mineral (or relative affinity of the same reagent with different minerals). While the detailed discussion on this topic is beyond the scope of this review, the readers are referred to excellent publications on reagent design based on molecular modeling computations (for more details [48, 61–68]).

As illustrated for both of the separation problems discussed in earlier sections, namely the flotation separation of spodumene from associated silicate minerals and the flotation separation of bastnaesite from other minerals present in the Mountain Pass carbonatite ore, the results of the molecular modeling computations matched well with experimental observations. Molecular modeling computations could thus be utilized in screening the most promising among several possible reagents (functional groups as well as different molecular architectures) available and/or designed, for a given separation problem, thus saving enormous experimental effort.

With the availability of enormous computing power as well as several easy to use computational tools for conducting molecular modeling simulations, it is now possible for mineral engineers to utilize this approach in the design and development of novel reagents tailor-made for a separation problem under investigation. The most promising part of this development is the possibility of designing novel reagents based on the surface crystal structure specificity of the mineral to be floated (on the lines illustrated in this paper in Section 4).

Pradip and coworkers [67, 68] further demonstrated how to account for the distribution of different adsorption sites

available on the surface so that not only the appropriate functional groups (polar part) are selected based on this information but the molecular structure of the reagent being designed is also made compatible with the distribution of sites on the surface. This approach is termed as the design of selective flotation reagents based on the molecular recognition methodology. The utility and power of such an approach were demonstrated for a reagent design problem involving apatite-dolomite separation [67, 68].

It is important to add that not only flotation collectors but the design of selective dispersants and flocculants [69, 70] as well as selective solvent extractants [71], is also possible using molecular modeling computations.

Several research groups are currently working on the studies related to the study of surface phenomena at mineral-water interfaces including the study of the structure of mineral-water interface [72] and the changes in the structure of water closer to the interface [73–78].

One of the important properties of surfactants, relevant to mineral flotation is, their critical micelle concentration (CMC). It requires modeling the adsorption of surfactants at the air-water interface as a function of bulk concentration in solution. Molecular modeling computations can help predict the CMC, as demonstrated by several research groups [68, 79–82].

A review of the important milestones in flotation research indicates that the experimental measurement of contact angles (a measure of the hydrophobicity achieved as a result of surfactant adsorption) and the determination of adsorption isotherms for a given surfactant-mineral system are the key to designing highly selective reagents. While it is not yet possible to compute the adsorption isotherms for a given surfactant-surface system [83–85], one can reliably predict the contact angles based on molecular modeling computations [68, 86–88]. The prediction of the interaction energies, as well as the contact angles for a given mineral surface-surfactant system based on molecular modeling computation, should, therefore, be leveraged in the design and development of reagents for mineral processing applications [88, 89].

## 7 Concluding Remarks

The design and development of highly selective flotation reagents remain a challenging area of contemporary research in mineral processing. Quantification of the relative affinity of surfactants based on electric double layer theory was an important milestone in flotation research. Results of electrokinetic measurements, that is, zeta potential-versus-pH (or pPD) curves, provided the means to distinguish between the physisorption (that is, adsorption due to electrostatic) and the chemisorption (which involves chemical

bonding and surface reactions at the interface) of surfactants and quantify the relative strength of interactions in terms of standard free energies of adsorption. In some important cases, specific adsorption phenomena do not involve chemical interactions and therefore fall under physisorption. Very important examples are the chain-chain association of adsorbed surfactants on hydrophilic minerals and adsorption through surfactant chains displacing water from the surface of hydrophobic minerals. The computed free energies of adsorption based on EDL theory and electrokinetic measurements matched well with those calculated from experimental adsorption isotherms.

Mineral crystal structure can lead to the availability of specific adsorption sites on cleavage planes in determining selectivity with chemisorbing collectors. An important example is the adsorption of oleate on spodumene in preference to other silicate minerals present in a pegmatitic ore, which, as illustrated in this work, provides a novel approach to designing more selective flotation reagents.

The successful separation of bastnaesite from associated semisoluble minerals (calcite and barite) with alkyl hydroxamate collectors was found to be more selective than conventional fatty acids and suggests the need for designing flotation collectors based on the specific chelating characteristics of the reagent with metal ions sites available on the surface. The role of temperature in enhancing selectivity of adsorption of the surfactant (higher entropy of adsorption) and hence selectivity of flotation was established in our work.

More recent work on molecular modeling computations to predict the interaction energies on the same systems confirmed the utility and power of such an approach. It is now possible to predict the contact angle for a given mineral-surfactant system based on molecular modeling computations, requiring no experiments. These computations thus provide a powerful tool to design/screen reagents for a given mineral separation problem, thereby selecting the most promising candidates only for more exhaustive experimental test work and saving cost in terms of time and resources in the development of novel, highly selective, and tailor-made reagents for a given separation system.

**Acknowledgements** Pradip acknowledges the encouragement and support provided by Mr. K. Ananth Krishnan, Chief Technology Officer, Tata Consultancy Services Ltd. during the preparation of this paper. Pradip thanks his colleague, Dr. Shankar Kausley at Tata Research Development and Design Centre for his help in the preparation of some of the figures included in this paper.

## Compliance with Ethical Standards

**Conflict of Interest** The authors declare that they have no conflict of interest.

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