

Chapter 6

QUANTITATIVE IN-SITU ANALYSIS OF COLLECTOR ADSORPTION REACTIONS BY FTIR INTERNAL REFLECTION SPECTROSCOPY

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ABSTRACT

Researchers in flotation chemistry have long sought to describe collector adsorption phenomena in greater detail including kinetics, orientation and interactions between adsorbed species. Now a quantitative description can be made in-situ using FTIR internal reflection spectroscopy. Details of the adsorption process at the surface of mineral crystals, machined into internal reflection elements, can be described from first principles, provided the refractive indices, incident angle, and wavelength of light are known. Collector orientation can be established based on spectral characteristics of plane polarized and perpendicular polarized light. Examples of the use of in-situ FTIR internal reflection spectroscopy are given for the sapphire-sodium dodecyl sulfate system and for the fluorite-sodium oleate system. It is expected that quantitative in-situ analysis of collector adsorption reactions by FTIR internal reflection spectroscopy will continue to grow in importance and will provide an important new dimension in our understanding of flotation chemistry.

INTRODUCTION

With the advent of commercially available Fourier transform infrared (FTIR) spectrometers in the mid-seventies, study of mineral/surfactant interactions by means of infrared spectroscopy increased greatly. Table 1 lists six commonly used experimental techniques (Harrick Scientific Corp., 1987).

The first four methods are most commonly utilized in studies of mineral/surfactant interactions. Internal reflection spectroscopy

Table 1. Infrared Experimental Techniques.

1. Transmission	4. External Reflection
2. Diffuse Reflection	5. Emission
3. Internal Reflection	6. Photo Acoustic

(IRS), alternatively referred to as attenuated total reflection (ATR), allows for in-situ measurements in aqueous solutions and as such is most useful for the study of flotation surface chemistry.

Shown in Figure 1 is a 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) which propagates a short distance, typically a few microns, away from the IRE. 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.

Two requirements must be met before total internal reflection can occur. First, the sample must be optically rarer, that is, have a lower refractive index than the IRE. Second, the incident angle of the light beam on the IRE must be greater than a critical angle, θ_c :

$$\theta_c = \sin^{-1} (n_2/n_1) \quad (1)$$

where n_2 and n_1 are the refractive indices of the sample and IRE, respectively.

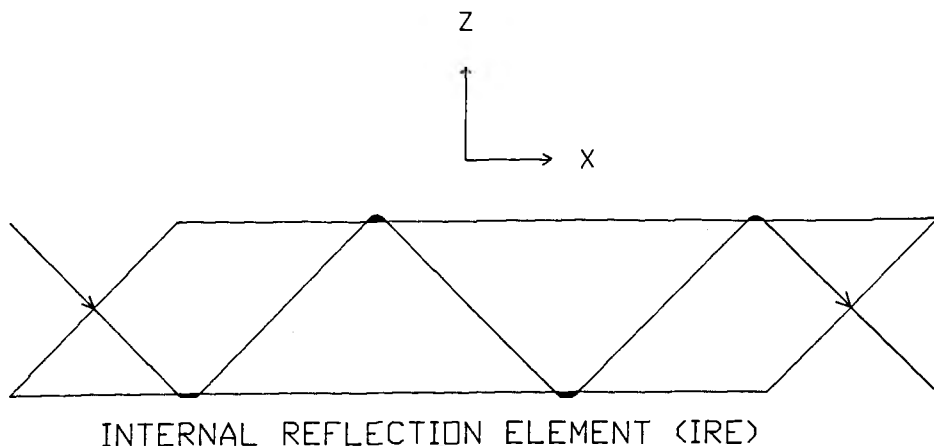


Figure 1. Schematic of light undergoing multiple internal reflections in an IRE.

Three possibilities exist for studying flotation systems by in-situ internal reflection spectroscopy: 1) direct adsorption of surfactants from solution onto a reactive IRE mineral substrate of interest (Kellar et al., 1988), 2) vacuum deposition of the desired mineral onto an "inert" IRE such as germanium and monitoring surfactant adsorption from the solution phase onto the evaporated mineral (Iskra and Kielkowska, 1980), and 3) pressing and dewatering a mineral/surfactant suspension against an "inert" IRE (Strojek and Mielczarski, 1974). Methods 2 and 3 have received the greatest attention among flotation chemists. Although the first method has been used by some researchers in other fields (Yang et al., 1973; Mattson et al., 1975; Sperline et al., 1987; Parry and Harris, 1988), only recently has it been applied to the study of flotation systems (Kellar et al., 1988). Direct adsorption onto a reactive mineral IRE provides much more quantitative information regarding the nature and structure of adsorbed collector species than Methods 2 and 3 and is the focus of this paper. Furthermore, with respect to methods 2 and 3, experimental evidence suggests that the commonly used "inert" IREs such as germanium are not completely inert but react with surfactant in some systems (Kellar et al., 1988).

THEORY OF INTERNAL REFLECTION SPECTROSCOPY

Harrick (1979) has devoted a monograph to the topic of internal reflection spectroscopy. Although originally written in 1967, this still serves as the most complete work to date. Reviews of IRS are given elsewhere (Haller et al., 1976; Hansen, 1973; Strojek et al., 1983; Mirabella, 1985), and only the equations essential for studying adsorption processes will be presented here.

Electric Field Amplitudes

Previously, it was mentioned that an evanescent wave passes from the IRE and decays exponentially into the sample. This wave is composed of three electric field vectors which can interact with the sample. Harrick (1979) defined two limiting cases in the analysis of these vectors:

- 1) Thick sample case, where the electric field amplitudes decay to a low value within the medium, and
- 2) Thin film case, where the electric field amplitudes are relatively constant through the film.

The equations for the three unit electric field amplitudes for case one are given below:

$$E_{y0} = \frac{2 \cos \theta}{(1 - n_{21}^2)^{1/2}} \quad (2)$$

$$E_{x0} = \frac{2(\sin^2 \theta - n_{21}^2)^{1/2} \cos \theta}{(1 - n_{21}^2)^{1/2} [(1 + n_{21}^2) \sin^2 \theta - n_{21}^2]^{1/2}} \quad (3)$$

$$E_{z0} = \frac{2 \sin \theta \cos \theta}{(1 - n_{21}^2)^{1/2} [(1 + n_{21}^2) \sin^2 \theta - n_{21}^2]^{1/2}} \quad (4)$$

where, $n_{21} = n_2/n_1$

θ = incident angle of light (degrees)

Perpendicular polarization of the IR radiation will contain an electric field with only E_{y0} as a component. Parallel polarization will result in elliptical polarization having both E_{x0} and E_{z0} components.

For the thin-film case, the unit electric field amplitudes are given by

$$E_{y0} = \frac{2 \cos \theta}{[1 - n_{31}^2]^{1/2}} \quad (5)$$

$$E_{x0} = \frac{2(\cos \theta)[\sin^2 \theta - n_{31}^2]^{1/2}}{(1 - n_{31}^2)^{1/2} [(1 + n_{31}^2) \sin^2 \theta - n_{31}^2]^{1/2}} \quad (6)$$

$$E_{z0} = \frac{2(\cos \theta \sin \theta) n_{32}^2}{(1 - n_{31}^2)^{1/2} [(1 + n_{31}^2) \sin^2 \theta - n_{31}^2]^{1/2}} \quad (7)$$

where, n_1 = refractive index of IRE

n_2 = refractive index of thin film

n_3 = refractive index of bulk

$n_{31} = n_3/n_1$

$n_{21} = n_2/n_1$

$n_{32} = n_3/n_2$

As mentioned above, for perpendicular polarized light, $E_0 = E_{y0}$. For parallel polarized light, $E_0 = (|E_{x0}|^2 + |E_{z0}|^2)^{1/2}$. It should

be kept in mind that the refractive indices for each phase are wavelength-dependent.

Depth of Penetration

An important parameter in IRS is the depth of penetration, d_p . The depth of penetration is arbitrarily defined to be the distance from the IRE where the electric field amplitude falls to $1/e$ of its value at the surface. The nomenclature involved with d_p is unfortunate, since it is often mistaken for an actual measurement depth in IRS. Nonetheless, d_p has remained as defined by Harrick (1979) and is given by:

$$d_p = \frac{\lambda}{n_1 2\pi(\sin^2\theta - n_{21}^2)^{1/2}} \quad (8)$$

where, λ = wavelength of light

n_1 = refractive index of IRE

n_2 = refractive index of the sample

$n_{21} = n_2/n_1$

Because d_p is dependent upon wavelength, λ , IRS spectra often differ from transmission spectra, in that bands at lower wavenumbers are often more intense than those at larger wavenumbers. An exception to this is for the thin-film case, where the electric field amplitudes are relatively constant, and IRS spectra closely resemble transmission spectra. In fact, thin-film spectra can be found for films which have a larger refractive index than the IRE. In other words, Equation (1) for the critical angle is determined by the IRE and the phase next to the film and not the film itself. A final point worth noting is that thin-film spectra do not become distorted near the critical angle, unlike bulk solution spectra.

By way of example, the ex-situ transmission spectrum (Hu et al., 1986) of precipitated calcium oleate, $\text{Ca}(\text{Ol})_2$, is compared with the in-situ IRS spectrum of oleate adsorbed (chemisorption and surface precipitation) by a fluorite IRE in Figure 2. The absorbance peaks in the region $1600\text{-}1400\text{ cm}^{-1}$ correspond to the carboxylate functionality of the $\text{Ca}(\text{Ol})_2$ species. Clearly, as expected from the above discussion, the IRS spectrum closely resembles the transmission spectrum.

Various researchers have derived an equation similar to Equation (8) above, with the exception that the factor 2 in the denominator is replaced by a factor of 4 (Hansen, 1973; Hirshfeld, 1977). In this study d_p will be used as defined by Equation 8.

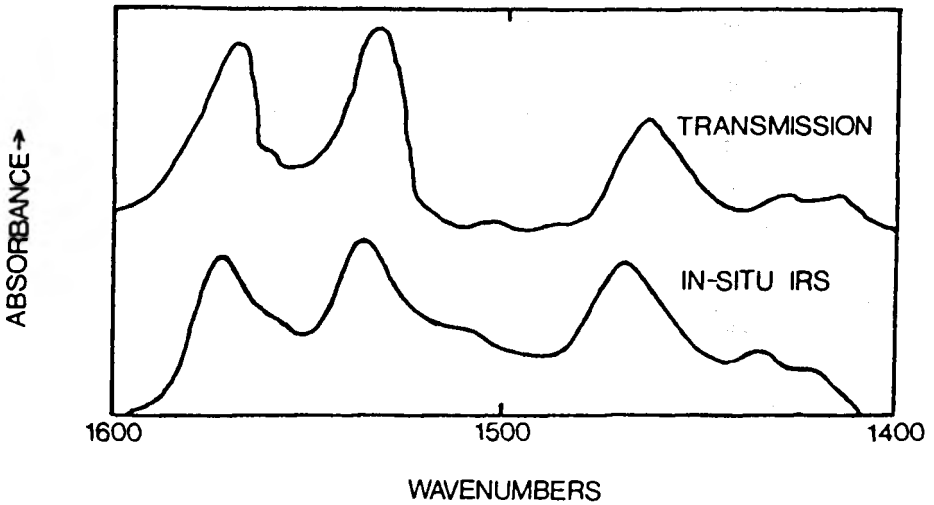


Figure 2. In-situ FTIR spectrum of calcium oleate adsorbed at a fluorite IRE and transmission spectrum of powdered calcium oleate.

Effective Depth

Harrick (1979) also defined an effective thickness, d_e , as the thickness of material which gives the same absorbance as a transmission spectra at normal incidence as that found from IRS:

$$d_e = (n_{21} E_o^2 d_p) / (2 \cos \theta) \quad (9)$$

Absorbance per Reflection

Tompkins (1974) derived an equation that describes the absorbance per reflection for multiple IRS when a thin film is adjacent the IRE. This equation is given below:

$$A/N = \frac{n_{21} E_o^2 \epsilon}{\cos \theta} \int_0^{\infty} c(z) e^{-2z/d_p} dz \quad (10)$$

where A = integrated absorbance (cm^{-1})

N = number of internal reflections

ϵ = integrated molar absorptivity ($\ell/(\text{cm}^2 \cdot \text{mol})$)

z = thickness (cm)

$c(z)$ = concentration as a function of distance from IRE
(mol/l)

Equation (10) was derived for a step-like concentration profile next to the IRE. In this heuristic derivation, Tompkins assumed that the distribution of species was not important, only that it be a maximum at the interface.

QUANTITATIVE DESCRIPTION OF THE ADSORBED STATE

Collector Orientation

A great deal of speculation still exists regarding collector orientation on mineral surfaces. Is the collector molecule in a supine position at low surface coverages, or is it always adsorbed in a perpendicular orientation with the aliphatic C-H groups parallel to the surface?

It can be seen from Figure 3 that, when a collector molecule is adsorbed perpendicular to the IRE surface, the C-H bonds lie in x,y planes parallel to the surface of the IRE. For a bond to be infrared active, there must be a component of the light's electric field which

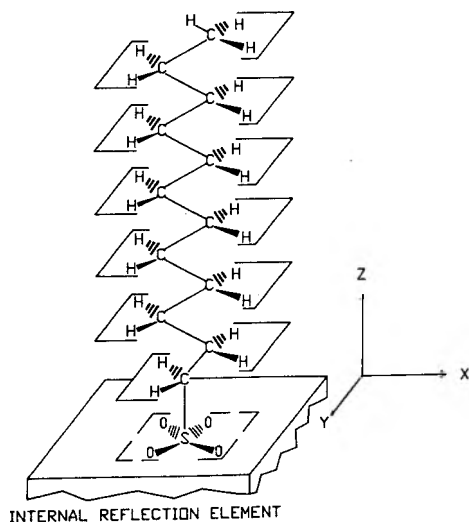


Figure 3. Schematic of an adsorbed collector molecule on an IRE oriented with C-H bonds parallel to the IRE surface.

can interact with the bond's dipole moment. In this case the electric field vectors in the x and y direction (E_{x_0} , E_{y_0}) affect the C-H dipole and light is absorbed. However, the z component of the electric field, E_{z_0} , will not interact with the C-H groups, and no absorbance will occur. Furthermore, since absorbance is proportional to the square of the electric field (see Equation 10), two limiting cases can be found by using Equations (5) through (7) to deduce the orientation of adsorbed collector species:

Case 1. C-H groups parallel to the IRE

$$\frac{A_{\perp}}{A_{\parallel}} = \frac{E_{y_0}^2}{E_{x_0}^2} \quad (11)$$

Case 2. C-H groups random to the IRE

$$\frac{A_{\perp}}{A_{\parallel}} = \frac{E_{y_0}^2}{E_{x_0}^2 + E_{z_0}^2} \quad (12)$$

Haller and Rice (1970) used Equations (11) and (12) to determine the orientation of a Langmuir-Blodgett calcium stearate monolayer deposited from the aqueous phase onto a sapphire IRE. Experimental A_{\perp}/A_{\parallel} ratios were found using conventional IRS techniques and a polarized infrared beam. Theoretical A_{\perp}/A_{\parallel} ratios were calculated using Equations (5-7) for the three spatial components of the electric field, E_{x_0} , E_{y_0} , and E_{z_0} , respectively. The absorbance ratio found spectroscopically, 1.90, was very similar to the Case 1 theoretical value of 2.13, suggesting a highly ordered monolayer. Interestingly, a calcium stearate monolayer formed by adsorption from a hexane solution gave quite dissimilar results. For these conditions, the spectroscopic A_{\perp}/A_{\parallel} ratio was 1.23, and the calculated ratio for Case 2 was 1.28, indicating a random orientation of the adsorbed calcium stearate molecules. A similar approach has been used by others for different IREs and surfactants (Fringeli et al., 1972; Higashiyama and Takenaka, 1974; Yacynych et al., 1976; Maoz and Savig, 1984). However, such measurements have not been made in-situ, and no flotation chemistry studies of this nature have been reported in the literature. Inherent in the above equations is the assumption that the adsorbed surfactants are isotropic, and that absorbance values vary linearly with concentration from monolayer coverage and below. Clearly, this technique could be used for determination of collector orientation on mineral surfaces.

Adsorption Density

Sperline et al. (1987) used Equation (10) and the approximation $\exp(-2t/d_p) = 1 - 2t/d_p$ (a thin film of thickness, t , is much smaller than the depth of penetration), along with Equations (8) and (9),

to give the following equation:

$$\frac{A}{N} = \epsilon C_b d_e + \epsilon (2d_e/d_p) (C_i t) \quad (13)$$

where C_b = surfactant concentration in the bulk (mol/l)

C_i = surfactant concentration at the interface (mol/l)

By using a reference solute, the number of internal reflections, N , was determined. However, N also can be found by geometric considerations (Harrick, 1979) from the relationship:

$$N = (\ell/h) \cot \theta \quad (14)$$

where ℓ = IRE length

h = IRE thickness

Replacing Equation (14) in Equation (13) and rearranging gives

$$C_i t = \left(\frac{A}{\ell/h \cot \theta} - \epsilon C_b d_e \right) / \epsilon \left(\frac{2d_e}{d_p} \right) \quad (15)$$

and recognizing that $C_i t/1000$ equals the Gibbs surface excess, Γ (mol/cm²), gives the following form:

$$\Gamma = \left(\frac{A}{\ell/h \cot \theta} - \epsilon C_b d_e \right) / 1000 \epsilon \left(\frac{2d_e}{d_p} \right) \quad (16)$$

Thus by appropriate choice of a mineral crystal for the IRE, collector adsorption density can be determined in-situ in real time. In Equations (13) through (16), it was assumed that the adsorbed surfactant layer's refractive index was similar to the bulk; therefore d_e and d_p are for the bulk case (Equations (8) and (9)).

Kinetics

Recently, rapid scan FTIR spectrometers have been used to monitor electrochemical reactions in real time (Yaniger and Vidrine, 1986; Daschbach et al., 1986). Scan rates of 84 scans/sec have been reported in one case (Yaniger and Vidrine, 1986). With such equipment it is now possible to study the adsorption kinetics of surfactants in-situ at the surface of IREs in real time.

EXPERIMENTAL CONSIDERATIONS

IRS, like all experimental FTIR techniques, has its limitations and subtleties. Some of these limitations are discussed below for in-situ flotation chemistry applications.

Solvents

Water is a very strong absorber in the infrared. These strong absorbance bands tend to mask the weaker bands from the mineral and surfactant. Spectral subtraction routines common to most FTIR spectrometers alleviate this problem somewhat. One alternative is to use deuterium oxide, D_2O , as a substitute for H_2O . Both H_2O and D_2O spectra are shown in Figure 4. It can be seen from Figure 4 that by judicious choice of either D_2O or H_2O one can have IR "windows" where solvent absorbance is either weak or nil. The refractive indices of H_2O and D_2O have been reported for a number of wavelengths (Downing and Williams, 1975; Sethna et al., 1978) and aid in quantitative analysis of the spectral data.

An immediate question regarding the use of D_2O in flotation studies is whether it behaves similarly to H_2O . Bubble attachment time measurements in the fluorite/oleate system with the two solvents are almost identical (Cross, 1988) and lend credibility to the use of D_2O for flotation studies. This response is not surprising when one considers that D_2O and H_2O have very similar physical properties (Nebergall et al., 1980).

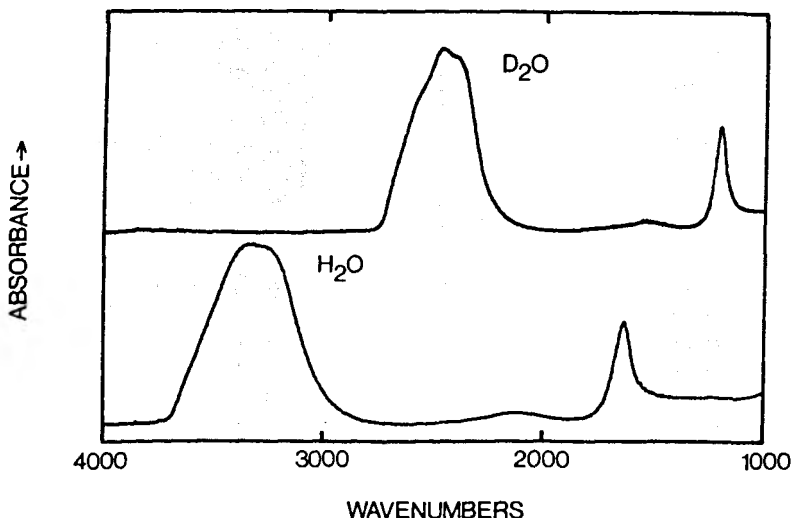


Figure 4. Infrared spectra of H_2O and D_2O in the region $4000-1000\text{ cm}^{-1}$.

Internal Reflection Elements

The focus of this paper has been on surfactant adsorption directly onto the IRE mineral of interest. Knutson and Lyman (1985) gave a good overview of the commonly used IREs. However, from a flotation standpoint, such IREs are not useful.

Possible synthetically grown single-crystal IREs which are readily available and useful from a flotation standpoint are listed in Table 2 (Harrick Scientific Corp., 1988a). Also listed in Table 2 is the useful transmission range of each IRE. The use of natural mineral crystals as IREs was postulated nearly 20 years ago (Harrick, 1979). To the authors' knowledge, natural mineral crystals have not been machined into IREs. The problem with using natural minerals as IREs is three-fold. First, many mineral crystals are not large enough (at least 20 mm) to be machined into a usable form. Second, adequate signal detection is difficult because of scattering caused by micro-cracks and voids. Finally, strong absorbance bands characteristic of some minerals also tend to limit their useful transmission range as IREs. Nevertheless, use of certain mineral crystals is possible, and a fluorapatite IRE has been fabricated, and its use will be shown later in the paper.

Table 2. Synthetic Single-Crystal IREs Which Are Useful for Flotation Studies.

Internal Reflection Element (IRE)	Useful Transmission Region (cm^{-1})	Average Refractive Index, n
SiO_2	50,000-4,000	1.44
Al_2O_3	33,000-2,800	1.75
MgO	20,000-1,700	1.68
CaF_2	66,000-1,300	1.40
NaCl	25,000- 900	1.5
KCl	20,000- 700	1.47
As_2S_3	12,500-1,300	2.4
ZnS	14,000-1,000	2.22
TiO_2	20,000-2,000	2.6; 2.9
ZrO_2	25,000-1,800	2.15

The most common geometry of IREs is that of a prism; however, cylindrical IREs which use Cassegrainian optics are more amenable to the circular infrared beam of FTIR spectrometers have recently become more widely used. Cylindrical IREs have the disadvantage that polar-

ization studies are not possible because the state of the polarized beam is scrambled during transmission through the IRE. Furthermore, in the case of the cylindrical IRE, the number of internal reflections must be established experimentally (Sperline et al., 1987).

A final point regarding IREs is their fabrication and cleaning. IREs should be fabricated such that the incident angle of incoming IR light meets the critical angle in Equation (1). However, as noted earlier for thin films, such as adsorbed surfactants, the critical angle requirement can be lessened somewhat.

Polishing or buffing IREs to remove adsorbed surfactants usually is not sufficient to remove the contamination. Two approaches to cleaning are usually used. The first involves immersion of the contaminated IRE in solvents which dissolve the surfactant. Alternatively, the IRE can be exposed to a high-energy plasma which has been shown to remove adsorbed species (Harrick Scientific Corp., 1988).

APPLICATION OF IRS TO SELECTED FLOTATION SYSTEMS

Physisorption--Sapphire/Sodium Dodecyl Sulfate

A sapphire (Al_2O_3) prism IRE purchased from Harrick Scientific was used as a model substrate. Deuterium oxide (D_2O) +99.9% purity (Cambridge Isotopes) and sodium dodecyl sulfate (SDS) +99% purity (Fluka Chemical) were used as solvent and surfactant, respectively. The aliphatic absorbance peaks ($3000\text{--}2800\text{ cm}^{-1}$), which are free from IRE and solvent absorbance bands, were used for all quantitative measurements. All spectra were recorded using a Digilab FTS-40 FTIR spectrometer. Experimental details are given elsewhere (Kellar and Miller, 1989).

Adsorption Density. It has been well-established that adsorption of sodium dodecyl sulfate by alumina is controlled to a large extent by coulombic forces. This classic physisorption reaction at pH 7.5 has been studied by IRS using Equation (16). The adsorption densities of SDS by the Al_2O_3 IRE were determined from IRS spectra after four hours of equilibration. Adsorption densities are given in Table 3. These in-situ results agree quite well with other results reported in the literature (Chandar et al., 1987; Somasundaran and Fuersteman, 1966; Yoon and Salman, 1976).

Orientation. The two limiting cases of orientation defined by Equations (11) and (12) were used to define the orientation of adsorbed SDS on Al_2O_3 . The refractive indices of D_2O (1.27), Al_2O_3 (1.70), and SDS (1.44) are known from the literature (Sethna et al., 1978; Malitson, 1962; Besio et al., 1988). Sapphire exhibits low to moderate birefringence (Deer et al., 1982). Because of this, it was assumed that the polarized light was not scrambled and that the

Table 3. Adsorption Density of SDS by Al_2O_3 as Calculated from Internal Reflection Theory.

Equilibrium Concentration (M)	Adsorption Density (mol/cm^2)
4.8×10^{-5}	1.54×10^{-10}
1.18×10^{-3}	4.37×10^{-10}
3.85×10^{-3}	5.25×10^{-10}

refractive index remained constant upon reflection through the sapphire IRE. The refractive indices along with the optical constants of the system give calculated A_{\perp}/A_{\parallel} ratios for Case 1 (Equation 11) and Case 2 (Equation 12), respectively. These ratios are compared with the experimental A_{\perp}/A_{\parallel} ratios determined spectroscopically as shown in Table 4 for two equilibrium SDS concentrations after four hours of equilibration. It should be noted that, at the lower SDS concentration, the adsorbed layer is less than monolayer coverage, and Equations (11) and (12) may be compromised somewhat. Many researchers (Chandar et al., 1987) have contended that these adsorbed species are ordered in a perpendicular orientation to the surface. However, these FTIR/IRS results suggest that at both equilibrium SDS concentrations the adsorbed species are mostly random in orientation at the sapphire surface.

Table 4. Orientation of SDS on Al_2O_3 as Established by Absorbance Ratios According to Internal Reflection Theory. See Equations (11) and (12).

Theoretical

Vertical Orientation, $A_{\perp}/A_{\parallel} = 4.85$

Random Orientation, $A_{\perp}/A_{\parallel} = 0.82$

Experimental

Equilibrium Concentration (M)	A_{\perp}/A_{\parallel}
2.0×10^{-6}	0.95
1.0×10^{-3}	1.42

Chemisorption--Fluorite/Sodium Oleate

Fluorite (CaF_2) IREs purchased from Optovac Inc. were used as model substrates. Deuterium oxide and sodium oleate +99% purity (Sigma Chemical) were used as solvent and surfactant, respectively. Aliphatic absorbance peaks ($3000\text{--}2800\text{ cm}^{-1}$) were used for all quantitative measurements.

Adsorption Density. The adsorption of oleate by fluorite is a classic example of a chemisorption/surface precipitation reaction. It has been well-established that at low equilibrium concentrations oleate is chemisorbed in what appears to be a horizontal monolayer (Hu et al., 1986). Figure 5 compares in-situ adsorption densities after 30 hours of equilibration at pH 9.5 calculated from Equation (16) with those determined by ex-situ radiotracer techniques (Hu et al., 1986). The IRS data supports the previous hypothesis of adsorption occurring as a chemisorption reaction at low equilibrium concentrations. Notice that adsorption densities at low equilibrium concentrations of oleate ($5 \times 10^{-7}\text{ M}$) can be determined by this method.

Shown in Figure 6 is a complete in-situ adsorption isotherm calculated from IRS theory. At approximately $1 \times 10^{-4}\text{ M}$ oleate, the adsorp-

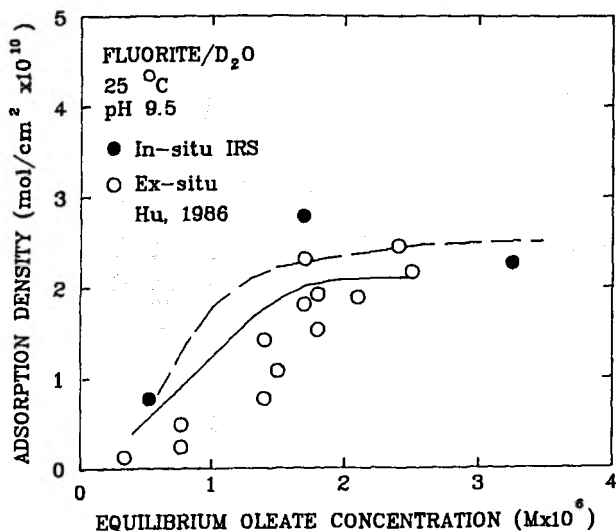


Figure 5. Adsorption isotherm of oleate by fluorite using ex-situ (radiotracer) and in-situ (IRS) techniques.

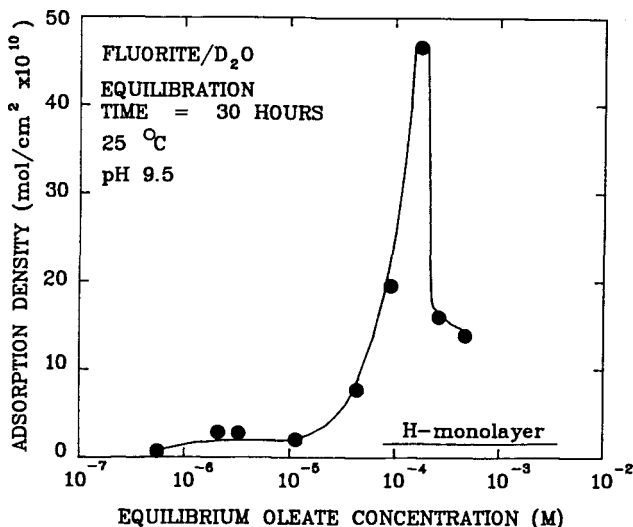


Figure 6. Adsorption isotherm of oleate by fluorite (IRE) as calculated from in-situ FTIR spectroscopic data using internal reflection theory.

tion density reaches a maximum and decreases at higher oleate concentrations. This adsorption phenomenon has been attributed to the surface precipitation of calcium oleate (Hu et al., 1986).

Kinetics. The kinetics of oleate adsorption at a cylindrical CaF₂ IRE are shown in Figure 7. Oleate is seen to adsorb rapidly at short equilibration times (<2 hours) and more slowly thereafter. Similar results have been found for the Al₂O₃/SDS system.

RESEARCH HORIZONS

The approach taken for this FTIR/IRS research (direct adsorption from solution onto reactive mineral crystal IREs) is unique in that it gives detailed quantitative information about adsorption phenomena, in-situ and in real time. It is expected that this method will continue to expand in use and give fundamental information about the flotation process. Discussed below are some of the possibilities that exist for the flotation chemist.

As mentioned previously, natural mineral crystals have never before been used as IREs. A fluorapatite crystal purchased from the

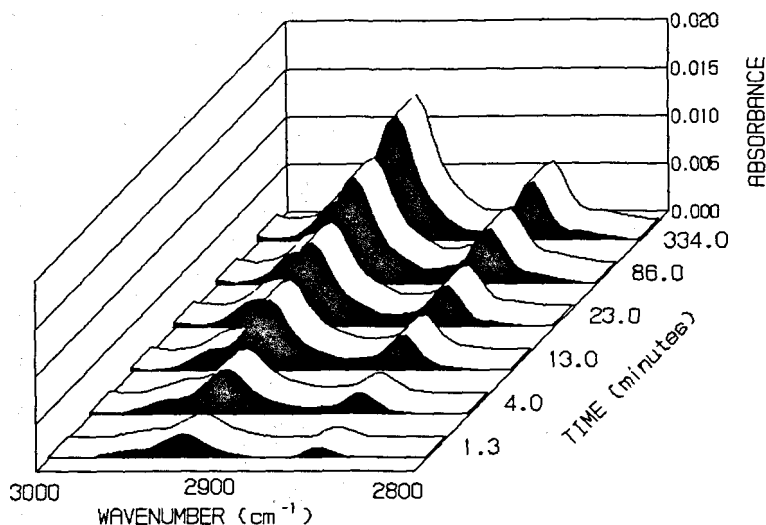


Figure 7. The kinetics of oleate adsorption at a fluorite surface as revealed by in-situ internal reflection spectroscopy.

Black Hills Institute of Geological Research was fabricated and polished by Harrick Scientific into an IRE with dimensions 23x7x3.5 mm. The unique dimensions of this IRE, dictated by its natural occurrence, don't readily allow for in-situ measurements like the $\text{Al}_2\text{O}_3/\text{SDS}$ and $\text{CaF}_2/\text{sodium oleate}$ systems. However, Figure 8 shows the aliphatic region ($3000\text{--}2800\text{ cm}^{-1}$) after soaking the fluorapatite IRE in a sodium oleate solution ($5 \times 10^{-3}\text{ M}$) and drying under ambient conditions. This spectrum demonstrates for the first time that natural minerals can be used as IREs.

Many mineral crystals do not become infrared transparent until the near-IR ($12,000\text{--}4,000\text{ cm}^{-1}$) where overtone and combination bands of the fundamental mid-IR ($4,000\text{--}700\text{ cm}^{-1}$) bands occur. These overtone/combination bands are inherently an order of magnitude weaker than the fundamental mid-IR bands. Could IRS be used to study adsorption phenomena in the near-IR as demonstrated for the mid-IR? For instance, natural calcite (CaCO_3) is not transparent in the mid-IR and therefore useless as an IRE in the mid-IR region. Calcite however is transparent in the near-IR. A three-inch calcite crystal could be machined into an IRE which would give 150 internal reflections! This large number of internal reflections, compared to the small number used in this study (5 to 30 reflections), would magnify the weak near-IR absorbance peaks of adsorbed collector species. A fluorite IRE which gives six internal reflections was soaked in an oleate sol-

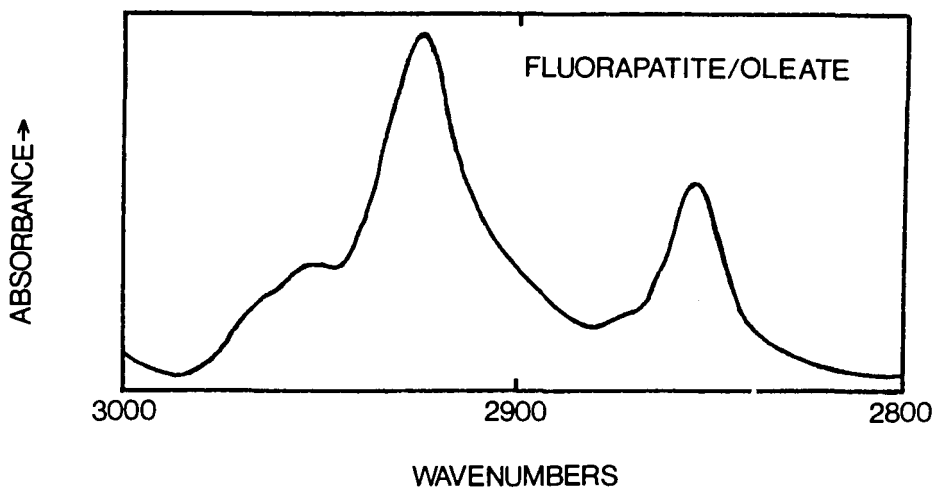


Figure 8. Infrared spectrum of oleate adsorbed on a natural crystal fluorapatite IRE.

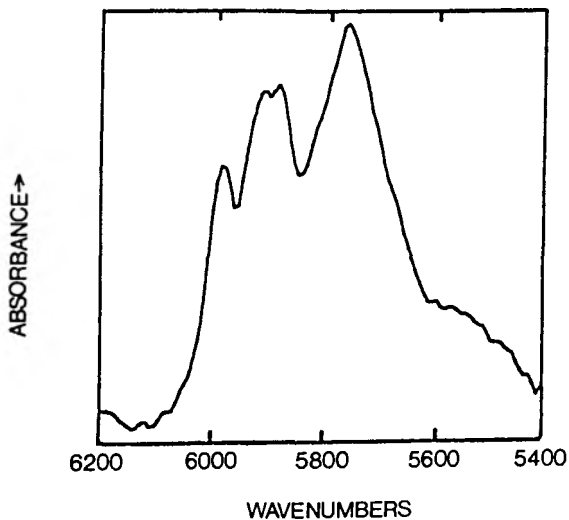


Figure 9. Near-infrared spectrum of aliphatic overtones of oleate adsorbed on a fluorite IRE.

ution, dried under ambient conditions, and examined in the near-IR. Figure 9 shows the resulting spectrum in the region $6200-5400\text{ cm}^{-1}$. The peaks can be positively identified as the first overtones of the C-H stretching vibrations (Weyer, 1985). Clearly, the use of natural minerals as internal reflection elements in the near-IR offers an exciting possibility for future in-situ FTIR internal reflection spectroscopy research in flotation chemistry and other areas of technology.

CONCLUSIONS

It has been demonstrated that quantitative in-situ FTIR/IRS collector adsorption measurements are possible using reactive mineral crystal internal reflection elements (IREs). These in-situ results show that adsorption kinetics, adsorption density, and collector orientation can be monitored in real time. The adsorption density measurements for the sapphire/SDS and fluorite/sodium oleate systems agree quite well with those using more traditional methods. It was also determined that SDS adsorbed by sapphire mostly exhibits random orientation. A natural mineral crystal (fluorapatite) has been used as an IRE, and the possibility of extending the use of such crystals to the near-IR represents an exciting new horizon for flotation chemistry research.

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