

MICELLE PROMOTION AGENTS

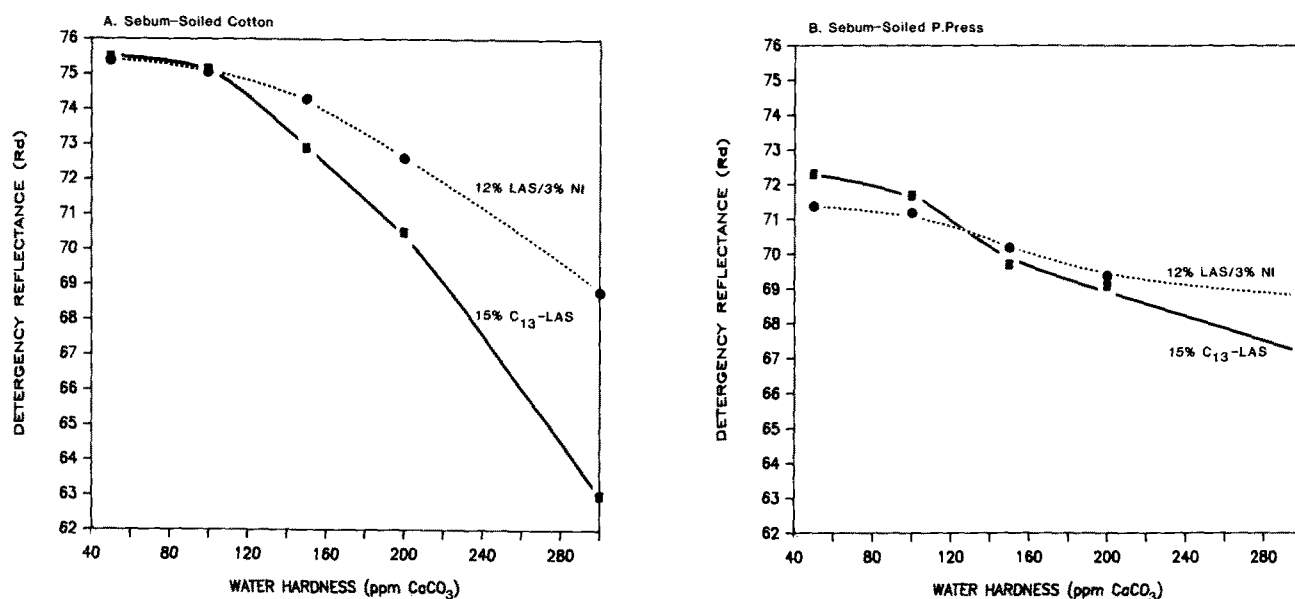


FIG. 6. Detergency performance of 15% LAS and 12% LAS/3% NI as a function of water hardness (Ca^{2+} only) on sebum soiled cotton (A) and sebum-soiled p.press (B) cloths using tridecyl LAS and 1214-70 NI surfactants. All test formulations contained 35% sodium sulfate, 25% sodium tripolyphosphate and 10% soluble silicate.

increasing ionic strength, because large changes in formulation are not required. However, as is the case with nonionic surfactants, the addition of cosurfactants can affect the processing characteristics of the formulation. Tentative studies also show that ether sulfates and high molecular weight polyethylene glycols act as micelle promotion agents.

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Interactions Between Linear Alkylbenzene Sulfonates and Water Hardness Ions. III. Solubilization and Performance Characteristics of $\text{Ca}(\text{LAS})_2$ ¹

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ABSTRACT

This paper compares the appearance and detergency properties of LAS solutions in which $\text{Ca}(\text{LAS})_2$ has formed either in the presence or absence of a micelle promotion agent.

INTRODUCTION

As one adds calcium ions to an aqueous solution of linear alkylbenzene sulfonate (LAS), $\text{Ca}(\text{LAS})_2$ eventually begins to precipitate from solution. As discussed in the second paper in this series (1), micelles solubilize $\text{Ca}(\text{LAS})_2$ so that the addition of a micelle promotion agent delays precipitation of $\text{Ca}(\text{LAS})_2$ (1). If sufficient calcium ion is added, however, the capacity of the micelles to solubilize the precipitate is exceeded and $\text{Ca}(\text{LAS})_2$ precipitate forms. The range of hardness concentrations investigated is shown as a shaded area in Figure 1.

EXPERIMENTAL

The properties of the LAS and the nonionic surfactant used in this study are shown in Table I.

We measured the detergency of two series of solutions. In one series, LAS was the sole surfactant; these are referred to as the all LAS solutions. In the other series, the surfactant was a 4:1 molar mixture of LAS and a nonionic surfactant (Alfonic® 1214-60). For both series, the hardness levels were 50, 150 and 250 ppm Ca as CaCO_3 . For microscopic examination of the precipitate, a solution containing a 4:1 molar ratio of LAS to nonionic surfactant with a hardness level of 1000 ppm Ca as CaCO_3 was prepared.

The presence of micelles was detected by using a 1×10^{-4} M solution of pinacyanol chloride (Eastman Kodak).

Detergency measurements were conducted using the method outlined in Table II.

We took photographs of the precipitate particles through an orthoplanar Leitz microscope equipped with a Polaroid camera back and a polarizing light attachment. Magnification was 520X for all photographs.

The concentration of LAS was measured by colorimetric determination of the LAS/methylene blue complex (2) using a spectrophotometer (Hewlett Packard, model 8451A). The intensity of complexes of the experimental solutions at

¹ Presented at the AOCS meeting in Philadelphia, May 1985.

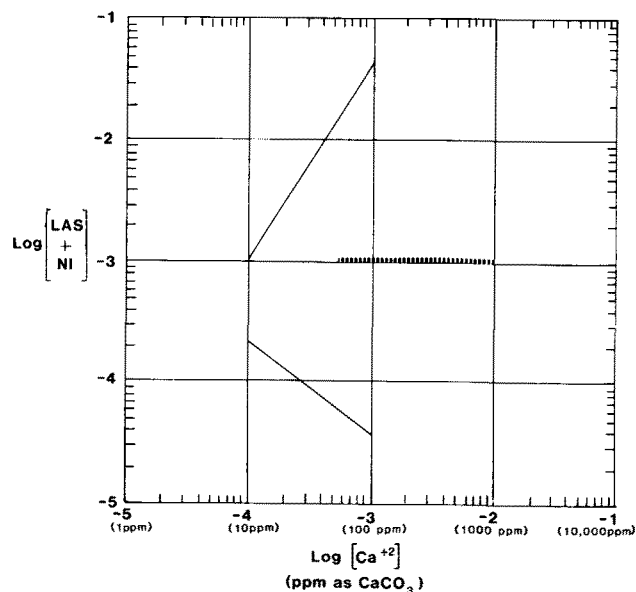


FIG. 1. Precipitation boundary for LAS and Alfonic® 1214-60 alcohol ethoxylate. The shaded area corresponds to the region examined in the paper.

TABLE I

Properties of Surfactants

Surfactant	Average molecular weight	Moles of EO
LAS (commercial dodecylbenzene sulfonate)	366	
Alfonic® 1214-60	456	6.7

TABLE II

Detergency Testing Conditions

Testing apparatus	Terg-O-Tometer
Wash cycle	10 min
Rinse cycle	5 min
Wash temperature	74 F
Water hardness	Ca ²⁺ only (as ppm CaCO ₃)
Number of soiled cloths	9
Soil	Sebum ^a
Cloth	Cotton, ^b Perm. Press ^c
Formulation use level	0.04%
Test procedure	Conoco CRS Lab Method 303-74 ^d

^aSpangler sebum (10).

^bTest Fabrics S/419.

^c65% Dacron/35% cotton with a permanent press finish (Test Fabrics S/7406).

^dSimilar to ASTM Standards, Part 30, 465-466 (1977).



FIG. 2. From left to right, solutions of LAS at 250 ppm, 150 ppm and 50 ppm hardness and LAS/Alfonic® 1214-60 alcohol ethoxylate at 250 ppm, 150 ppm and 50 ppm hardness.

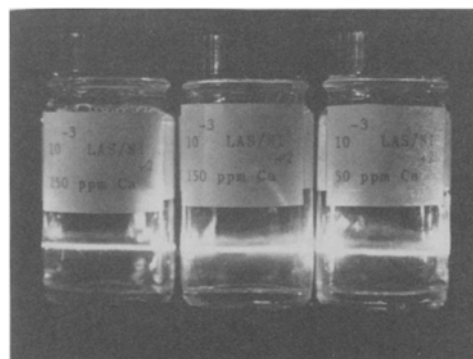


FIG. 3. Scattering of laser beam by solutions of LAS/Alfonic® 1214-60 alcohol ethoxylate containing 250 ppm, 150 ppm and 50 ppm hardness.

TABLE III

Active Content of Solutions of Various Hardness

Active type	Hardness (ppm)	Active (ppm)
LAS	50	170
LAS	150	23
LAS	250	20
LAS/nonionic	50	178
LAS/nonionic	150	173
LAS/nonionic	250	177

652 nm was compared to a standard reference curve.

The all-LAS solutions were centrifuged prior to determination of LAS concentrations.

RESULTS AND DISCUSSION

A photograph of the six solutions from the two series used in the detergency measurements is shown in Figure 2. The all-LAS solutions showed obvious precipitation of Ca(LAS)₂. Mixtures of LAS with nonionic surfactant at the same hardness levels appear to be clear. However, when a helium neon laser beam is passed through these solutions (632 nm), scattering of the beam is clearly evident, indicating the presence of small particles (Fig. 3).

The concentration of LAS with increasing hardness showed different trends for the all-LAS solutions on the one hand and for the LAS/nonionic surfactant mixture on the other. Thus, analysis of the centrifuged supernatant of the all-LAS solutions showed decreasing concentrations of surfactant with increasing hardness; in LAS/nonionic surfactant solutions, the surfactant level remained nearly constant with increasing hardness. These results are shown in Table III.

The precipitation of LAS from solution with increasing hardness also was reflected in the absence of micelles from certain solutions. Micelle detection with pinacyanol chloride dye depends on a color change from pink to blue when micelles are present (3). The all-LAS solution was blue at 50 ppm hardness, but pink at 150 and 250 ppm, indicating sufficient loss of monomer from these solutions to be below the cmc. LAS/nonionic surfactant solutions were blue at all hardness levels, indicating all were above the cmc.

Detergency data for cotton cloth soiled with sebum are shown in Figure 4. As expected, the highest detergency values were found for the solutions without hardness. For the solutions that contained hardness, the detergency of the

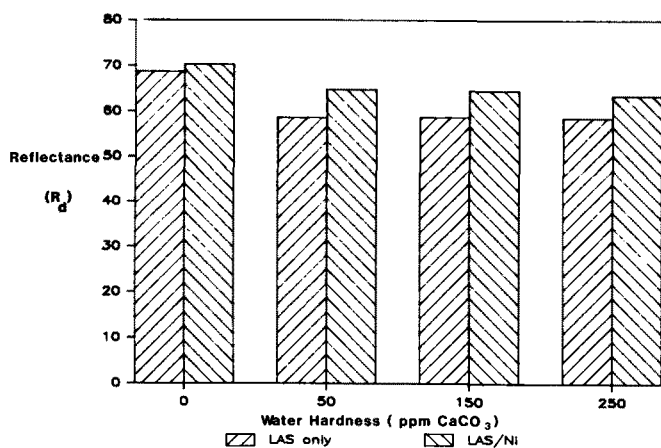
Ca(LAS)₂ AND DETERGENCY

FIG. 4. Detergency of solutions for sebum soiled cotton at 74 F.

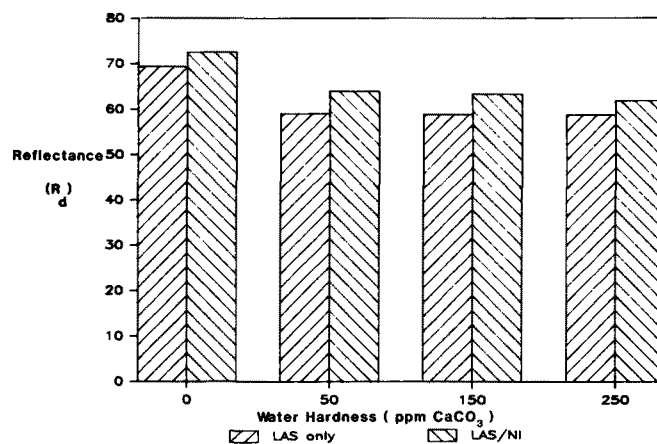
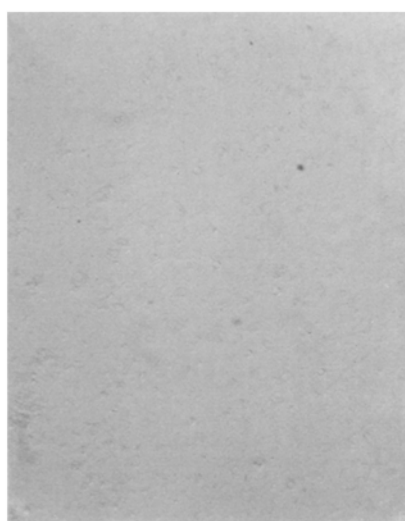
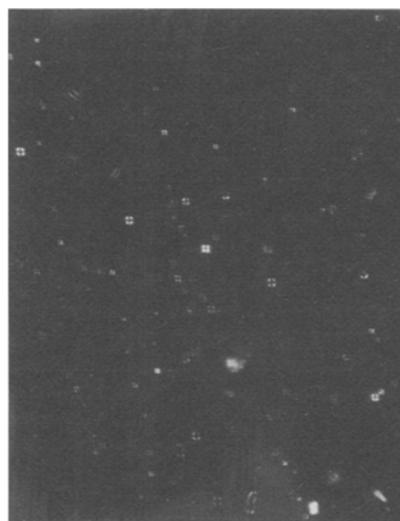


FIG. 5. Detergency of solutions for sebum soiled permanent press at 74 F.



520X



520X

FIG. 6. Photomicrograph of LAS/alcohol ethoxylate containing 1000 ppm Ca as CaCO₃. Photo on the left is with an ordinary light source. The photo on the right is with a plane polarized light source, 520X.

LAS/nonionic surfactant solutions was higher than the LAS only solutions.

Detergency data for permanent press cloth soiled with sebum are shown in Figure 5. The sequence of detergency results is similar to that found with cotton cloth. The decrease in the detergency of the all-LAS solutions with increasing hardness is not surprising, because the concentration of LAS in these solutions is reduced as a result of precipitation.

Precipitate also was present in the LAS/nonionic surfactant mixtures as evidenced by the scattering of the laser beam, yet the LAS/nonionic surfactant solutions suffered a relatively small loss of detergency as the hardness level increased. The focus of this paper is to investigate the role Ca(LAS)₂ precipitate may play in the detergency of LAS/nonionic surfactant solutions.

To investigate the properties of the precipitate in the LAS/nonionic surfactant mixtures, the hardness level was increased to 1000 ppm Ca as CaCO₃. The resulting solution was hazy but did not separate into a clear supernatant and a solid white precipitate phase on standing. This is in contrast to the precipitate formed in the all-LAS solutions. In these solutions, the precipitate readily settles out of solution.

As seen through the microscope, the precipitate formed in the LAS/nonionic surfactant solution containing 1000

ppm hardness consisted of spherical entities about 2 μ in diameter. Viewed through the crossed polarizers of the microscope, these spherical precipitate particles showed a Maltese cross pattern characteristic of a liquid crystal (Fig. 6). The presence of the nonionic surfactant in the mixture was not responsible for the precipitate being a liquid crystal, however, as precipitate from the all-LAS solution also exhibited Maltese cross patterns, as seen in Figure 7.

The effect of a nonionic surfactant on the form of the precipitate is seen by comparing Figure 6 with Figure 7. In the presence of a nonionic surfactant, the precipitate is kept in a suspension of finely divided particles (Fig. 6). Without a nonionic surfactant, the precipitate clumps together into large particles that readily settle out of solution (Fig. 7). A number of mechanisms by which polyethoxylates suspend solids in aqueous solutions have been proposed (4-6). We believe nonionic surfactants suspend Ca(LAS)₂ precipitate particles by similar mechanisms.

All of the mechanisms explain the stabilization of solid particles by the presence of an adsorbed layer on the solid. Adsorption of a nonionic surfactant on the precipitate could decrease the Hamaker constant and so decrease van der Waals attraction between particles (6,7). A bias against coagulation also may arise from a loss of configura-

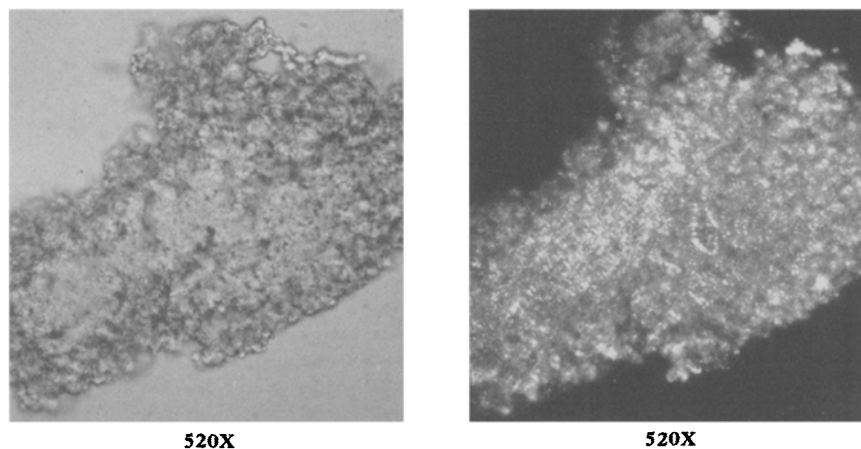


FIG. 7. Photomicrograph of $\text{Ca}(\text{LAS})_2$ precipitate. Photo on the left is with an ordinary light source. Photo on the right is with a plane polarized light source, 520X.

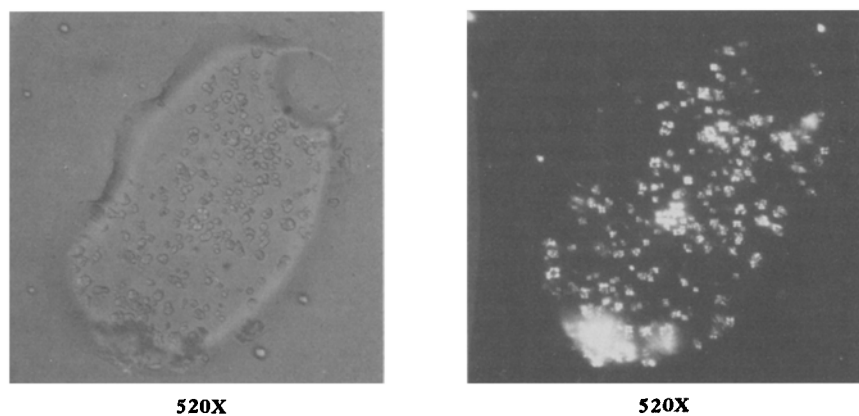


FIG. 8. Photomicrograph of a mineral oil droplet in an LAS/alcohol ethoxylate solution containing $\text{Ca}(\text{LAS})_2$ precipitate. Photo on the left is with an ordinary light source. Photo on the right is with a plane polarized light source, 520X.

tional entropy that occurs as the particle's adsorbed layers interpenetrate when the particles approach one another (8). Finally, the solvent is expected to interact with the adsorbed nonionic surfactant and stabilize particles against coagulation (9). The quantitative contribution of each of these mechanisms to the stability of the $\text{Ca}(\text{LAS})_2$ suspension is not known, but qualitatively, each is expected to contribute to the stability of the suspension. The physical manifestation of the stabilization of the suspension is the hazy appearance of the solutions when precipitation occurs in the presence of a nonionic surfactant.

In the suspended form, the precipitate can solubilize mineral oil. This was demonstrated by adding a sample of the hazy LAS/nonionic surfactant solution containing 1000 ppm hardness to a test tube. To another test tube we added a sample of the LAS/nonionic surfactant solution without hardness. This solution was clear. A few drops of mineral oil containing a red dye was floated on top of both solutions. After a few hours the hazy solution was a uniform red color, indicating the dye had been carried into the aqueous phase, presumably by the suspended precipitate. The solution without hardness remained clear.

The surface active property of the precipitate was also evident when a drop of mineral oil was added to the LAS/nonionic surfactant solution containing 1000 ppm Ca. In Figure 8 the drop of mineral oil is seen to be covered by the $2\ \mu$ size precipitate particles. When viewed through the crossed polarizers, the mineral oil droplet is visible because of the clustering of precipitate particles on its surface, which again show the Maltese cross pattern typical of a

liquid crystal.

Because of their finely divided form and surface active property, $\text{Ca}(\text{LAS})_2$ particles formed in the presence of a nonionic surfactant may be able to contribute to the detergency of solutions. When the $\text{Ca}(\text{LAS})_2$ particles clump together as in the absence of a nonionic surfactant, the precipitate probably is still surface active but the efficacy with which the large clumps can interact with the soil is likely to be reduced. As a result, the precipitate's contribution to the detergency is likely to be lost in solutions which do not contain a dispersing agent such as a nonionic surfactant.

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