# Conformation of chemisorbed oleate at a calcite surface

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## Abstract

*The surface chemistry of the calcite/oleate flotation system was examined by in situ FT-NIR/IRS. Spectra of combination and overtone bands of aliphatic stretching vibrations revealed gauche/trans conformational changes that occurred solely as a function of temperature. The conformational changes were attributed to the simple "melting" behavior associated with phase transitions. It was concluded that chemisorbed oleate at calcite surfaces is gel-like at temperatures below 22°C, resembles a coagel between 22°C and 31°C, and becomes micelle-like at temperatures above 31°C. By comparison, chemisorbed oleate at fluorite surfaces also undergoes these phase transitions but is additionally dependent on adsorption density. The conformational changes were observed at high chemisorption densities (> $2.0x10^{-10}$ mol/cm$^2$) and attributed to molecular forces, primarily van der Waal's interactive forces, among neighboring chemisorbed oleate molecules. Similar analysis of in situ FT-NIR/IRS spectra of surface-precipitated calcium dioleate at calcite surfaces did not exhibit this behavior thereby confirming that surface-precipitated calcium dioleate remains in an all-trans conformation. The results help explain why surface polymerization is not observed at calcite surfaces but is observed at fluorite surfaces.*

Key Words: Chemisorption, Oleate, Calcite, Gauche/trans conformation, Rotational isomerism

## Introduction

Comprehensive reviews have shown that fatty acids in solution have been characterized since the turn of the century according to physical and chemical properties associated with phase transitions (e.g., Winsor, 1974; Laughlin, 1978; Small, 1986). Various optical and spectroscopic techniques were used to identify the phase transitions depending on changes in temperature or concentration of the fatty acid. In early work, phases were generically identified as "middle soaps," "soap boiler's neat soaps," "superneat soaps," "waxy soaps," "curds," "supercurds," and "nigre." Presently, the phases are more commonly called hexagonal liquid crystals, lamellar liquid crystals, discs, gels (hydrated liquid crystals) and coagels (binary mixtures of gels and nigre). Nigre or "isotropic liquid" refers to dissolved species such as micelles (spherical and cylindrical), dimers (acid, acid-soap, and soap), and monomers (acid, soap and ionic).

Although the phases found at high fatty acid concentrations and/or low temperatures are more applicable to studies involving adhesives, cosmetics, corrosion inhibitors, inks, lipid membranes, and biomembranes (Johnson, 1979; Mead et al., 1986), some are believed to form at the solid surface upon adsorption. Of particular importance and application are mineral-collector systems in flotation separations. For example, in proposing the *Hemi-micelle Theory of Adsorption*, Gaudin and Fuerstenau (1955) stated that adsorbed collectors should appear similar to spherical micelles in solution and therefore should form rounded patches at the mineral surface. Cases et al. (1986) described adsorption at heterogeneous mineral surfaces as a two-dimensional condensation process that formed crystalline hemihydrates (i.e., gels or hydrated liquid crystals) in order to explain the step-wise adsorption isotherms found for various collectors. In a recent in situ Fourier-transform infrared internal reflection spectroscopic (FT-IR/IRS) investigation in the mid-infrared (MIR) with reactive internal reflection elements (IREs), Kellar et al. (1991) showed that fundamental C-H asymmetric and symmetric stretching vibrations (2800-3050 cm$^{-1}$) for chemisorbed oleate at fluorite ($CaF_2$) surfaces exhibited band shifts which coincided with the change in adsorption density. Because the band shifts were equivalent to that observed in solution (Cameron et al., 1982), these results were attributed

Nonmeeting paper number 99-353. Original manuscript submitted for review November 1999. Revised paper accepted for publication April 2000. Discussion of this peer-reviewed and approved paper is invited and must be submitted to SME Publications Dept. prior to Aug. 31, 2001. 

to a coagel-to-micelle phase transition caused by gauche/trans rotational isomerism about carbon-carbon single bonds which occur to minimize hydrogen repulsive forces between adjacent -$CH_2$- groups.

Further in situ FT-IR/IRS studies regarding gauche/trans conformations of adsorbed surfactants have since been reported for other mineral flotation systems. Yalamanchili et al. (1991) observed that adsorbed octylamine at sylvite (KCl) surfaces exhibited micellar characteristics independent of surface coverage. The behavior was attributed to the high ionic-strength brines that were needed and was later related to the adsorption of surfactant colloids (Miller et al., 1992). On the other hand, Cross et al. (1991) illustrated that dodecylsulfate physisorbed at alumina ($Al_2O_3$) surfaces in a monomeric state at low adsorption densities but progressively became coagel-like and micelle-like at higher adsorption densities. Cross and Miller (1993) further established that the various conformational states of adsorbed dodecylsulfate could also be observed with changes in temperature and that the behavior could be related to changes in hydrophobicity. Recently, Young and Miller (1999 and 2000) reported that in situ FT-IR/IRS spectra of aliphatic overtone and combination bands in the near infrared (NIR) did not exhibit band shifts during oleate chemisorption at calcite ($CaCO_3$) surfaces but that the band positions of the spectra were dependent on temperature.

This study was undertaken to explore further the effect of adsorption density and temperature on the band positions. In this regard, in situ FT-NIR/IRS spectra of chemisorbed oleate at a calcite surface were collected at $9x10^{-6}$ M equilibrium oleate concentrations as a function of temperature. Corresponding equilibrium spectra were analyzed to show the influence of temperature on infrared band positions as well as adsorption densities. Results are compared to those obtained at an equilibrium oleate concentration of $9x10^{-5}$ M where calcium dioleate surface precipitation is known to predominate (Young and Miller, 1999).

## Experimental procedures

Details of in situ FT-IR/IRS experiments have been presented in full for calcite by Young and Miller (1999, 2000) and for fluorite by Kellar et al. (1991). Oleate adsorption isotherms for calcite and fluorite were reported and discussed in these references as well. Additional experiments were carried out in the present investigation with the BioRad/Digilab Division FTS-40N near infrared (NIR) spectrometer and 3240 Data Station as outlined previously by Young and Miller (1999, 2000). A Haake F3 constant temperature bath recirculator was used to control the temperature between 16°C and 60°C. All solutions were prepared using $D_2O$ of +99.9% deuterium (Cambridge Isotopes), adjusted to pH 9.2 with +99.5% NaOD and DCl (Sigma Chemical) and sparged for two hours with dry nitrogen. The $D_2O$ solutions were kept under the dry nitrogen atmosphere using either a glovebag or glovebox.

In situ FT-NIR/IRS experiments were conducted using calcite IREs prepared from optically pure, natural specimens of Iceland Spar calcite (Mexico) and sodium oleate of 99.5% purity (Sigma Chemical). The high purity oleate was needed to satisfy the analytical and spectroscopic needs of the study and is in keeping with many previous studies (e.g., Kellar et. al., 1991; Young and Miller, 1999, 2000). In this regard, it is important to note that oleate is usually the most common fatty

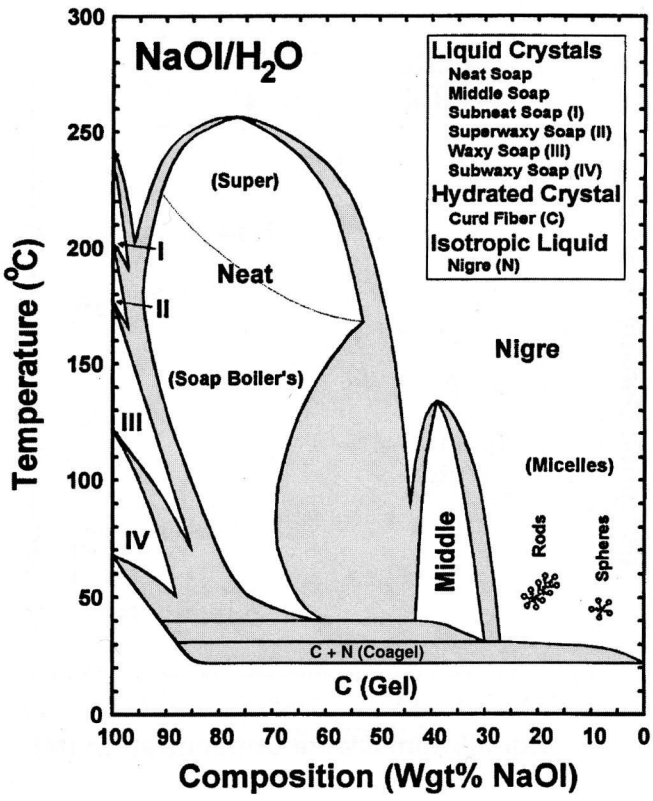


**Figure 1** — Binary phase diagram for the sodium oleate/water system (after Vold, 1939; McBain and Lee, 1943; Laughlin, 1978; and Small, 1986).

acid in tall oil and that tall oil is typically the preferred collector for the flotation separation of calcium semi-soluble salts such as calcite and fluorite. Hence, oleate is simply used to represent tall oil.

When the optical setup was readied, a single beam background was taken. An oleate-free $D_2O$ solution was then injected and, after two to three hours, an equilibrium absorbance spectrum was recorded. Next, a syringe pump was connected to deliver a $D_2O$ solution containing either $9x10^{-6}$ or $9x10^{-5}$ M oleate at 3 ml/hour for 24 hours. Successive $D_2O$/oleate spectra were then collected. Adsorbed oleate spectra were obtained by subtracting the $D_2O$ spectrum from each of the $D_2O$/oleate spectra using subtraction factors as reasonably close to one as possible. All spectra consisted of 4096 co-added scans at a resolution of 8 $cm^{-1}$ and were baseline-corrected and smoothed to remove noise. Equilibrium spectra were used to determine band positions and integrated absorbances and thereby calculate equilibrium adsorption densities.

## Discussion

Gel/coagel and coagel/micelle phase transitions for oleate in bulk solution are known to occur between 22°C and 31°C as shown by the binary phase diagram in Fig. 1, originally established by Vold (1939) and McBain and Lee (1943) but modified here according to Laughlin (1978) and Small (1986). In order to consider conformational changes (i.e., gauche/trans rotational isomerism) as oleate chemisorbs at calcite surfaces, a series of in situ FT-NIR/IRS experiments with calcite IREs was performed in which oleate chemisorption (Region I of Fig.

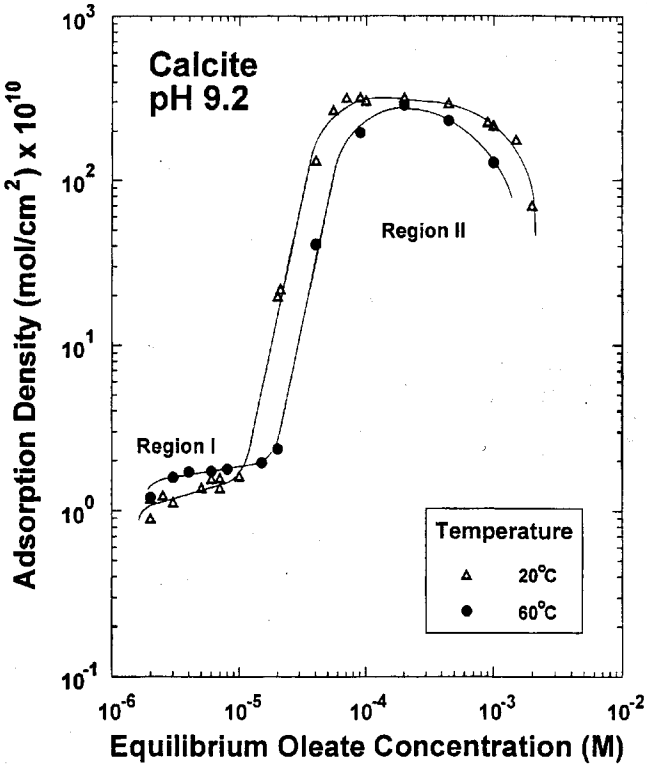


**Figure 2** — Oleate adsorption isotherms determined for calcite at 20°C and 60°C at pH 9.2 by in situ FT-NIR/IRS with aliphatic overtone and combination bands (from Young and Miller, 1999 and 2000).

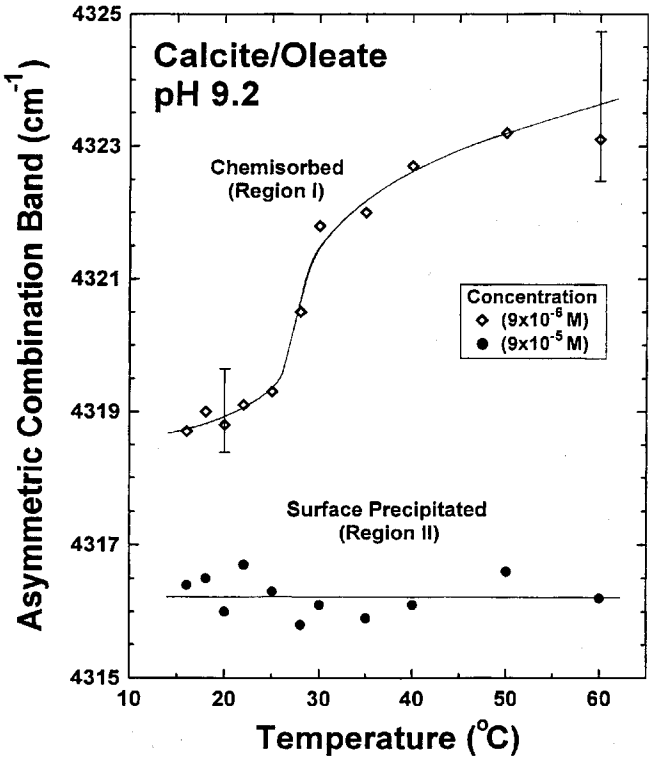


**Figure 4** — Band positions of the asymmetric C-H combination band versus temperature for chemisorbed oleate (9 x 10$^{-6}$ M) and surface-precipitated calcium dioleate (9 x 10$^{-5}$ M) at a calcite IRE surface as determined from in situ FT-NIR/IRS experiments.

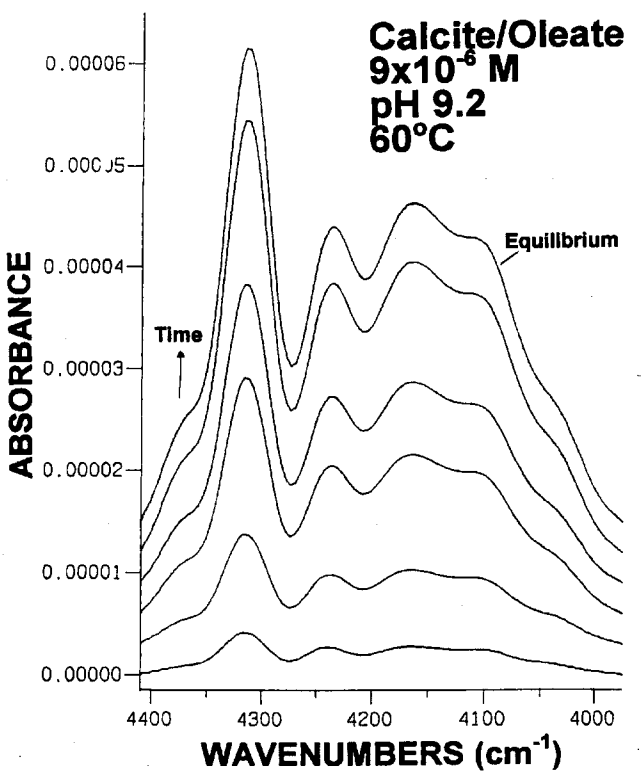


**Figure 3** — In situ FT-NIR/IRS spectra of the C-H combination region for oleate chemisorbing at a calcite surface until equilibrium is reached in pH 9.2 solutions at 60°C.

2) was monitored at a constant oleate concentration of 9x10$^{-6}$ M and a specified temperature ranging between 16°C and 60°C. Equilibrium spectra were then used to determine band positions and calculate adsorption densities. Results are compared to those obtained with 9x10$^{-5}$ M oleate where calcium dioleate surface precipitation predominates (Region II of Fig. 2).

Typical in situ FT-NIR/IRS spectra of aliphatic C-H combination bands are shown in Figure 3 as oleate (9x10$^{-6}$ M) chemisorbs at the calcite surface at 60°C. Clearly, as time passes, the spectra increase in absorbance until equilibrium is established, in this case, after about 10 hours. Furthermore, the C-H asymmetric and symmetric band positions near 4320 and 4245 cm$^{-1}$ respectively do not change as chemisorption occurs thereby confirming previous observations. Equilibrium spectra collected at other temperatures were found to be similar to those shown in Fig. 3 but exhibited band positions dependent on temperature. The C-H asymmetric and symmetric combination band positions of the equilibrium spectra were therefore plotted as a function of temperature as illustrated in Figs. 4 and 5, respectively. Both plots illustrate that, at temperatures below 26°C, a gauche/trans conformational change is not observed. Because a gel/coagel phase-like transition was expected at 22°C, it could be concluded that the gel and coagel phases could not be distinguished from one another using this in situ FT-NIR/IRS technique and would concur with similar results obtained with FT-MIR (Cameron et al., 1982) and FT-NIR (Cross et al., 1992) liquid transmission experiments. However, at temperatures greater than 26°C, a gauche/trans conformational change occurs where a

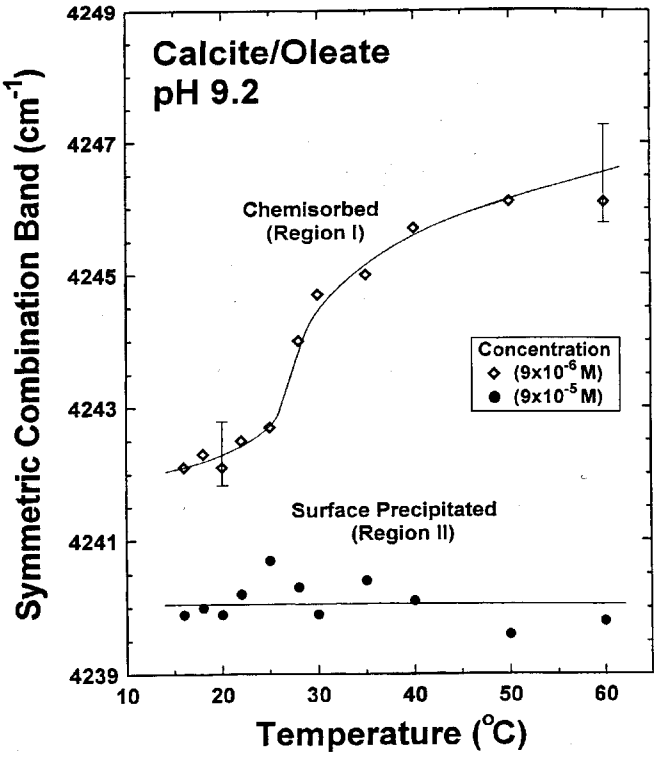


**Figure 5** — Band positions of the symmetric C-H combination band versus temperature for chemisorbed oleate ($9 \times 10^{-6}$ M) and surface-precipitated calcium dioleate ($9 \times 10^{-5}$ M) at a calcite IRE surface as determined from in situ FT-NIR/IRS experiments.

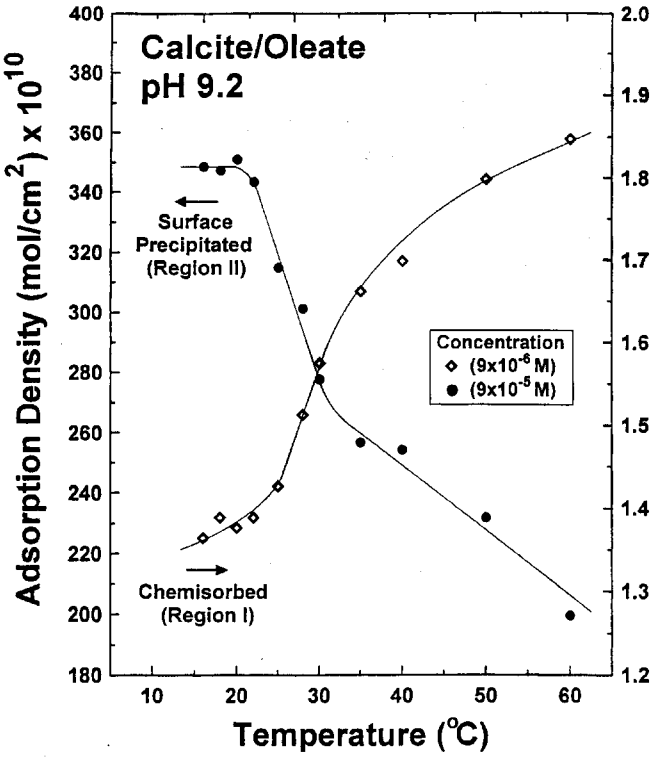


**Figure 6** — Adsorption densities determined from in situ FT-NIR/IRS spectra of the aliphatic C-H combination band for chemisorbed oleate ($9 \times 10^{-6}$ M) and surface-precipitated calcium dioleate ($9 \times 10^{-5}$ M) at a calcite surface as a function of temperature.

coagel/micelle phase-like transition would be expected. Initially, the band positions change quickly with initial increase in temperature but appear to slow to a constant slope at higher temperatures similar to that observed at fluorite surfaces (Kellar et al., 1991).

Because the band positions measured for chemisorbed oleate in Figures 4 and 5 were determined from one-time experiments, average band positions with 90% confidence intervals are also revealed. These intervals were determined from the previous in situ FT-NIR/IRS spectra (Young and Miller, 1999 and 2000) used to construct the adsorption isotherms shown in Fig. 2. Results indicate that asymmetric and symmetric combination band positions determined at 20°C are accurate to within ±0.7 and ±0.5 $cm^{-1}$ whereas those determined at 60°C were only accurate to within ±1.1 and ±0.8 $cm^{-1}$, respectively. Although these confidence intervals are very acceptable considering that the spectra were smoothed and collected at resolution of 8 $cm^{-1}$, it is apparent that the accuracy of both band positions decreased at higher temperatures and that the accuracy of the asymmetric band position was worse.

Comparing these confidence intervals to the equilibrium spectra shown in Figure 3 suggests that the asymmetric band position was more difficult to determine and can be attributed to problems associated with the strong carbonate absorbances which exist near the combination band region. Carbonate absorbances, of course, emanate from the reactive calcite ($CaCO_3$) IRE.

Results of in situ FT-NIR/IRS experiments conducted with $9 \times 10^{-5}$ M oleate are also shown in Figs. 4 and 5. They indicate that the combination band positions of surface precipitated calcium dioleate do not shift with change in temperature. Furthermore, the combination bands also appear from 2 to 8 $cm^{-1}$ below those observed for chemisorbed oleate depending on the temperature. This is attributed to the calcium dioleate being in an all-trans conformation at each of the temperatures thereby confirming observations found for in situ FT-MIR/IRS experiments conducted in the mid-infrared to characterize oleate adsorption at the surface of fluorite IREs (Kellar et al., 1991).

A plot of adsorption density versus temperature is shown in Fig. 6. Results show that chemisorption (Region I) gradually increases from $1.35 \times 10^{-10}$ mol/$cm^2$ at 16°C to $1.85 \times 10^{-10}$ mol/$cm^2$ at 60°C in a manner similar to the increase in band positions with temperature. Oleate adsorption at calcite surfaces is clearly endothermic and therefore is attributed to chemisorption behavior. Thermodynamic evaluation of the adsorption isotherms has verified this position (Young and Miller, 2001).

On the other hand, the extent of calcium dioleate surface precipitation (Region II) is observed to decrease with increasing temperature. Young and Miller (2000) previously stated that, at elevated temperatures, the amount of surface precipitation decreases due to both the increased solubility of calcium dioleate and the increased surface passivation caused by the increased amount of chemisorption. The sudden decrease in the amount of surface precipitation as the temperature is increased above 20°C suggests surface passivation plays a more important role. It is interesting that this decrease also coincides where gel/coagel phase transition would be ex-

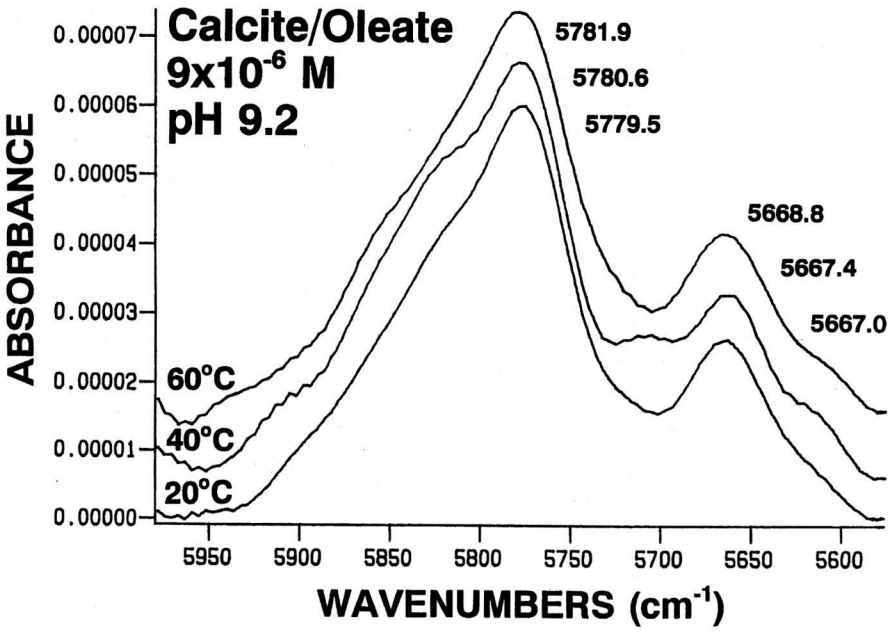


**Figure 7** — In situ FT-NIR/IRS spectra of the C-H overtone band for oleate chemisorbed at a calcite surface in equilibrium with 9 x $10^{-6}$ M oleate solutions at pH 9.2 and either 20°C, 40°C and 60°C.

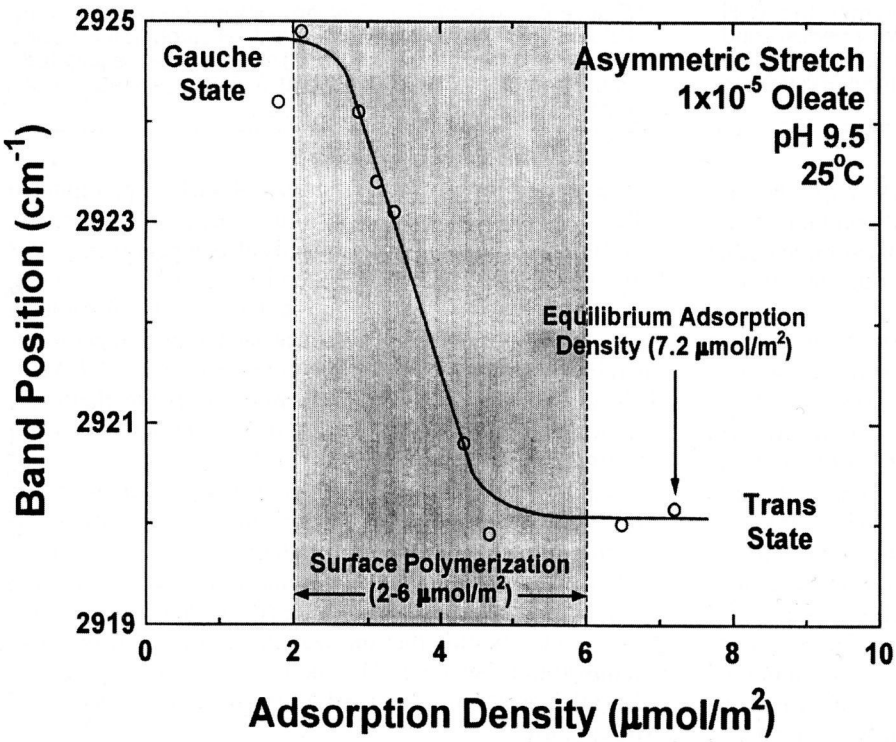


**Figure 8** — Band position of the fundamental asymmetric C-H stretching vibration of chemisorbed oleate at a fluorite surface as a function of adsorption density. Shaded region corresponds to gauche/trans conformational changes and appears to coincide with the surface polymerization phenomenon.

pected. Clearly, these events are inter-related: increased chemisorption, surface passivation, and decreased surface precipitation.

Although previous discussions about the combination band positions presented in Figs. 4 and 5 were inconclusive regarding whether a gauche/trans conformational change was observed for the gel/coagel phase-like transition, this appears to be evidence that it does occur. It is important to note that a second inflection point in Fig. 6 also appears near 32°C where coagel/micelle phase transition would likely occur and therefore in agreement with Figs. 4 and 5.

Finally, in situ FT-NIR/IRS experiments were also conducted with calcite IREs in the aliphatic C-H overtone region (6,000 to 5,500 $cm^{-1}$) at 20°, 40° and 60°C. Symmetric and asymmetric bands near 5,780 and 5,667 $cm^{-1}$ did not change position as oleate chemisorbed but did change position depending on the temperature at which adsorption was monitored (see Fig. 7).

This behavior is also attributed to gauche/trans rotational isomerism and is therefore equivalent to that observed for the combination band as just discussed. Because Fig. 7 confirms that rotational isomerism can be observed with aliphatic overtone bands, then it can be concluded that in situ FT-NIR/IRS research can be extended to other minerals such as gypsum ($CaSO_4 \cdot 2H_2O$) which are opaque in both the aliphatic combination region in the NIR and the aliphatic fundamental region in the MIR.

## Significance of results

By comparison, Kellar et al. (1991) observed for oleate chemisorption at fluorite surfaces that band positions of the fundamental C-H stretching vibrations also shifted with change in temperature but additionally noted that they shifted with adsorption density (see Fig. 8). Clearly, the asymmetric stretching band position decreases from a gauche state at approximately 2,924.5 $cm^{-1}$ to a predominantly all-trans state at 2,920 $cm^{-1}$ as adsorption densities increase beyond $2.0 \times 10^{-10}$ mol/$cm^2$. Because this lower limit on adsorption density exceeds the maximum adsorption density observed for calcite, it is reasonable to conclude that rotational isomerism of chemisorbed oleate at calcite surfaces occurs but is only caused by changes in temperature and therefore can be attributed to a simple "melting" of the aliphatic chain of chemisorbed oleate.

Furthermore, because this thermotropic behavior of chemisorbed oleate at fluorite surfaces appears at constant temperature but requires adsorption densities to exceed $2.0 \times 10^{-10}$ mol/$cm^2$, it can also be concluded that there is a critical distance between neighboring chemisorbed oleate molecules which must be exceeded in order for rotational isomerism to occur. If a circle

of equivalent surface area to the 2.0 x $10^{-10}$ mol/cm$^2$ is assumed, than this critical distance can be approximated from the diameter and shown to be 10.3 Å. Miller and Young (1999) used Raman spectroscopy and showed that neighboring chemisorbed oleate molecules should come within 11.28 Å (i.e., 1.67 x $10^{-10}$ mol/cm$^2$) before surface polymerization could occur in order to explain why such behavior was so commonly observed at fluorite surfaces and not at calcite surfaces.

Likewise, Arad et al. (1993) used similar calculations to show that, if polymerization occurred on calcite, it would be limited by the spacing between calcium sites due to the C-O bond length of 1.4 Å and would, at best, only involve a few molecules, if at all. In any case, the 10.3 and 11.28 Å distances are close to the 1-nm distance (i.e. 10 Å) commonly associated with van der Waal's attractive forces (Hiemenz, 1986; Adamson, 1990; Israelachvili, 1992). Therefore, it can be concluded that adjacent chemisorbed oleate molecules would begin interacting with one another when adsorption densities exceed 2.0 x $10^{-10}$ mol/cm$^2$ due to van der Waal's attractive forces and possibly to the extent that surface polymerization reactions would be induced. Clearly, the onset of rotational isomerism closely coincides with the surface polymerization phenomenon.

In this same manner, Jang et al. (1993) showed that LB-transferred films of oleate do not polymerize. Because LB-transferred films also exhibit all-trans conformations, it can be concluded that there is also an upper limit on adsorption density at which polymerization would be observed. This value appears to be near 6.0 x $10^{-10}$ mol/cm$^2$, where gauche conformational behavior is minimal and the trans-state predominates.

It can therefore be concluded that an adsorption density window exists between approximately 2.0 x $10^{-10}$ and 6.0 x $10^{-10}$ mol/cm$^2$, where oleate surface polymerization might be observed. Because adsorption densities determined for oleate chemisorption at calcite surfaces were below this critical range, surface polymerization can not be observed for calcite. In addition, because adsorption densities for chemisorbed oleate at fluorite surfaces can be below, within, or above this critical range, surface polymerization may or may not be observed. This would help explain the sporadic observations of surface polymerization with the fluorite/oleate system (Kellar et al., 1991). In this regard, the region in Fig. 8 between 2.0 x $10^{-10}$ and 6.0x$10^{-10}$ mol/cm$^2$ has been shaded. Although it seems that the kinetics of both the chemisorption process and the surface polymerization reaction need to be investigated further, these results show how elevated temperatures enhance the flotation separation of fluorite and calcite.

## Summary and conclusions

Collectors adsorbed at mineral surfaces are constrained to two dimensions but nevertheless exhibit characteristics similar to bulk solution phases. Resulting adsorption states can therefore be dependent on temperature and adsorption density (i.e., surface concentration). In this regard, in situ FT-IR/IRS with reactive IREs has proven to be a valuable technique for identifying the state of the adsorbed collectors at mineral surfaces as determined from the aliphatic C-H band positions and shifts of the resulting infrared spectra. These band positions and shifts have been attributed to the gauche/trans conformational changes associated with phase transitions. Previous studies were conducted in the mid-infrared (MIR) predominantly using the fundamental aliphatic C-H stretching region (2,800 to 3,050 cm$^{-1}$).

In the present investigation, gauche/trans conformational changes were observed for oleate chemisorbed at calcite surfaces using the aliphatic C-H combination (4,400 to 3,900 cm$^{-1}$) and overtone (6,000 to 5,500 cm$^{-1}$) regions in the near infrared (NIR). Conformational changes were only found dependent on temperature. However, the conformational changes were not associated with a change in adsorption density and did not change as adsorption occurred. This behavior was attributed to low adsorption densities (< 2.0 x $10^{-10}$ mol/cm$^2$), where van der Waal's attractive forces are not expected to predominate between adjacent chemisorbed oleate molecules at the calcite surface. It therefore appears that chemisorbed oleate at calcite surfaces resembles a gel state at low temperatures but becomes coagel-like and micelle-like at temperatures above approximately 22° and 31°C, respectively. Similarly, in situ FT-NIR/IRS analysis showed that surface-precipitated calcium dioleate at calcite surfaces did not exhibit this thermotropic behavior which suggests calcium dioleate remains in an all-trans conformation in agreement with a previous study with fluorite.

Further comparison of the results obtained with calcite to previous results obtained with fluorite indicates that an adsorption density window exists between approximately 2.0x$10^{-10}$ mol/cm$^2$ and 6.0 x $10^{-10}$ mol/cm$^2$ in which surface polymerization of the chemisorbed oleate may occur. Because adsorption densities of chemisorbed oleate at calcite surfaces do not exceed 2.0 x $10^{-10}$ mol/cm$^2$, surface polymerization is never observed for calcite. Likewise, because LB-transfer films of oleate have packing densities that exceed 6.0 x $10^{-10}$ mol/cm$^2$, they are difficult to polymerize after transfer to a crystal surface. Consequently, it is concluded that conformation of chemisorbed oleate must be between a gauche state and a predominantly all-trans state in order for surface polymerization to occur. These results help explain how elevated temperatures enhance the flotation separation of fluorite and calcite.

## Acknowledgements

This paper is dedicated to the memory of Felix Fahland, stepfather of C.A. Young. He was a good man and is sorely missed. Many thanks are also extended to Dr.'s Jon Kellar and William Cross for their valuable discussions. This work was partially supported by DOE Basic Sciences Division Grant No. DE-FG-03-93ER14315.

## References

Adamson, A.W., 1990, *Physical Chemistry of Surfaces*, 5th Ed., John Wiley and Sons, New York, NY.

Arad, D., Kaftory, M., Zolotoy, A.B., Finkelstein, N.P. and Weissman, A., 1993, "Molecular modeling for oxidative cross-linking of oleates adsorbed on surfaces of minerals." *Langmuir*, Vol. 9, pp. 1446-1448.

Cameron, D.G., Umemura, J., Wong, P.T.T., and Mantsch, H.H., 1982, "A Fourier transform infrared study of the coagel to micelle transitions of sodium laurate and sodium oleate," *Colloids and Surfaces*, Vol. 4, pp. 131-145.

Cases, J.M., Levitz, P., Poirier, J.E., and Damme, H.V., 1986, "Adsorption of ionic and nonionic surfactants on mineral solids from aqueous solutions," *Advances in Mineral Processing*, P. Somasundaran, ed., SME of AIME, Littleton, CO, pp. 171-188.

Cross, W.M., Kellar, J.J. and Miller, J.D., 1991, "Conformation of adsorbed surfactant species in the alumina/sodium dodecylsulfate/water system as determined by in situ FT-IR/IRS," *Proceedings of the XVII International Mineral Processing Congress*, Dresden, Germany, Vol. 2, pp. 319-338.

Cross, W.M. and Miller, J.D., 1992, "Hydrocarbon chain conformations of surfactants adsorbed at mineral oxide surfaces," presented at the 19th Annual Meeting of FACCS, September 20-25, Philadelphia, PA.

Cross, W.M. and Miller, J.D., 1993, "Adsorbed hydrocarbon chain conformation and its effect on hydrophobicity," presented at the 122nd Annual SME of AIME Meeting, Reno, Nevada, February 15-18.

Gaudin, A.M. and Fuerstenau, D.W., 1955, "Quartz flotation with cationic collectors," *Transactions of AIME*, Vol. 202, pp. 958-962.

Hiemenz, P.C., 1987, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, NY, NY.

Israelachvili, J., 1992, *Intermolecular and Surface Forces*, 2nd Ed., Academic Press, San Diego, CA.

Jang, W.H. and Miller, J.D., 1993. "Verification of the IRS adsorption density equation by FT-IR analysis of transferred Langmuir-Blodgett films." *Langmuir*, Vol. 9, pp. 3159-3165.

Johnson, R.W., 1979, "Miscellaneous industrial uses," *Fatty Acids*, E.H. Pryde, ed., Amer. Chem. Soc., Champagne, IL, pp. 608-615.

Kellar, J.J., Young, C.A., Knutson, K. and Miller, J.D., 1991, "Thermotropic phase transitions of adsorbed oleate species at a fluorite surface by in situ FT-IR/IRS spectroscopy," *Journal of Colloid and Interface Science*, Vol. 144, pp. 381-389.

Laughlin, R.G., 1984, "Phase equilibria and mesophases in surfactant systems," *Surfactants*, Th. F. Tadros, ed., Academic Press, New York, pp. 53-81.

McBain, J.W. and Lee, W.W., 1943, "Vapor pressure data and phase diagrams for some concentrated soap-water systems above room temperature," *Oil and Soap*, Vol. 20, pp. 17-25.

Mead, J.F., Alfin-Slater, R., Howton, D.R. and Popjak, G., 1986, *Lipids: Chemistry, Biochemistry and Nutrition*, Plenum Press, New York, pp. 1-68.

Small, D.M., 1986, *The Physical Chemistry of Lipids, Handbook of Lipid Research*, Plenum Press, New York, NY.

Vold, R.D., 1939, "The phase rule behavior of concentrated aqueous systems of typical colloidal electrolyte: sodium oleate," *Journal of Physical Chemistry*, Vol. 43, pp. 1213-1231.

Winsor, P.A., 1974, "the influence of composition and temperature on the formation of mesophases in amphiphilic systems. The R-theory of fused micellar phases," *Liquid Crystals and Plastic Crystals*, G.W. Gray and P.A. Winsor, eds., Ellis Horwood Limited, Sussex, England, Vol. 1, pp. 199-287.

Yalamanchili, M.R., Kellar, J.J. and Miller, J.D., 1991, "In situ FT-IR internal reflection spectroscopy of collector adsorption phenomena in soluble-salt flotation systems," *Proceedings of the XVII International Mineral Processing Congress*, Dresden, Germany, Vol. 6, pp. 135-143.

Young, C.A. and Miller, J.D., 1999. "In situ FT-IR/IRS and MLRS examination of adsorbed oleate at fluorite and calcite surfaces." In: L.J. Cabri, C.H. Bucknam, E.B. Milosavljevic, S.L. Chryssoulis and R.A. Miller (Editors), *Analytical Technology in the Mineral Industries*, TMS, Warrendale, PA, 119-136.

Young, C.A. and Miller, J.D., 2000. "Effect of temperature on oleate adsorption at a calcite surface: an FT-NIR/IRS study and review." *Intern. J. Miner. Proc.*, Special Edition in honor of Dr. Frank F. Aplan, Vol. 58, pp. 331-350.

Young, C.A. and Miller, J.D., 2001. "Thermodynamic evaluation of oleate chemisorption at calcium semisoluble salt surfaces." Submitted to *Miner. and Metall. Proc.*