Surface phase transitions of adsorbed collector molecules as revealed by in situ FT-IR/IRS spectroscopy

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Introduction

Researchers have long speculated regarding the adsorption state of collectors on mineral surfaces. Only recently have analytical techniques become available that allow direct in situ analysis of adsorbed layers. With reactive internal reflection elements (IREs), Fourier transform infrared spectroscopy coupled with internal reflection spectroscopy (FT-IR/IRS) allows for unobtrusive investigation of the adsorbed layer (Harrick, 1979). This technique has been used both for the in situ identification of adsorbed species and for the direct calculation of collector adsorption density in real time from infrared spectral data (Miller and Kellar, 1988).

The reactive mineral IRE serves both to internally reflect the infrared light and to act as a substrate at which collector adsorption can be monitored. Shown in Fig. 1 is a schematic of light being internally reflected in an IRE. As the light is totally reflected at the interface, an evanescent wave propagates a short distance (typically a few microns) away from the IRE, and sampling of the interfacial region occurs. Because of multiple internal reflections, great sensitivity can be obtained. Flotation systems for which this method has been demonstrated include CaF_2/oleate, Al_2O_3/dodecylsulfate, $CaCO_3$/oleate, ZnS/xanthate and KCl/octylamine (Miller and Kellar, 1988; Kellar et al., 1989, 1990; Miller et al., 1990).

Of particular interest to flotation chemists is the conformational behavior of the alkyl chain of adsorbed collector molecules. In the simplest sense, conformation can be thought of as the relative flexibility of the hydrocarbon chain caused by rotations about carbon-carbon single bonds. The flexibility is described by the amount of gauche/trans conformations in the alkyl chain.

Figure 2 shows examples of gauche and trans conformations (rotational isomers or rotamers) in a hydrocarbon chain. These two conformations are observed when the terminal methylene groups in any four-carbon subchain are on the same side (gauche) or opposites sides (trans) of the plane of the middle carbon-carbon bond. A gauche conformer (rotamer) is thus a state of maximum potential energy, whereas a trans conformer is a state with minimum potential energy. The difference between these states has been found to be approximately 0.5 to 0.8 kcal/mole (Mead et al., 1986).

The relative number of butane molecules present as gauche conformers with respect to trans conformers can be calculated from the Boltzmann equation (Mead et al., 1986). At 25° C approximately 66% of the butane molecules are trans rotamers.
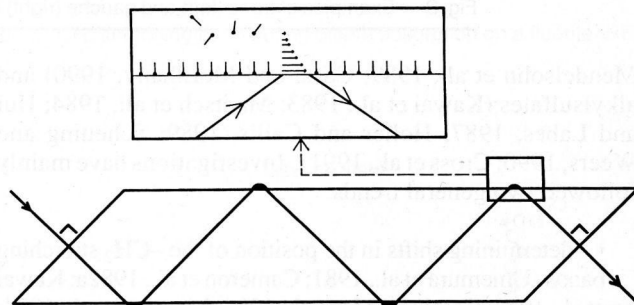

Fig. 1— Schematic of light undergoing multiple internal reflections in an IRE.

However at 100° C, only 33% of butane molecules are trans rotamers.

Exposing the hydrocarbon chain to a polar, rather than an apolar, medium should also cause an increase in the number of gauche butylene groups in a hydrocarbon chain, although this effect has been difficult to observe experimentally (Mead et al., 1986). Forming a crystalline hydrocarbon is equivalent to decreasing the temperature, which greatly increases the amount of trans butylene groups present in the chain.

From the preceding discussion, a picture of the solution species of concern can be developed. The collector monomer should exhibit the greatest number of gauche rotamers and most likely will look crumpled or balled-up to reduce the surface area in contact with water. The micellar form is expected to be aggregated, with the hydrocarbon chain existing in a less polar environment.

These characteristic conformational features have been examined by FT-IR spectroscopy for various liquid phases of alkanoic acids (Umemura et al., 1981; Cameron et al., 1982a; Yang et al., 1986; Wong, 1987; Wong and Mantsch, 1983; Cross et al., 1992), phospholipid membranes (Fringeli, 1980; Casal and Mantsch, 1985; Wong et al., 1988;

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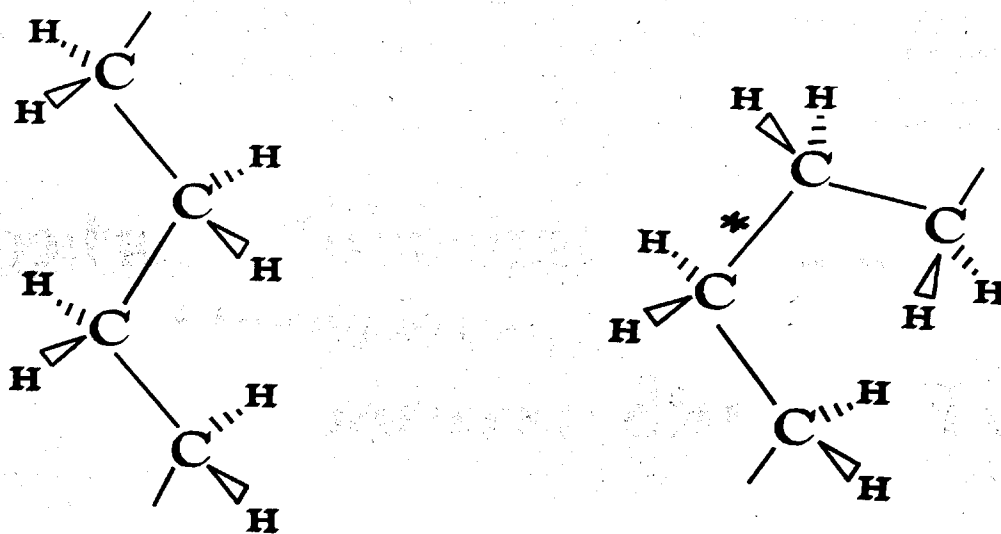
Fig. 2 — Examples of trans (left) and gauche (right) butylene linkages. The asterisk indicates the gauche bond.

Mendelsohn et al., 1989; Casal and McElhany, 1990) and alkylsulfates (Kawai et al., 1983; Mantsch et al., 1984; Hui and Labes, 1987; Holler and Callis, 1989; Scheuing and Weers, 1990; Cross et al., 1991). Investigations have mainly followed two general trends:

- determining shifts in the position of the –CH_2 stretching bands (Umemura et al., 1981; Cameron et al., 1982a; Kawai et al., 1983; Casal and Mantsch, 1984; Mantsch et al., 1984; Wong and Mantsch, 1985; Yang et al., 1986; Wong, 1987; Hui and Labes, 1987; Wong et al., 1988; Scheuing and Weers, 1990; Cross et al., 1991) and, more recently,
- examining –CH_2 wagging bands that are specific to certain gauche or trans conformations (Holler and Callis, 1989; Mendelsohn et al., 1989; Casal and McElhany, 1990).

In both cases, these bands give data characteristic for each phase studied. Thus it is clear that phase transitions can be distinguished by specific infrared spectral changes. In terms of the –CH_2 stretching bands, higher wavenumbers are indicative of a high population of gauche rotamers. Conversely, lower wavenumbers are indicative of more trans rotamers.

In this paper FT-IR/IRS with reactive internal reflection elements has been used to examine some of the conformational characteristics exhibited in three flotation systems: CaF_2/oleate, Al_2O_3/dodecylsulfate and KCl/octylamine.

Experimental

Infrared spectra were recorded with a nitrogen gas- or dry-air-purged Digilab FTS-40 FT-IR spectrometer using a narrow-band liquid, nitrogen-cooled, mercury-cadmium-telluride detector. All spectra were at least 1024 co-added scans at resolutions of 8, 4 or 1 cm^{-1}, as noted in the text. A Twin Parallel Mirror Reflection 320 liquid, internal reflection accessory (Harrick Scientific) was used with a Haake F3 constant-temperature bath to obtain thermostated in situ IRS spectra. Transmission spectra were collected with a Spectra-Tech demountable, liquid transmission cell with fluorite windows. All chemicals used were reagent-grade. Single-crystal minerals were machined and polished into 50- x 10-mm internal reflection elements. All IREs were 1 mm in thickness. IRE angles were verified by goniometric measurement.

Spectra of adsorbed collector were obtained by subtracting a deuterium oxide, D_2O, spectrum from a D_2O/collector spectrum, both of which were ratioed against the clean IRE background. More complete experimental details can be found elsewhere (Miller and Kellar, 1988; Kellar et al., 1989, 1990, 1991; Kellar, 1991; Cross et al., 1991; Yalamanchili et al., 1991; Kellar et al., 1992).

Results and discussion

The conformational analysis of the surface state is based on a detailed examination of systematic shifts in the asymmetric –CH_2 and symmetric –CH_2 stretching vibrations. Specifically, liquid transmission spectra of collector/solution are compared with spectra of the adsorbed collector at the surface of a particular mineral IRE. From similarities in the band positions of these spectra, the conformations of adsorbed collectors are thus determined.

Shown in Table 1 is the frequency of the asymmetric –CH_2 stretching band for solution phases of various collectors common to froth flotation systems. The monomeric and micellar phases are well known to most flotation chemists. The liquid crystalline and coagel phases are somewhat less familiar. The most common liquid crystals found are hexagonal and lamellar. The hexagonal liquid crystal can be thought of as an aggregate

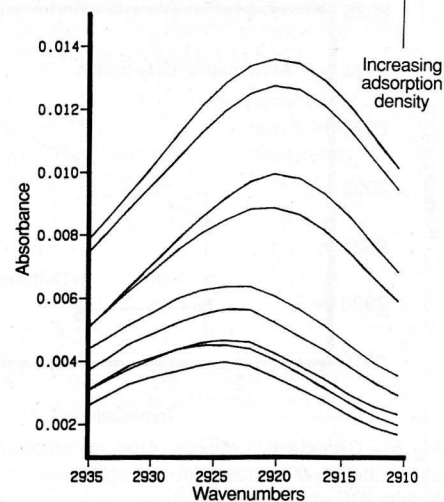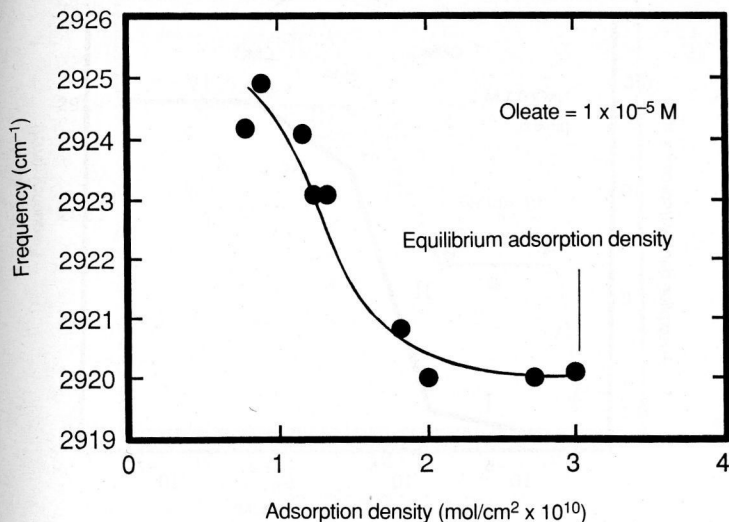| Table 1 — Asymmetric –CH_2 stretching frequency wavenumbers (cm^{-1}) for selected surfactants in various states.						
Surfactant	**Monomer**	**Micelle**	**Coagel**	**Liquid crystal**	**Solid**	**Reference**
Sodium n-octanoate	2936	2928				Umemura, et al., 1981
Sodium oleate		2926	2920			Cameron, et al., 1982
Sodium dodecylsulfate	2934	2928	2918	2924		Cross, et al., 1991
n-octylamine hydrochloride	2937	2933			2924	Yalamanchili, et al., 1991
n-octylamine hydrochloride (KCl-saturated D_2O)	2935	2929			2924	Yalamanchili, et al., 1991

Fig. 3 — Frequency change (a) and corresponding spectra (b) of the asymmetric –CH$_2$ stretching band during oleate adsorption on a fluorite IRE at 25° C and 1 x 10^{-5} M oleate.

of cylindrical micelles with each micelle positioned according to a hexagonal lattice. The lamellar liquid crystals are planar, bilayered aggregates of single molecules. Common examples of liquid crystals are the thick soap/water mixture found on the bottom of soap dishes, as well as biological cell membranes.

The coagel phase is most often described as a poorly hydrated crystalline solid. In appearance this phase is usually opaque and microscopically heterogeneous, most resembling toothpaste. An example of a coagel occurs during the transformation of cell membranes in biological systems. These membranes are lamellar liquid crystals at normal body temperatures but transform to coagels when exposed to a body temperature drop of 5 to 10 degrees. Also, cholesterol buildup in arteries can result in coagel formation. The liquid crystalline and coagel phases each have a specific amount of conformational order (Tardieu et al., 1973; Collings, 1990).

From Table 1, one can determine the relative conformation of various phases. For example, the monomer of sodium dodecylsulfate has an asymmetric –CH$_2$ stretching frequency of 2934 cm^{-1} and a significant population of flexible gauche rotamers in comparison to the coagel phase, which has a frequency of 2918 cm^{-1}. At the lower frequency, the alkyl chain is predominantly in the all-trans conformation. Armed with bulk phase information regarding conformational states of the various surfactants, attention can now be turned to adsorbed collectors and their alkyl conformational state.

Fluorite/oleate

Recently, using in situ FT-IR/IRS, the fluorite/oleate flotation system was thoroughly investigated (Kellar, 1991; Kellar et al., 1991). In these analyses it was determined from infrared spectral data that, at solution concentrations less than 3 x 10^{-5} M, oleate was chemisorbed. Also, at concentrations greater than this, a surface-precipitated calcium oleate resulted.

Conformational analysis has been performed for adsorbed oleate at concentrations that give these two, different, adsorbed oleate species. Shown in Fig. 3a is the band position of the asymmetric –CH$_2$ band as a function of adsorption density at 25° C from an oleate concentration of 1 x 10^{-5} M. This dependence was established from peak maxima determined by a peak-picking algorithm (Digilab,
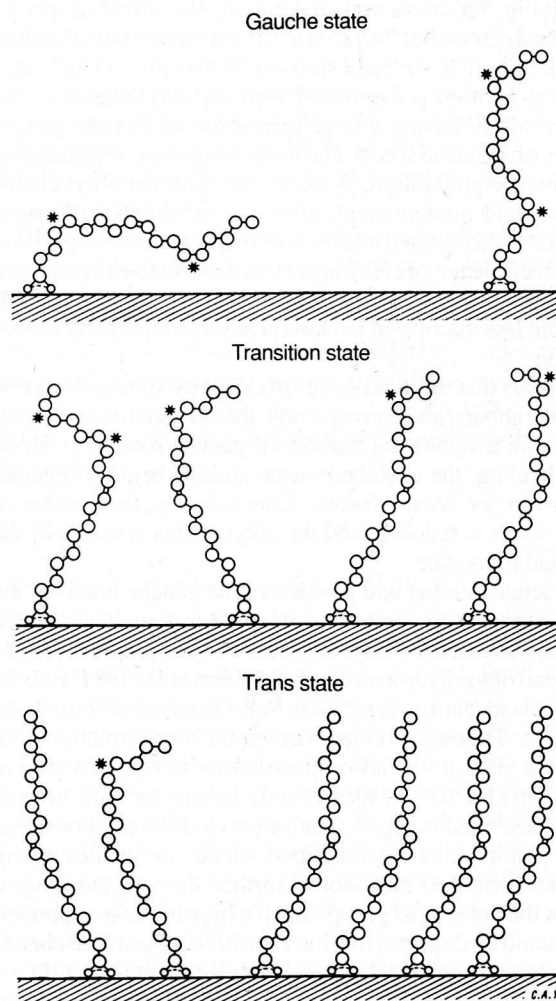

Fig. 4 — Conformation of the chemisorbed oleate species at the surface of fluorite for different levels of adsorption density revealing the transition from the gauche state at submonolayer coverage to the more rigid trans state at near monolayer coverage. Gauche bonds are designated with asterisks (*).
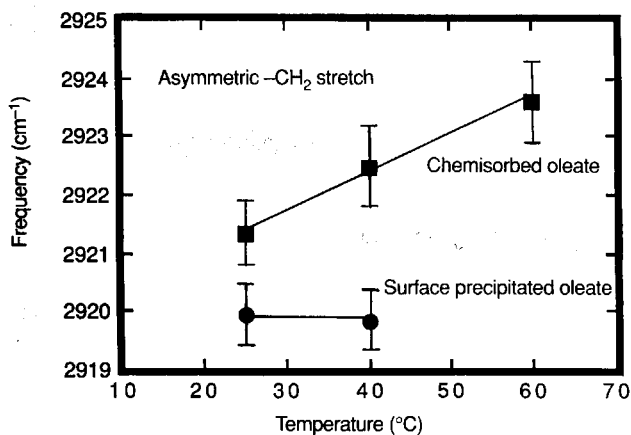
Fig. 5 — Change in frequency of the asymmetric –CH$_2$ stretching band as a function of temperature for equilibrium oleate adsorption on a fluorite IRE at each temperature.
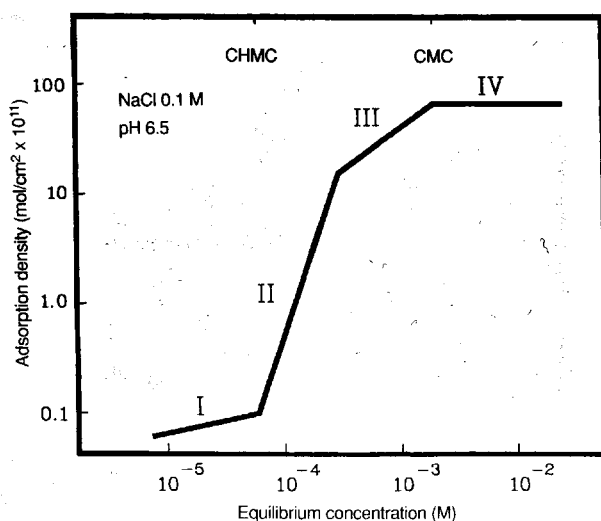

Fig. 6 — Adsorption isotherm for the physisorption of surfactant SDS at an alumina surface. CHMC indicates the critical hemimicelle concentration, and CMC shows the critical micelle concentration (adapted from Somasundaran et al., 1988).

1988) from the overlaid spectra (resolution 4 cm^{-1}) presented in Fig. 3b. Using a similar algorithm, Cameron and co-workers have shown that changes in peak maxima can be accurately determined for changes as small as a hundredth of a wave number (Cameron et al., 1982).

From Fig. 3 it can be seen that initially the adsorbed species have a band centered at 2924.5 cm^{-1}, but with continued loading on the fluorite IRE, the band shifts to 2920.0 cm^{-1}. The higher frequency position is associated with the alkyl chains of the adsorbed oleate having a large proportion of flexible gauche rotamers (the gauche state). The lower frequency, reached after 30 hours of equilibration, is associated with the alkyl chains being in a rigid, predominantly all-trans conformation (the trans state). It should be noted that the spectra presented in Fig. 3b are for adsorbed oleate species and not for oleate species in solution. Even in the worst case, the oleate species in solution (1 x 10^{-5} M) contribute less than 1% at the lowest adsorption density shown in Fig. 3a.

It appears that the initially adsorbed oleate species have few nearest neighbors, and consequently, the alkyl chains are highly mobile with a significant number of gauche rotamers. Upon further loading, the adsorbed oleate species begin to interact through van der Waals' forces. Consequently, the number of gauche bonds is reduced, and the alkyl chains stabilize in the more rigid trans state.

The actual number and position of the gauche bonds in the adsorbed species were not determined. However, it is believed that, with increased loading, the gauche bonds progress toward the tail-end of the hydrocarbon chain (Zerbi et al., 1981; Rabolt, 1987). This scenario is depicted in Fig. 4 from top to bottom and left to right. The transition state depicts the transformation from the gauche state at low adsorption density to the trans state at equilibrium (1 x 10^{-5} M oleate) and explains the shift in band position described in Fig. 3. Unlike previous illustrations, Fig. 4 also pictures the chemisorbed oleate molecules being monocoordinated to the fluorite surface through the oxygen atoms in the polar head group. Such a hypothesis is supported by in situ infrared spectra that have positively identified chemisorbed oleate on fluorite (Kellar, 1991; Kellar et al., 1991).

After 30 hours of equilibration at 25° C, the temperature of the fluorite IRE and oleate solution was raised to 40° C, 60° C and 80° C. Each temperature was held for 10 hours. Shown in Fig. 5 is the band position of the asymmetric –CH$_2$ band at each of these temperatures. This increase in frequency with increased temperature is the reverse of what was witnessed at 25° C with an increase in oleate adsorption, namely a change in the alkyl

chains from the rigid, predominantly trans state to the more mobile and disordered gauche form. The frequency shift occurs primarily between 25° and 40° C, which is the temperature range where Cameron et al. (1982a) found a coagel-to-micelle transition of sodium oleate. Thus, the results presented here for oleate adsorption suggest that, at room temperature, these adsorbed aggregates behave more like a gel or coagel; they resemble a micelle only at elevated temperatures.

In addition to the conformational state of chemisorbed oleate, a similar analysis was performed on surface-precipitated oleate. It was found that at both 25° and 40° C, the asymmetric –CH$_2$ stretching frequency remained constant between 2920 to 2919 cm^{-1}. From this behavior one can conclude that surface-precipitated species have alkyl chains in the predominantly all-trans conformation. Furthurmore, this packing of the calcium oleate remains, even at elevated temperatures.

Alumina/sodium dodecylsulfate

In the absence of chemisorption, the isotherm for collector adsorption at a mineral oxide surface is generally divided into four regions, as shown for the alumina/SDS (sodium dodecylsulfate) system in Fig. 6 (Scamehorn et al., 1982; Bitting and Harwell, 1987; Besio et al., 1988; Somasundaran et al., 1988). Region I is attributed to Henry's Law-type adsorption of monomers. The increase of adsorption in region II is often characterized as the onset of surface aggregation. The boundary between region I and II is called the critical hemimicelle concentration. The cause of the slope change in region III is more debatable and is ascribed to a reversal in sign of the surface charge (Somasundaran et al., 1988) or to the distribution of patch adsorption energies (Bitting and Harwell, 1987). Region IV usually occurs at a solution concentration exceeding the CMC (critical micelle concentration), and the plateau region is most often attributed to the solution monomer concentration attaining a constant value.

Comparison of the transition between regions I and II and regions II and III with the solution behavior of SDS has shown that there are very good correlations both between the adsorption density at the region I/II boundary and the CMC and between the adsorption density at the region II/III boundary and the micelle/coagel transition (Cross et al., 1991). This enabled
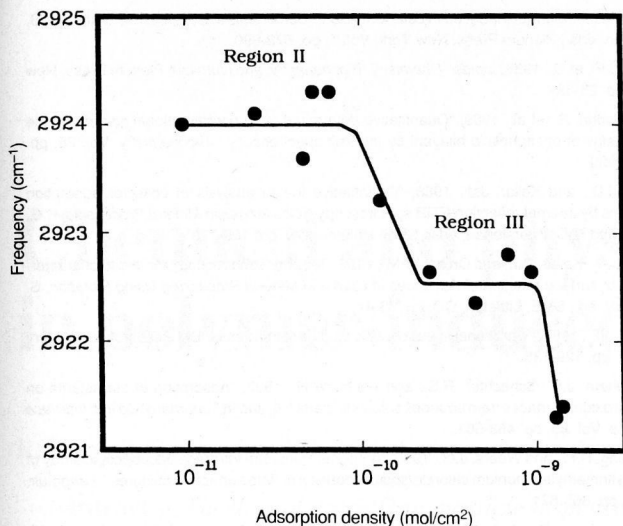
Fig. 7— Effect of adsorption density on the asymmetric –CH$_2$ stretching band frequency. These in-situ FT-IR/IRS spectral data were obtained at different times for adsorption from various solutions.

Table 2 — Adsorption density, predicted surface phase, and predicted asymmetric –CH$_2$ stretching frequency for alumina/SDS at pH 6.5 and 0.1 M NaCl.

Region	Adsorption density (10^{-11} x mol/cm^2)	Surface phase	Asymmetric –CH$_2$ stretching frequency (cm^{-1})
I	<0.1	monomer	2934
II	0.1–15.0	micelle	2928, 2924
III	15.0–67.0	coagel	2920
IV	>67.0	coagel	2920

Table 3 — Asymmetric –CH$_2$ stretching frequencies of adsorbed octylamine at various adsorption densities.

Adsorption density (mol/cm^{2}x10^{-10})	–CH$_2$ stretching frequency (cm^{-1})
1.55	2928.0
2.80	2927.9
4.92	2924.0
3.51	2927.8
3.40	2927.5
4.02	2924.0
11.57	2927.9
21.27	2927.8

the prediction of the surface phase for the adsorbed SDS species. These predictions are shown in Table 2.

Adsorbed SDS on alumina was evaluated for adsorption densities that correspond to regions II and III of Fig. 6. Shown in Fig. 7 is a plot of adsorption density determined from spectral data (Cross et al., 1991) vs. frequency of the asymmetric –CH$_2$ stretching band. For adsorption densities that correspond to region II of Fig. 6, it can be noted that a plateau frequency occurs at approximately 2924 cm^{-1}. In comparison to reported bulk SDS phases (Table 1), this value corresponds most closely to a hexagonal liquid crystal-type species. It is not possible at the present time to differentiate between the hexagonal liquid crystal and the cylindrical micelle that composes the liquid crystal solely on the basis of the asymmetrical –CH$_2$ stretching band.

In Fig. 7, the second plateau, at approximately 2922.5 cm^{-1}, corresponds to adsorption densities represented by region III of Fig. 6. The asymmetric –CH$_2$ stretching frequency of 2922.5 cm^{-1} for the adsorbed SDS appears to be a mixture of coagel (2918 cm^{-1}) and liquid crystalline (2924 cm^{-1}) components. It is interesting to note that at adsorption densities greater than 1 x 10^{-9} mol/cm^2, the asymmetric –CH$_2$ stretching frequency decreases rapidly, indicative of a substantial increase in the trans character of the alkyl chains of adsorbed SDS molecules.

Sylvite/octylamine

The asymmetric –CH$_2$ stretching frequency also was monitored for the sylvite/n-octylamine flotation system (Yalamanchili et al., 1991). The primary difference between this system and the previous systems is that adsorption occurred from a saturated KCl brine that was necessary to prevent the dissolution of the IRE. Shown in Table 3 is the asymmetric –CH$_2$ stretching frequency as a function of n-octylamine adsorption density. As before, the adsorption density was determined from in situ spectral data.

The –CH$_2$ asymmetric stretching frequencies of adsorbed octylamine on the sylvite IRE do not change appreciably with time, as shown in Table 3. Initially, the adsorbed octylamine has an asymmetric –CH$_2$ stretching band position of about 2929 cm^{-1}, which decreases only slightly after about 10 hours of equilibration time. Of greater significance is the fact that the asymmetric –CH$_2$ stretching frequency for the adsorbed

octylamine generally remains constant at about 2927 to 2928 cm^{-1} throughout the complete adsorption isotherm (see Table 3). The anomalous results at 4.92 x 10^{-10} mol/cm^2 and at 4.02 x 10^{-10} mol/cm^2 may be due to crystallization or etching effects during the experiment.

These results suggest that, in the KCl/octylamine system, the surface state of the adsorbed species is of a micellar structure for both monolayer coverage and high adsorption densities. In contrast to these results, the surface state of the adsorbed species in the CaF$_2$/oleate and Al$_2$O$_3$/dodecylsulfate systems was found to have coagel- or liquid crystal-type structures at room temperature. Thus it appears that the high ionic strength conditions inhibit conformational changes that are favored in more conventional flotation systems.

Summary

It has been shown by inspection of FT-IR/IRS spectra that the alkyl conformation of adsorbed collectors can be determined. The conformations of adsorbed collectors were interpreted in terms of bulk solution phases of the collectors. Such analysis was performed on the CaF$_2$/oleate, Al$_2$O$_3$/SDS and KCl/octylamine flotation systems. It was found that each system has unique conformational behavior, depending upon variables such as adsorption density and temperature. For the CaF$_2$/oleate system, the adsorbed species resemble a coagel at room temperature. Raising the temperature of the chemisorbed species to 40° C caused the adsorbed oleate to become micellar. Liquid crystalline-adsorbed species were observed in the Al$_2$O$_3$/dodecylsulfate system at low adsorption densities. As the adsorption density increased, the adsorbed species resembled a coagel/liquid crystal mixture. In all cases, octylamine adsorbed by KCl appeared micellar in nature. ♦

Acknowledgments

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