Precipitation of Anionic Surfactants in the Presence of Sodium Oleate and Calcium Ions

S. Das, N. Nayyar, R.G. Bhirud, K.S. Narayan and **V.V. Kumar***
Hindustan Lever Research Centre, Chakala, Andheri East, Bombay—400 099, India

Precipitation of anionic surfactants, linear alkylbenzene sulfonate (LAS) and alpha olefin sulfonate (AOS), by calcium ions was studied in the presence of sodium oleate. Lather stability was determined by the Ross-Miles method, precipitation was followed by measuring the optical density (OD), and equilibrium surface tension (EST) and Fourier transform infrared (FTIR) spectroscopy were used to characterize the nature of the precipitate formed. For the 5 mM LAS-0.7 mM oleate system, lather was unstable, and the OD was high in the 2–5°FH region of calcium hardness, while at higher calcium hardness levels, lather was stable and the turbidity of solutions decreased. On the other hand, in the 5 mM AOS-0.7 mM oleate system, lather was unstable throughout the calcium hardness region studied (0–20°FH). Also, the turbidity buildup was much higher in the AOS system than in the LAS system. Analysis of the precipitates formed in these systems by FTIR spectroscopy indicated that the precipitate from the AOS system had an additional band at 1190 cm^{-1}, corresponding to the sulfonate group. These results, together with the EST data, confirm that the precipitate formed in the LAS system between 2–5°FH calcium is calcium oleate, and that formed in the AOS system is likely to be calcium (AOS) oleate. It is tempting to hypothesize that the similarity of AOS and oleate in chainlength could be responsible for the coprecipitation of AOS and oleate with calcium, whereas LAS, which has a larger headgroup with a benzene ring and two smaller chains (average length is C8) is unlikely to precipitate with the oleate.

KEY WORDS: Alpha olefin sulfonate, infrared, lather, LAS, precipitation, surface tension, water hardness.

Calcium and magnesium ions present in hard water are known to interact with anionic surfactants and precipitate them as insoluble calcium salts. This leads to reduced detergency of formulations that contain anionics as the sole or main active ingredient. Interaction of calcium ions with anionic surfactants, such as linear alkyl benzene sulfonate (LAS), alpha olefin sulfonate (AOS) and soap, has been studied extensively (1–8). Such surfactants have different calcium tolerance levels. For example, calcium can precipitate fifteen times its own weight of soap, 150 ppm calcium is sufficient to precipitate significant LAS from wash liquor (5,6) and AOS is shown to have better calcium tolerance (9,10). However, none of those studies mentioned above characterized the interaction of AOS and LAS with calcium ions in the presence of soil or the precipitates formed. Fatty acids are present in human sebum, and free fatty acids (FFA) from oils and fats (11,12) that are likely to deposit on fabrics get saponified in the highly alkaline wash solution, leading to the formation of sodium soaps. In view of this, we have selected Na oleate as the model soil in our studies. We have recently demonstrated by proton nuclear magnetic resonance (NMR) spectroscopy (13) and fluorescence spectroscopy (14) the interaction between Na-LAS and Na-oleate in the absence of calcium ions.

We studied lather behavior of LAS-oleate and AOS-oleate systems at various calcium ion concentrations by the Ross-Miles method. Precipitation was followed by measuring the optical density (OD), Fourier transform infrared (FTIR) and equilibrium surface tension (EST) data were utilized to characterize the nature of the precipitate formed.

MATERIALS AND METHODS

Na-LAS (Reliance Industries, Bombay, India) and Na-AOS (Godrej Soaps, Bombay, India) were purified commercial-grade samples and were mixtures of homologs and isomers. Nondetergent organic matter was removed by ether extraction in a Soxhlet apparatus. Thereafter, the sodium salts were extracted in methanol and the inorganics were rejected. Solvent was removed by distillation, and the final traces were evaporated in a vacuum oven. The samples were characterized by gas chromatography (GC), and LAS was found to have 12 carbon atoms in the alkyl chain (75% inner isomers). AOS has an average chainlength of 16 carbon atoms. Reagent-grade $CaCl_2 \cdot 2H_2O$ was used for the preparation of hard water. All the solutions except calcium chloride were prepared at pH 10.5. All the measurements were carried out at room temperature (25 ± 1°C).

Preparation of surfactant solutions. Stock solutions of LAS and AOS (5×10^{-2} M) were prepared and adjusted to pH ≈10.5. Water used for the required dilutions was also adjusted to pH ≈10.5 with sodium hydroxide. Sodium oleate was prepared by neutralizing oleic acid with sodium hydroxide and making up the volume to get 0.1 M solution.

Analysis of the precipitates formed in LAS and AOS systems. FTIR spectra were recorded on a Nicolet model SX20 FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI). The insolubles formed in the AOS-oleate and the LAS-oleate systems at 2°FH were separated by centrifugation. The wet precipitate was dried under an infrared (IR) lamp and mixed with potassium bromide before IR spectra were recorded. The spectra were compared with the IR spectra of freshly prepared precipitates of calcium LAS, calcium AOS, calcium oleate and calcium carbonate for identification. Surface tension of the solutions was measured by the Wilhelmy plate method on a Krüss K10 digital tensiometer (Krüss GmbH, Borsteler, Chaussee, Hamburg, Germany). For turbidity measurements, absorbance was recorded at 620 nm in a Shimadzu (Tokyo, Japan) double-beam spectrophotometer with water as reference, five minutes after all the materials were mixed.

Lather stability. The standard Ross-Miles method was employed to determine lather stability. The concentration of surfactant was fixed at 5×10^{-3} M, the required amount of calcium ions was introduced and Na oleate was added to get a concentration of 0.7 mM in the solution. The above solution (50 mL) was transferred into the Ross-Miles apparatus along the walls by means of a pipette. Lather was generated by dropping 200 mL more of the above solution into the center of the solution pool. Lather

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*To whom correspondence to be addressed.

height was measured at 30 s and after 5 min, and the ratio of these values is expressed as the lather stability.

In the results presented and in all the figures, calcium ion concentration is expressed in terms of °FH: 1°FH corresponds to 0.1 mM Ca^{2+}.

RESULTS AND DISCUSSION

Lather stability of 5 mM LAS and 5 mM AOS in the presence of 0.7 mM oleate is presented in Figure 1 as a function of calcium hardness. Each point represents a discrete measurement. Figure 1 shows clearly that LAS and AOS exhibit a minimum in lather stability with increasing calcium concentration. For LAS, lather falls sharply to a minimum around 2-3°FH and for AOS, the minimum spans a larger region, i.e., 4-10°FH. Also, at higher calcium hardness levels (ca. °FH = 10), lather of the LAS-oleate system is highly stable, and stability is comparable to that around 0°FH. However, for AOS, lather stability was always low and never reached that of zero calcium level stability. These differences in the behavior of LAS and AOS are likely to reflect the different types of interaction of LAS and AOS with calcium ions in the presence of soil that lead to different types of precipitates.

In Figure 2, OD at the end of 5 min in 5 mM LAS and 5 mM AOS solutions containing 0.7 mM oleate is presented as a function of calcium ion concentration. Figure 2 shows that the OD in the LAS system increases slightly and reaches a maximum around 3°FH and then falls off. However, for the AOS system, the OD increases significantly (as compared to LAS), and a broader maximum is seen between 3-7°FH, which falls slightly at higher calcium ion concentrations. These OD results indicate that for LAS, precipitation takes place around 3°FH, and around this region of calcium hardness the lather was highly unstable (Fig. 1). However, the OD behavior of the AOS system indicates that precipitation takes place at 7°FH. Theoretically, if calcium oleate were precipitating from both systems, precipitation should be complete around 3°FH because 0.7 mM oleate can only react with 0.35 mM calcium (i.e., 3.5°FH). Hence, the turbidity buildup, measured as OD, should be maximal around this region of 3°FH. This indicates that the species precipitating from the AOS system may not be calcium oleate because the OD maximum is seen around 7°FH. In both systems, the decrease in OD after the precipitation indicates that either the size of the particle precipitated is decreasing or the oleate formed is solubilized in the surfactant micelles.

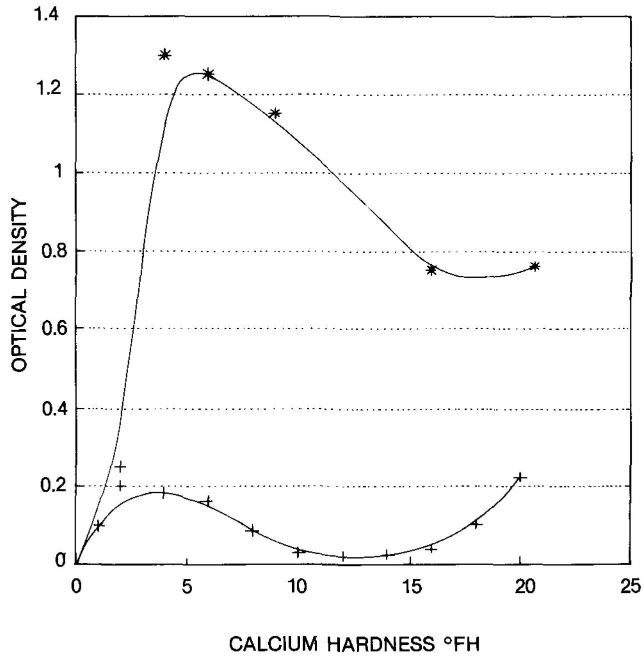

FIG. 2. Optical density (620 nm) of the 5 mM linear alkylbenzene sulfonate (+ + +) and 5 mM alpha olein sulfonate (* * *) systems in the presence of 0.7 mM sodium oleate as a function of calcium ion concentration (in °FH). Each point in the figure is a discrete measurement.

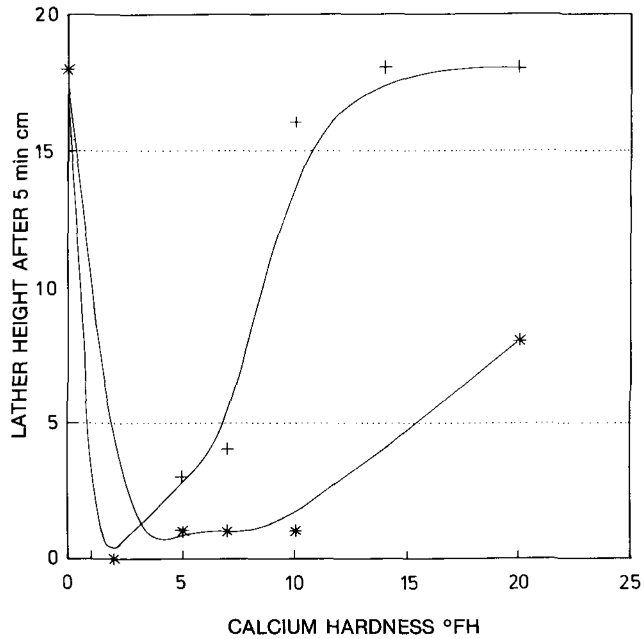

FIG. 1. Lather stability of the 5.mM linear alkylbenzene sulfonate (+ + +) and 5 mM alpha olefin sulfonate (* * *) systems in the presence of 0.7 mM sodium oleate as a function of calcium ion concentration (in °FH). Each point in the figure represents a discrete measurement, i.e., the points in the figure are not generated by continuously increasing the calcium ion concentration.

Taken together, Figures 1 and 2 indicate that in the LAS system, calcium oleate precipitate is formed, but in AOS, the precipitate formed is not calcium oleate. Thus it would be interesting to characterize the nature of the precipitate formed. For this purpose, precipitates from the LAS and AOS systems at 2°FH were centrifuged, and the precipitates were separated and dried. These dried precipitates were characterized by FTIR spectroscopy. The FTIR spectra of the precipitates from the LAS and AOS systems are presented in Figure 3. Although the IR spectra of both precipitates are identical, in the AOS system an additional absorption band around 1190 cm^{-1} is noticeable. This corresponds to the sulfonate group, and such a peak is normally observed in pure LAS and AOS. The results of the IR spectra can be interpreted to indicate that, in the AOS system, the precipitate formed is likely to contain

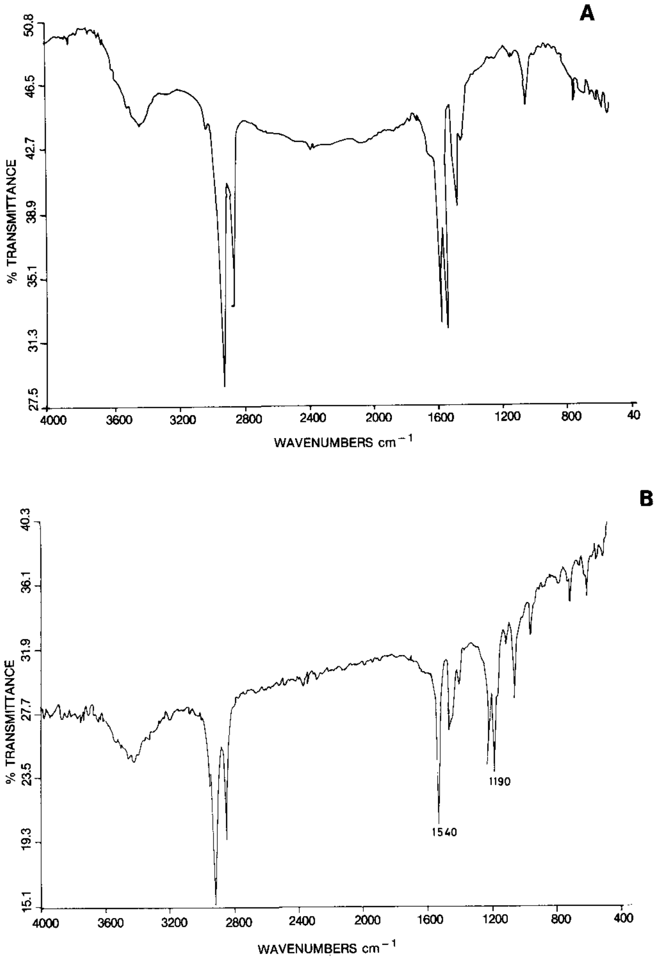

FIG. 3. A. Fourier transform infrared (FTIR) spectrum of the precipitate formed in the 5 mM linear alkylbenzene sulfonate through 0.7 mM sodium oleate system at 2°FH calcium ion concentration. B. FTIR spectrum of the precipitate formed in the 5 mM alpha olefin surfactant through 0.7 mM sodium oleate system at 2°FH calcium ion concentration.

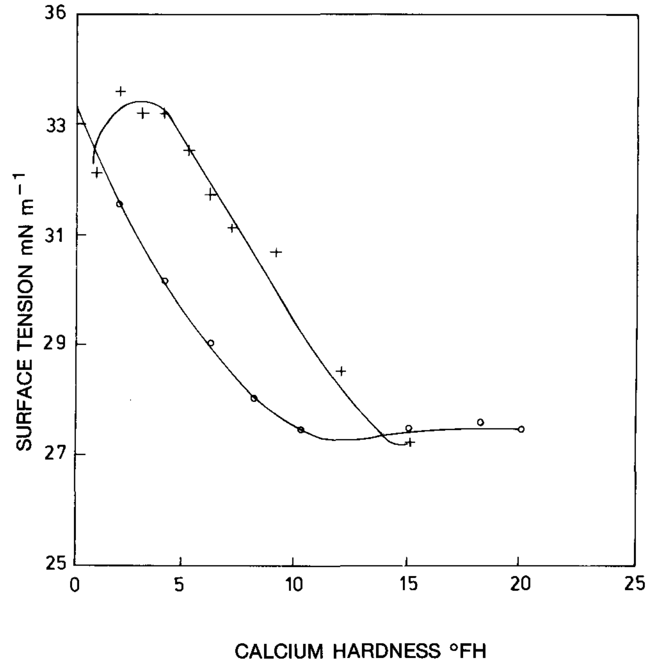

FIG. 4. Changes in the equilibrium surface tension of 5 mM linear alkylbenzene surfactant solution in the absence (o o o) and in the presence (+ + +) of 0.7 mM sodium oleate as a function of calcium ion concentration (in °FH). Each point in the figure represents a discrete measurement.

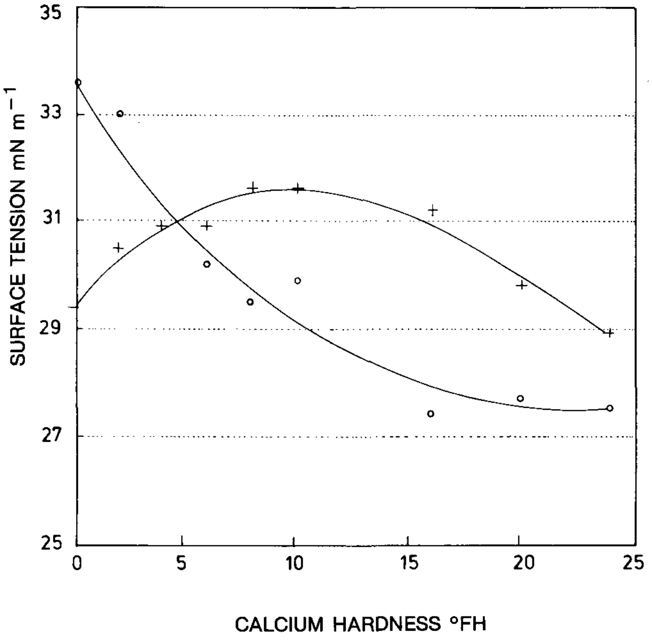

FIG. 5. Changes in the equilibrium surface tension of 5 mM alpha olefin sulfonate solution in the absence (o o o) and in the presence (+ + +) of 0-7 mM sodium oleate as a function of calcium ion concentration (in °FH). Each point in the figure represents a discrete measurement.

AOS, whereas in the LAS system, the precipitate formed does not contain LAS. In fact, the precipitate formed in the LAS system is identical to that of calcium oleate that was separately prepared and characterized (see Materials and Methods section). The IR spectra also indicate that the precipitate formed in the AOS system is not calcium oleate, and we tentatively characterized this precipitate to be Ca (AOS) oleate because of the presence of carbonyl and sulfonate peaks in the spectrum.

Changes in the EST of the 5 mM LAS (Fig. 4) and 5 mM AOS (Fig. 5) systems, with and without 0.7 mM oleate, as a function of calcium hardness are presented in Figures 4 and 5. Sodium oleate (0.7 mM) has an EST of 27 mN m^{-1}, where as 5 mM AOS and 5 mM LAS have surface tension values of 36 and 34 mN m^{-1}, respectively. Figure 4 shows that, in the case of LAS system (in the absence of oleate), the EST value decreases from 34 to 28 mN m^{-1} and remains constant. Decrease in the surface tension could be due to the electrolyte effect of $CaCl_2$, which makes the surface more compact due to a decrease of the electrostatic repulsion that leads to enhanced surface occupancy. It is likely that calcium LAS is formed in this system, which has a lower surface tension than Na-LAS. The surface tension (ST) profile of the Na-LAS system in the presence of 0.7 mM oleate shows a different, but interesting trend. In this case, the EST value increases from 32 to 34 mN m^{-1} from 1 to 4°FH and is followed

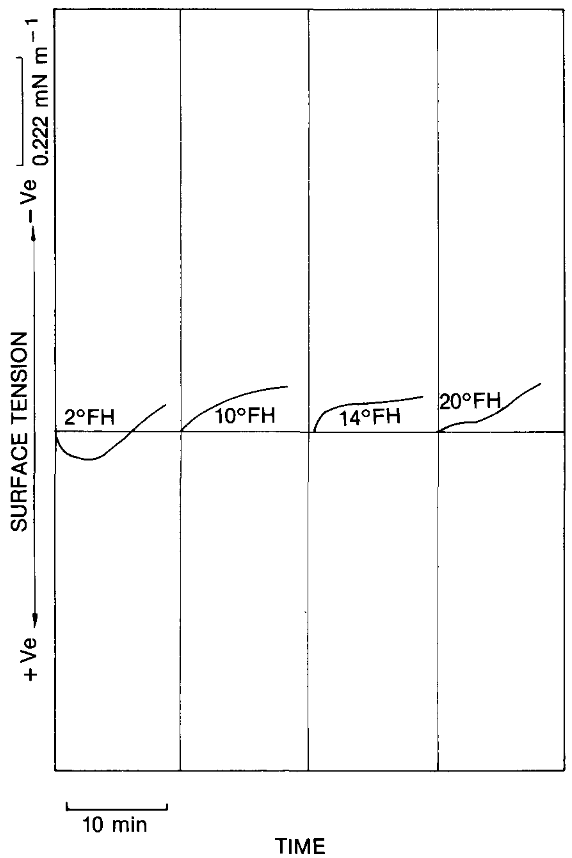

FIG. 6. Changes in the equilibrium surface tension of the 5 mM linear alkylbenzene sulfonate through 0.7 mM sodium oleate system as function of time at various calcium ion concentrations.

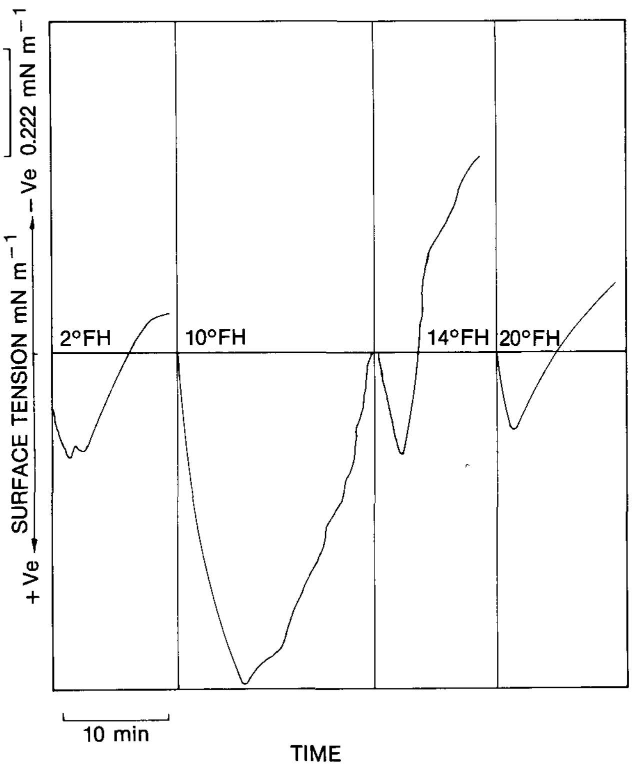

FIG. 7. Changes in the equilibrium surface tension of the 5 mM alpha olefin sulfonate through 0.7 mM sodium oleate system as a function of time at various calcium ion concentrations.

by a decrease. The region of initial increase corresponds to a stoichiometric amount of the calcium needed to precipitate oleate as calcium oleate. The ST increases because the calcium oleate formed is not surface-active (15). When all the oleate is precipitated as calcium oleate, the system will have only Na-LAS, and the ST profile should be similar to that of Na-LAS and Ca ions. This trend can be seen in Figure 4. The results presented in Figure 4 clearly indicate that calcium oleate is precipitated in the Na-LAS system up to 4°FH. For the AOS system (in the absence of oleate), as expected, the EST values decrease from 36 to 27 mN m^{-1} as a function of the calcium ion concentration. On the other hand, in the presence of oleate ions, the EST values do not peak around 3–4°FH calcium, which is the stoichiometric amount of calcium needed to precipitate the oleate as calcium oleate. This indicates that the precipitate formed in the AOS-oleate system in the presence of calcium ions is not calcium oleate. At higher levels of oleate, the surface tension is low at 0°FH Ca due to the increased population of oleate ions. However, the decrease of surface tension takes place at higher levels of Ca after all the oleate present has been precipitated. However, no fixed trend was observed at higher levels for AOS. There was a broad maximum indicating that the precipitate was Ca (AOS) oleate.

Precipitation kinetics were followed by measuring the change in the ST with time. Variation of the ST as a function of time was monitored after addition of 0.7 mM oleate to the 5 mM LAS (Fig. 6) and 5 mM AOS (Fig. 7) systems containing known amounts of calcium ions. In the LAS-oleate system, the ST value increased in the first 5 min at 2°FH calcium ion concentration and then decreased. This is likely due to the fact that the ST of oleate is lower than that of the LAS. Any depletion of oleate should lead to an increase in the ST value. Thus, the increase in the ST can be attributed to the depletion of the surfactant (oleate), i.e., removal of oleate as calcium oleate. However, at higher calcium ion concentrations, a decrease in the surface tension was always observed. This indicates that no depletion of the surfactant from the surface is taking place at these calcium levels.

For the AOS-oleate system, the ST increased initially, indicating depletion of the surfactant from the surface at all calcium ion concentrations studied. This indicates that the precipitating species and the kinetics are different in the two systems. Taken together, IR and ST data indicate the possibility of Ca (AOS) oleate precipitating out in this system.

All results presented in Figures 1–7 indicate that the precipitate formed in the LAS system between 2–4°FH calcium ion concentration is calcium oleate. In the AOS system, however, the precipitate formed is not calcium oleate but is more likely to be calcium (AOS) oleate. Although the results presented do not clearly confirm the precipitation of Ca (AOS) oleate, it is tempting to hypothesize the following: commercial LAS, used in the studies here, has 12 carbon atoms in the alkyl chain, with linear isomers virtually absent. The molecules are mostly (75%) 3,4,5,6 phenyl isomers with an average alkyl chainlength of 8 carbon atoms for the LAS. On the other hand, the AOS has an average chainlength of 16 carbon atoms. The similarity between AOS and the oleate (in chainlength) could be the reason for the coprecipitation of AOS and oleate with calcium ions, whereas LAS with its larger head group of a benzene ring and smaller chains, may not fit well into the calcium oleate precipitate.

REFERENCES

1. Scamehorn, J.F., and J.H. Harwell, in *Mixed Surfactant System*, Surfactant Science Series Vol. 46, edited by K. Ogino, and M. Abe, Marcel Dekker, New York, 1993, p. 283.
2. Peacock, J.M., and E. Matijevic, *J. Colloid Interface Sci. 77*:548 (1980).
3. Stellner, K.L., and J.F. Scamehorn, *Langmuir 5*:70 (1989).
4. Hato, M., and K. Shinoda, *J. Phys. Chem. 77*:378 (1973).
5. Fan, X.J., P. Stenius, N. Kallay and E. Matijevic, *J. Colloid Interface Sci. 121*:571 (1988).
6. Matheson, K.L., M.F. Cox and D. Smith, *J. Am. Oil Chem. Soc. 62*:1391 (1985).
7. Cox, M.F., and K.L. Matheson, *Ibid. 62*:1396 (1985).
8. Suri, S.K., N. Homendra and S. Bharadwaj, *Chemical Business 45*, June (1991).
9. Noik, C., M. Baviere and D. Defives, *J. Colloid Interface Sci. 36*:115 (1987).
10. Ogino, K., and M. Abe, *J. Am. Chem. Soc. 52*:465 (1975).
11. Powe, W.C., in *Detergency: Theory and Test Methods*, Part 1, edited by W.G. Cutlet, and R.C. Davis, Marcel Dekker, New York, 1972, p. 31.
12. Nagarajan, M.K., *J. Am. Oil Chem. Soc. 62*:949 (1985).
13. Das, S., R.G. Bhirud, N. Nayyar, K.S. Narayan and V. V. Kumar, *J. Phys. Chem. 96*:7454 (1992).
14. Nayyar, N., S. Das, R.G. Bhirud, K.S. Narayan, A.P. Singh and V.V. Kumar, *J. Colloid Interface Sci. 160*:496 (1993).
15. Pepper, H., *Ibid. 13*:199 (1958).

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