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Internal Reflection Spectroscopy for FTIR Analysis of Carboxylate Adsorption by Semi-Soluble Salt Minerals

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Flotation chemists have long sought to unravel the mechanisms of carboxylate collector adsorption by semi-soluble salt minerals. In particular, the adsorption density of adsorbed carboxylates, adsorption kinetics, speciation (chemisorbed, physisorbed), orientation, and conformation are of interest. Given the importance of these phenomena in establishing the hydrophobic state at a mineral surface, in-situ surface spectroscopy studies certainly are justified. Such measurements traditionally have been difficult to perform. However, beginning in the late 1980s, a Fourier transform infrared (FTIR) spectroscopic technique was developed that has allowed for the acquisition of a wealth of detailed information concerning carboxylate adsorption in semi-soluble salt flotation systems. The technique, internal reflection spectroscopy using single-crystal internal reflection elements, is reviewed, as it applies to semi-soluble salt flotation systems.

BACKGROUND

Prior to availability of the Fourier transform infrared spectrometer, the flotation chemist was often limited by the sensitivity of the dispersive infrared spectrometer. Specifically, due to low-energy throughput, most studies involved transmission techniques such as the KBr disk or Nujol mull methods.

With the advent of FTIR spectrometers, many low-energy throughput experimental techniques (almost all exclusively reflectance based) previously unused by flotation researchers could be utilized on a routine basis.

For example, FTIR analysis of flotation systems by diffuse reflection (Sivamohan et al., 1990) and external reflection (grazing angle) (Poling and Leja, 1963) techniques can be found in the literature. These techniques are generally performed ex-situ (no water

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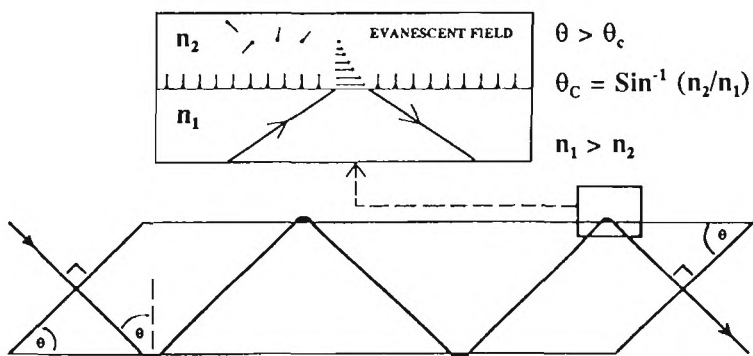


FIGURE 1 Schematic of light undergoing multiple internal reflections in an IRE

present). Since the froth flotation process involves an aqueous phase, an in-situ infrared technique is preferred.

In-Situ FTIR Internal Reflection Spectroscopy

Internal reflection spectroscopy (IRS), alternatively referred to as attenuated total reflection (ATR), allows for in-situ measurements. Shown in Figure 1 is a simple schematic representation of a ray of light undergoing multiple internal reflections in an internal reflection element (IRE). As the light is totally reflected at the interface, an exponentially decaying evanescent wave is set up in the outer phase (sample). It is through this evanescent wave that sampling occurs. The wave has components in all three spatial directions, x, y, and z, which interact with the sample. Typically the depth of penetration and the number of internal reflections vary between 0.1 to 1 microns and 10 to 50 reflections, respectively.

There are several reasons why FTIR/IRS has become an important method of analysis for flotation chemists. First, it can be used to evaluate many conclusions based on previous ex-situ measurements. Second, the short sampling depth minimizes the strong infrared absorbance of water, a condition that generally has limited the use of in-situ IR spectroscopy. Finally, because of the multiple reflections at the IRE/sample interface, sensitivity is greatly increased over more routine sampling methods.

One of the earliest applications of in-situ IRS analysis involved pressing and dewatering a fine particulate suspension against an "inert" IRE such as germanium. Since the sampling depth is short, the particles must be in intimate contact with the "inert" IRE. Reproducible contact between experiments is very difficult, and consequently only qualitative measurements are possible. Also, collector contamination of the "inert" IRE cannot be ignored. Surface contamination can be significant, as has been shown by residual contamination of potassium amyl xanthate on a germanium IRE (Miller et al., 1990).

Another method of studying adsorption reactions in-situ involves coating, usually by vacuum deposition, of the desired mineral onto an inert IRE. The coated IRE can then be placed in solution, and surfactant adsorption occurs directly onto the exposed mineral surface. Again, reproducibility of the mineral surface and quantitative analysis of adsorption processes limit the utility of this technique.

TABLE 1 Synthetic single-crystal IREs that are useful for flotation studies

Internal Reflection Element (IRE)	Useful Transmission Range (cm ⁻¹)	Average Refractive Index, n
SiO ₂	50000–4000	1.44
Al ₂ O ₃	33000–2800	1.75
MgO	20000–1700	1.68
CaF ₂	66000–1300	1.40
NaCl	25000–900	1.5
KCl	20000–700	1.47
As ₂ S ₃	12500–1300	2.4
ZnS	14000–1000	2.22
TiO ₂	20000–2000	2.6; 2.9
ZrO ₂	25000–1800	2.15

Beginning in the late 1980s, researchers demonstrated the utility of fabricating the desired substrate into a reactive IRE and directly studying surface reactions in-situ at the IRE surface. Sperline et al. (1987) first used this approach to quantitatively monitor the adsorption density of the surfactant cetylpyridinium chloride onto a zinc selenide IRE. Of course, this method is limited to systems where IR-transparent IRE crystals are available, and appropriate care must be taken to avoid and/or correct for any impurity contamination of the system. Synthetically grown single-crystal IREs that are readily available and useful from a flotation standpoint are listed in Table 1. Also listed in Table 1 is the useful transmission range of each IRE. Since the initial investigation by Miller and Kellar (1989), numerous IREs have been used to describe adsorption processes associated with flotation chemistry. The use of natural mineral crystals as IREs was first postulated by Harrick over 30 years ago and now has been developed for flotation chemistry studies (Harrick, 1979; Harrick Scientific, 1988). In the case of semi-soluble salt-type minerals, fluorite, calcite, and fluoroapatite crystals have been used as reactive IREs (Miller and Kellar, 1989; Kellar et al, 1990; Lu et al., 1998; Young and Miller 1998).

The focus of this paper is a review of the FTIR/IRS technique for the analysis of carboxylate adsorption in the flotation chemistry of semi-soluble salt minerals, using these same minerals as reactive IREs.

ADSORPTION DENSITY

In the first demonstrated use of reactive IREs for in-situ flotation chemistry research, Miller and Kellar (1989) and Kellar et al. (1989) showed that the adsorption density of oleate at the surface of a fluorite IRE could be calculated from in-situ spectral data. Subsequently, this approach was refined by Free et al. (1994). The general utility of the FTIR/IRS adsorption density equation for reactive IREs has now been established.

$$\Gamma = \frac{A/N - \epsilon C_b d_e}{1000\epsilon(2d_e/d_p)}$$

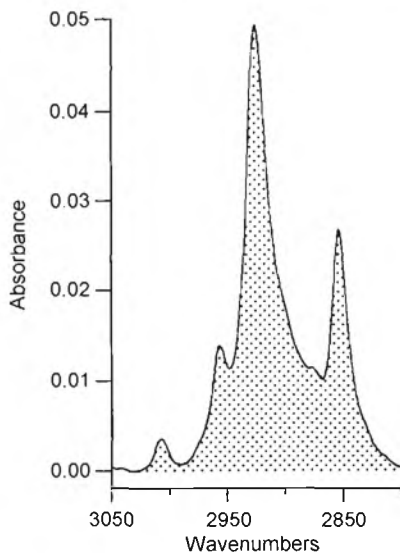


FIGURE 2 Spectra of CH stretching bands showing the integrated area chosen for quantitative analysis of adsorbed carboxylates at the surface of reactive IREs

- where Γ = adsorption density (mole/cm²)
 A = integrated absorbance (1/cm)
 N = number of internal reflections
 ϵ = molar absorptivity (1/mole·cm)
 C_b = bulk species concentration (mole/l)
 d_e = effective depth (cm)
 d_p = depth of penetration (cm)

Typically the adsorption density is determined by the intensity (integrated absorbance, A) of the CH stretching vibrations such as shown in Figure 2, together with the optical constants of the system (incident angle and refractive indices) that allow calculation of N , d_e , and d_p .

From such calculations the adsorption isotherms can be determined as shown for fluorite, calcite, and apatite in Figure 3 (Lu et al., 1998). Frequently in these studies D₂O can be used instead of H₂O in order to allow easier examination of collector absorption bands.

These FTIR/IRS results were encouraging in that the adsorption isotherms agreed well with some previous studies and demonstrated the great sensitivity (sub-monolayer coverages could be detected) of the reactive IRE method.

Subsequently, Jang and Miller (1993), in the case of fluorite, compared the measured adsorption density as determined by IRS theory with that found using well-defined monolayers transferred by the Langmuir-Blodgett method. See Figure 4. This comparison shows that the IRS technique gives highly reliable, quantitative results.

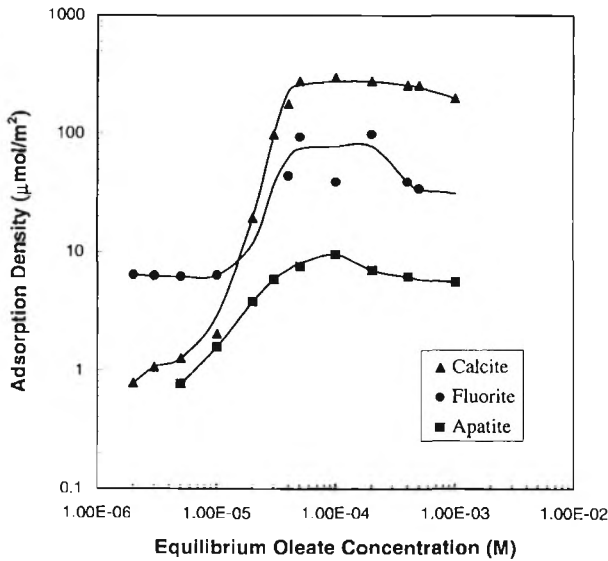


FIGURE 3 Comparison of oleate adsorption isotherms at apatite, fluorite, and calcite surfaces at about pH 9.5 and a temperature of 20 °C to 25 °C (Lu et al., 1998)

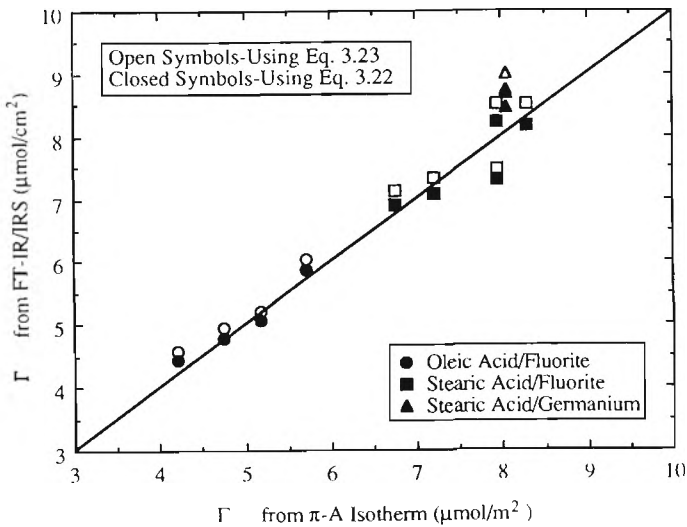
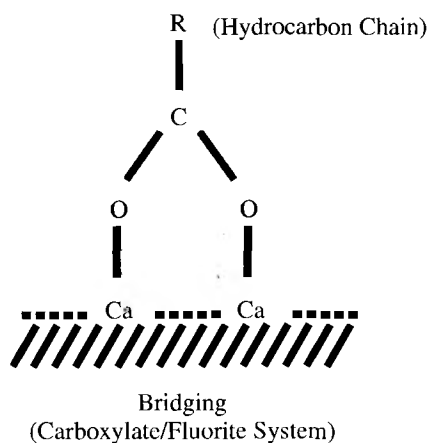


FIGURE 4 Adsorption density values for transferred LB monolayers of fatty acids calculated by the FTIR/IRS adsorption density equation vs. those determined from the π -A isotherms (Jang and Miller, 1993)

TABLE 2 Calcium surface site densities for apatite, fluorite, and calcite (Lu et al., 1998)

Surface	Calcium density ($\mu\text{mole}/\text{m}^2$)	Area per calcium (\AA^2)
Apatite (0001)	6.6	25.3
Apatite (1000)	5.2	32.2
Fluorite (111)	12.9	12.9
Calcite (1011)	8.2	20.2

**FIGURE 5 The bridging coordination believed to define the nature of carboxylate chemisorption at the fluorite surface**

In general, the oleate adsorption isotherms presented in Figure 3 are characterized by at least two regions. At low equilibrium oleate concentrations ($< 1 \times 10^{-5} \text{ M}$), in the absence of calcium dioleate precipitation, the density of the calcium surface sites (Table 2) dictates the adsorption density in this plateau region for the endothermic chemisorption reaction (Lu et al., 1998). In the case of fluorite, the adsorption density plateau for adsorbed oleate is 6.5 to 6.8 $\mu\text{mole}/\text{m}^2$ such as would be expected for a close-packed monolayer. Taking into consideration the density of calcium sites, this corresponds to a calcium-to-carboxylate ratio of about 2 to 1 and suggests that bridging occurs between a carboxylate group and two calcium ions at the fluorite surface. See Figure 5. On the other hand, the chemisorption plateau for calcite and apatite as determined from Figure 3 is significantly less, approximately 1 $\mu\text{mole}/\text{m}^2$. Clearly a close-packed monolayer is not achieved in these systems at low concentrations, which accounts for a diminished state of hydrophobicity for calcite and apatite under these circumstances when compared to fluorite. For example, it has been found that for a $1 \times 10^{-5} \text{ M}$ equilibrium oleate concentration, fluorite exhibits a contact angle of close to 90° , whereas bubble attachment at a calcite surface does not occur under these circumstances (Young and Miller, 1998).

In region two ($> 1 \times 10^{-4} \text{ M}$), where adsorption exceeds an effective close-packed monolayer, the maximum adsorption densities were found to be about 300 $\mu\text{mol}/\text{m}^2$ at a calcite surface, 100 $\mu\text{mol}/\text{m}^2$ at a fluorite surface, and only 11 $\mu\text{mol}/\text{m}^2$ at an apatite surface. In this

TABLE 3 Comparison of the measured heats of adsorption of oleate at the fluorite/water interface with isosteric heats of adsorption for different levels of surface coverage (Miller et al., 1989)

	Heats of adsorption of oleate (kcal mol ⁻¹)	
	Measured by microcalorimetry	Calculated from adsorption isotherm data
Chemisorption (monolayer coverage)	2.36	2.77
Surface precipitation (above monolayer coverage)	-5.31*	-6.60

*At oleate surface coverage $\theta_2 = 0.59$ (i.e., $\theta = 1.59$).

region it appears that the adsorption is mainly due to surface precipitation of calcium dioleate or heterocoagulation of calcium dioleate collector colloids. Therefore, it is reasonable to relate adsorption density to the extent and kinetics of calcium ion release to solution as has been discussed in the literature (Young and Miller, 1998; Free and Miller, 1997). In this regard, it should be noted that the adsorption isotherm is quite sensitive to the level of dissolved calcium, particularly region one, the chemisorbed layer. If even a modest amount of calcium is present in solution prior to oleate addition, the precipitation event can overwhelm chemisorption and the plateau, so characteristic of the chemisorbed monolayer, can be eliminated as demonstrated for the fluorite system by Free and Miller (1997).

The two regions of oleate adsorption (chemisorption and surface precipitation) are also revealed from thermochemistry studies of the fluorite/oleate system (Miller et al., 1989). As shown in Table 3, adsorption at low equilibrium oleate concentrations reveals an endothermic reaction of oleate at the fluorite surface, whereas at high equilibrium oleate concentrations, an exothermic reaction associated with multilayer adsorption by surface precipitation of calcium dioleate is observed. Similar results that indicate an endothermic chemisorption reaction of oleate at a calcite surface have been reported (Young and Miller, 1998).

In summary, based on these adsorption density and thermochemistry considerations, chemisorption predominates at low equilibrium concentrations (low adsorption densities) and a precipitated calcium dioleate predominates at higher adsorption densities. In the case of fluorite, a close-packed monolayer of oleate forms during the chemisorption reaction, creating a strong hydrophobic state at the fluorite surface. On the other hand, in the case of calcite and apatite, monolayer formation is incomplete during chemisorption and, at best, a weak hydrophobic state is created at these surfaces.

ADSORPTION KINETICS

Detailed studies of adsorption kinetics are relatively uncommon in the flotation literature. There are numerous reasons for the dearth of such data, including lack of instrumentation capable of giving real-time results. Furthermore, most kinetic studies have been performed ex-situ. An exception to this occurred in 1997, when Free and Miller (1997) examined the adsorption kinetics of oleate and linoleate in-situ using a reactive fluorite IRE. It was found that the adsorption process was not controlled by convective diffusion or mass transport but rather by the reaction of the collector molecules at the fluorite IRE substrate. Another significant finding from this analysis was that, once oleate chemisorbed at the fluorite surface,

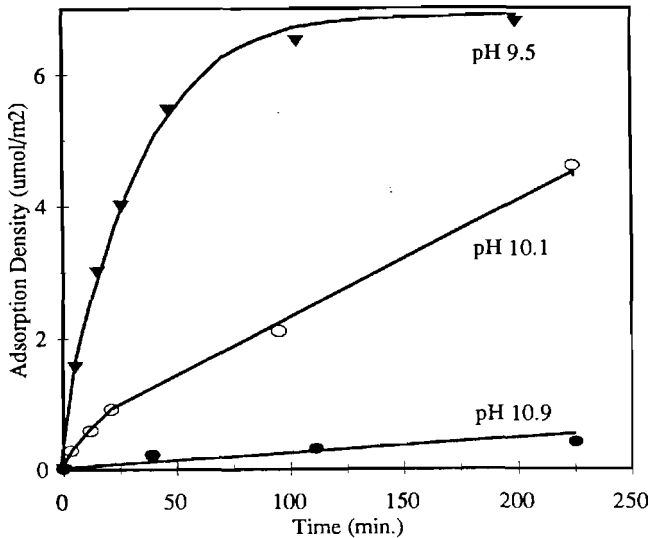


FIGURE 6 Effect of pH on the kinetics of oleate adsorption by fluorite IRE as revealed by in-situ FTIR/IRS. Each experiment was conducted with 1×10^{-5} M sodium oleate in D_2O at $25^\circ C$ (Free and Miller, 1997).

desorption could not be detected. Finally, it was shown that anions such as F^- , CO_3^- , and OH^- strongly influenced the rate of collector adsorption. For example, shown in Figure 6 is the effect of pH on the adsorption kinetics of oleate at the surface of a fluorite IRE. The rate of adsorption is significantly reduced at high pH, presumably due to competition with the hydroxyl ion for surface sites or due to a surface carbonation reaction (Miller and Hiskey, 1972).

SPECIATION OF ADSORBED COLLECTOR

Dating as far back as the 1950s there was a great deal of speculation concerning the speciation of adsorbed carboxylate collectors at the surface of semi-soluble salt minerals. Even during that time period it was recognized that infrared spectroscopy had the potential to determine whether the adsorbed layers were chemisorbed, physisorbed, or precipitated on the substrate. However, while useful, ex-situ analyses often tended to cloud the understanding of the nature of the adsorbed collectors. Specifically, the presence of water in ex-situ analyses often confused the researcher and caused misinterpretation of the resulting spectra. Interpretation was based upon the location and splitting (singlet or doublet) of the COO^- asymmetric stretching band in the region 1600 to 1500 cm^{-1} . Using FTIR/IRS spectra, Kellar et al. (1991) were the first to show from in-situ spectroscopy that the chemisorbed carboxylate is characterized by a single absorbance band $\sim 1550\text{ cm}^{-1}$ and that surface-precipitated calcium dicarboxylates are characterized by a doublet with bands on either side of $\sim 1550\text{ cm}^{-1}$. A summary of results that demonstrates these characteristic surface spectroscopic features of oleate adsorption is presented in Table 4 (Young and Miller, 1998).

TABLE 4 Band positions (cm^{-1}) of chemisorbed and surface-precipitated oleate at fluorite, apatite, and calcite surfaces from selected references (Young and Miller, 1998)

Reference	Mineral	Band Positions (cm^{-1})		Detection Method
		Chemisorb	Precipitate	
Fluorite (CaF_2)				
Kellar et al. (1991)	synthetic	1549	1573, 1535	In-situ FTIR/IRS
Jang and Miller (1994)	synthetic	1550	—	LB FTIR/IRS
Bahr et al. (1978)	natural	1550	1575, 1538	KBr transmission
Sivamohan et al. (1990)	natural	1555	1575, 1540	Diffuse reflection
Rao and Forssberg (1991)	synthetic	1555	1576, 1540	Diffusion reflection
Peck and Wadsworth (1965)	natural	1555	1577, 1543	Nujol Mull
Hu et al. (1986)	synthetic	1557	1577, 1540	KBr transmission
Apatite [$\text{Ca}_5(\text{PO}_4)_3\text{X}$]				
Gong et al (1992)	X = OH^-	1550	1574, 1593	Diffuse reflection
Antti and Forssberg (1989)	X = F^-	1550	1577, 1541	Diffusion reflection
Lu and Miller (1998)	X = F^-	1554	1575, 1540	Ex-situ FTIR/IRS
Calcite (CaCO_3)				
Peck (1963)	natural	1562	—	KBr transmission
Antti and Forssberg (1989)	natural	unable	unable	Diffuse reflection
Young and Miller (1998)	natural	1551	1569, 1534	Ex-situ FTIR/IRS

Not all researchers agree with this position. The above analysis touched off significant debate in subsequent publications (Miller et al., 1995). Complete understanding of the phenomena that cause the formation of a singlet and doublet was not fully resolved until the IRS work of Lu and Miller (1998) with fluorite showed that the 1550 cm^{-1} singlet and the doublet at 1540 and 1575 cm^{-1} could be explained in terms of the coordination structure of carboxylate groups with calcium ions. (For example, splitting of the asymmetrical stretch is not observed for magnesium and barium carboxylates, and in fact, such splitting reveals the unique multiple coordination states, characteristic of calcium in such aqueous systems.) In this analysis it was shown that constrained calcium carboxylate groups in a chemisorbed state at the surface (monolayer coverage) give rise to the singlet, whereas carboxylate groups associated with calcium ions in three-dimensional seven- or eight-fold coordination (multilayer coverage) give rise to the doublet. It is now clear that the singlet peak is indicative of the chemisorbed oleate when it is constrained at the surface and limited in coordination with calcium. This is true even if a calcium dicarboxylate is formed in such a constrained state (Lu and Miller, 1998). In view of the adsorption density observed for monolayer coverage at a fluorite surface and the calcium surface site density (Table 2), the bridging structure for the chemisorbed oleate (Figure 5) is justified by the carboxylate singlet position observed at $\sim 1550 \text{ cm}^{-1}$. Such close packing of the oleate monolayer and the ordered arrangement (see next section) account for the great stability of oleate at fluorite surfaces and the excellent hydrophobicity observed (Jang et al., 1995).

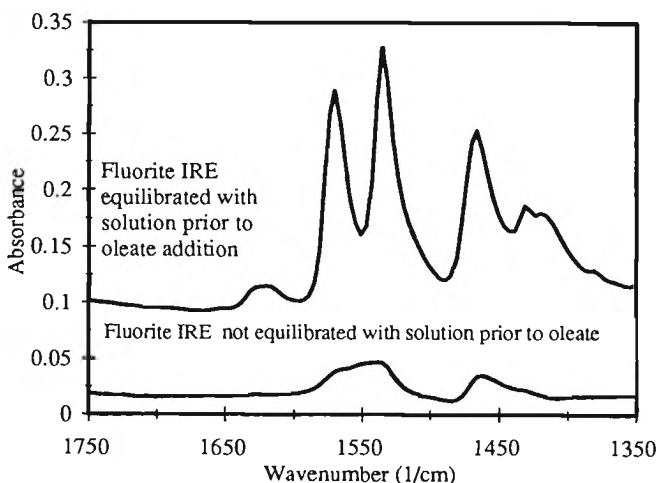


FIGURE 7 FTIR/IRS ex-situ spectra of the oleate adsorption product with and without prior equilibration of the fluorite IRE in water. Adsorption occurred for 14 hours in each test. The oleate concentration was 1×10^{-4} M, the temperature was 25°C, and the pH was 9.8 (Free and Miller, 1996).

Again, the spectral features of the adsorbed state are quite sensitive to the calcium ion concentration in solution. If sufficient calcium is present in solution to stimulate the calcium dioleate precipitation reaction, the doublet will be observed. For example, if fluorite is first equilibrated with water prior to oleate addition, the asymmetric vibration for the carboxylate is split and a doublet is observed rather than a singlet, which is the case when fluorite is not equilibrated in the water prior to oleate addition. See Figure 7 (Free and Miller, 1996).

Also, in-situ IRS has been used to monitor the reactivity of adsorbed carboxylate species. It was shown that the C=C double bond of chemisorbed oleate at a fluorite surface exhibited significant cross-linking when subjected to elevated temperature and/or oxygen-saturated solutions. These results were correlated with adsorption density measurements (Kellar et al., 1992; Young and Miller, 1999).

ORIENTATION OF THE HYDROCARBON CHAIN AND SURFACE PHASE TRANSITIONS

As mentioned above, band location allows one to determine the speciation of adsorbed collector molecules. Another feature associated with absorbance band position involves subtle changes in the band position that are associated with the molecular environment of the alkyl chain. The bands most often used in such an analysis are the strong asymmetric -CH stretching bands (3200 to 2800 cm^{-1}) of the collector. The high resolution associated with FTIR spectrometers allows the band positions to be determined at sub-wavenumber resolution. Consequently, slight changes in the alkyl environment can be monitored. For example, alkyl conformations termed either gauche or trans can be observed by FTIR spectroscopy. Figure 8 shows examples of gauche and trans conformations in a hydrocarbon chain. The two conformations are observed when the terminal methylene groups in any

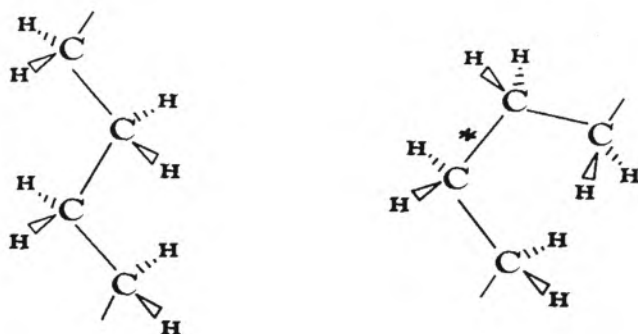


FIGURE 8 Examples of trans (left) and gauche (right) butylene linkages. The asterisk indicates the gauche bond (Kellar et al., 1993).

four-carbon subchain are on the same side (gauche) or opposite sides (trans) of the plane of the middle carbon/carbon bond. Typically, if the sample has a predominantly gauche population, the band location will occur at higher wavenumbers than when the population is predominantly of the trans conformation. Such analyses have been performed by researchers studying surfactant chemistry (Kellar et al., 1990). For example, when the surfactant is predominantly in the monomer form, the alkyl band position occurs at higher wavenumbers than when the micellar form of the surfactant prevails.

Kellar et al. (1993) used this concept to better understand the conformational behavior of adsorbed oleate on a fluorite IRE. It was found that at very low adsorption densities, the oleate molecules adsorbed initially in predominantly the gauche conformation, and as the adsorption density approached monolayer coverage, the trans conformation predominated. These results, together with more recent results, are shown in Figure 9 (Drelich et al., 1997). Also, it should be noted that Jang and Miller (1995) used polarized-light FTIR/IRS experiments to analyze the conformational behavior of self-assembled (SA) and Langmuir-Blodgett (LB) layers of stearate molecules at the surface of a fluorite IRE. They found that for both the SA and LB monolayers, the predominant conformation was the trans state.

Finally, with respect to orientation, Jang and Miller (1995) determined the orientation angle (relative to surface normal) from the same FTIR/IRS polarization experiments. It was found that this angle was 21° to 22° for the SA layer and from 9° to 16° for the LB layer. These orientation/conformation results complement the previous adsorption density and speciation results and demonstrate, in the case of fluorite, that a well-ordered/organized, tightly packed, chemisorbed monolayer layer forms at low oleate concentrations.

CONCLUSIONS

A Fourier transform infrared spectroscopic technique has been developed that has allowed for the acquisition of fundamental information concerning carboxylate collector adsorption in semi-soluble salt flotation systems. The technique allows for in-situ measurements on both synthetic and naturally occurring minerals. In general, the in-situ measurements, which include adsorption density, kinetic, speciation, and orientation/conformation studies, have provided additional information that was not available with other spectroscopic

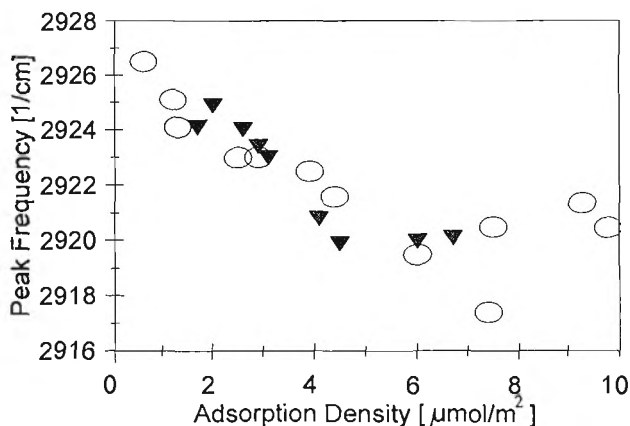


FIGURE 9 Peak frequency change of the asymmetric C-H stretching mode of the $-\text{CH}_2-$ group with increasing adsorption density of oleate at a fluorite surface (Drelich et al., 1997)

techniques. Specifically, the spectroscopic evidence and thermochemical data show that, in the absence of dissolved calcium, chemisorption predominates at low equilibrium oleate concentrations (low adsorption densities) and a precipitated calcium dioleate predominates at higher adsorption densities. In the case of fluorite, a close-packed monolayer of oleate forms during the chemisorption reaction, creating a strong hydrophobic state at the fluorite surface. On the other hand, in the case of calcite and apatite, monolayer formation is incomplete during chemisorption and a weak hydrophobic state is created at these surfaces. At high equilibrium oleate concentrations, a surface precipitation reaction occurs that leads to multilayer calcium dioleate coverage in the case of fluorite and calcite.

ACKNOWLEDGMENT

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