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Wetting Characteristics and Stability of Langmuir–Blodgett Carboxylate Monolayers at the Surfaces of Calcite and Fluorite

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Although surface chemistry fundamentals of semisoluble minerals have been studied by many researchers, detailed understanding of these systems is still incomplete. In situ Fourier transform infrared internal reflection spectroscopy (FT-IR/IRS) techniques have recently been used to successfully describe the adsorption of carboxylates at semisoluble mineral surfaces. The wetting characteristics of these adsorbed films, however, require further consideration. In this regard, the hydrophobicity and stability of transferred Langmuir–Blodgett (LB) monolayers of fatty acids at fluorite and calcite surfaces have been studied by contact angle measurements with water and diiodomethane. Generally, it was found that the transferred LB monolayers of fatty acids at a calcite surface are unstable whereas such monolayers transferred onto a fluorite surface are stable, as revealed from advancing and receding contact angle measurements. These results are believed to be due to incomplete reaction of the fatty acid monolayer at the calcite surface. In addition it was found that a closely packed well-ordered stearate monolayer similar to that of a transferred LB monolayer can be formed at fluorite surfaces by spontaneous adsorption and self-assembly from aqueous solutions.

Introduction

Semisoluble salt minerals such as fluorite (CaF_2), calcite (CaCO_3), apatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$ ($\text{X} = \text{F}, \text{OH}, \text{or Cl}$)), scheelite (CaWO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), magnesite (MgCO_3), and barite (BaSO_4) are commonly used by industry as raw materials for fillers, fluxes, fertilizers, cements, chemicals, etc. These semisoluble salt minerals are naturally hydrophilic, and fatty acids are frequently used to establish a hydrophobic state and thus modify their surface-wetting properties. Without such modification the separation of semisoluble salt minerals by flotation cannot be achieved. Also, such treatment facilitates the use of these semisoluble salt minerals as fillers for plastics in the production of polymer–mineral composites. In this regard, an understanding of the surface chemistry of fatty acid adsorption at semisoluble salt mineral surfaces is important from both a fundamental and a practical point of view.

It has been recognized from infrared studies that a fatty acid adsorbs at the surfaces of semisoluble salt minerals through chemisorption of the carboxylate group with a lattice cation at low collector concentrations, typically less than $1.0 \times 10^{-5} \text{ M}$.^{1–5} At higher concentrations of the collector and/or the cation, and at higher pH values, surface precipitation or collector colloid adsorption occurs by reaction of the carboxylate collector with cations released from the lattice.^{2–8} Because the fatty acid interacts not only with the lattice cation sites of the semisoluble salt mineral but also with the dissolved cations in solution, the solution chemistry of these minerals and the pH of

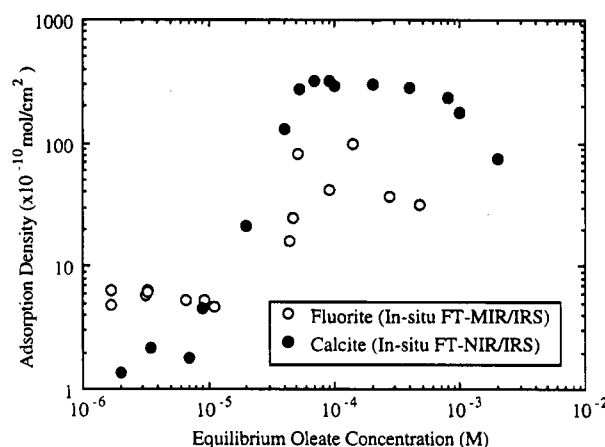


Figure 1. Oleate adsorption isotherms for fluorite (pH 9.5)⁹ and calcite (pH 9.2)¹² as determined by in situ FT-IR/IRS experiments (the original isotherms have been reconstructed using correction factors of 2.3 for fluorite and 1.2 for calcite, based upon sample area considerations¹⁴).

the system play an important role in determining the nature of the adsorbed species.

Oleate adsorption isotherms for semisoluble salt minerals have been established by several researchers.^{9–13} Figure 1 presents the adsorption isotherms for oleate at fluorite⁹ and calcite¹² surfaces (pH \approx 9) as determined using in situ FT-IR/IRS (note that the original isotherms from refs 9 and 12 have been reconstructed using correction factors of 2.3 for fluorite and 1.2 for calcite, based upon sampling area considerations¹⁴). Although the shape of the oleate adsorption isotherm is similar at both fluorite

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and calcite surfaces, the adsorption density values differ significantly. At an equilibrium oleate concentration of less than 1.0×10^{-5} M (monolayer region) the adsorption densities of oleate at a fluorite surface (from 4.6 to 6.3×10^{-10} mol/cm²) are found to be about 3 times larger than the adsorption densities at a calcite surface (from 1.4 to 2.2×10^{-10} mol/cm²). In contrast, at an oleate concentration greater than 1×10^{-5} M, the adsorption density of oleate at a calcite surface is found to be considerably higher than at a fluorite surface (multilayer region of precipitated calcium dioleate, the collector colloid). It has been suggested that the well-packed chemisorbed oleate monolayer at the fluorite surface inhibits the release of lattice calcium ions to solution and thus minimizes the surface precipitation phenomenon.¹² Note that the maximum monolayer adsorption density for oleate determined from the surface pressure-specific area isotherm is 6.1×10^{-10} mol/cm², i.e., $27 \text{ \AA}^2/\text{molecule}$.¹⁵ On the other hand, such a closely packed chemisorbed oleate monolayer is not formed at a calcite surface (1.4 to 2.2×10^{-10} mol/cm²). This low surface coverage at a calcite surface does not prevent calcium release and the subsequent precipitation of calcium dioleate at the surface.¹²

It has been proposed that for the chemisorbed monolayer region the increased adsorption density of oleate at the fluorite surface, when compared to that at the calcite surface, is due to a difference in the crystallographic structures of the minerals.¹² The average distance between the calcium ions is 3.86 \AA along the natural (111) cleavage plane for fluorite and 4.05 \AA and 4.99 \AA along the natural (10 $\bar{1}$ 4) cleavage plane for calcite.¹⁶ Based upon the distance between calcium ions, the calculated densities of lattice calcium ions at the fluorite and calcite surfaces are 14.5×10^{-10} and 8.3×10^{-10} mol/cm², respectively. Thus, in both cases, the lattice calcium ions are in excess of that required for the chemisorption of an uniform and densely packed oleate monolayer in one-to-one coordination with surface calcium sites. Such simple calculations do not explain the different adsorption density values determined at fluorite and calcite surfaces. Not all surface calcium ions are involved in the oleate chemisorption reaction, and the maximum monolayer adsorption density is determined by the dimensions of the surfactant species and its organization at the surface. Some research has been reported on this issue^{16,17} which describes this molecular arrangement at the surface.

The difference in the mechanisms of adsorption of fatty acids at fluorite and calcite surfaces is not fully understood. The stability of the fatty acid monolayers at fluorite and calcite surfaces has not been studied. It is not clear why a self-assembled, densely packed and stable monolayer of carboxylate is not formed at a calcite surface by adsorption from aqueous solutions whereas such a densely packed and stable monolayer of carboxylate is self-assembled at a fluorite surface. On this basis, it is particularly interesting to investigate if the formation of a well-packed and stable fatty acid monolayer is possible at a calcite surface under certain experimental conditions. In this regard the stability of transferred LB monolayers was examined using the sessile-drop contact angle technique. Both advancing and receding contact angles were measured for polar (water) and apolar (diiodomethane) drops of varying size. The usefulness of this experimental technique in the examination of surface chemistry phenomena associated with flotation systems will be demonstrated.

Ideal solid surfaces with homogeneity and smoothness at the atomic/molecular level are extremely difficult to prepare; nearly all surfaces examined are, to some extent, heterogeneous and rough.¹⁸ Even uniform and closely packed LB films, when transferred at a smooth and pure surface, may still be unstable when in contact with certain liquids. Obviously, the film instability affects the contact angle measurements. A liquid in contact with nonideal surfaces (heterogeneous, rough, and/or unstable films) exhibits more than one contact angle. Two contact angles are important in the characterization of such surfaces: (1) the advancing contact angle, θ_A , which is the largest contact angle for the system and is measured for the advancing liquid front and (2) the receding contact angle, θ_R , which is the smallest contact angle for the system and is measured for the receding liquid front. The difference between the advancing and receding contact angles ($\theta_A - \theta_R$) is called the contact angle hysteresis. The contact angle hysteresis is a good parameter to describe the quality of surfaces examined and does not exceed a few degrees for well-prepared and stable surfaces. A minimized or zero contact angle hysteresis is an indication of a well-prepared surface. Nevertheless, it should be noted that a large contact angle hysteresis may be a reproducible characteristic for a particular surface. High-quality surfaces require appropriate surface preparation (using a substrate with a smooth surface, cleaning the solid substrate, and careful transferring of the homogeneous LB monolayer), handling, and preservation.

The advancing and receding contact angles were measured using the sessile-drop technique for a drop of varying size. The effect of drop size on advancing and receding contact angles has been demonstrated for several systems by Drelich and Miller.¹⁹ It was shown that the contact angle/drop size relationship becomes an important feature of the three-phase system, especially when the surface exhibits imperfections, i.e., the surface is heterogeneous and/or rough.^{19–22} For such systems, the contact angle hysteresis may vary significantly with drop volume and examination of the relationship between contact angle hysteresis and drop size is one way to obtain more information regarding the quality of the surface being examined.

Experimental Section

Materials. Fluorite (CaF₂) single-crystal parallelepiped internal reflection elements (IRE) with dimensions of $52 \times 10 \times 2$ mm and $52 \times 14 \times 2$ mm and acute angles of 72 – 75° were purchased from Optovac Inc. Optically pure, naturally cleaved crystals of Iceland Spar (Mexico) calcite (CaCO₃) were purchased from Ward's Natural Science Establishment, Inc. Before experimentation both the fluorite and calcite crystals were placed in a Tegal plasma chemistry reactor and subjected to argon plasma for 30–40 min to remove any organic contaminants. In some cases, the surfaces of the crystals were polished with alumina powders ($0.05 \mu\text{m}$) on Texmet polishing pads (Buehler) and washed with high-purity water to create a fresh surface.

The chemicals used in the experiments were as follows: stearic acid (CH₃(CH₂)₁₆COOH) with purity greater than 99% (Aldrich Chemical Co.), oleic acid (CH₃(CH₂)₇CH=CH(CH₂)₇COOH, cis form) with purity greater than 99% (Sigma Chemical Co.), sodium stearate (CH₃(CH₂)₁₆COONa) with purity greater than 99% (Sigma), diiodomethane (CH₂I₂) with purity greater than 99% (Janssen Chimica), reagent grade calcium chloride dihydrate

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($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Mallinckrodt, Inc.), reagent grade sodium hydroxide (NaOH, Mallinckrodt), reagent grade hydrochloric acid (HCl, EM Science), and spectrograde chloroform (CHCl_3 , EM Science). A Milli-Q water system, supplied with distilled water, provided high-purity water with a resistivity of $+18 \text{ M}\Omega$ and a surface tension of 72 ± 0.4 at 22°C . The pH of this high-purity water was stabilized at $\text{pH } 5.8 \pm 0.1$ after equilibrating with the atmosphere.

Langmuir-Blodgett (LB) Film Preparation and Transfer. A Lauda Langmuir film balance (Langmuir trough) manufactured by SYBRON/Brinkmann was used for LB film preparation and transfer. The film balance was kept in a special housing to provide a dust-free environment. The experiments were performed at room temperature ($22\text{--}23^\circ\text{C}$). The Langmuir trough was filled with water from a Milli-Q system ($\text{pH } 5.8 \pm 0.1$). In selected experiments, Milli-Q water with $1 \times 10^{-3} \text{ M}$ calcium ions (as $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and $\text{pH } 9.2 \pm 0.2$ (adjusted with NaOH) was used in order to maintain conditions for the formation of calcium distearate.

The compounds to be studied (stearic acid and oleic acid) were weighed on a balance and dissolved in chloroform (7.6 and 4.8 mM, respectively). The monolayers were spread from the spreading solutions onto the subphase with a Hamilton syringe (typically $40 \mu\text{L}$). The solvent was permitted to evaporate completely (20–30 min). The surface pressure of the monolayer was measured as a function of the area occupied by the amphiphilic molecule for the surface pressure-specific area isotherm studies.

For LB deposition, the mineral crystal (fluorite or calcite) was dipped into the subphase (water) before spreading the monolayer. After spreading, the solvent was evaporated for 20–30 min and the film was transferred from the subphase onto the crystal surface at a speed of 3 mm/min with the surface pressure held at the desired level. In all LB experiments a constant film pressure was maintained at 23 mN/m for stearic acid and calcium distearate and 24 mN/m for oleic acid. The corresponding molecular areas were found to be $20 \text{ \AA}^2/\text{molecule}$ for stearic acid, $40 \text{ \AA}^2/\text{molecule}$ for calcium distearate, and $30 \text{ \AA}^2/\text{molecule}$ for oleic acid. While the monolayers were transferred at the crystal surfaces, all the transfer curves were recorded to ensure that each monolayer was transferred at a constant pressure. The variation in the film pressure was found to be within $\pm 1 \text{ mN/m}$. Other details of the Langmuir-Blodgett technique are provided elsewhere.^{23–26}

Self-Assembled (SA) Monolayer Preparation. For SA monolayer preparation $1.4 \times 10^{-3} \text{ g}$ of sodium stearate was dissolved into 0.5 L of Milli-Q water which had been heated to $75\text{--}80^\circ\text{C}$. The solution was diluted with water to $3 \times 10^{-7} \text{ M}$, and the initial pH was typically adjusted to $\text{pH } 9.5 \pm 0.1$ with NaOH. In selected experiments, the solution pH was adjusted to higher or lower pH values. A clean fluorite crystal was clamped in Teflon-coated tweezers and suspended in the solution of sodium stearate. The solution was agitated with a magnetic stirrer at a constant speed. The solution was isolated from the atmosphere by covering it with aluminum foil. After reaction for a given time (10 min to 5 h), the fluorite IRE was rinsed with water at $\text{pH } 9.5 \pm 0.1$ and dried in a vacuum.

Adsorption Density Determinations. Fourier transform infrared internal reflection spectroscopy (FT-IR/IRS) experiments were conducted with a Bio-Rad Digilab Division FTS-40 FT-IR spectrometer equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. The spectrometer was purged with dry air supplied by a Balston 75-60 air dryer. Digilab software, version 4.45, was used for spectral manipulation with the SPC 3200 data station. An internal reflection cell with a variable angle holder (a twin-parallel mirror reflection 320 internal reflection accessory, Harrick Scientific) was used to measure the FT-IR/IRS spectra. The dial reading of the variable angle holder was adjusted to satisfy the condition for total internal

reflection inside the IRE. Then, the intensity of the infrared beam internally reflected through the IRE was maximized by adjusting the mirrors of the variable angle holder. After alignment of the IRE, the spectrometer was purged with dry air for at least 30 min before a background spectrum of the clean IRE was collected in order to minimize possible interferences from water vapor.

Substantial care was taken to reposition the IRE in its holder for ex situ internal reflection experiments. Absorbance spectra of the surfactant films (LB or self-assembled films) were ratioed against the background spectra of a clean calcium fluoride IRE. All the spectra were the result of 1024 coadded scans at a resolution of 8 cm^{-1} . In all cases, the size of the IR beam was adjusted to allow it to pass through only the area of the transferred LB monolayer film with the same IR beam size for both background and sample spectra to eliminate any error that could be caused by the difference between IR beam area and the sample area. Detailed analysis of the effect of sampling area on adsorption density measurements is provided elsewhere.^{14,27}

The FT-IR/IRS adsorption density equation was initially derived by Sperline et al.²⁸ and later developed for different systems by Miller et al.^{29–31} The FT-IR/IRS adsorption density is given below:

$$\Gamma = (A_{\text{IRS}}/N - \epsilon C_b d_e)/(1000\epsilon(2d_p/d_p)) \quad (1)$$

where A_{IRS} = integrated absorbance (cm^{-1}) from the IRS spectrum, N = number of internal reflections, ϵ = integrated molar absorptivity of collector ($\text{L}/(\text{cm}^2 \text{ mol})$), C_b = bulk concentration of the surfactant (mol/L), d_p = depth of penetration (cm), and d_e = effective thickness (cm). The N , d_e , and d_p values can be calculated from optical constants of the system (wavelength in the absorbance region, refractive indices of the IRE and the sample, and incident angle for internal reflection). The integrated absorbance due to internal reflections, A , can be determined from FT-IR/IRS spectra. The integrated molar absorptivity, ϵ , can be evaluated from transmission experiments using the Beer-Lambert equation.^{32,33} The validity of the FT-IR/IRS adsorption density equation has been confirmed by the FT-IR/IRS analysis of transferred LB films.^{14,15} Because calcite is not transparent in the midIR range, the adsorption densities of transferred LB monolayers of stearic acid and calcium distearate at a calcite surface were determined from the π -A isotherms.^{15,26}

Contact Angle Measurements. The sessile-drop technique for contact angle measurements was employed in these studies using a NRL goniometer (Ramè-Hart, Inc.). The optical system of the NRL goniometer has independently rotatable cross hairs and an internal protractor-readout calibrated in 1° increments. The supporting stage of the instrument is calibrated on the vertical axes in 0.02 mm divisions, and this allows for accurate measurement of the drop base diameter.

The mineral substrate (fluorite or calcite) with the transferred LB monolayer or with the adsorbed monolayer was placed on Teflon posts in a rectangular glass chamber. The glass chamber with the substrate was partially filled with water and covered with a polyethylene film to maintain conditions of constant humidity. A water drop was introduced onto the substrate through a microsyringe, and the needle was maintained in contact with the drop. A special precaution was taken in the measurements to avoid vibrations of the needle and to avoid distortion of the drop shape by the needle. The three-phase contact line of the liquid drop was made to advance or recede by adding or

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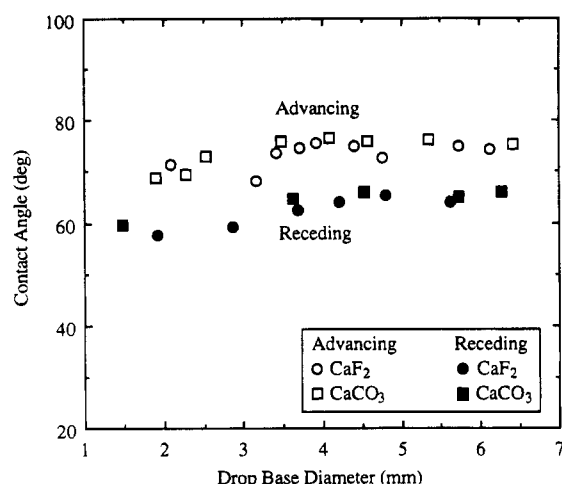


Figure 2. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at fluorite (circles) and calcite (squares) surfaces as measured for a diiodomethane drop of varying size.

withdrawing a small volume of liquid, and the advancing and receding contact angles were measured after 15–30 s on both sides of the drop (the average contact angle value was taken for each drop diameter). The contact angles were measured for liquid drops of varying size at room temperature (22–23 °C).

Results and Discussion

Wetting Characterization of LB Monolayers with an Apolar Liquid. LB monolayers of stearic acid in the condensed state (i.e., having a molecular cross-sectional area of 20 Å²/molecule, as determined from the π -A isotherm) were transferred at both fluorite and calcite surfaces. A diiodomethane drop was placed at a freshly deposited and dried monolayer surface, and both advancing and receding contact angles were measured. As shown in Figure 2, the same wetting characteristics were obtained for both transferred LB monolayers. The advancing and receding contact angles for the LB monolayer of stearic acid were found to be 74–76° and 64–66°, respectively, for a drop base diameter of 3–7 mm. Also, it appeared that the prepared LB monolayers remained stable during the contact angle measurements with diiodomethane. The same advancing and receding contact angles were obtained when contact angle measurements were repeated at the same location on the transferred monolayer.

When the drop size was reduced to a drop base diameter of approximately 2 mm, both advancing and receding contact angles were found to decrease by 5–6°. It was found from the surface roughness analysis by atomic force microscopy that the fluorite crystal had an average surface roughness of about 5 nm with a maximum of 100 nm whereas the calcite crystal had a surface roughness of 7–15 nm with a maximum of 100–300 nm depending upon the specific locations examined. Therefore, both the fluorite and calcite surfaces exhibit surface irregularities which could affect, to a certain extent, both the contact angle hysteresis and the contact angle/drop size relationship. Also, although the system examined appeared to be stable during contact angle measurements, the effect of diiodomethane on the destabilization of the transferred LB monolayer of stearic acid cannot be ignored. For example, Johnson and Dettre³⁴ observed that LB monolayers of stearic acid and barium stearate deposited onto glass slides were slowly desorbed into hexadecane during

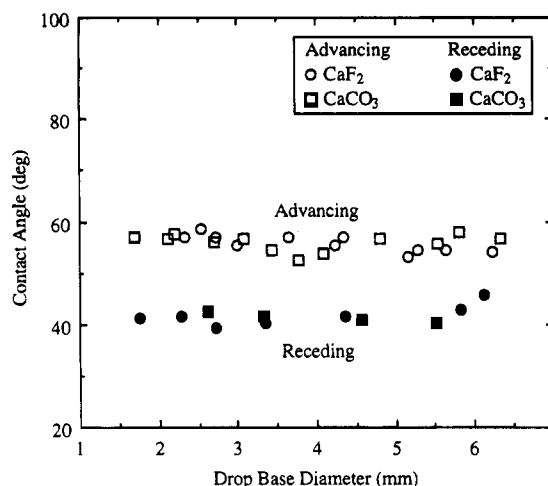


Figure 3. Advancing and receding contact angles for a transferred LB monolayer of oleic acid at fluorite (circles) and calcite (squares) surfaces as measured for a diiodomethane drop of varying size.

contact angle measurements (note that the contact angle hysteresis was only 1–2° in these measurements).

The advancing contact angles as measured for the larger drops were 74–76° (Figure 2) and are close to the contact angles, 73–74°, which were measured at a highly ordered CH₃ surface of a self-assembled octadecyltrichlorosilane (OTS) monolayer on SiO₂.³⁵ This similarity between the contact angles measured in this study and those published in the literature indicates that the transferred LB monolayers of stearic acid at fluorite and calcite surfaces remained closely packed during the advancing contact angle measurements. For such systems, in which the interaction involves only Liftshitz–van der Waals forces between the transferred LB monolayer of stearic acid and the diiodomethane (apolar surface–apolar liquid), the surface tension (γ_s) of this monolayer can be calculated based on Fowkes' concept³⁶ using the following equation:

$$\gamma_s = \gamma_L(\cos \theta + 1)^2/4 \quad (2)$$

where γ_L is the surface tension of the apolar liquid (γ_L = 50.8 mN/m for diiodomethane) and θ is the contact angle as measured for the apolar liquid at the solid surface (the advancing contact angle for diiodomethane at the transferred LB monolayer of stearic acid was 74–76°). Thus, the surface tension of a closely packed LB monolayer of stearic acid calculated using eq 2 is found to be from 19.6 to 20.7 mN/m.

LB monolayers of oleic acid were transferred at fluorite and calcite surfaces for contact angle measurements. In both cases the molecular cross-sectional area of the transferred LB monolayer of oleic acid was 30 Å²/molecule, as determined from the π -A isotherm. The contact angles as measured for diiodomethane at the surface of transferred LB monolayers of oleic acid are presented in Figure 3. Again, the same advancing (54–58°) and receding (40–43°) contact angles were obtained for transferred LB monolayers of oleic acid at both the fluorite and calcite surfaces. Also, the same advancing and receding contact angles were obtained when contact angle measurements were repeated at the same location on the transferred monolayer. No significant decrease in contact angle with decreasing drop size was observed for these systems. The observed scatter in contact angle data with varying drop

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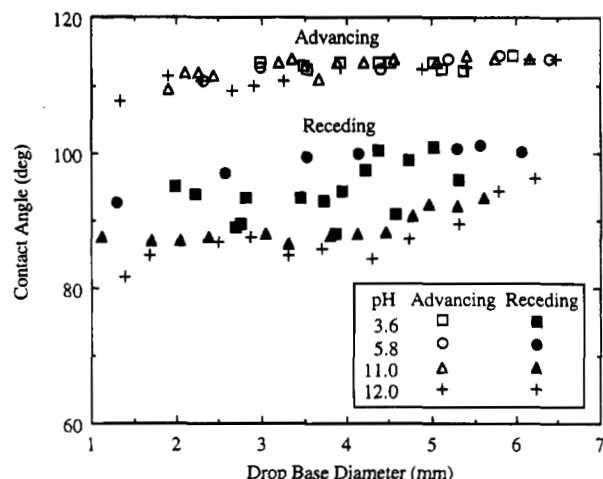


Figure 4. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at a fluorite surface as measured for a water drop of varying size at different pH values (squares = pH 3.6, circles = pH 5.8, triangles = pH 11.0, and crosses = pH 12.0).

size suggests that the contact angle measurements were affected by surface roughness. Larger contact angle hysteresis was observed for the transferred LB monolayers of oleic acid ($12\text{--}18^\circ$) than for the transferred LB monolayers of stearic acid (about 10°). Such a difference may be due to a difference in molecular arrangements. Note that one stearic acid molecule covered 20 \AA^2 of the crystal surface whereas one oleic acid molecule covered 30 \AA^2 of the crystal surface. As a simple calculation, there might be one-third of the surface area which was not covered by methyl groups of adsorbed oleate species (of course, a detailed calculation of the surface heterogeneity should also include the hydrocarbon chain conformation and the presence of the C=C bond). If this hypothesis is correct, such a surface needs to be considered as heterogeneous and the surface tension of a transferred LB monolayer of oleic acid cannot be calculated based on eq 2 which requires surface homogeneity.

Hydrophobicity and Stability of Transferred LB Monolayers at a Fluorite Surface. The hydrophobicity of transferred LB monolayers of fatty acids at a fluorite surface was examined with the sessile-drop contact angle technique. Both advancing and receding contact angles were measured for water drops of varying size at different pH values. The contact angle data are presented in Figures 4 and 5. The advancing contact angle for water was found to be $110\text{--}114^\circ$ and was not affected by the pH of the aqueous phase, as shown in Figure 4. Note that the advancing contact angle of $110\text{--}114^\circ$ is a characteristic value for closely packed methyl groups of organic LB films and self-assembled monolayers.^{35,37,38} A contact angle hysteresis of $10\text{--}20^\circ$, depending on the pH value, was observed for water drops with a base diameter of $2\text{--}6.5\text{ mm}$ (see Figure 4). The contact angles as measured for water drops with varying pH at the surface of a transferred LB monolayer of stearic acid on a fluorite surface were reproducible. For example, at pH 5.8 the same advancing and receding contact angles were obtained when contact angle measurements were repeated at the same location on the transferred monolayer, i.e., by increasing and reducing the drop size and then again increasing and reducing the drop size (see Figure 5). FT-IR/IRS analysis

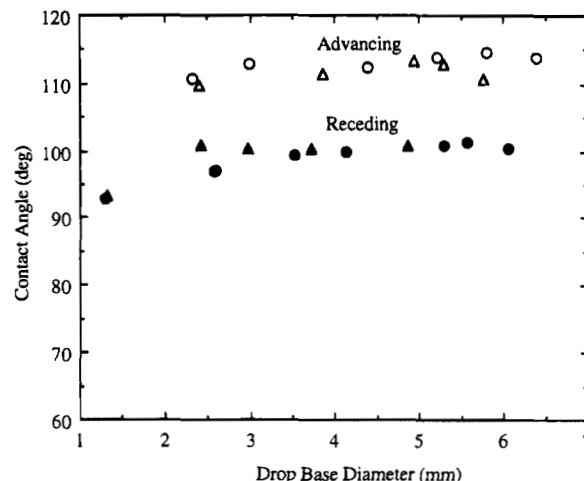


Figure 5. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at a fluorite surface as measured for a water drop of varying size at pH 5.8. The measurements were performed for two runs at the same location on the LB monolayer surface (circles = first run, triangles = second run).

of the transferred LB monolayers of fatty acids at a fluorite surface showed that the carboxylate head group of the fatty acid monolayer reacts with surface calcium sites of the fluorite surface to form a chemisorbed monolayer.¹⁵ It is probable that carboxylate chemisorption at a fluorite surface after LB transfer caused immobilization of the stearate molecules at the fluorite surface, thus providing substantial stability for this monolayer. A similar stability has been observed for a chemisorbed OTS monolayer at a mica surface.³⁸

Smaller receding contact angles were measured for water drops at alkaline pH values (see Figure 4). These contact angle data indicate that a transferred LB monolayer of stearic acid at a fluorite surface which has reacted to form the chemisorbed monolayer exhibits some instability in a strongly alkaline environment. This relatively small instability of the transferred LB chemisorbed monolayer of stearate at a fluorite surface in water of high pH requires further investigation. A small decrease in both advancing and receding contact angles with decreasing drop size, especially for drops with a base diameter smaller than 2 mm , was obtained (see Figure 4). As mentioned in the previous section, this may be due to surface roughness features of the fluorite crystal.

In another experiment, an LB monolayer film of calcium distearate was transferred at a fluorite surface. The hydrophobic properties and stability of this transferred LB calcium distearate monolayer were also examined by contact angle measurements using water drops of varying size at different pH values. The contact angle data are shown in Figure 6. The advancing contact angles of $109\text{--}114^\circ$ were found to be very similar to those measured for the transferred LB chemisorbed monolayer of stearate, $110\text{--}114^\circ$ (see Figure 5). The receding contact angle values for the transferred LB calcium distearate monolayer were found to differ from those measured for the transferred LB chemisorbed monolayer of stearate. As shown in Figures 5 and 6, the contact angle hysteresis as measured for a water drop at pH 5.8 was $20\text{--}30^\circ$ for the transferred LB calcium distearate monolayer at the fluorite surface whereas it was about 10° for the transferred LB chemisorbed monolayer of stearate at the same surface.

The transferred LB calcium distearate monolayer was found to be unstable in acidic and alkaline solutions. As shown in Figure 6, the contact angle hystereses were found

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(38) Chen, Y. L.; Helm, C. A.; Israelachvili, J. N. *J. Phys. Chem.* **1991**, *95*, 10736–10747.

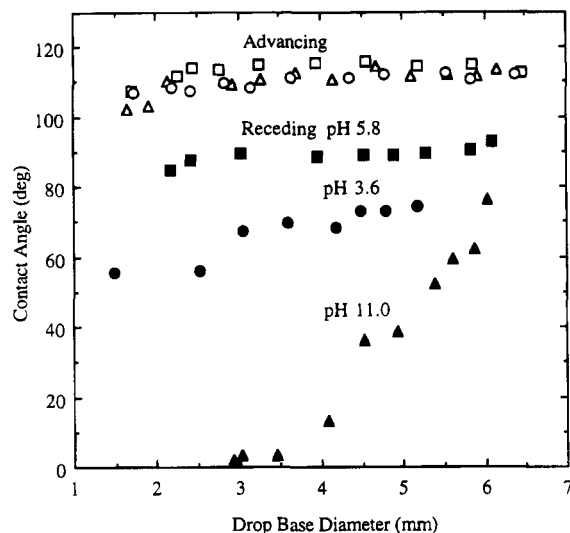


Figure 6. The effect of pH on receding contact angles of a transferred LB monolayer of calcium distearate at a fluorite surface as measured for water drops of varying size at different pH values (circles = pH 3.6, squares = pH 5.8, triangles = pH 11.0).

to be roughly 40–50° at pH 3.6 and 40–110° at pH 11.0 depending upon the drop size. Also, significantly smaller advancing contact angles were observed for repeated measurements at the same location of the transferred LB film (experimental data not shown here). Therefore, it can be concluded that a transferred LB calcium distearate monolayer at a fluorite surface is much less stable than a transferred LB chemisorbed monolayer of stearate at the same surface. It seems clear that after contact with water, some disorganization of the transferred LB calcium distearate monolayer occurred through desorption, molecular reorientation, and probably water penetration. It is speculated that the calcium distearate monolayer is attracted to the fluorite surface through Coulombic interaction. Such a monolayer is expected to be less stable than a chemisorbed stearate monolayer.

Further, contact angle measurements for a transferred LB monolayer of oleic acid at a fluorite surface were conducted. As in the case of transferred stearic acid monolayers, the transferred oleic acid monolayer reacted with the fluorite surface to form a chemisorbed monolayer of oleate.¹⁵ The advancing and receding contact angles were measured for water drops of varying size at different pH values, and the contact angle data are presented in Figure 7. The molecular area of the transferred LB chemisorbed monolayer of oleate was found to be 30 Å²/molecule. The advancing contact angle was found to be 100–104° at pH 3.5 and at pH 5.8 when contact angle measurements were performed on freshly deposited monolayers. The receding contact angles were primarily between 58° and 65° at pH values of 3.5 and 5.8. Both the advancing and receding contact angles decreased slightly when contact angle measurements were repeated at the same location on the transferred LB monolayer (experimental data not shown here). This change was quite clear when contact angle measurements were conducted with a water drop of pH 11.1. The advancing and receding contact angles were found to be 95–98° and approximately 20°, respectively (Figure 7). Also, the advancing contact angles decreased by 40° when contact angle measurements were repeated at the same location on the transferred monolayer (experimental data not shown here). It seems very clear that because of the larger molecular spacing of the transferred LB chemisorbed monolayer of oleate (30 Å²/molecule) compared to that of the transferred LB

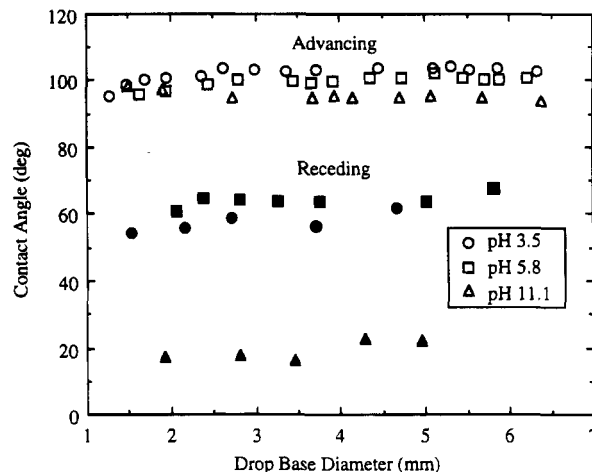


Figure 7. The effect of pH on advancing (open symbols) and receding (closed symbols) contact angles for a transferred LB monolayer of oleic acid at a fluorite surface as measured for water drops of varying size at different pH values (circles = pH 3.5, squares = pH 5.8, triangles = pH 11.1).

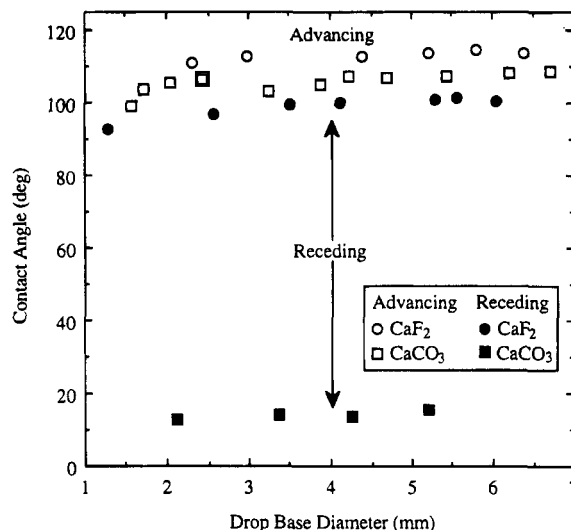


Figure 8. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at fluorite (circles) and calcite (squares) surfaces as measured for a water drop of varying size at pH 5.8.

chemisorbed monolayer of stearate (20 Å²/molecule) and because of the presence of the more polar C=C bond (cis form) in the hydrocarbon chain, water molecules can penetrate the oleate monolayer more easily and lead to reorganization of oleate species at the surface, thus affecting the wetting characteristics of the transferred oleate monolayer.

Hydrophobicity and Stability of Transferred LB monolayers at a Calcite Surface. The advancing contact angles for a water drop (pH 5.8) at a calcite surface with a transferred LB monolayer of stearic acid (perhaps only partially reacted and chemisorbed) were found to be 105–108° which are 5° smaller than those measured in the case of fluorite. In the case of receding contact angle measurements, a considerably larger difference was observed between the two minerals. As shown in Figure 8, the receding contact angles for a transferred LB monolayer of stearic acid at a calcite surface were only 13–15° compared to 100–102° for a transferred LB monolayer of stearic acid at a fluorite surface. It was observed that both the advancing and receding contact angles for a water drop (pH 5.8) at a transferred LB monolayer of stearic acid at the calcite surface decreased significantly when

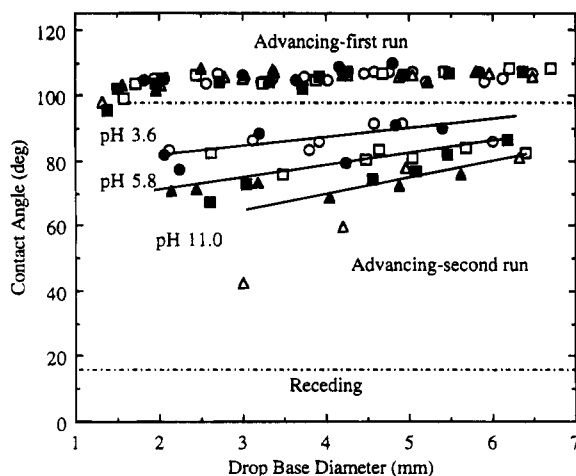


Figure 9. Advancing and receding contact angles for transferred LB monolayers of stearic acid (open symbols) and calcium distearate (closed symbols) at a calcite surface as measured for water drops of varying size at different pH values (circles = pH 3.6, squares = pH 5.8, triangles = pH 11.0).

the contact angle measurements were repeated at the same location on the transferred monolayer (experimental data not shown here). These experimental results briefly demonstrate the instability of transferred LB stearate monolayers at the calcite surface. The destructive effect of the aqueous phase on transferred LB monolayers of stearic acid at a calcite surface increased with increasing pH of the aqueous phase, as shown in Figure 9.

A contact angle/drop size relationship similar to that observed for the transferred LB monolayer of stearic acid at the calcite surface was obtained when a calcium distearate monolayer was transferred at a calcite surface (see Figure 9). Even repeated measurements at the same location on the transferred monolayer showed similar advancing and receding contact angles for both systems. In view of these experimental results, it seems that the adsorption force(s) between the transferred LB stearate monolayer and the calcite surface is(are) similar in nature to the adsorption force(s) between the transferred LB calcium distearate monolayer and the calcite surface. It has been reported that fatty acid molecules are chemisorbed at a calcite surface,⁵ but this may not necessarily be true for all molecules of the transferred LB monolayer. It is expected that only some portion of the transferred LB monolayer of stearic acid might be adsorbed at the active sites of the calcite surface through carboxylate chemisorption, whereas the remaining molecules of the transferred monolayer remain unreacted in the acid form and are adsorbed at the calcite surface through weaker interactions, possibly through hydrogen bonding.

Fluorite vs Calcite. As shown in Figures 2 and 3, the same wetting characteristics were obtained for LB monolayers of fatty acids at both fluorite and calcite surfaces when probed with an apolar liquid (diiodomethane). In this regard, it seems evident that the instability of the transferred LB monolayer of fatty acid at a calcite surface when in contact with the aqueous phase is due to a greater tendency for hydration of the calcite surface. Just after argon plasma cleaning, the advancing contact angles for the fluorite and calcite surfaces were always close to zero ($<10^\circ$). On the other hand, the advancing contact angle for the fluorite surface was found to increase (up to 27°) after being in contact with air for 30 min whereas there was no change in the contact angle of the calcite surface.³⁹ The hydration free energies of CO_3^{2-} and F^- are reported

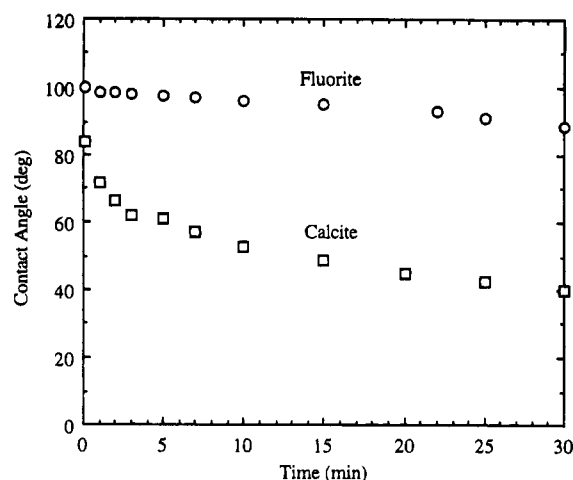


Figure 10. Advancing contact angle for a transferred LB monolayer of oleic acid at fluorite (circles) and calcite (squares) surfaces as measured for a water drop (pH 5.8) as a function of time.

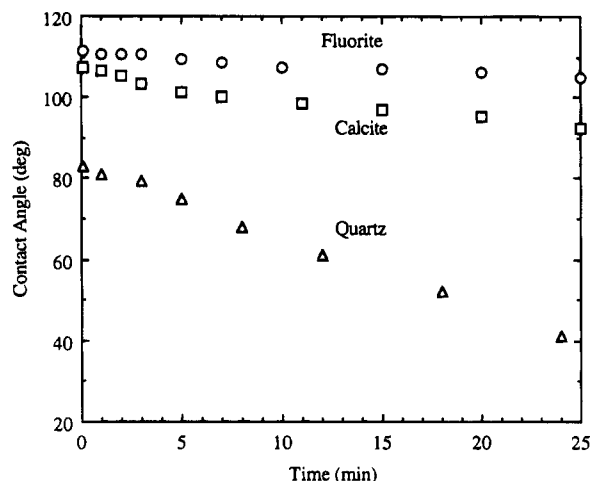


Figure 11. Advancing contact angle for a transferred LB monolayer of stearic acid at fluorite (circles), calcite (squares), and quartz (triangles) surfaces, as measured for a water drop (pH 5.8), as a function of time.

as -402.6 and 26.6 kJ, respectively.⁴⁰ On the basis of the contact angle data and hydration free energy, it is speculated that the trend toward greater hydration of the calcite surface leads to weaker adsorption force(s) between the LB monolayer of fatty acid and the calcite surface. Thus, in the aqueous phase water is able to penetrate the monolayer and results in the disorganization/desorption of the unreacted portion of the fatty acid monolayer.

Time-Dependent Contact Angle Measurements. The kinetics of destabilization of LB monolayers in contact with water drops was examined for several systems by monitoring the contact angle change as a function of time. In these experiments a drop of water (pH 5.8) with a base diameter of 5 mm was placed on an LB monolayer (both stearate and oleate). The contact angle changes for the transferred LB monolayers of oleic and stearic acids are presented in Figures 10 and 11, respectively. The initial contact angle ($t = 0$ min) corresponds to the advancing contact angle which was measured 15–30 s after the drop was placed at the surface.

As shown in Figure 10, the contact angle for a water drop at the transferred LB monolayer of oleic acid at a fluorite surface ($30 \text{ \AA}^2/\text{molecule}$) decreased from 100° to

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(40) Krestov, C. A. *Thermodynamics of Solution*; Ellis Horwood Limited: West Sussex, England, 1991; pp 121–122.

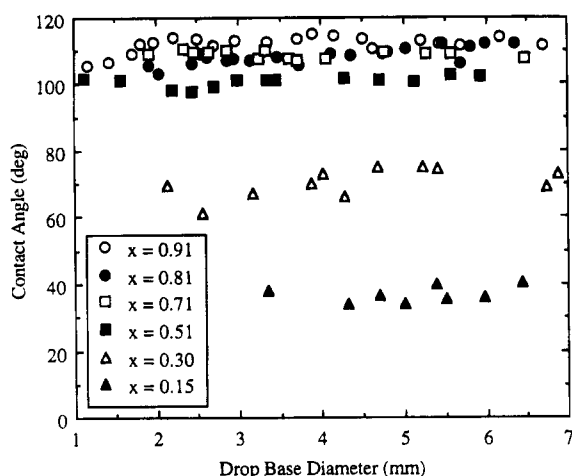


Figure 12. Advancing contact angle changes for SA stearate adsorbed at a fluorite surface as measured for a water drop at pH 5.8 as a function of surface coverage (an adsorption density of 8.3×10^{-10} mol/cm² is equivalent to $x = 1$).

89° in 30 min. A few degrees of change in the contact angle is expected for most systems due to an equilibration effect. Hayes and Ralston⁴¹ postulated that an imbalance in interfacial energies in the vicinity of the three-phase contact line exists for even longer times than examined here. This hypothesis cannot be validated from these experimental results. The instability of LB monolayers at mineral surfaces can have a significant effect on contact angle relaxation. The contact angle of a transferred LB monolayer of oleic acid at a calcite surface was found to decrease rapidly during the first 5 min (by 23°). In 30 min, the contact angle of the LB oleate monolayer decreased from 84° to 40°.

The destructive effect of the aqueous phase over time on a transferred LB monolayer of stearic acid (20 Å² per molecule) was found to be less pronounced (see Figure 11). After 25 min the contact angle of the transferred LB monolayer of stearic acid at fluorite and calcite surfaces decreased by 7° and 15°, respectively. These results agree with the previous observation that LB monolayers of fatty acids are less stable at a calcite surface than at a fluorite surface. Note that destabilization of the transferred LB monolayer of stearic acid by the aqueous phase is even more pronounced at a quartz surface (see Figure 11). Chemisorption does not occur at the quartz surface, and the transferred LB monolayer remains as stearic acid and is physically adsorbed on the quartz surface.

Hydrophobicity and Stability of Self-Assembled Stearate Monolayers at a Fluorite Surface. The advancing and receding contact angles for water drops of varying size (pH 5.8) at stearate monolayers self-assembled (SA) at the fluorite surface were measured as a function of surface coverage. Surface coverage (x) of the fluorite surface by SA stearate was determined spectroscopically. The maximum monolayer coverage ($x = 1$) corresponds to 8.3×10^{-10} mol/cm², as determined from the LB study.¹⁵

Figure 12 shows the change of the advancing contact angle as a function of drop base diameter for different levels of surface coverage (x). The measured advancing contact angles increased significantly with a surface coverage up to 0.5. At $x = 0.15$, advancing contact angles of less than 40° were observed. The advancing contact angles increased to 98–103° at $x = 0.51$. Further increase in surface coverage from $x = 0.51$ to $x = 0.91$ changed the advancing contact angle by only about 10°.

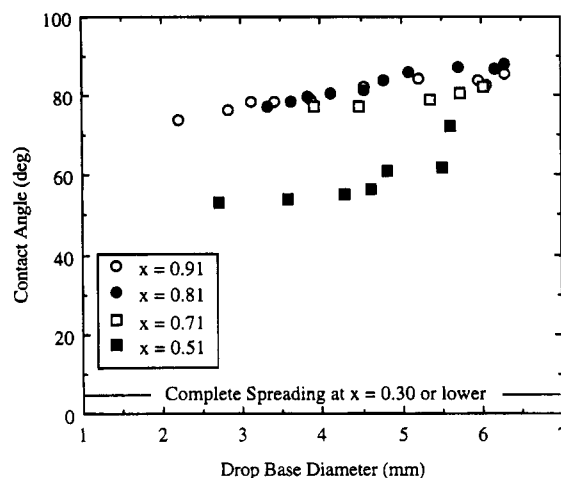


Figure 13. Receding contact angle changes for SA stearate adsorbed at a fluorite surface as measured for a water drop at pH 5.8 as a function of surface coverage (an adsorption density of 8.3×10^{-10} mol/cm² is equivalent to $x = 1$).

In contrast, the receding contact angle values obtained for fluorite crystals with self-assembled stearate at submonolayer coverage (Figure 13) decreased continuously with decreasing drop size over a range of drop base diameter from 2 to 6.5 mm. Examination of larger drops is required in order to identify characteristic values of the receding contact angles. The receding contact angles of the SA stearate were found to be close to zero at $x = 0.30$ or below, as shown in Figure 13. At $x = 0.51$, the receding contact angles were found to be mostly 55–65°. Further increase in surface coverage up to $x = 0.71$ changed the receding contact angles by about 20°. However, the measured receding contact angles did not change appreciably with an increase in surface coverage from $x = 0.71$ to 0.91. Importantly, with regard to the flotation systems in mineral processing, these results along with the results from the advancing contact angle measurements suggest that good hydrophobicity and stability of the SA stearate layer can be obtained at $x = 0.71$. Further increase in surface coverage does not enhance the hydrophobicity appreciably even at coverage greater than 0.71. The observed receding contact angles were no larger than 75–85°.

It is clear from comparison of the measured contact angles of LB and SA stearate layers that the receding contact angle for the transferred LB stearate monolayer is always greater than the receding contact angle for the SA stearate monolayer by 17–25° (see Table 1²⁶). On the basis of linear dichroism theory, it was found that the transferred LB monolayer of stearic acid at a fluorite surface is oriented at 13° from the surface normal whereas the SA stearate monolayer at $x = 0.91$ (adsorption density of 7.6×10^{-10} mol/cm²) is oriented at 21° from the surface normal.^{17,26} In addition, it was found that the adsorption density of stearate has no significant influence on the molecular orientation of the adsorbed stearate species.^{17,26} These results suggest that formation of a stearate monolayer by SA with perfect homogeneity and a molecular orientation angle equivalent to that of the LB monolayer is not possible at a fluorite surface, although the SA monolayer is still of fairly high quality. See Table 1.

Summary and Conclusions

It has been shown in previous research¹⁵ that transferred LB monolayers of fatty acids react completely with the fluorite surface to form a chemisorbed carboxylate monolayer. Such a reaction appears to be incomplete at

(41) Hayes, R. A.; Ralston, J. *Colloids Surf.* **1993**, *80*, 137–146.

Table 1. Contact Angle Data for Transferred LB and SA Stearate Monolayers at a Fluorite Surface (Drop Size Varied from 2 to 6.5 mm, pH 5.8)²⁶

type	adsorption density ($\times 10^{-10}$ mol/cm ²)	molecular orientation angle (degrees)	advancing contact angle (degrees)	receding contact angle (degrees)
LB	8.1	13	110–114	98–102
SA	7.6	21	110–115	75–85

a calcite surface, and this difference in the extent of the reaction at fluorite and calcite surfaces accounts for distinct differences in wettability and stability of the monolayer film.

The hydrophobicity and stability of fatty acid monolayers at fluorite and calcite surfaces have been analyzed using the contact angle—sessile-drop technique. The wetting characteristics for the transferred LB monolayers of fatty acids were observed to be the same at both fluorite and calcite surfaces when probed with an apolar liquid (diiodomethane). The contact angle results indicate that the transferred LB monolayers of fatty acids are stable during the contact angle measurements when exposed to an apolar liquid (diiodomethane).

The hydrophobic properties and stability of transferred LB monolayers of fatty acids were also examined by contact angle measurements using water drops of varying size and at different pH values. The transferred LB monolayer of stearic acid exhibits good hydrophobicity and stability at the fluorite surface. The advancing contact angle was found to be 110–114° and was not affected by the pH of the aqueous phase. A contact angle hysteresis of 10–20°, depending on the pH value, was observed. The advancing and receding contact angles were reproducible when contact angle measurements were repeated at the same location on the transferred monolayer. It seems that carboxylate chemisorption causes immobilization of the transferred stearate molecules at a fluorite surface, thus providing for the stability of this monolayer. A slight instability of transferred LB chemisorbed stearate monolayers at a fluorite surface in water of alkaline pH requires further investigation.

The water advancing contact angles for the transferred LB monolayer of calcium distearate at the fluorite surface were found to be similar to those for the transferred LB monolayer of stearic acid. However, the contact angle hysteresis for water drops at the calcium distearate monolayer was larger, especially for acidic and alkaline solutions. It seems that after contact with water, some disorganization of the calcium distearate monolayer such as desorption and molecular reorientation occurred at the fluorite surface.

A considerable difference in the water receding contact angles between the transferred LB monolayer of stearic acid at the fluorite surface and the transferred LB

monolayer of stearic acid at the calcite surface was observed. For example, at pH 5.8, the receding contact angles for water drops (pH 5.8; drop base diameter = 2 to 6.5 mm) at the surface of transferred LB monolayer of stearic acid on calcite were only 13–15° compared to 100–102° for an LB stearate monolayer at the fluorite surface. Further, both the advancing and receding contact angles decreased significantly when the contact angle measurements were repeated at the same location of the monolayer. It seems clear that only some portion of the transferred LB monolayer of stearic acid adsorbs at the active sites of the calcite surface through carboxylate chemisorption whereas the rest of the stearic acid monolayer remains unreacted and is adsorbed at the calcite surface through weaker intermolecular forces. Interestingly, a similar contact angle/drop size relationship was obtained when a calcium distearate monolayer was transferred at the calcite surface. In view of these experimental results, it seems that the adsorption force(s) between the transferred LB monolayer of stearic acid and the calcite surface is similar in nature to the adsorption force(s) between the transferred LB monolayer of calcium distearate and the calcite surface.

The kinetics of destabilization of transferred LB monolayer films of fatty acid was also examined at fluorite and calcite surfaces by monitoring contact angle change with time. The results again agree with the previous observation that transferred LB monolayers of stearic acid are less stable at a calcite surface than at a fluorite surface. In addition, destabilization of the transferred LB monolayer of stearic acid by the aqueous phase was found to be even more pronounced at a quartz surface, supporting a general consensus that choosing a proper surfactant is critical for hydrophobization of the surface.

Changes in the contact angles of self-assembled (SA) stearate monolayers at a fluorite surface were examined as a function of surface coverage (x). The results showed that good hydrophobicity and stability of the SA stearate monolayer can be obtained at $x > 0.7$. It is evident from the results of contact angle measurements for SA monolayers that formation of a SA stearate monolayer of structure and order equivalent to those of the surface created by a transferred LB monolayer does not occur, although the SA monolayer is still of fairly high quality.

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