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DOE RESEARCH GRANT
NO. DE-FG-02-84ER13181

"The Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double-Bond Reactions of Adsorbed Unsaturated Collector Species"

PROGRESS REPORT

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June 1992

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INTRODUCTION

Froth flotation is a physico-chemical process that is used to separate particles in an aqueous suspension via differences in hydrophobicity as established by the interaction of various reagents at the solid/water, solid/gas and water/gas interfaces. Surfactants called collectors are added to the suspension to selectively adsorb at the surface of specific particles, rendering these particles hydrophobic. Regulators are employed to promote collector adsorption at the desired surfaces, while preventing such reactions at other surfaces. When air is dispersed into the suspension, the bubbles generated attach to hydrophobic particles. The resulting bubble/particle aggregates float to the suspension surface and are collected in a froth phase as a concentrate. Frothers are used to stabilize the froth and prevent the concentrate from collapsing back into the suspension before removal. Hydrophilic particles remain in suspension and are eventually discarded as tailings. Clearly, froth flotation is one of the most outstanding examples of applied surface chemistry, and is used in the food, petroleum, pulp/paper and mineral industries. The use of this technology is perhaps most significant in the mineral industry.

Nonsulfide minerals are generally divided into three classes [1]:

1) soluble salt minerals such as sylvite (KCl) and halite (NaCl),
2) semi-soluble salt minerals, such as fluorite (CaF_2) and apatite ($Ca_5(PO_4)_3X$, where X = F, Cl, OH or CO_3), and
3) insoluble oxide and silicate minerals, such as quartz (SiO_2) and rutile (TiO_2).

Due to differences in mineral solubility and collector adsorption, a wide variety of flotation strategies have been employed for the selective separation and recovery of these nonsulfide minerals. For soluble-salt minerals (alkali halide and oxyanions), the ionic strength of the suspension can be 5 molar or greater, making collector solubility an important issue. Long-chain tallow amines (mixtures of palmityl, stearyl and oleyl amine) are used commercially for sylvite flotation from halite. Demand for potash, the mineral sylvite, has increased considerably in the last 30 years. Agricultural fertilizers account for about 95% of the world potash usage.

Other uses include high-quality glass production, electronic components and ceramics [2]. The importance of soluble-salt flotation world wide was demonstrated by the special session on this topic held at the XVII International Mineral Processing Congress at Dresden, Germany, in September 1991.

Semi-soluble salt minerals (alkaline earth and metallic oxyanions) are often concentrated by flotation with tall oils, which are long chain saturated and unsaturated carboxylic acids such as stearic, oleic and linoleic acids. These collectors are thought to adsorb at the surface of the semi-soluble salt minerals through chemical bonding of the carboxylic acid head group and the mineral cation. Such reactions can occur with cations in the crystal lattice or with cations in solution due to the slight solubility of the mineral. Among the common semi-soluble salt minerals, apatite is used in the production of fertilizers, while fluorite is used as flux in steel and glass-making and to produce fluorine chemicals [2]. Calcite ($CaCO_3$) is a common gangue mineral in nearly all ore bodies. Other important semi-soluble salt minerals include the rare-earth minerals especially bastnaesite, a rare earth fluocarbonate. The production of rare earths is of particular importance in many high-tech areas including permanent magnets, high-temperature superconductors, nuclear power generators and lasers.

Insoluble oxide and silicate minerals are also recovered by flotation. Furthermore, the ubiquitous presence of quartz and clay minerals such as kaolinite in all types of ores makes knowledge of their flotation behavior of paramount importance. Also large quantities of low-grade oxide minerals of strategic metals (mainly titanium) are contained in ore deposits in the southwestern United States. Utilization of these resources would be very useful in maintaining Federal Emergency Management Agency (FEMA) stockpiles and reducing dependence on imports of these critical materials.

During the past two decades, the flotation of nonsulfide minerals has grown substantially. For instance in 1965, approximately 240,000 tons per day (tpd) of nonsulfide minerals were processed by flotation. This production capacity had grown to 560,000 tpd by 1975 and about 640,000 tpd in 1985 [3]. Nevertheless, understanding of the interfacial chemistry and optimum conditions necessary for improved separation efficiencies are incomplete.

Energy consumption in flotation has only been recognized as a significant process variable during the last 15 years. Most of the energy is used to generate bubbles and maintain the particles in suspension. ERDA [4] and NRC [5] reports have concluded that initiatives to maximize flotation response can also result in a reduction in the energy consumed during flotation. Most previous strategies proposed to enhance flotation response have concentrated on new reagents and modifying reagent schedules or on improving the performance of the flotation equipment.

Techniques for detailed, direct observation of the solid/liquid interface have only been developed within the last ten years. The advent of these sophisticated experimental methods now allows for the investigation of the critical role that the interfacial chemistry plays in flotation separations. Understanding the interfacial chemistry will allow flotation chemists to design new procedures for improved flotation efficiency and reduced energy consumption.

This report summarizes the last thirty-six month period of Grant No. DE-FG-02-84ER13181. Research has focused on extending previous results from model systems to minerals representative of each of the nonsulfide mineral types discussed previously. The research supported by the DOE during this period has led to 17 presentations at special seminars and professional society meetings. Further, eleven publications have resulted from this work in a broad range of journals, including publications in ***Langmuir*,** **Applied Spectroscopy, The Journal of Colloid and Interface Science** and in more engineering-related journals. All efforts to communicate these results to our colleagues are documented in APPENDICES 2, 3 and 4.

Our research laboratories at the University of Utah were visited on two occasions by program officers from the Division of Chemical Sciences, Department of Energy. In April of 1989, Dr. Richard Gordon visited our laboratories and reviewed the status of our research program. Later, in January of 1992 Dr. Clem Yonker visited us for a similar purpose.

As a result of the research performed during this grant period, fundamental *in situ* measurements of many interfacial chemical properties for several nonsulfide mineral systems have been made using FT-IR/IRS with reactive internal reflection elements. Significant advancements have been achieved particularly in the examination of surfactant aggregation phenomena at mineral surfaces for both chemisorption (fluorite/oleate) and physisorption (sapphire/SDS) systems. Among these advances are the first adsorption density calculations from real-time near-IR spectral data and the discovery that phase transitions of adsorbed surfactant aggregates can be described from the spectral data.

Substantial contributions to the lattice ion hydration theory have been made to help describe the surface chemistry of soluble salt minerals. Basically, the lattice ion hydration theory explains the sign of the surface charge for these minerals. In this regard, a nonequilibrium technique for the measurement of electrophoretic mobilities has been developed which allows the sign of the surface charge to be determined for alkali halide particles in their saturated brines. These were the first such measurements to be made; the results substantiate the lattice ion hydration theory and represent a significant breakthrough in understanding the flotation behavior of soluble salt minerals.

PROGRAM OBJECTIVES

The primary goal of this research is to improve the flotation efficiency of nonsulfide mineral systems by establishing the fundamental features of collector adsorption reactions and developing appropriate chemical control strategies. *In situ* real-time FT-IR/IRS measurements, nonequilibrium electrophoresis, vacuum flotation, contact-angle goniometry, and laser Raman spectroscopy have been used to accomplish this goal. These experimental techniques have led to the determination of important information concerning collector adsorption phenomena in each nonsulfide mineral system. For example, the demonstration of polymerization of adsorbed unsaturated surfactant species has added a new dimension to semi-soluble salt flotation chemistry and may have more general utility. Furthermore, refinement of the *in situ* FT-IR/IRS analysis has been accomplished particularly for the examination of surfactant aggregation phenomena at nonsulfide mineral surfaces. Finally, the significance of the lattice ion hydration theory has been demonstrated by nonequilibrium electrophoretic mobility measurements, and the new results will provide a better basis for the understanding of soluble-salt flotation phenomena. These accomplishments represent original contributions to applied surface chemistry in general and to flotation chemistry in particular.

Clearly, many program objectives have been realized during this grant period, and a strong foundation for future research efforts has been established.

IN SITU FT-IR INTERNAL REFLECTION SPECTROSCOPY

Throughout the course of this grant, *in situ* Fourier transform infrared internal reflection spectroscopy (FT-IR/IRS) with reactive internal reflection elements (IREs) has been developed to probe the properties of surfactants adsorbed at mineral surfaces. In this experimental technique, the IRE is machined from a material of interest (either synthetic single crystals or naturally occurring mineral crystals) and adsorption is monitored at the IRE surface, hence the term reactive IRE. FT-IR/IRS has been shown to provide direct, real-time, spectral data to quantify adsorption reactions. These spectra can be interpreted to give information concerning three different areas of surfactant behavior.

First, the absorbance of the $-CH_2$ stretching bands has been used to calculate the adsorption density of surfactant at the IRE surface in real-time. From these measurements detailed adsorption isotherms have been constructed. Second, *in situ* FT-IR/IRS spectra contain information concerning the state of adsorption of the surfactant species. Thus, the type of adsorption (chemisorption or physisorption) can be examined. Third, the characteristic features of hydrocarbon chain order in the adsorbed layer can be identified. This allows the type of aggregation, position and orientation of adsorbed surfactant molecules to be determined. In short, *in situ* FT-IR/IRS provides a veritable plethora of information concerning the adsorption of surfactants at mineral surfaces.

For nonsulfide flotation systems, spectral information has been used to distinguish the chemisorbed state from the surface-precipitated state at a fluorite IRE. Also, the interactions and cross-linking/polymerization of adsorbed unsaturated collectors has been examined. Furthermore, conformational analysis has detailed the structural changes (monomer to micelle to coagel) of adsorbed collectors at mineral surfaces. Finally, from this research it is fairly evident that adsorbed collector species in all systems do not exist in a well-ordered vertical orientation as typically described in even the most recent texts.

General Experimental Procedure

Shown in Figure 1 is a schematic representation of light undergoing multiple internal reflections in a parallelipiped-shaped IRE. Two requirements must be met for total internal reflection to occur. First, the IRE must be optically denser, that is have a higher refractive index, than the sample phase. Second, the incident angle of the light beam within the IRE must be greater than the critical angle (θ_c) given by Snell's law ($\theta_c = \sin^{-1}(n_2/n_1)$). Upon total reflection at the IRE interface, an evanescent field is established at the surface. It is through this evanescent field that sampling of the interface occurs. Since the evanescent field decays exponentially away from the surface, with a decay length on the order of the wavelength of the light beam, and because of the relatively low bulk concentration of the surfactant, at least 90% and usually more than 95% of the signal comes from the adsorbed layer.

Figure 2 shows a schematic diagram of the cell used in *in situ* FT-IR/IRS experiments. The IRE, which has been cleaned by a combination of solvents and radio frequency plasma, is

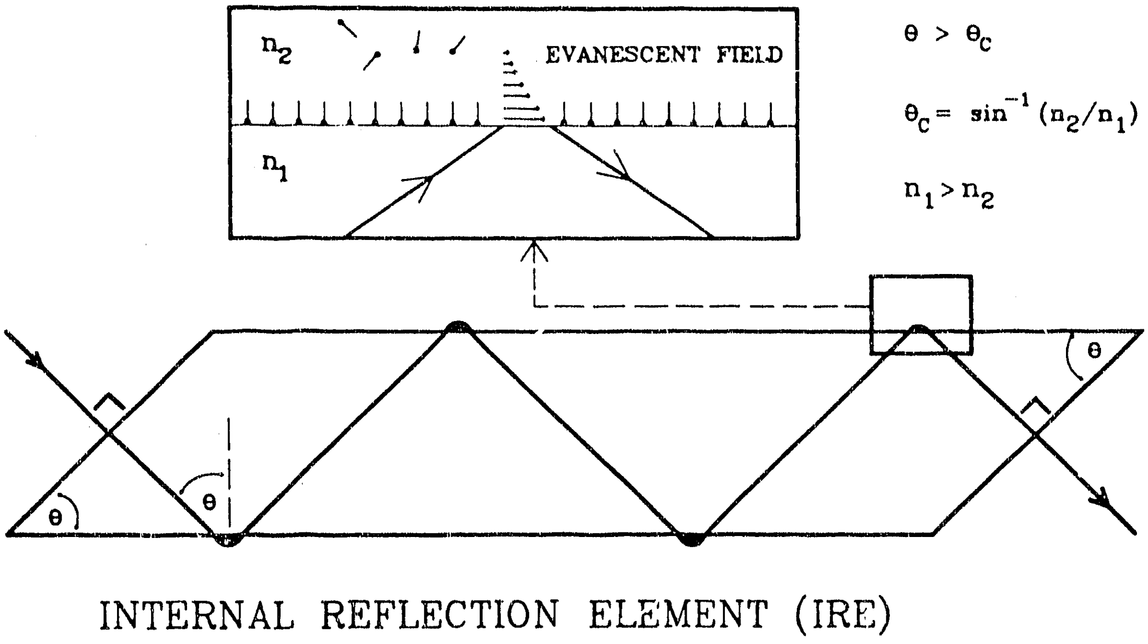
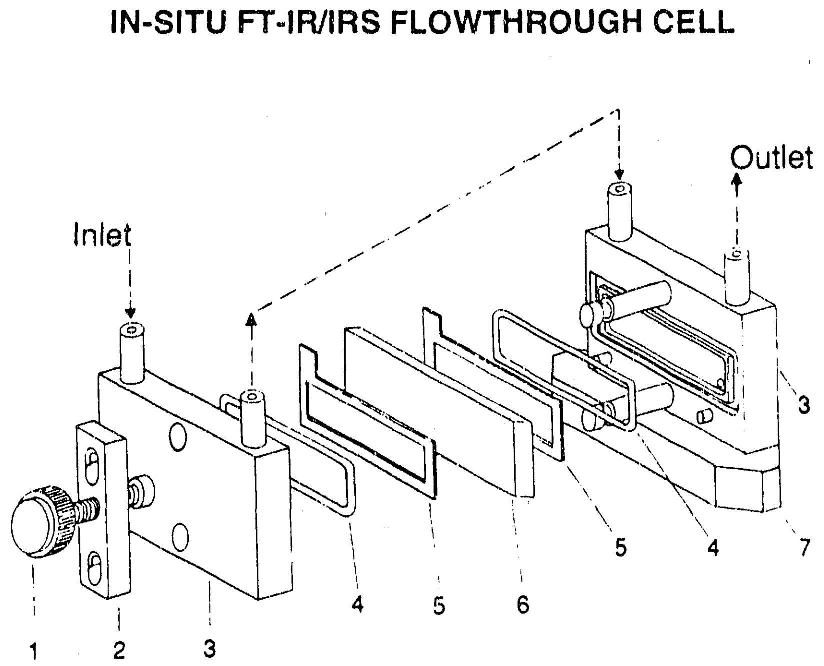


Figure 1. Schematic representation of light undergoing multiple internal reflections in a reactive IRE.



1. Clamping Screw
2. Clamping Bar
3. Flowthrough Cell
4. "O" Rings
5. Teflon or Al Spacers
6. Reactive IRE
7. Mounting Base

Figure 2. Exploded view of an *in situ* FT-IR/IRS flowthrough cell.

placed in the *in situ* FT-IR/IRS flowthrough cell. This cell is placed in the FT-IR sample compartment on a variable-angle holder manufactured by Harrick Scientific. At this point, the efficiency of the cleaning procedure is determined by collecting a spectrum of the cleaned crystal. A background spectrum of the IRS is collected and the surfactantless solvent, usually D_2O, is injected into the inlet port. This solution is allowed to equilibrate with the IRE, and the solvent spectrum is recorded. Surfactant solution is injected through the inlet port to replace the barren solvent solution and spectra of the adsorbing surfactant are recorded as a function of time. Injections are performed at regular intervals to insure that the surfactant concentration in solution has not changed. The solvent spectrum is subtracted from the spectrum of the adsorbed species and the resultant spectrum undergoes the manipulations necessary to obtain the data used to evaluate the adsorbed surfactant.

Adsorption Density Calculations

In the previous grant period, equation 1, initially suggested by Sperline et al. [6], was shown to give accurate determinations of the adsorption density for collectors adsorbed at mineral surfaces.

$$\Gamma = \frac{(A/N) - \epsilon C_b d_e}{2000 \epsilon d_e/d_p} \qquad (1)$$

where
N = number of internal reflections
ϵ = surfactant molar adsorptivity $[1/(cm^2 \cdot mol)]$,
C_b = bulk surfactant concentration (M),
d_e = effective depth, and
d_p = depth of penetration.

Our research group has evaluated and applied this equation to yield the first direct, *in situ* determinations of adsorption isotherms for a number of different systems [7, 8]. Also, we have pioneered the *in situ* examination of adsorption from dilute bulk solutions, so that the spectral data obtained is due almost exclusively to adsorbed species. Finally, research at the University of Utah has extended the *in situ* determination of adsorption densities to the near infrared spectral region to allow the use of mineral crystals which are not transparent in the mid-IR region.

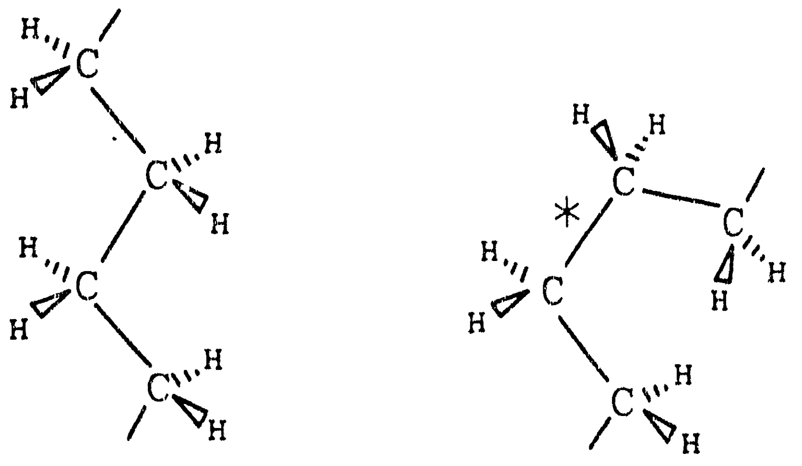
Adsorption State

In situ FT-IR/IRS has also been used to confirm previous indirect solution and *ex situ* spectroscopic measurements concerning the adsorption of oleate at the fluorite surface. In these experiments it was shown for the first time *in situ* that oleate chemisorbed at the fluorite surface for solution concentrations less than 1×10^{-5} M, while at higher concentrations, surface precipitation of calcium dioleate results in multilayer adsorption [8].

Order Phenomena

Order, as applied to surfactants, is used to describe the interactions between the surfactant molecules. For many years surfactants have been thought to aggregate at the solid-water interface. FT-IR spectroscopy can readily distinguish two types of order, orientational and conformational. The orientational order is determined by polarizing the incoming light and ratioing the absorbance under perpendicular and parallel polarization states. The resulting quotient is termed the dichroic ratio. Conformational order is described by the relative frequency of gauche rotational isomers (rotamers).

Figure 3 shows a trans and a gauche rotamer. The difference between these two states is that the gauche conformer is rotated 110° about the middle carbon-carbon bond giving a higher energy (500 cal/mole) conformation [9]. Because the gauche form has higher energy, there will be more gauche rotamers as the temperature is increased. Also, the gauche conformer has a greater cross-sectional area than the trans form, so that as the degree of aggregation increases (and the area per molecule decreases) the number of gauche rotamers will decrease at constant temperature. Prior to the advent of FT-IR/IRS direct *in situ* spectroscopic examination of surfactant aggregation phenomena was impossible. Research performed during this grant provided the first *in situ* measurements of the dichroic ratio of self-assembled surfactant species at an IRE surface and the first determination of the conformational order of adsorbed surfactant species [7, 10].



TRANS GAUCHE

Figure 3. Examples of trans (left) and gauche (right) butylene linkages. The asterisk indicates the gauche bond.

SOLUBLE-SALTS

Excellent progress has been made in the research on soluble-salt systems during the period of this grant. The selective flotation of alkali halide salts such as sylvite (KCl) and halite (NaCl) is of great industrial significance and has been considered sporadically by flotation chemists for many decades. These soluble-salt flotation systems have not been investigated thoroughly because of experimental difficulties associated with high ionic strength brines and collector insolubility in saturated brines. FT-IR/IRS alleviates these problems and is a valuable technique for the study of collector adsorption reactions in soluble-salt flotation systems. In this regard, the adsorption of octylamine by KCl was selected as a model system with KCl serving as the reactive internal reflection element for the *in situ* FT-IR/IRS experiment. After development of appropriate experimental procedures, the results from this study have provided the first *in situ* surface chemistry information for this model system including adsorption density determinations, adsorption kinetics and conformation features of adsorbed collector species.

Of even greater significance, a nonequilibrium technique for the measurement of electrophoretic mobilities has been developed which allows for the determination of the sign of the surface charge for alkali halides. These were the first such measurements to be made and the experimental results were found to support the lattice ion hydration theory. This represents quite a significant breakthrough in understanding the behavior of alkali halides and other soluble salts in their saturated brines. Importantly, particle/particle interaction and flotation behavior from saturated brines can now be explained with confidence and from first principles.

FT-IR/IRS (KCl/n–Octylamine)

The FT-IR/IRS spectra of adsorbed octylamine at the sylvite IRE surface were obtained using the procedure described in the previous section on FT-IR/IRS. The adsorption densities at different molar concentrations were calculated using the adsorption density equation, Equation 1.

Adsorption Kinetics

Octylamine adsorption by the sylvite IRE was studied using D_2O as solvent, since the strong absorbance bands of H_2O tend to mask the bands from the octylamine collector. Figure 4 shows the time dependent *in situ* spectra for octylamine adsorption on KCl from a saturated brine in the aliphatic stretching region (3000-2800 cm^{-1}) at an octylamine concentration of 5.3×10^{-2} M. From spectral data such as that presented in Figure 4, the adsorption density values were calculated and plotted as a function of time for two different concentrations as shown in Figure 5. It can be observed that the adsorption density increases rapidly at first and then levels off at an apparent equilibrium point after about 10 hours equilibration time.

Adsorption Isotherm

An equilibrium adsorption isotherm for the sylvite/octylamine system has been established from the *in situ* spectral data as shown in Figure 6. It was found that monolayer coverage occurred at collector concentrations below 1×10^{-2} M. Above this concentration aggregation of

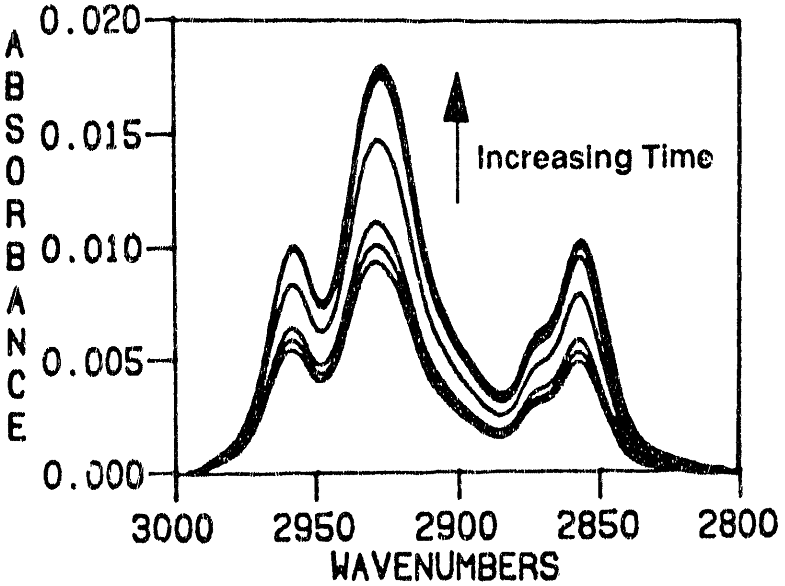


Figure 4. *In situ* spectra of octylamine adsorbed by KCl IREs from a saturated brine containing 5.3×10^{-2} M octylamine.

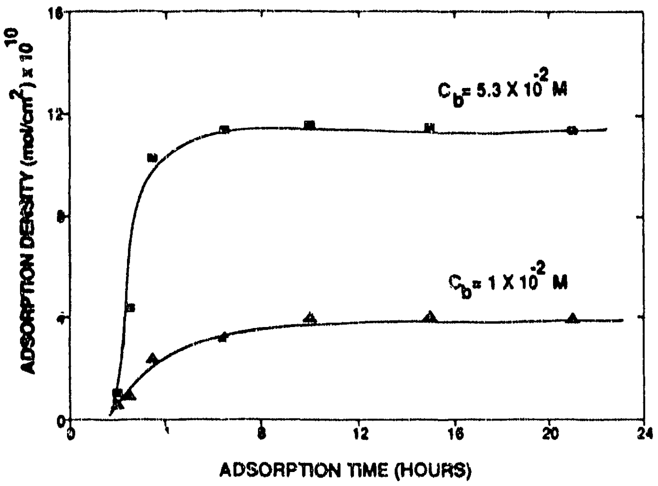


Figure 5. Adsorption density of octylamine on KCl as a function of time.

collector micelles occurs at the surface of sylvite IRE. The rapid increase in adsorption density shown in Figure 6 is somewhat similar to the isotherm reported by Schubert [11] for n-alkyl ammonium chlorides adsorbed on KCl particles.

Conformational Features of the Adsorbed Octylamine

FT-IR/IRS has also been used to determine the alkyl chain conformation of the adsorbed collector state. Similar to the CaF_2/oleate and sapphire/SDS systems, the conformational analysis of the surface state was performed by the examination of systematic shifts in the asymmetric $-CH_2$ stretching frequencies which had been correlated with solution spectra. Unlike other systems (CaF_2/oleate and sapphire/SDS), where surface-phase transitions were found to occur with change in adsorption density, adsorbed n-octylamine maintained a micellar-like conformation at all adsorption densities. This behavior is attributed to the high ionic strength environment for the adsorbed species.

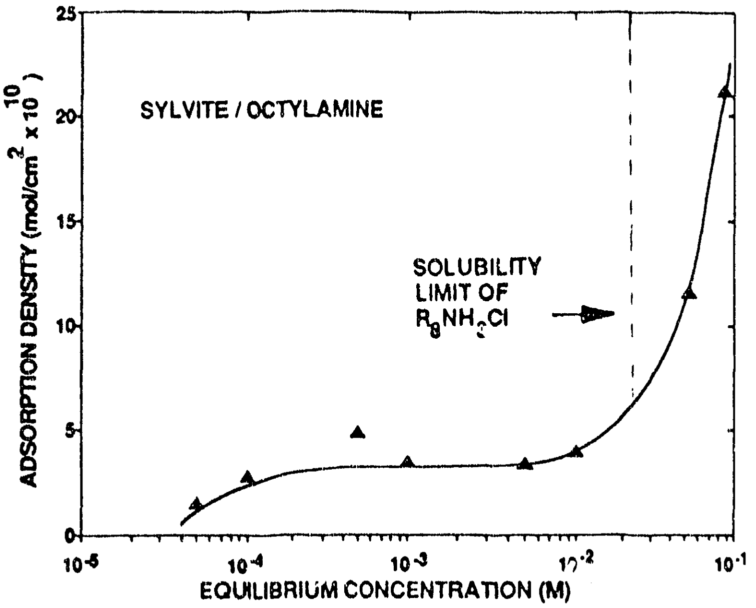


Figure 6. Equilibrium adsorption isotherm for the sylvite/octylamine system at 25°C.

The Significance of Surface Charge in Soluble-Salt Systems

How does selective flotation of sylvite or halite from saturated brines take place? What is the mechanism of collector adsorption in these soluble-salt flotation systems? These questions have intrigued flotation researchers, and during the past fifty years several models [12–18] have been advanced to explain the mechanism of collector adsorption in soluble-salt systems. None of these hypotheses can be used to adequately explain flotation and the collector adsorption phenomena observed in these systems. During the past year, nonequilibrium electrophoretic mobility measurements by laser-Doppler electrophoresis have been done for the first time. On the basis of these measurements, it is now possible to examine the significance of surface charge in soluble-salt systems. In this regard, vacuum flotation experiments, bubble attachment studies and particle interaction experiments for various soluble salt minerals have been completed. These results supplemented by the FT-IR/IRS information will enable us to develop a more complete understanding of collector adsorption phenomena in soluble-salt flotation systems.

Laser-Doppler Electrophoresis

The nonequilibrium electrophoretic mobilities of alkali halides including fluorides, chlorides, bromides, and iodides have been measured during dissolution by laser-Doppler electrophoresis. These measurements were possible because of certain advantages of laser-Doppler electrophoresis over conventional electrophoresis in which the measurements are limited to low ionic strength solutions. The details of the laser-Doppler technique have been reported in "Surface Charge of Alkali Halides as Determined by Laser-Doppler Electrophoresis," published in *Langmuir,* May, 1992. It should be noted that, even though the double layer is collapsed in saturated brines, the surface charge will still be present for these soluble salt particles. In order to describe the electrokinetic behavior of soluble salt particles, nonequilibrium electrophoretic mobility measurements of the alkali halide particles were made after injection into fresh water solutions. Such measurements are dynamic in the sense that the salt particles are dissolving in the aqueous phase during the course of the electrophoretic mobility measurement by the laser-Doppler electrophoresis equipment. Importantly, however, these measurements should give a relative indication of the sign of the surface charge of the salt particles in their saturated brine.

The electrophoretic mobility results obtained were quite reproducible with respect to the sign of the electrophoretic mobility. Figure 7 shows typical electrophoretic mobility distributions for KCl and NaCl. It can be observed from this figure that KCl exhibits a negative electrophoretic mobility of -0.47 ± 0.263 μm/sec/v/cm, while NaCl exhibits a positive electrophoretic mobility of $+0.171 \pm 0.148$ μm/sec/v/cm. Table 1 presents the electrophoretic mobility results for 21 different alkali halides, for which as many as nine replicate measurements were made. It should be emphasized that, for a given salt, the measured electrophoretic mobility was consistently of the same sign.

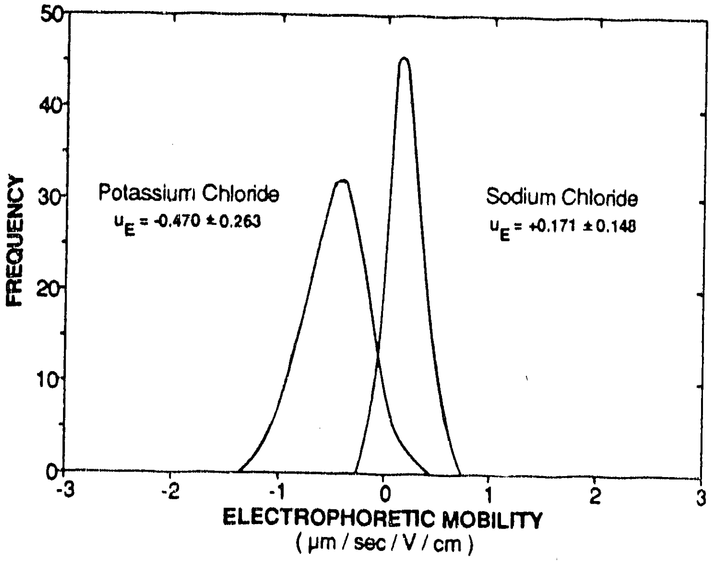


Figure 7. Nonequilibrium electrophoretic mobility distributions for KCl and NaCl.

Table 1. Results from Laser-Doppler Electrophoresis Experiments — Nonequilibrium Conditions.

Alkali Halide	Number of Observations	Electrophoretic mobility, μm/sec/v/cm Range	Mean
Fluorides			
LiF	5	+0.175 to +0.271	+0.221
NaF	4	+0.112 to +0.171	+0.162
KF	5	+0.061 to +0.083	+0.084
RbF	9	+0.040 to +0.135	+0.065
CsF	3	+0.486 to +0.813	+0.582
Chlorides			
LiCl	4	-0.497 to -0.733	-0.641
NaCl	5	+0.124 to +0.216	+0.163
KCl	6	-0.330 to -0.467	-0.421
RbCl	3	+0.164 to +0.270	+0.213
CsCl	4	+0.325 to +0.495	+0.397
Bromides			
LiBr	7	-0.224 to -0.375	-0.320
NaBr	3	-0.252 to -0.342	-0.311
RbBr	3	-0.388 to -0.496	-0.459
KBr	5	-0.078 to -0.106	-0.086
CsBr	3	+0.064 to +0.081	+0.072
Iodides			
LiI	4	-0.741 to -0.803	-0.761
NaI	8	-0.662 to -0.791	-0.741
KI	4	+0.057 to +0.109	+0.079
RbI	4	-0.098 to -0.348	-0.253
CsI	3	+0.025 to +0.061	+0.041
$NaI \cdot 2H_2O$	4	+0.026 to +0.050	+0.039

The validity of these nonequilibrium measurements was demonstrated by making equilibrium measurements for LiF and NaF. Table 2 presents the experimental results, which show the nonequilibrium electrophoretic mobilities to be equivalent in sign to the equilibrium electrophoretic mobilities measured after one hour of equilibration between the salt and the aqueous brine solution. On this basis, it is expected that the nonequilibrium electrophoretic mobility measurements can be used to establish the sign of the surface charge for each alkali halide salt.

Table 2. Comparison of Nonequilibrium Electrophoretic Mobilities with Equilibrium Electrophoretic Mobilities for Two Alkali Halide Salts.

		Mean Electrophoretic Mobility,[a] μm/sec/v/cm	
Salt	Solubility	Nonequilibrium	Equilibrium
LiF	0.27 g/100 cc	+0.221 (5)	+0.155 (8)
NaF	4.22 g/100 cc	+0.162 (4)	+0.099 (6)

[a] Number of observations reported in parentheses.

Lattice Ion Hydration Theory

How do the results from electrophoretic measurements compare with the expected behavior based on lattice ion hydration theory? The lattice ion hydration theory [19] describes the surface charge developed by nonreactive ionic solids when placed in water. This theory applies to ionic solids that do not react with water to form weak surface acid groups (hydrolysis) and to ionic solids that do not undergo surface oxidation reactions. Either reaction type would modulate the surface charge that the solid develops in water. The only reaction of consequence then is the hydration of lattice ions and differential hydration of these lattice ions at the surface of the solid determines the sign of the surface charge.

For the alkali halides, the surface charge should be established simply by comparing the gaseous ion hydration free energies of the respective lattice ions. The results from the laser-Doppler electrophoresis are compared to the predictions using the simplified lattice ion hydration theory in Table 3. The gaseous hydration free energy values given in Table 3 were determined based on the Born model [20], which allows for the calculation of free energies that are accurate to within a few percent [21].

Table 3. Sign of the Surface Charge for Selected Alkali Halides.

	Negative Gaseous Hydration Free Energies, kcal/mole		Sign of Surface Charge	
	Cation	Anion	Predicted[a]	Experimental[b]
Fluorides				
LiF	112.0	109.6	?	+
NaF	88.4	109.6	+	+
KF	71.1	109.6	+	+
RbF	65.9	109.6	+	+
CsF	58.2	109.6	+	+
Chlorides				
LiCl	112.0	82.5	-	-
NaCl	88.4	82.5	-	+
KCl	71.1	82.5	+	-
RbCl	65.9	82.5	+	+
CsCl	58.2	82.5	+	+
Bromides				
LiBr	112.0	75.7	-	-
NaBr	88.4	75.7	-	-
KBr	71.1	75.7	+	-
RbBr	65.9	75.7	+	-
CsBr	58.2	75.7	+	+
Iodides				
LiI	112.0	66.5	-	-
NaI	88.4	66.5	-	-
KI	71.1	66.5	-	+
RbI	65.9	66.5	?	-
CsI	58.2	66.5	+	+
$NaI \cdot 2H_2O$	NA	NA	NA	+

[a] Simplified lattice ion hydration theory.
[b] Electrophoretic-mobility measurements by laser-Doppler electrophoresis.

As can be noted from Table 3, the measurements for five salts are in disagreement with the predictions from the simplified lattice ion hydration theory; of particular interest is KCl. These discrepancies might be due to differences in lattice energy contributions of cation and anion in the salt, lattice defects and/or relaxation effects [22–24]. When gaseous ion hydration free-energy values based on enthalpies reported by Kanevskii [25] are used, the lattice ion hydration theory predictions match most of the experimental results, with KCl, KBr, and RbBr being the only exceptions.

Flotation of KCl and NaCl

The nonequilibrium electrophoretic mobility results from the previous section allow for the sign of the surface charge to be predicted for alkali halides in their saturated brines. On this basis, the hypothesis regarding the role of surface charge in the flotation of alkali halides was examined in detail. For example, the flotation response of KCl and NaCl salts was studied with dodecylamine hydrochloride and sodium laurate collectors.

It is known that most amine and carboxylate collectors used in alkali halide flotation systems form insoluble collector colloids at relatively low collector concentrations. Similar to the results reported by Roman et al. [18], Figure 8 shows that KCl floats well with $R_{12}NH_3Cl$ collector only after precipitation of the $R_{12}NH_3Cl$ collector colloid from solution. It has been reported that $R_{12}NH_3Cl_{(s)}$ is positively charged at natural pH [26]. Because the charges on KCl (see Table 1) and $R_{12}NH_3Cl_{(s)}$ are opposite in sign, it is reasonable to suspect that heterocoagulation occurs between the positively charged $R_{12}NH_3Cl_{(s)}$ collector colloids and the negatively charged KCl particles. This heterocoagulation event appears to account for the effective flotation of KCl with $R_{12}NH_3Cl$ collector. It should also be noted from Figure 8 that NaCl is not floated by the positively charged $R_{12}NH_3Cl_{(s)}$ collector colloid, because NaCl carries the same charge as the collector colloid (see Table 1), and heterocoagulation does not occur. Similar arguments hold for the negatively charged $R_{12}COONa_{(s)}$ collector colloid. In this case, positively charged NaCl is floated with the carboxylate collector colloid, whereas negatively charged KCl is not, as shown in Figure 9.

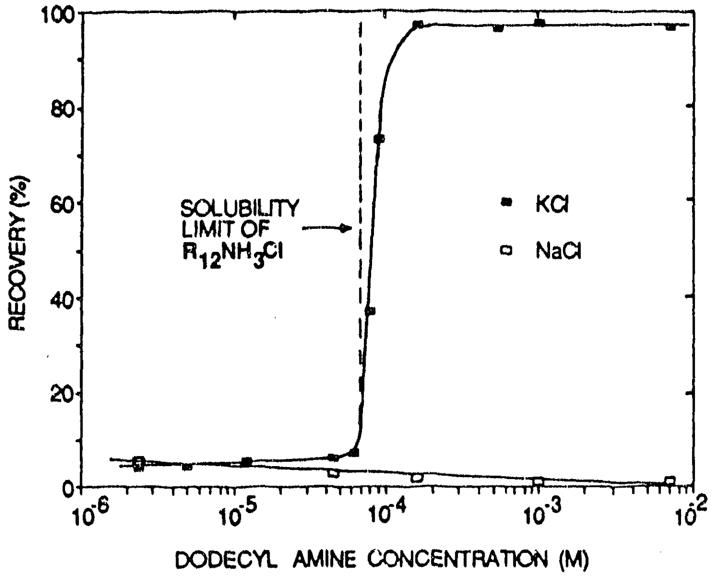


Figure 8. Flotation behavior for sylvite and halite with dodecylamine as collector.

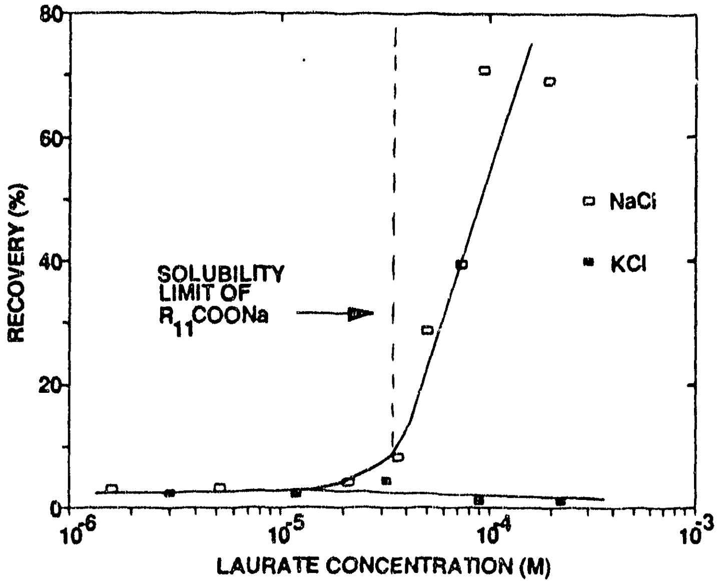


Figure 9. Flotation behavior of sylvite and halite with sodium laurate as collector.

It was also found that the flotation response of sylvite and halite is sensitive to the pH of the system and to the solution activity of K^+ ions, as was reported in "The Significance of Surface Charge in Alkali Halide Flotation by Adsorption of Collector Colloids," presented at the 121st Annual SME Meeting, Phoenix, Arizona, February, 1992. These results again indicate that the alkali halide flotation is determined by the interaction forces associated with the surface charge of the collector colloid and the surface charge of the alkali halide mineral. This hypothesis has further been tested for different alkali halides based on bubble attachment studies and particle interaction experiments.

Bubble Attachment Studies

Table 4 gives the results of the bubble attachment studies for alkali fluorides, chlorides, bromides, and iodides. This table also presents the experimentally determined sign of the surface charge and the expected flotation behavior/bubble attachment for these alkali halides. Excellent agreement between theory and experiment is observed. As is evident from Table 4, only two alkali halide salts, namely CsCl and CsBr, deviated from the expected flotation behavior according to the suggested adsorption mechanism of heterocoagulation between the collector colloid and the alkali halide particles. Further analysis is underway to explain these deviations.

Particle Interactions

The results of particle interaction experiments reported in "Interaction of Alkali Halide Particles in Their Saturated Brines and the Significance of the Attractive Hydration Forces" to be published in the *Proceedings of the Engineering Foundation Conference on Dispersion and Aggregation: Fundamentals and Applications,* Palm Coast, Florida, March, 1992, indicate that the surface charge developed by alkali halides in their saturated brines plays a very important role in the stability of such particulate suspensions. Clearly, DLVO theory is only of limited utility in describing the suspension stability at these high ionic strengths. The extent of particle interaction has been studied by optical microscopy which clearly shows that when oppositely

Table 4. Bubble attachment studies for alkali halides with dodecylamine hydrochloride (3×10^{-4} M) as collector.

Alkali Halide	Surface Charge	Bubble Attachment Predicted	Bubble Attachment Experimental
LiF	+	N	N
NaF	+	N	N
KF	+	N	N
RbF	+	N	N
CsF	+	N	N
LiCl	-	Y	Y
NaCl	+	N	N
KCl	-	Y	Y
RbCl	+	N	N
CsCl	+	N	Y
LiBr	-	Y	Y
NaBr	-	Y	Y
KBr	-	Y	Y
RbBr	-	Y	Y
CsBr	+	N	Y
LiI	-	Y	Y
NaI	-	Y	Y
KI	+	N	Some
RbI	-	Y	Y
CsI	+	N	N
$NaI \cdot H_2O$	+	N	N

charged alkali halide particles are examined as a binary mixture of particles, significant aggregation occurs relative to the behavior of salt particles of the same sign of surface charge, in which case they tend to remain dispersed.

In summary, it is evident from this research program that surface charge analysis of soluble-salt systems is now possible based on reliable electrokinetic measurements by laser-Doppler electrophoresis. On the basis of this analysis, the nature of collector adsorption and the flotation behavior of alkali halide salts from their saturated solutions can now be described more accurately by the heterocoagulation of collector colloids with alkali halide particles of opposite charge.

Research in Progress

Further research is in progress to explain the deviations in behavior of certain alkali halide salts, most importantly KCl, from that predicted by lattice ion hydration theory. Preliminary results indicate that these deviations are due to the presence of lattice defects and consequent changes in the lattice energy contributions. Efforts are also underway to physically examine the presence of adsorbed collector colloids on the salt mineral particles using an appropriate experimental technique such as transmission electron microscopy or scanning force microscopy. Also, interaction forces will be examined by atomic-force microscopy. These forces are believed to be responsible for the proposed heterocoagulation event which occurs between the oppositely charged collector colloids and the salt mineral particles at these high ionic strengths. Already preliminary results from this work have opened up a new perspective for soluble-salt flotation and should lead to significant improvements in soluble-salt flotation practice.

SEMI-SOLUBLE SALTS

Semi-soluble salt minerals are distinguished from other mineral types due to their moderate aqueous solubilities having solubility products on the order of 1×10^{-10}. The most common semi-soluble salt minerals are alkaline earth halides or salts of oxyanions as exemplified by fluorite, CaF_2; calcite, $CaCO_3$; fluorapatite, $Ca_5(PO_4)_3F$; scheelite, $CaWO_4$; and gypsum, $CaSO_4 \cdot 2H_2O$. Because single crystals of fluorite and calcite are readily available, detailed *in situ* FT-IR/IRS spectroscopy investigations have been restricted to these two minerals. However, FT-IR/IRS with reactive IREs has been successfully demonstrated for fluorapatite [7] and should not be a problem for scheelite and gypsum, since they are also IR-transparent.

Tall oil, a mixture of various organic acids predominated by the 18–carbon fatty acids (n–alkyl carboxylates) shown in Figure 10, is the most common collector for the industrial flotation of semi-soluble salt minerals. Of the components, the most abundant is oleic acid

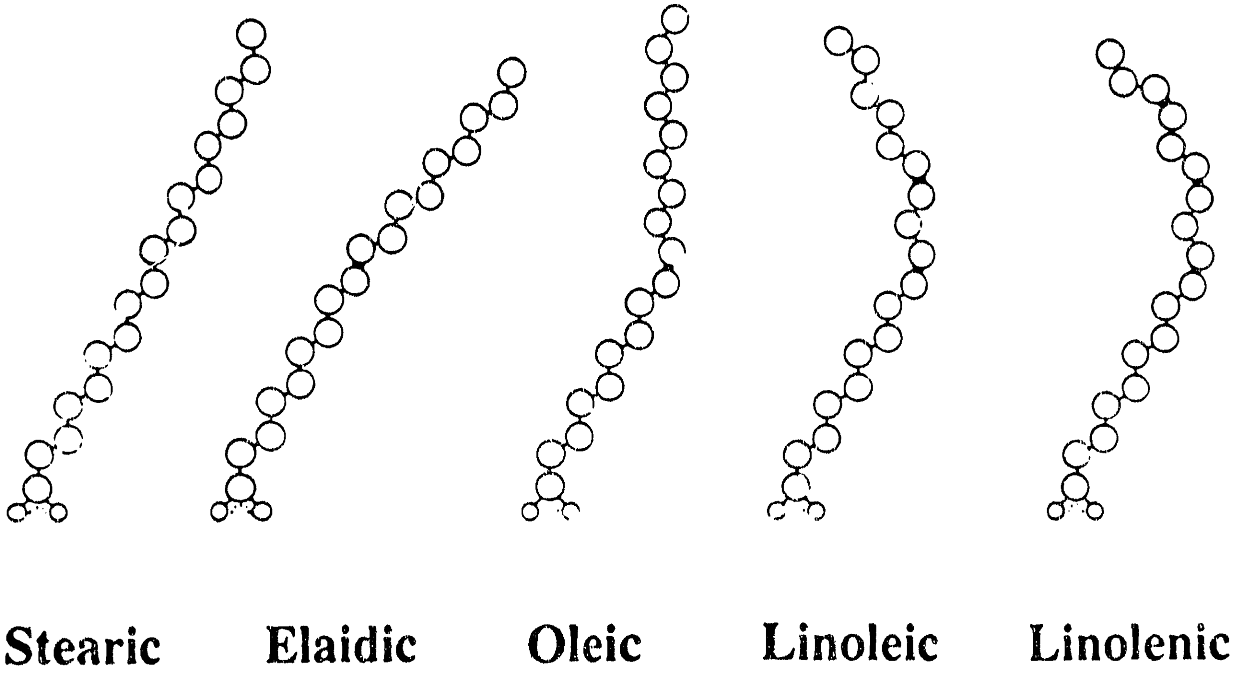


Figure 10. Typical 18-carbon fatty acids in tall oil. Hydrogen atoms are omitted for clarity.

which is also known by its IUPAC name of cis-9-octadecenoic acid. Stearic (octadecanoic) acid does not contain a double bond and is therefore hydrogen-saturated. On the other hand, because oleic, elaidic (trans-9-octadecenoic), linoleic (cis-9,cis-12-octadecadienoic) and linolenic (cis-9,cis-12,cis-15-octadecatrienoic) acids contain double bonds, they are referred to as unsaturated surfactants. Linolenic acid contains three double bonds and is therefore the most unsaturated of the five fatty acids mentioned. The prefix 'cis' indicates hydrogen atoms on the double-bonded carbons are on the same side of the molecule and 'trans' means they are on opposite sides. Consequently, elaidic and oleic acids are geometric isomers of one another.

Fluorite/Oleate

Because fluorite is frequently floated from calcite at temperatures between 40 and 80°C with tall oil as collector, oleate adsorption isotherms were determined for fluorite at room temperature and 40°C by *in situ* FT-IR/IRS as shown in Figure 11. Both the mid-IR and the near-IR spectral regions were used to quantify the fundamental aliphatic stretching and aliphatic combination bands, respectively. The isotherms show three distinct adsorption regions (labelled

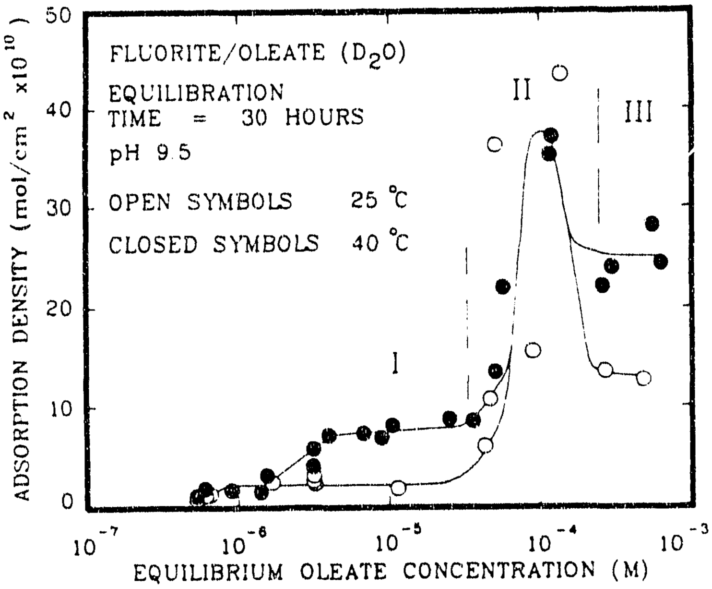


Figure 11. Adsorption isotherm of oleate by fluorite at 25°C and pH 9.5 as calculated from *in situ* FT-IR/IRS data.

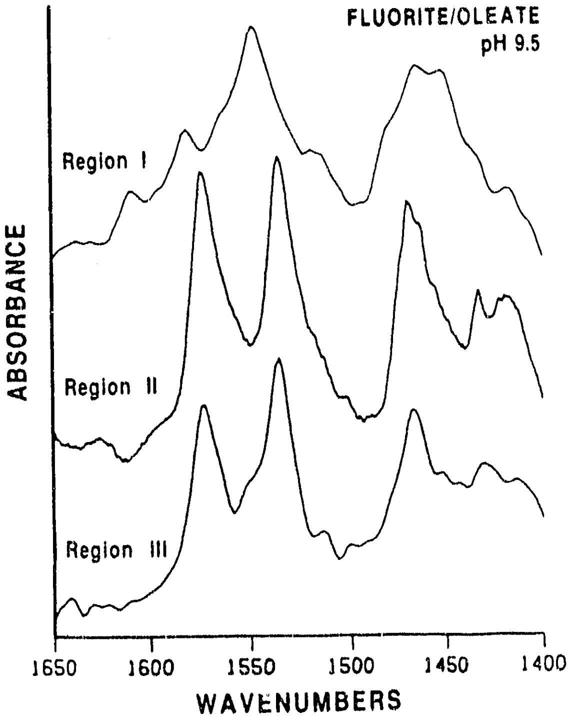


Figure 12. *In situ* FT-IR/IRS spectra of chemisorbed oleate (Region I) and surface-precipitated calcium dioleate (Regions II and III) at a fluorite surface.

I, II, and III in Figure 11) and compare quite well to previous research conducted at the University of Utah [27] and elsewhere [28, 29] with various *ex situ* and solution-depletion methods. However, the *in situ* FT-IR/IRS technique was found to be more sensitive than other methods at dilute concentrations below 1×10^{-5} $\underline{M}$ where a monolayer of oleate forms (Region I). Spectra of the carboxylate stretching bands in Figure 12 shows that adsorbed oleate in this region contains only a single C=O stretching band at 1546 cm^{-1}. Consequently, oleate is believed to chemisorb as a monocoordinated species in Region I. This would explain why a large free energy change of −10 kcal/mole has been measured for the adsorption process in this region and why the adsorption reaction is endothermic and thereby gives rise to increased adsorption density at elevated temperatures [30]. In addition, it also explains why this layer can only be removed by plasmod combustion [31] and why repulping and refloating fluorite particles does not appreciably change flotation recoveries or grades [32].

At higher concentrations, the appearance of a doublet at 1576 and 1535 cm^{-1} is evident from the spectra presented in Figure 12 for Regions II and III. The multilayer species has been identified as surface-precipitated calcium dioleate. This claim is substantiated by the fact that multilayer formation begins near 4×10^{-5} M (see Figure 11), a concentration which can be approximated from the solubility products of calcium dioleate (4×10^{-14}) and fluorite (6×10^{-11}). Since the critical micelle concentration for oleate is 2×10^{-3} M, Region II appears to be in equilibrium with monomeric oleate and Region III with micellar oleate. However the decrease in calcium dioleate precipitation can also be explained by the nature of the surface calcium dioleate. If the surface precipitation results in a protective film, calcium ion diffusion from the fluorite lattice will be prevented and the extent of surface precipitation will be reduced [33].

In situ FT-IR/IRS provides real-time information about the adsorption process, and kinetic analysis of the chemisorption process in Region I shows that the $-CH_2$ asymmetric stretch in Figure 13 exhibits a frequency shift from 2925 cm^{-1} at low adsorption density near 0.8×10^{-10} mol/cm^2 to 2920 cm^{-1} at monolayer coverage. This shift is analogous to the gauche-trans conformational change observed for the micelle to coagel phase transition [34]. When equilibrium was obtained, the reverse transition (melting) was observed upon increasing the temperature from 20°C to 40°C and 60°C. Further confirmation of this thermotropic effect was observed by monitoring the frequency shift of the symmetric $-CH_2$ stretch between 2851 and 2853 cm^{-1}. Consequently, a micellar-like state for chemisorbed oleate on fluorite is believed to exist at low adsorption densities and/or elevated temperatures; under other conditions, the coagel-like state appears to predominate. By comparison, the calcium dioleate surface precipitate did not exhibit this frequency-shift phenomenon and was found to only possess the all-trans conformation.

It therefore appears that oleate initially chemisorbs with few neighboring oleate species and has highly mobile alkyl chains with a significant number of gauche bonds. As adsorption continues, neighboring oleate molecules begin to interact through van der Waal's forces causing the number of gauche bonds to diminish. In lieu of investigations ascribing gauche bonds to

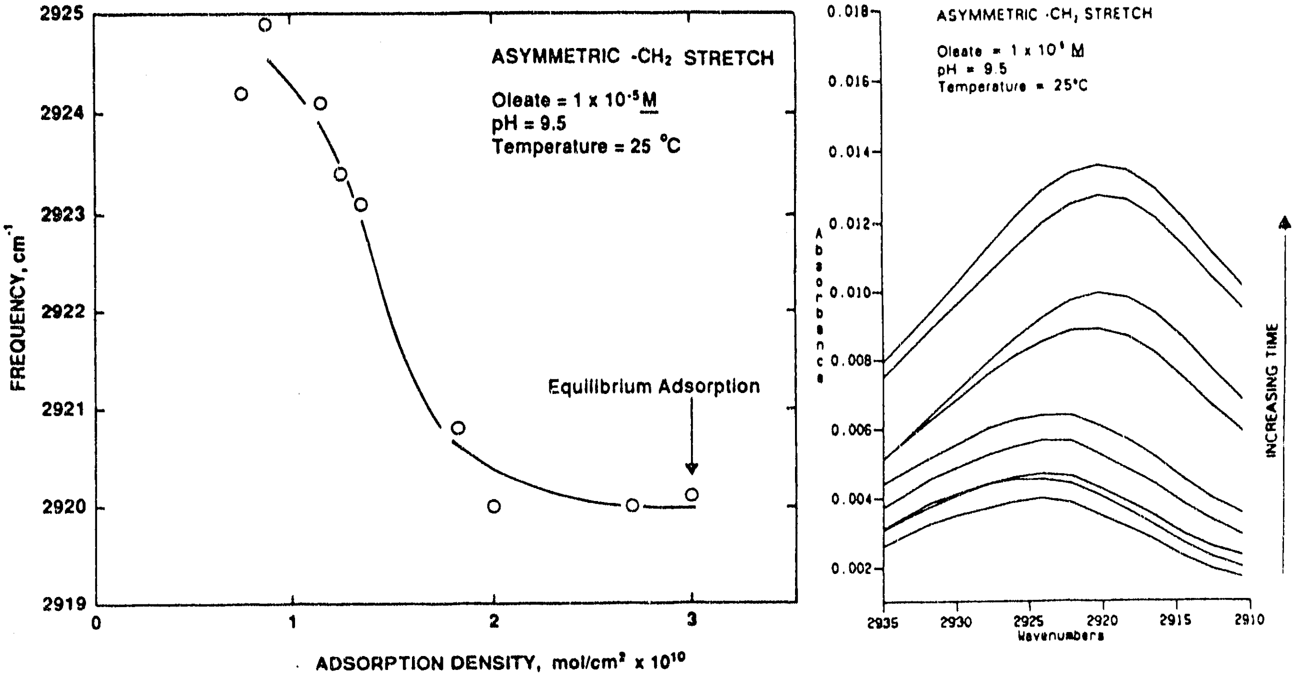


Figure 13. Frequency shift of the asymmetric $-CH_2$ stretching band as oleate chemisorbs at a fluorite surface.

specific conformations (e.g., end gauche, double gauche, kink, and jog) [35-37], it is believed that gauche bonds are more prevalent towards the tail-end of the hydrocarbon chain, as shown in Figure 14. Unlike previous illustrations, Figure 14 also pictures the head groups of the chemisorbed oleate being monocoordinated at the fluorite surface.

By ratioing the integrated absorbance of the =CH band at 3005 cm^{-1} to that of all the aliphatic stretching region between 3050 and 2800 cm^{-1}, reactions involving the double bond were also examined using *in situ* FT-IR/IRS with reactive IREs. Specifically, the decrease in this integrated area ratio with increasing temperature (Figure 15a) and increasing oxygen pressure (Figure 15b) indicates that oxidation of the double bond occurred for the chemisorbed oleate in Region I but was more pronounced at elevated temperatures and oxygen-saturated conditions. The chemisorbed oleate on fluorite was believed to polymerize in the presence of

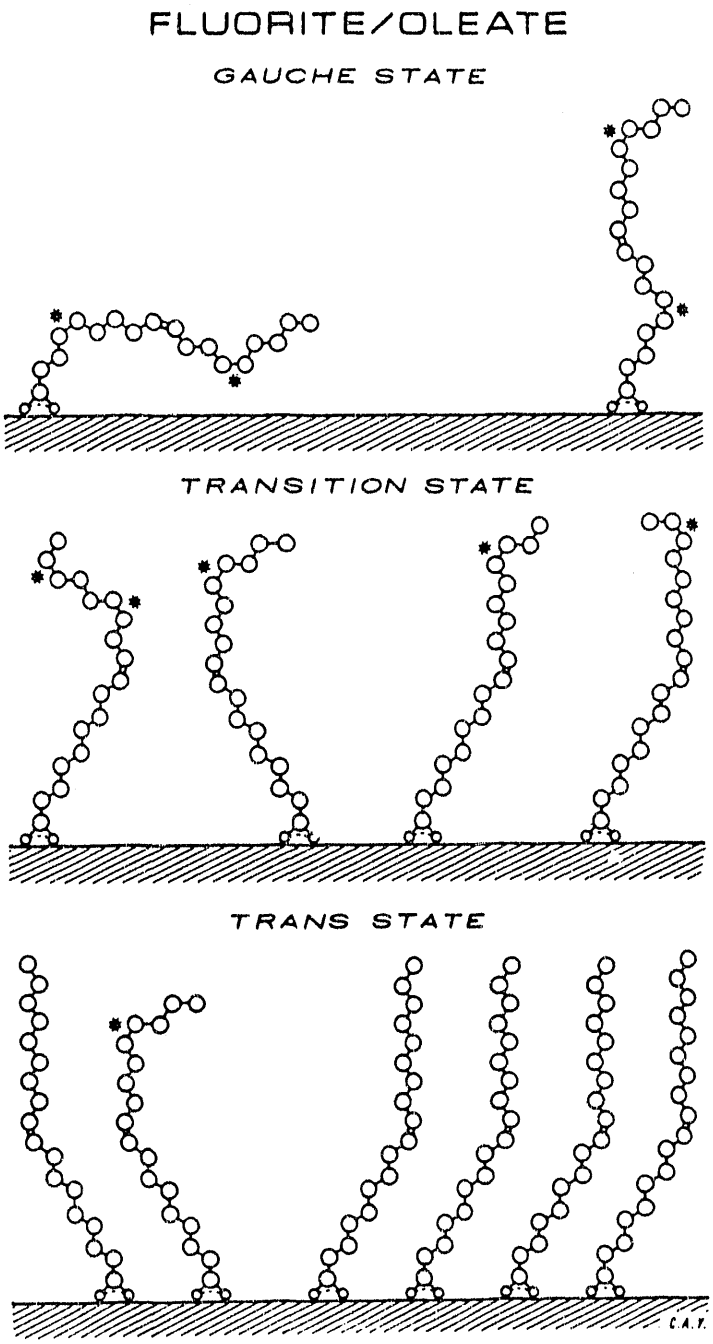


Figure 14. Conformation of chemisorbed oleate at a fluorite surface for different levels of adsorption density revealing the transition from the gauche state at submonolayer coverage to the trans state at near monolayer coverage. Gauche bonds are designed with asterisks (*).

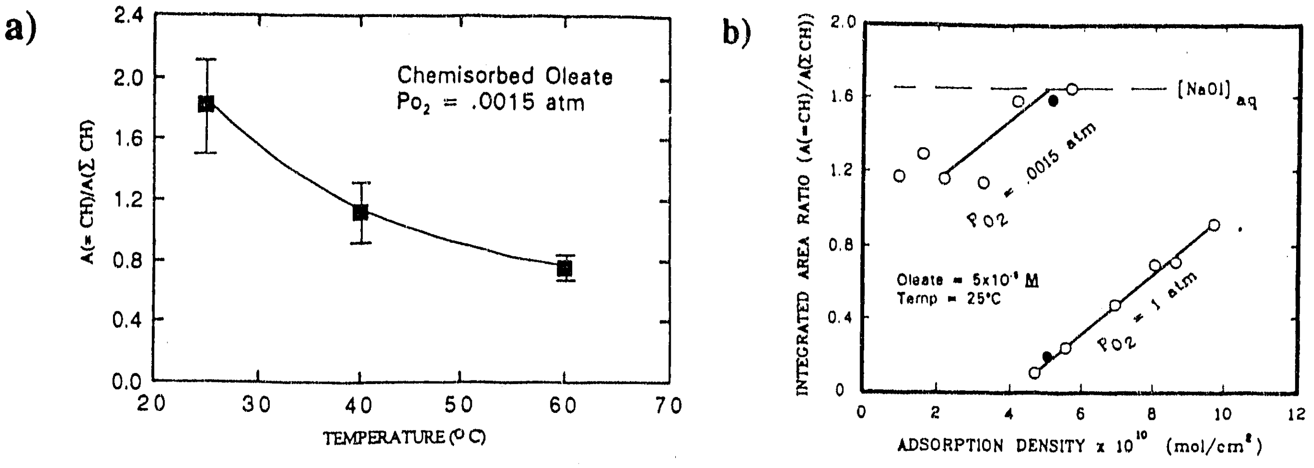


Figure 15. Effect of oxygen (a) and elevated temperature (b) on the double-bond reactivity of chemisorbed oleate at a fluorite surface.

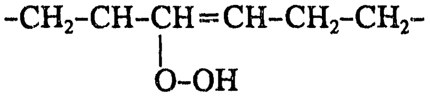
Table 5. Effect of oxygen and temperature on the hydrophobic characteristics of fluorite [39].

Oleate Concentration = 1×10^{-5} M
Conditioning Time = 20 min
pH = 8.1

Gas	Temperature	Contact Angle	Bubble Attachment Time	Recovery
Air	22°C	70-73°	260-270 ms	60%
Air	60°C	90-95°	20-22 ms	88%
O_2	22°C	90-92°	20-25 ms	83%

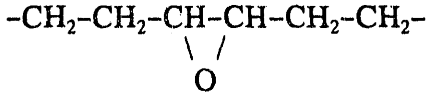
oxygen and/or elevated temperatures according to the reaction sequence outlined below [38] resulting in the enhanced hydrophobic surface characterized in Table 5 [39]:

1. Autoxidation of oleate molecules to hydroperoxides;



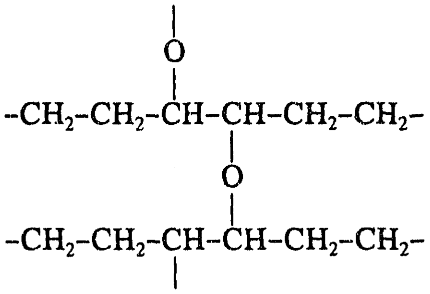
$$-CH_2-CH-\underset{\substack{|\\ O-OH}}{CH}=CH-CH_2-CH_2-$$

2. Surface catalysis of hydroperoxides to epoxides;



$$-CH_2-CH_2-\underset{\substack{\backslash\ /\\ O}}{CH-CH}-CH_2-CH_2-$$

3. Polymerization of epoxides to a polyether;



$$\begin{array}{l} -CH_2-CH_2-\overset{\substack{|\\ O\\ |}}{CH}-\underset{\substack{|\\ O\\ |}}{CH}-CH_2-CH_2- \\ -CH_2-CH_2-\underset{|}{CH}-CH-CH_2-CH_2- \end{array}$$

The surface-precipitated calcium dioleate (regions II and III of the adsorption isotherm) did not show any double-bond reactivity, which may be related to steric hindrance due to its all-trans conformation and/or the high adsorption density of the calcium dioleate at the fluorite surface. These findings are in agreement with those reported by *ex situ* techniques [40, 41], although the appearance of polyether/epoxide bands near 1100 cm^{-1} was impossible to detect since fluorite is opaque below approximately 1200 cm^{-1}.

Since fluorite is opaque below 1200 cm^{-1}, laser Raman spectroscopy (LRS) was employed to retrieve information in this and other spectral regions. Preliminary *ex situ* results demonstrated that the double-bond of chemisorbed oleate at the surface of a high-surface-area fluorite powder (14 m^2/g) may have reacted under oxygen but not under nitrogen atmosphere due to the disappearance of the =CH at 3005 cm^{-1} (see Figure 16a). Although the signals in Figure 16a are weak, the appearance of the epoxide band at 1090 cm^{-1} in Figure 16b clearly confirms that the double-bond reaction occurs and that the polymerization phenomenon may

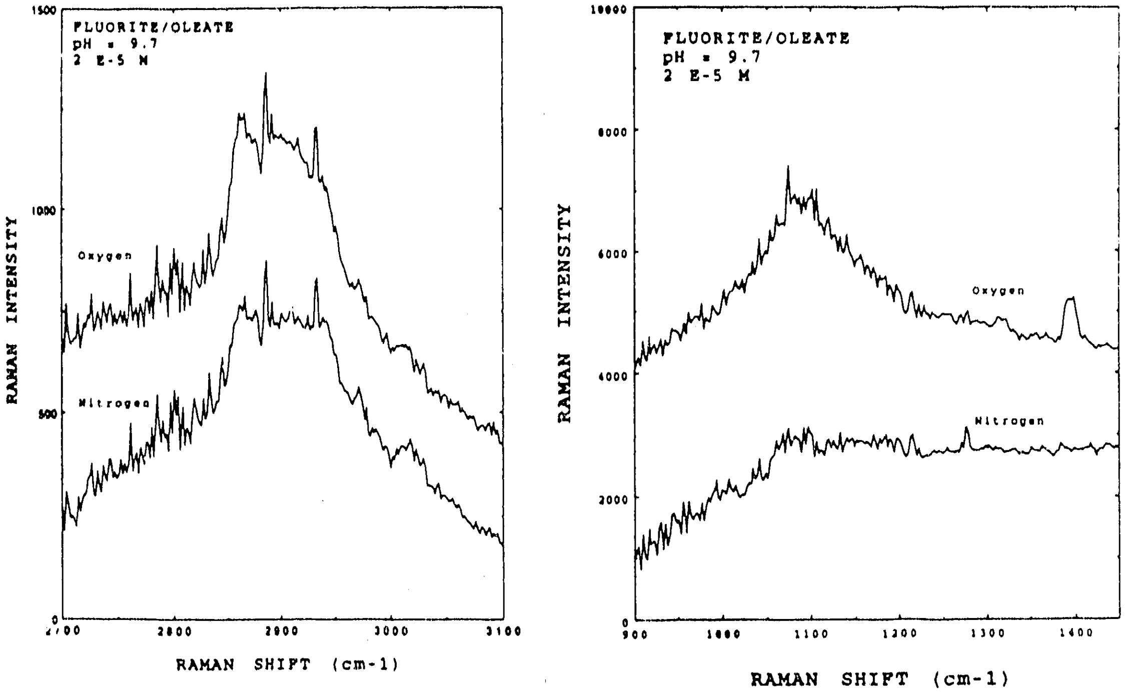


Figure 16. Raman spectra of chemisorbed oleate at a fluorite surface indicating (a) double-bond reactivity and (b) subsequent epoxide formation.

account for enhanced hydrophobicity of fluorite under oxygen atmosphere at room temperature.

Calcite/Oleate

Rather than using synthetically grown minerals, calcite IREs were prepared from optically-pure, natural specimens of Iceland Spar (Mexico). Because calcite is not transparent below 3300 cm^{-1}, the overtone and combination absorbance regions of the aliphatic stretch were monitored. However, in order to overcome the well-known birefringence of calcite, specific geometries for the IREs were established. For the overtone band, the incident angle was 58° in order to satisfy total internal reflection for only the higher refractive index. For the combination band, an incident angle of 71° was needed to minimize carbonate absorbances.

The resulting isotherm for oleate adsorbed on calcite is shown in Figure 17 and is in excellent agreement with one study reported in the literature [41]. The adsorption isotherm has some similarities to that determined for fluorite presented previously in Figure 11. However,

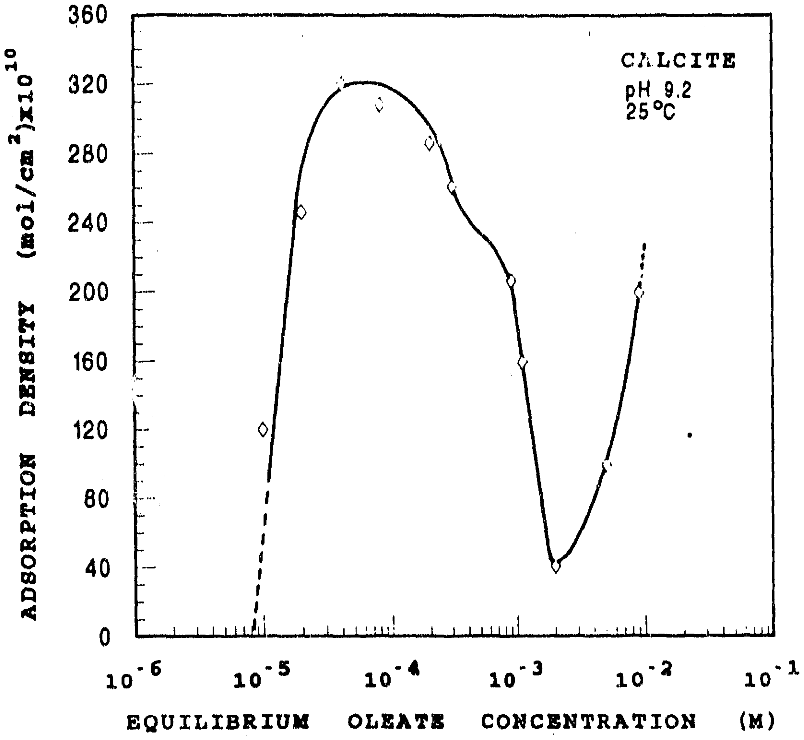


Figure 17. Adsorption isotherm of oleate by calcite at 25°C and pH 9.2 as calculated from *in situ* FT-NIR/IRS data.

because the aliphatic CH overtone and combinations bands could not be detected for concentrations below 1×10^{-5} M on at least ten occasions, it is believed that oleate does not chemisorb on calcite. Furthermore, the adsorption density for what appears to be calcium dioleate surface precipitation is nearly an order of magnitude greater for calcite than that for fluorite under similar conditions. Assuming the adsorbed oleate is in the liquid crystal state and occupies a surface area of 34.2 Å^2 per molecule [30], about 67 vertical monolayers would form on calcite as opposed to 8 on fluorite. Consequently, in oleate solutions calcite might be expected to possess the more hydrophobic surface, but, as is known throughout the literature, fluorite is much more hydrophobic.

Based on the above information, it would be reasonable to conclude that the lack of oleate chemisorption (and therefore double-bond reactivity!) on calcite might account for the difference in flotation behavior. However, it is also possible that the calcium dioleate surface precipitate is not tenaciously held to the calcite surface, so upon bubble attachment, the precipitate is merely displaced from the surface and the calcite particles remain in suspension. As mentioned below, research is presently underway to confirm and/or deny these hypotheses.

Research in Progress

Because of the transmission limitations of calcite, complete information can not be obtained using the novel *in situ* FT-IR/IRS technique with reactive IREs. Consequently, laser Raman spectroscopy (LRS) is receiving attention, particularly with respect to chemisorption and double-bond reactivity of adsorbed oleate on calcite. Since water is not very Raman-active, LRS experiments are being conducted *in situ* as opposed to the exploratory *ex situ* tests demonstrated earlier for fluorite. Finally, in order to characterize the hydrophobicity of calcite in the presence of oleate, plans have been formulated to perform flotation tests and measure contact angles as well as bubble attachment times in order to answer questions regarding the tenacity of the calcium dioleate precipitate at the calcite surface.

INSOLUBLE OXIDES

In situ FT-IR/IRS has been used to characterize surfactant adsorption at the surface of several insoluble oxide minerals. Most of the effort thus far has characterized the adsorption density and conformational order of sodium dodecylsulfate (SDS) adsorbed at the surface of sapphire (α-Al_2O_3). In addition, experiments have been conducted to determine the adsorption characteristics of SDS, sodium oleate and dodecylammonium chloride ($R_{12}NH_3Cl$) at germanium oxide, rutile and quartz IREs. $R_{12}NH_3Cl$ and SDS both adsorb at mineral oxide surfaces primarily through Coulombic or electrostatic forces. Thus, their adsorption is highly dependent on the charge at the surface of the mineral. For oxide minerals hydronium and hydroxide ions are potential determining, so that the pH of the solution determines the surface charge and hence the amount of surfactant adsorbed.

Effect of pH (Al_2O_3/SDS and SiO_2/DDA)

The point-of-zero-charge (pzc) of sapphire occurs at pH 9.1 [42]. SDS adsorption by sapphire was examined by *in situ* FT-IR/IRS at pH values of 1.9, 3.0, 6.9 and 11.1. Since SDS is anionic, it is expected to adsorb strongly at pH values less than the pzc, where the sapphire is positively charged. Figure 18 shows a plot of adsorption density versus pH for this system. As expected the adsorption density increases as pH decreases.

The pzc of quartz is known to be at pH 1.8 [42], so that adsorption of the cationic $R_{12}NH_3^+$ should be strong at most pH values. There are two solution-phase reactions which must be considered [43]. The first reaction is the equilibrium between dodecylamine ($R_{12}NH_2$) and the protonated $R_{12}NH_3^+$.

$$H^+ + R_{12}NH_{2(aq)} \rightarrow R_{12}NH_3^+ \qquad pK_1 = 10.6 \qquad (2)$$

The second reaction is the solubility of $R_{12}NH_2$.

$$R_{12}NH_{2\,(\ell)} \rightarrow R_{12}NH_{2\,(aq)} \qquad pK_2 = 4.7 \qquad (3)$$

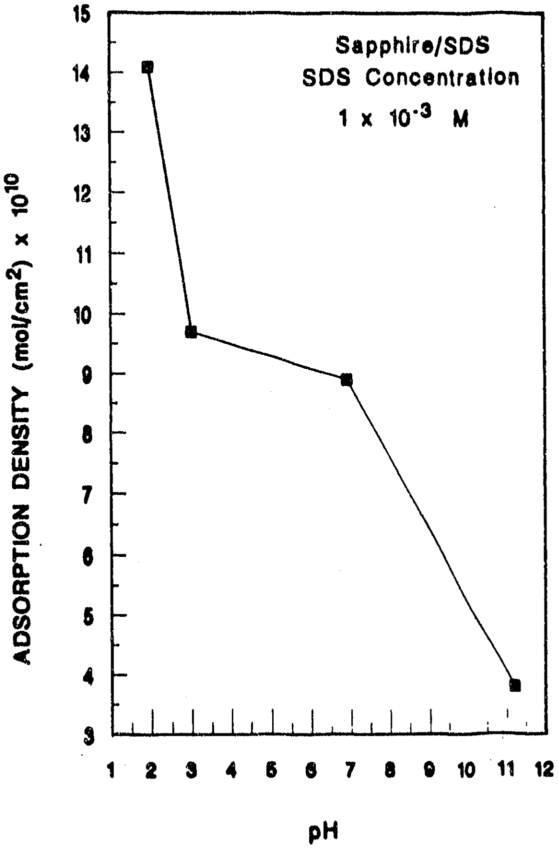


Figure 18. SDS adsorption by sapphire as a function of pH. The equilibrium concentration of SDS in solution is approximately 1×10^{-3} M.

Thus for $R_{12}NH_2$ concentrations exceeding 2×10^{-5} M, some $R_{12}NH_2$ will exist as a colloidal liquid rather than as a dissolved species. Equation 2 shows that at pH 10.6 the $R_{12}NH_2$ and $R_{12}NH_3^+$ concentration will be equal. At higher pH values, $R_{12}NH_2$ will predominate, while at lower pH values $R_{12}NH_3$ will predominate. Figure 19 shows the adsorption density as determined by FT-IR/IRS for the dodecylamine/quartz system at pH 6 and pH 8.2. Several interesting points are apparent from this figure. First, it can be seen that adsorption at pH 6 is always less than at pH 8.2. This is somewhat surprising considering that the concentration of $R_{12}NH_3Cl$ is slightly greater at pH 6. Second, at solution concentrations greater than pK_2, adsorption at pH 6 is nearly constant, while adsorption continues to increase at pH 8.2.

This behavior may be explained in the following manner. Dodecylamine in $R_{12}NH_3Cl$ solutions has been shown to precipitate in solution in a fashion similar to equation 2, and, of

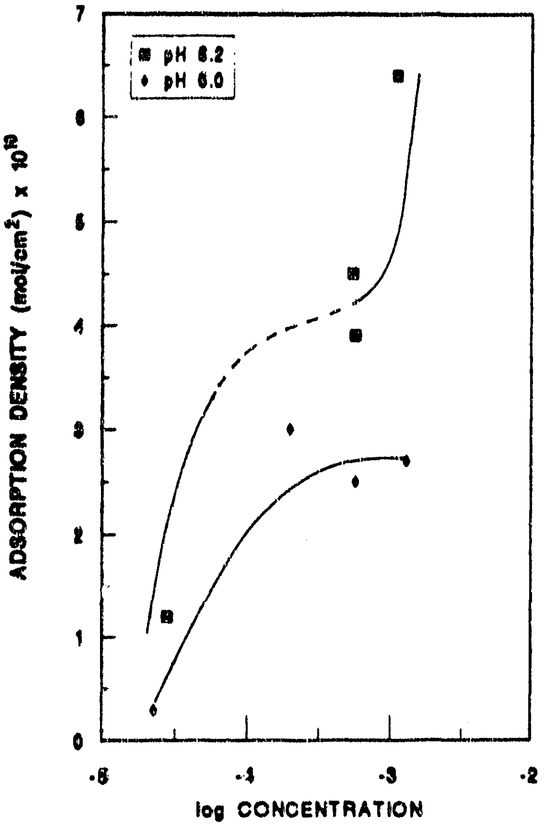


Figure 19. Partial adsorption isotherms for the quartz/ dodecylamine system at pH values 6.0 and 8.2.

course, the concentration at which precipitation occurs is a strong function of pH. Considering the pH values examined, at pH 6 solution precipitation will occur at approximately 3×10^{-2} M, while at pH 8.2 precipitation should occur at about 1×10^{-3} M [26]. Thus the adsorption isotherm can be interpreted as showing typical monolayer adsorption behavior at pH 6, while adsorption of the collector colloid species causes an increase in adsorption at concentrations greater than 1×10^{-3} M. At low concentration, adsorption at pH 8.2 is slightly greater than the adsorption at pH 6 because of the coadsorption of $R_{12}NH_2$.

Comparison of D_2O and H_2O

Adsorption of SDS at slightly oxidized germanium IREs has been examined. Because germanium has a very high refractive index, adsorption can be measured in both H_2O and D_2O. Table 6 shows the results of SDS adsorption at pH 6. As would be expected, the calculated adsorption densities are essentially equivalent. Adsorption of SDS and sodium oleate by rutile has also been attempted, but so far the extreme birefringence of the rutile IRE has prevented quantitative interpretation of the spectral data.

Surface Aggregation, Order Phenomena (Al_2O_3/SDS)

Another major area of emphasis for the *in situ* examination of collector adsorption at mineral oxide surfaces has been the determination of surfactant aggregation and order phenomena. The aggregation of surfactants in solution has been known since 1920 [44], and surfactant aggregation at surfaces was first suggested in 1955 [45]. Only recently have experimental techniques been developed to directly examine these surface aggregates. Generally, aggregation phenomena are divided into three types of order; positional, orientational, and conformational. Positional order is used to describe any crystalline packing and the distance between molecules. Orientational order denotes the angle between the hydrocarbon chain and an axis of symmetry. Conformational order describes the energetic state of the surfactant hydrocarbon chains. FT-IR spectroscopic techniques can be used, in principle, to determine all three types of order.

Table 6. Adsorption density of SDS at germanium IRE, pH = 6.0.

Solvent	[SDS], M	[NaCl], M	Adsorption density, mol/cm^2
H_2O	2.0×10^{-3}	0	5.95×10^{-10}
H_2O	1.9×10^{-3}	2.14×10^{-2}	9.94×10^{-10}
D_2O	1.8×10^{-3}	2.17×10^{-2}	9.79×10^{-10}

In the initial phase of this investigation, the conformational order of the various SDS solution phases was determined as described by the relative frequency of gauche rotational isomers (rotamers). Changes in the number of gauche conformers will cause a shift in the position of the asymmetric -CH_2 stretching band, and the band position can be used as a measure of the conformational order within the aggregate. Figure 20 shows the asymmetric -CH_2 stretching frequency as a function of SDS solution concentration. It can be seen that the band position changes significantly (4-6 wavenumbers) as the concentration is increased, and new phases are encountered.

The importance of these solution phases can be seen by examining the adsorption isotherm of the SDS/sapphire system (see Figure 21). Aggregation at the sapphire surface has been shown to begin at the boundary between regions I and II. The adsorption density at this boundary is about 1×10^{-12} mol/cm^2. In view of the fact that the thickness of the adsorbed layer

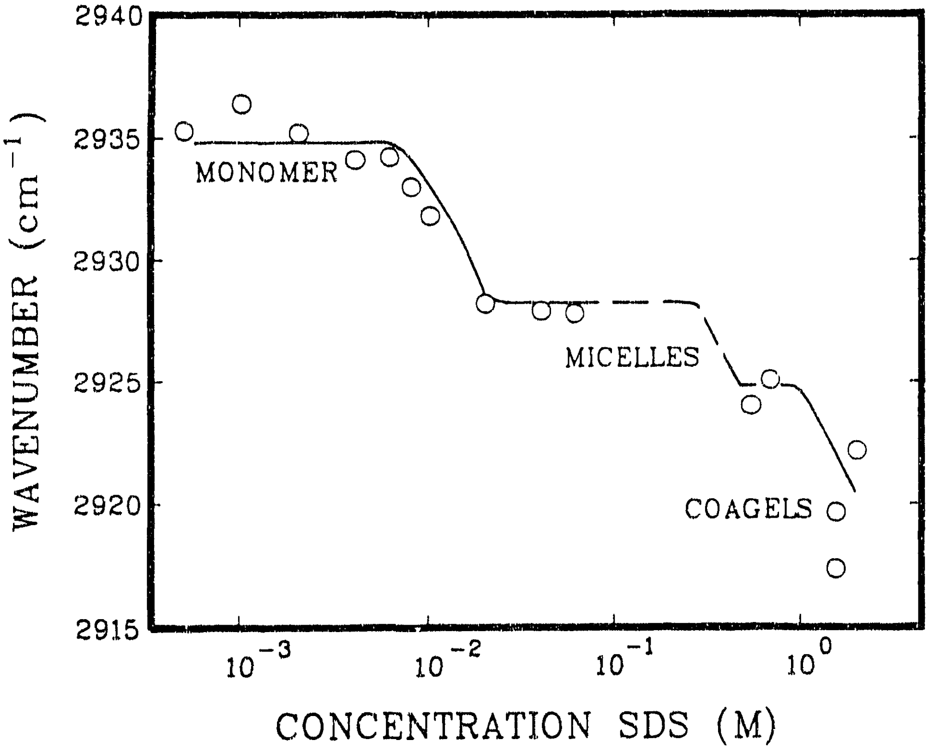


Figure 20. Plot of asymmetric -CH_2 stretching frequency versus solution SDS concentration as determined from liquid transmission spectra.

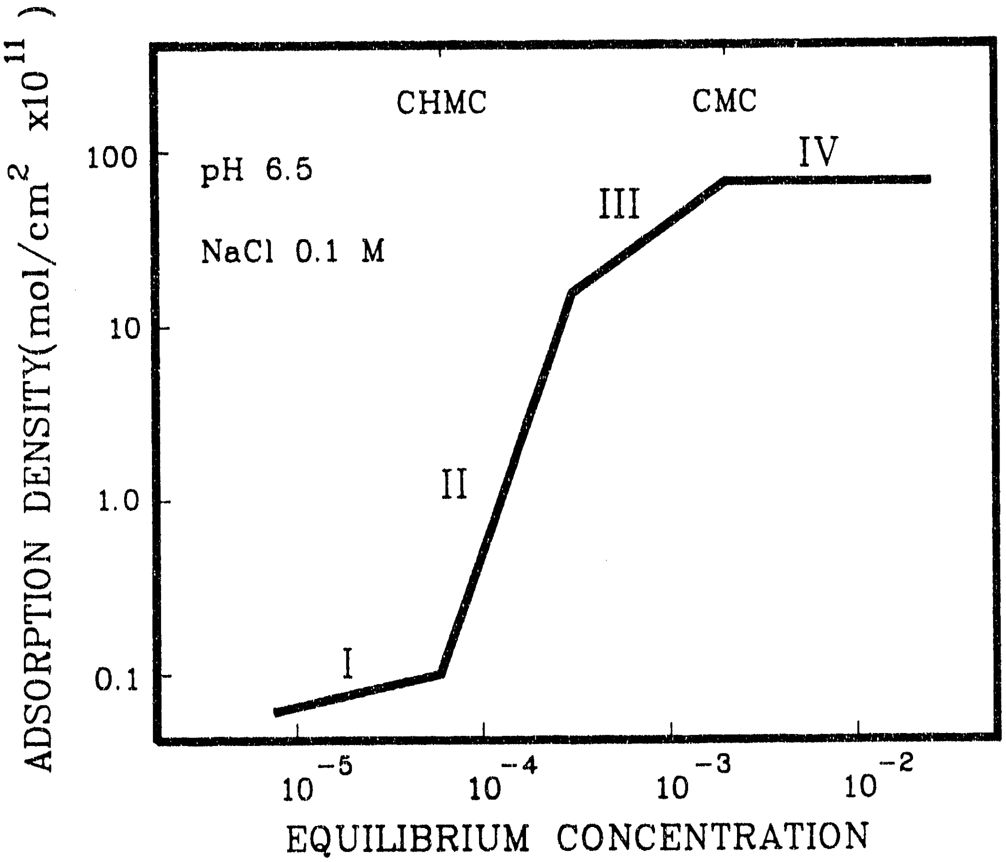


Figure 21. Generic isotherm for the sapphire/SDS system [48].

has been found to be about 10 angstroms [46], an equivalent molar concentration of the adsorbed layer can be calculated. For this case, the equivalent concentration is about 1×10^{-2} M, which is very similar to the solution phase critical micelle concentration (8.1×10^{-3} M) [47]. Similarly, examination of the division between regions II and III gives an equivalent concentration of 1.5 M, which is approximately the concentration at which solution micelles exhibit a phase transition to the coagel phase [49]. This analysis suggests that the solution phase behavior of SDS can be used to predict the state of aggregation of SDS adsorbed at the sapphire surface.

Table 7 presents the results of these predictions. At adsorption densities of less than 1.5×10^{-10} mol/cm^2 (the transition between regions II and III), the asymmetric -CH$_2$ stretching frequency of the adsorbed SDS is quite similar to the position of the band for the cylindrical

Table 7. Conformational analysis for the sapphire/SDS system

Adsorption density (mol/cm^2)	Asymmetric -CH$_2$ Stretching Frequency Predicted (cm^{-1})	Asymmetric -CH$_2$ Stretching Frequency Experimental (cm^{-1})
9.6×10^{-12}	2924-2925	2924.0
6.7×10^{-11}	2924-2925	2924.3
1.3×10^{-10}	2924-2925	2923.3
3.3×10^{-10}	2920-2922	2922.3
1.3×10^{-9}	2920-2922	2921.4

micelle in solution as shown in Figure 20. The position of the asymmetric stretching band at adsorption densities greater than 1.5×10^{-10} mol/cm^2 has decreased by 1-3 wavenumbers and the values observed are very similar to the frequencies of solution phase coagels. In both cases the band position was similar to the value of the position predicted by the solution phase diagram.

As stated previously, altering the temperature of the system should also affect the conformational order of the system. Figure 22 shows the thermotropic behavior of SDS (adsorption density = 7×10^{-10} mol/cm^2) adsorbed from a 1.85×10^{-3} M solution at pH 2.92 and ionic strength 2.8×10^{-2} M. At this adsorption density, the surface aggregate is predicted to undergo a transition from a hexagonal liquid crystal to a coagel as the temperature is decreased below 25°C. From the data in Figure 22, it can be seen that at temperatures greater than 25°C, the asymmetric -CH$_2$ stretching frequency occurs at approximately 2924 wavenumbers. This value is the same as the asymmetric -CH$_2$ stretching frequency for the hexagonal liquid crystal. At temperatures less than 25°C, the asymmetric -CH$_2$ stretching band position has shifted to less than 2920 wavenumbers. These values are very similar to solution phase coagels.

It is evident from these results and from results in the section on semi-soluble salt that the solution phase diagram can be used as a template to describe the conformational order of adsorbed aggregates. Both thermotropic and lyotropic data have confirmed this observation.

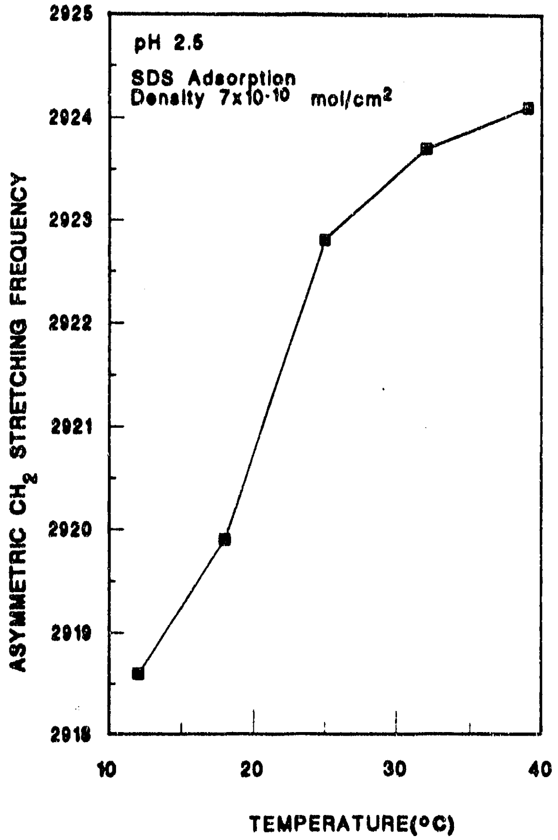


Figure 22. Thermotropic behavior of SDS adsorbed at a sapphire IRE. The adsorption density is approximately 7×10^{-10} mol/cm^2 in all cases.

Research in Progress

Adsorption density isotherms will be completed for the sapphire/SDS and quartz/$R_{12}NH_3Cl$ systems at several pH values. In addition, attempts will be made to ameliorate the birefringence problems of rutile as was done previously with calcite. The thermotropic behavior of the sapphire/SDS system is also being studied in greater detail. Of special interest in these experiments will be the determination of the heat of adsorption and the enthalpy and entropy of melting for the surface phase transitions.

The orientational order of the sapphire/SDS system will be examined in more detail through the use of polarized light. Polarizing the incoming IR radiation allows a measure of the average tilt direction of any band's transition moment. Finally, the effect of the various surface phases upon the hydrophobicity will be examined by contact-angle goniometry.

FUTURE RESEARCH ACTIVITIES — PROPOSAL RENEWAL

Excellent progress has been made in analyzing several nonsulfide mineral/collector systems. Important features investigated include collector adsorption phenomena, particularly double-bond reaction and conformational order of surface species, and surface-charge effects in saturated-brine solutions. Research performed at the University of Utah during this grant period has demonstrated the significance of these features in different nonsulfide flotation systems. Most importantly, *in situ* FT-IR/IRS has been shown to be a powerful, versatile technique for nonintrusive, real-time quantitative analysis of all aspects of mineral/collector adsorption phenomena. Nevertheless, many issues remain unresolved, and the research effort should be sustained. In this regard, a proposal renewal has been prepared, which in addition to the continued development of *in situ* FT-IR/IRS includes several other new techniques which will be developed to examine specific aspects of nonsulfide mineral flotation systems in detail. Preliminary results indicate that laser Raman spectroscopy can provide important surface spectroscopic information complementary to the results from FT-IR/IRS spectroscopy. This information will be especially useful in the determination of the nature and extent of double-bond reactions. The laser Raman technique has convincingly demonstrated its utility in *ex situ* experiments, and preliminary *in situ* results appear very promising.

Langmuir-Blodgett deposition has been used extensively [50, 51] to prepare specifically oriented thin surfactant films on solid substrates. Preliminary research under the auspices of this grant has determined the orientation of these deposited films, but the relationship between orientation, the extent of double-bond interaction, and hydrophobicity remains to be investigated. Atomic-force microscopy (AFM) has demonstrated the ability to examine both the positional order inherent in surface aggregates and the force-distance profile in the vicinity of solid surfaces. The results from these types of experiment should provide convincing evidence for the characterization of surface aggregates and for the mechanism of adsorption and interaction, particularly in the soluble-salt systems.

Other areas in need of further study are the aspects of order phenomena within self-assembled systems, especially regarding the thermodynamics and orientation associated with the various surface phases, and the relationship between the surface phases and flotation behavior.

Controlling the oxidation of double-bonds of unsaturated collectors in flotation systems offers the possibility of regulating the hydrophobicity of specific minerals in a suspension. Experiments to control double-bond oxidation will be attempted through the use of inorganic initiators and electrochemical techniques. If successful, the techniques developed will offer a new dimension for selective separation in many flotation systems.

Finally, adsorption phenomena for many important flotation systems remain to be investigated. Among the various aspects to be studied are: the effect of position and isomerism of double bonds on their reactivity; the effect of the mineral cation, anion and crystal structure on adsorption and double-bond reaction; the effect of hydrocarbon chain structure; and the flotation characteristics of industrially important soluble-salt systems in addition to potash.

Already the results obtained during the course of this grant have provided considerable insight into many aspects of adsorption phenomena critically important to flotation and many other surface chemical areas. In view of the significance of these findings and the great potential for future breakthroughs, a renewal proposal has been submitted to the Office of Basic Energy Science, DOE, to extend this research program an additional three years.

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APPENDIX I. STUDENT PARTICIPATION (1989-92)

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   Former University Research Fellow
   Ph.D., Met. Engg., University of Utah, 1991
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   B.S., 1990, Met. Engg., University of Utah
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APPENDIX 2. PRESENTATIONS LIST (1989-92)

1. J. J. Kellar, W. M. Cross, and J. D. Miller, "In-Situ Internal Reflection Spectroscopy for the Study of Surfactant Adsorption Reactions Using Reactive Internal Reflection Elements," presented at the 5th Symposium on Separation Science and Technology for Energy Applications, Knoxville, Tennessee, October 22-27, 1989.
2. J. D. Miller, J. J. Kellar, and W. M. Cross, "Infrared Spectroscopy for In-Situ Characterization of Surface Reactions," presented Engineering Foundation/SME Topical Conference on Advances in Coal and Mineral Processing Using Flotation, Palm Coast, Florida, December 3-8, 1989.
3. J. J. Kellar, W. M. Cross, and J. D. Miller, "In-Situ Near-Infrared Internal Reflection Spectroscopy of Collector Adsorption Reactions Using Reactive Internal Reflection Elements," presented at the 119th SME/AIME Meeting, Salt Lake City, Utah, February 26-March 1, 1990.
4. J. D. Miller, J. J. Kellar, and W. M. Cross, "In-Situ Examination of Adsorbed Surfactants by FTIR/IRS Using Reactive Internal Reflection Elements," presented at 199th ACS Annual Meeting, Boston, Massachusetts, April 23-25, 1990.
5. J. D. Miller, "FTIR/IRS Spectroscopy for the In-Situ Analysis of Collected Adsorption Phenomena," presented at South Dakota School of Mines and Technology, Rapid City, South Dakota, April 26, 1990.
6. J. D. Miller, "Fundamentals of Flotation," presented at the 3rd Congress of Nonferrous Extractive Metallurgy, Universidad de Sonora, Hermosillo, Sonora, Mexico, May 21-24, 1990.
7. J. J. Kellar, and J. D. Miller, "Surfactant Adsorption Density Calculations from In-Situ Real Time NIR Spectroscopic Data," presented at the 17th Meeting Federation of Analytical Chemistry and Spectroscopy Societies, Cleveland, Ohio, October, 1990.
8. C. A. Young, J. J. Kellar, and J. D. Miller, "FTIR Study of Oleate Double-Bond Reactions at a Fluorite Surface," presented at the SME Annual Meeting, Denver, Colorado, February 25-28, 1991.
9. W. M. Cross, J. J. Kellar, and J. D. Miller, "Conformation of Adsorbed Surfactant Species in the Alumina/Sodium Dodecyl Sulfate System as Determined by FTIR/IRS," presented at the XVII International Mineral Processing Congress, Dresden, Germany, September 23-28, 1991.
10. M. R. Yalamanchili, J. J. Kellar, and J. D. Miller, "In-Situ FTIR Internal Reflection Spectroscopy of Collector Adsorption Phenomena in Soluble Salt Flotation Systems," presented at the XVII International Mineral Processing Congress, Dresden, Germany, September 23-28, 1991.
11. J. D. Miller, "In-Situ FTIR Spectroscopy for the Study of Surfactant Adsorption Phenomena," presented as a Special Seminar for the Faculty of Chemistry, Politechnika Gdanska, Gdansk, Poland, October 3, 1991.

12. J. D. Miller, "The Significance of Surface Charge in Soluble Salt Flotation Systems," presented at Virginia Polytechnic Institute, Blacksburg, Virginia, November 21, 1991.

13. C. A. Young, Q. Yu, K. Knutson, and J. D. Miller, "Laser Applications of Vibrational Spectroscopy to Mineral and Coal Processing," presented at the 3rd topical meeting of the Optical Society of America on Laser Applications to Chemical Analysis, Salt Lake City, Utah, January 27-30, 1992.

14. J. D. Miller, "In-situ FTIR/IRS Analysis of Surfactant Adsorption Reaction Using Reactive Internal Reflection Elements," presented at the John Butler Extractive Metallurgy Lecture Series, Mackay School of Mines, University of Nevada-Reno, February 6, 1992.

15. J. D. Miller, and M. R. Yalamanchili, "The Significance of Surface Charge in Alkali Halide Flotation by Adsorption of Collector Colloids," presented at 121st SME Annual Meeting, Phoenix, Arizona, February 24-27, 1992.

16. J. J. Kellar, W. M. Cross, M. R. Yalamanchili, C. A. Young, and J. D. Miller, "Surface Phase Transitions of Adsorbed Collector Molecules as Revealed by Insitu FT-IR/IRS Spectroscopy," presented at 121st Annual SME Meeting, Phoenix, Arizona, February 24-27, 1992.

17. M. R. Yalamanchili and J. D. Miller, "Interaction of Alkali Halide Particles in Their Saturated Brines and the Significance of Attractive Hydration Forces," presented at the Engineering Foundation Conference Dispersion and Aggregation: Fundamentals and Applications, Sheraton Palm Coast, Palm Coast, Florida, March 15-20, 1992.

APPENDIX 3. PUBLICATIONS LIST (1989-92)

1. J. D. Miller, and J. J. Kellar, "Quantitative In-Situ Analysis of Collector Adsorption Reactions by FTIR Internal Reflection Spectroscopy," in: *Challenges in Mineral Processing,* K. V. Sastry and M. C. Fuerstenau, eds., AIME/SME, 1989, pp. 109–129.
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