

PROGRESS REPORT

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15 December 1990-14 December 1991

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

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Technical Progress during the Second Budget Period

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In the previous budget period, a unique in-situ sampling technique was developed which allowed for real-time analysis of surfactant adsorption processes on mineral single crystals. This technique couples FT-IR spectroscopy and internal reflection spectroscopy (FT-IR/IRS) and the mineral single crystal is referred to as a "reactive" internal reflection element (IRE). The single crystal is reactive in the sense that the adsorption occurs directly upon the surface of the IRE, which also serves to transmit IR electromagnetic radiation.

The in-situ FT-IR/IRS method was previously demonstrated for the fluorite (CaF_2)/oleate flotation system. Information obtained from this system included adsorption density (from mid- and near-infrared spectra), adsorption state and reactivity of adsorbed collector, and alkyl chain conformational analysis. In the second budget period, similar analyses have been performed for three other mineral systems. These systems are as follows:

Insoluble Oxides: sapphire ($\alpha\text{-Al}_2\text{O}_3$)/sodium dodecylsulfate,

Soluble Salts: sylvite (KCl)/n-octylamine, and

Semisoluble Salts: calcite (CaCO_3)/sodium oleate and fluorite (CaF_2)/sodium oleate.

Insoluble Oxide Minerals

The primary insoluble oxide flotation system studied in the past year has been the sapphire ($\alpha\text{-Al}_2\text{O}_3$)/sodium dodecylsulfate (SDS) system. The main area of emphasis was examination of the surface phase behavior of adsorbed dodecylsulfate by FT-IR/IRS. This has been accomplished by measurement of shifts in the asymmetric $-\text{CH}_2$ stretching frequency of the SDS surfactant. See Figure 1. The shift in the $-\text{CH}_2$ stretching frequency, which is on the order of 1-2 wavenumbers, occurs due to changes in the conformational order of the methylene tail as the surfactant undergoes a phase transition with increasing adsorption density. The position of the $-\text{CH}_2$ stretching band has been correlated to the position of this band for solution-phase SDS

species. The adsorption density at which this shift in stretching frequency occurs, when expressed as equivalent concentration, is nearly identical to the concentration in solution at which SDS micelles exhibit a phase transition to coagels.

Soluble-Salt Minerals

Soluble-salt flotation systems have not been investigated thoroughly because of experimental difficulties associated with high ionic strength brines. FT-IR/IRS alleviates these experimental difficulties somewhat and has been used to calculate the adsorption densities of the n-octylamine collector at the surface of sylvite (KCl) single-crystal internal reflection elements. A complete adsorption isotherm has been established for the sylvite/n-octylamine system from in-situ spectral data as shown in Figure 2. It was observed that monolayer coverage occurred at collector concentrations below 1×10^{-2} M. Above this concentration surface precipitation of collector micelles occurs at the surface of the sylvite IRE.

FT-IR/IRS has also been used to determine the conformation of the adsorbed collector's alkyl chain. Similar to the sapphire/SDS system, the conformational analysis of the surface state was performed by the examination of systematic shifts in the asymmetric $-\text{CH}_2$ stretching frequencies which had been correlated with solution spectra. Unlike other systems (CaF_2 /oleate, Al_2O_3 /SDS), where surface-phase transitions with adsorption density occur, it was found that the adsorbed n-octylamine resembled a micellar-like conformation at all adsorption densities. This behavior is attributed to the high ionic strength environment of the adsorbed species, and similar findings have been reported in the literature (Weers and Scheuing, ACS Symposium Series #447).

Semisoluble Salt Minerals

Previous in-situ FT-IR/IRS research has shown that polymerization of adsorbed oleate via reaction of the double bond with oxygen seems to take place at the fluorite surface, resulting in enhanced hydrophobicity. Attention is now focused on analyzing the reaction of adsorbed unsaturated carboxylates at the calcite (CaCO_3) surface in order to understand the nature of this

phenomenon. Present efforts using FT-IR/IRS with reactive IREs has proved to be difficult because:

- 1) the fundamental CH stretching bands of adsorbed surfactants cannot be analyzed, since calcite is opaque below 3200 cm^{-1} ,
- 2) strong interference bands exist in the combination region ($4500\text{-}4000\text{ cm}^{-1}$) due to carbonate stretching frequencies, and
- 3) the signal in the overtone region ($6000\text{-}5500\text{ cm}^{-1}$) may be too weak to be detected.

Alternative experimental techniques that are being considered include in-situ FT-IR/IRS of mineral suspensions and laser-Raman spectroscopy using a charge-coupled detector. Preliminary Raman spectra of adsorbed oleate on fluorite seem to indicate that the double bond has reacted under oxygen-saturated conditions as evidenced by the diminished intensity of the $=\text{CH}$ band (3005 cm^{-1}) as shown in Figure 3.

Publications and Presentations

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Miller, J. D., Kellar, J. J., and Cross, W., 1990. In-Situ Examination of Adsorbed Surfactants by FTIR/IRS Using Reactive Internal Reflection Elements. 199th ACS Annual Meeting, Boston, Massachusetts, 23-25 April 1990.

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Kellar, J. J. and Miller, J. D., 1990. Surfactant Adsorption Density Calculations from In-Situ Real Time NIR Spectroscopic Data. 17th Meeting Federation of Analytical Chemistry and Spectroscopy Societies, Cleveland, Ohio, October 1990.

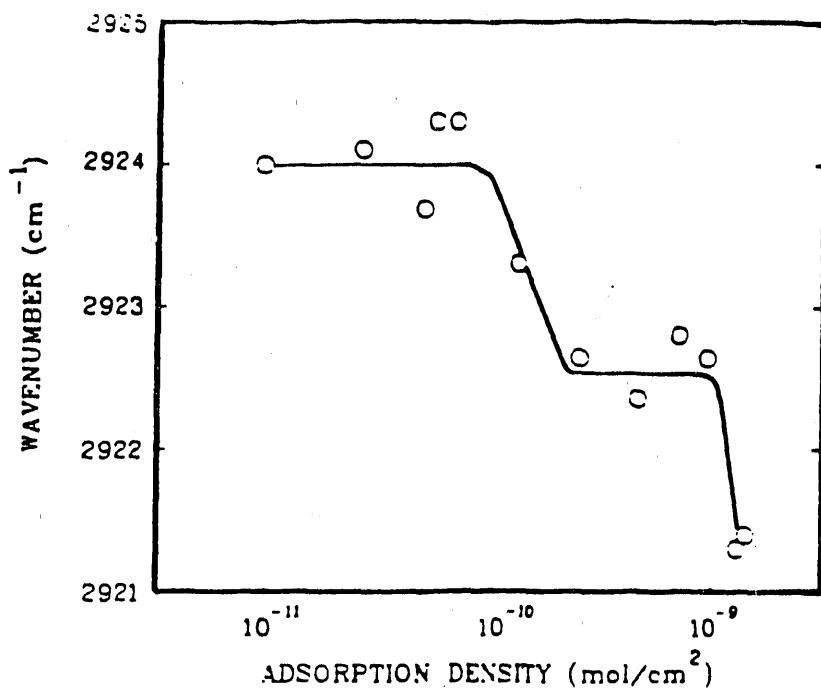


Figure 1. Effect of adsorption density on the asymmetric $-\text{CH}_2$ stretching frequency of adsorbed SDS.

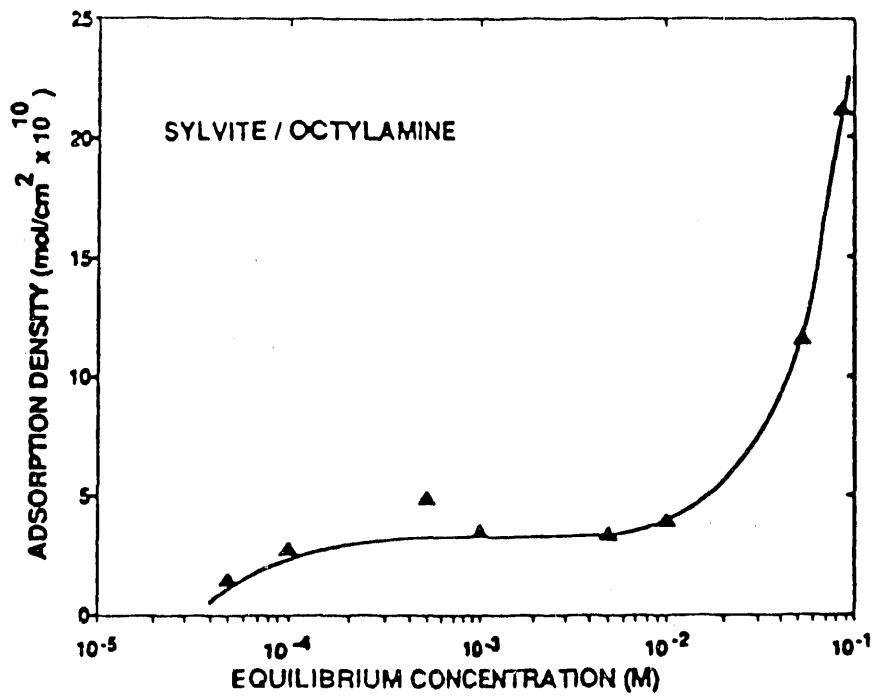


Figure 2. Adsorption isotherm for octylamine adsorption by a sylvite IRE as calculated from in-situ FT-IR/IRS spectral data ($\text{pD} = 4.9$).

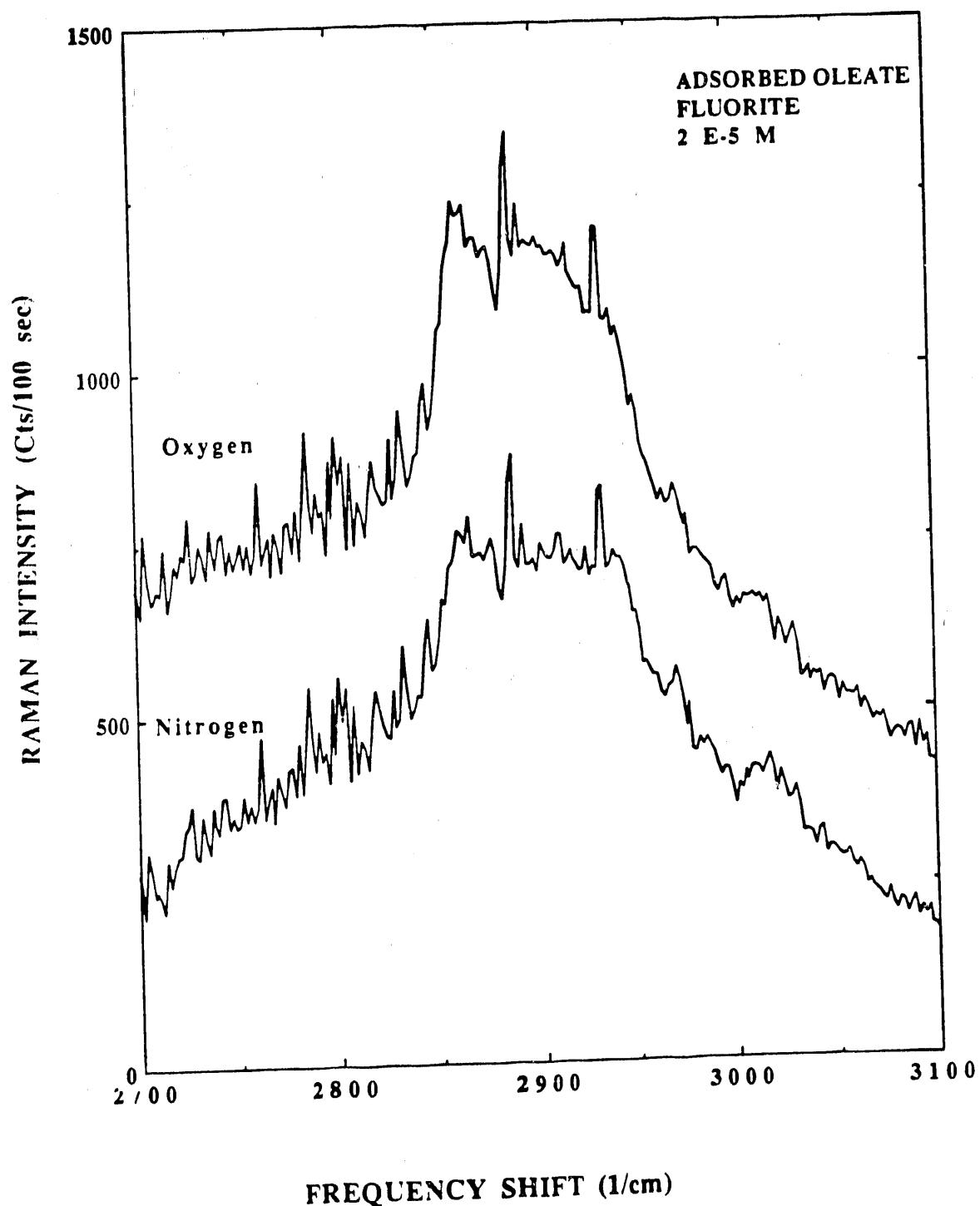


Figure 3. Raman spectra of adsorbed oleate on fluorite under oxygen (top) and nitrogen (bottom) atmospheres.

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