

FIG. 10. Detergency performance of C<sub>13</sub> ave. LAS in 15% LAS/25% STPP/10% silicate/35% Na<sub>2</sub>SO<sub>4</sub>, 100 F, .15% conc., sebum on cotton.

about 100 ppm hardness, the performance drop-off which starts at about 135 ppm Ca<sup>+2</sup> hardness does coincide with about 32 ppm residual [Ca<sup>+2</sup>].

These data confirm the widely held belief that at under-use concentrations, the detergency performance can suffer. The reduced level of surfactant plays a minor role. The major effect is an increase in residual Ca<sup>+2</sup> resulting from a

decrease in builder level. This could now put the initial [LAS<sup>-</sup>] and [Ca<sup>+2</sup>] concentrations beyond the line of stoichiometric equivalence where [Ca<sup>+2</sup>] ion is in excess and the loss of surfactant by precipitation is much greater. The Ca<sup>+2</sup>/LAS precipitation boundary diagrams provide a systematic way to study and evaluate the interactions of Ca<sup>+2</sup> and LAS. Although the diagrams are based on experimental observations after the Ca<sup>+2</sup>/LAS system has reached equilibrium conditions, some conclusions can be drawn which apply to detergency performance during the ten-minute wash time scale. In the following two papers, we will discuss how certain additives can moderate the Ca<sup>+2</sup>/LAS interaction to alleviate the deleterious effect of precipitation.

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## Interactions Between Linear Alkylbenzene Sulfonates and Water Hardness Ions. II. Reducing Hardness Sensitivity by the Addition of Micelle Promotion Agents<sup>1</sup>

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#### ABSTRACT

Agents which promote micellization of linear alkylbenzene sulfonates (LAS) improve LAS hard-water detergency performance by reducing water hardness sensitivity. A model is proposed which correlates micellization and water hardness tolerance. The ability of inorganic salts and cosurfactants to act as micelle promotion agents is discussed.

#### INTRODUCTION

As discussed in paper I (1), linear alkylbenzene sulfonates (LAS) interact with free calcium ions to form insoluble Ca(LAS)<sub>2</sub>. Formation of these complexes reduces the concentration of surfactant available for detergency. Several methods are available for minimizing the effect of this interaction. The most common involves the use of builders to reduce the concentration of water hardness ions. Another is to add more surfactant to make up for the amount lost in the formation of insoluble complexes. A third method, which is the subject of this paper, involves the use of micelle promotion agents to reduce the extent of interaction by effectively lowering the concentrations of both surfactant monomer and water hardness ions.

#### EXPERIMENTAL

##### Detergency Testing

Detergency tests were performed using the materials and procedures outlined in Table I. All tests were performed in duplicate. Performance was determined by measuring reflectance (in Rd units) of the washed cloths.

TABLE I

##### Detergency Test Materials and Procedures

Testing apparatus	Terg-O-Tometer
Wash cycle	10 min
Rinse cycle	5 min
Wash temperature	100 F (38 C)
No. soiled cloths	6 (3 cotton, 3 p.press)
No. unsoiled cloths	3 (cotton)
Soil	Sebum
Cotton cloth	Test Fabrics S/419
P.Press cloth	Test Fabrics S/7406 (65% Dacron/35% Cotton)
Formulation use level	0.15%
Test procedure	Vista CRS 303-74 <sup>a</sup>
Reflectance measuring device	Gardner (Model XL20) Colorimeter

<sup>1</sup> Presented at the AOCS meeting in Philadelphia, May 1985.

<sup>a</sup> Similar to ASTM Standards, Part 30, 465-466 (1977).

## MICELLE PROMOTION AGENTS

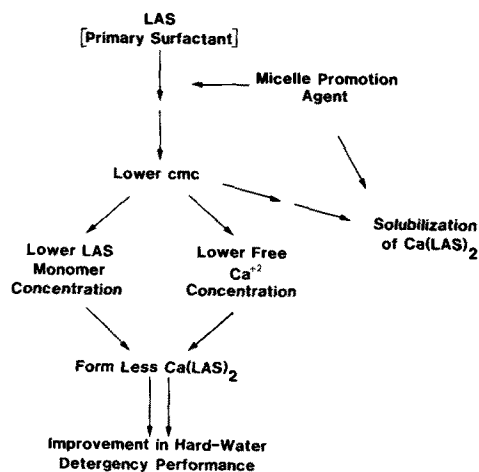


FIG. 1. Proposed model correlating micellization and hard-water detergency performance.

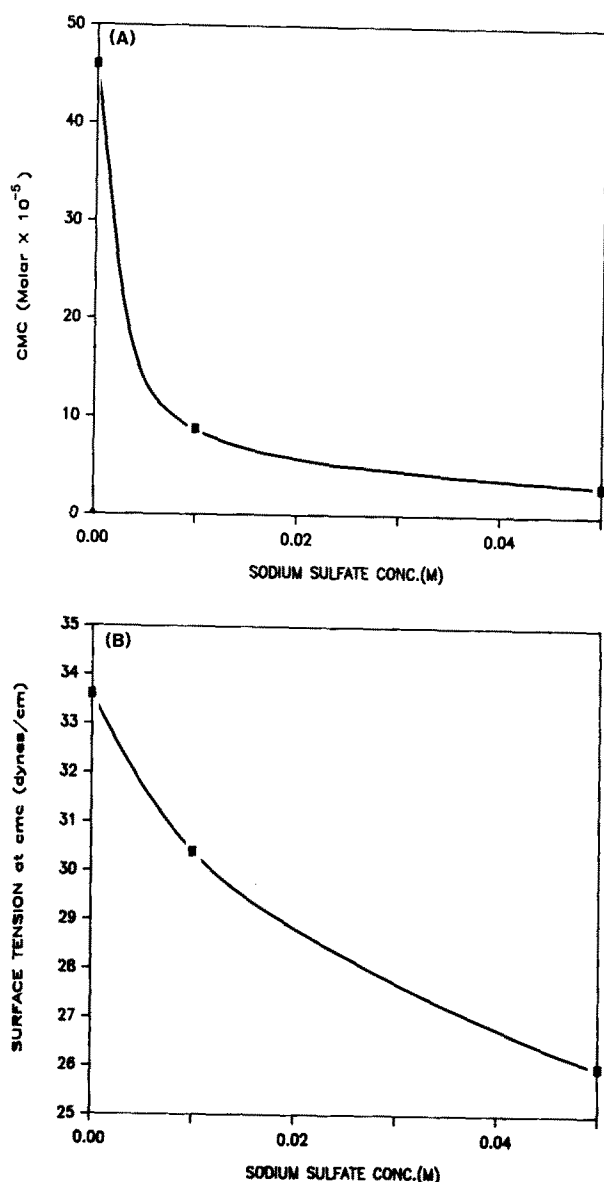


FIG. 2. Critical micelle concentration (A) and surface tension (B) of tridecyl LAS as a function of sodium sulfate concentration.

## cmc Measurements

Critical micelle concentration and surface tension measurements (Gibbs' Plots) were obtained using a Spinning Drop Tensiometer (University of Texas, Model 300). Measurements were made at 100 F (38 C) with 0 ppm water hardness. Unless otherwise stated, all test solutions contained 0.01 M  $\text{Na}_2\text{SO}_4$  to buffer ionic strength.

## Precipitation Boundary Diagrams

Precipitation boundary diagrams were obtained as described earlier (1).

## Surfactants

Surfactants used in these studies are listed below.

Surfactant	Composition
$\text{C}_{13}$ -LAS	Tridecyl LAS - Avg Mol Wt = 363
1214-70 NI	55% $\text{C}_{12}$ /45% $\text{C}_{14}$ linear alcohol with 70% (10.6 moles) ethylene oxide

## RESULTS AND DISCUSSION

Any agent which promotes micelle formation improves the hard-water detergency performance of LAS by the mechanism shown in Figure 1. Lowering critical micelle concentration (cmc) performs two functions. LAS monomer concentration is reduced due to incorporation of surfactant into micelles. The concentration of free hardness ions is also reduced through counterion binding of the cations with micellar surfaces. Effectively, micelles act as a sink for both surfactant and water hardness ions. Less surfactant is lost due to formation of insoluble  $\text{Ca}(\text{LAS})_2$  and  $\text{Mg}(\text{LAS})_2$  because less surfactant monomer and water hardness ions are available to interact. This results in an improvement in hard-water detergency.

As discussed below, some micelle promotion agents also help solubilize  $\text{Ca}/\text{Mg}(\text{LAS})_2$ , either through a micellar process or by interacting with the insoluble material directly.

There are two main types of micelle promotion agents, salts and cosurfactants. Examples of each are discussed below.

## Salts as Micelle Promotion Agents

Increasing ionic strength is one method of lowering the cmc of LAS. As shown in Figure 2, the addition of sodium sulfate lowers both cmc and surface tension of  $\text{C}_{13}$ -LAS. These effects result from a decrease in the repulsion of head groups in the micelle and by a reduction in surfactant solubility (2). The reduction in cmc also accounts for the decrease in hardness sensitivity observed with the addition of sodium sulfate in the precipitation boundary diagrams of the previous paper. Lowering cmc and surface tension also improve detergency performance, as shown in Figure 3.

Although increasing ionic strength is effective in lowering cmc, it is often impractical to add salts to a detergent because of restrictions on the formulation itself. In addition, most detergent powders already contain the equivalent of 0.01 M  $\text{Na}_2\text{SO}_4$  in ionic strength. Consequently, the addition of salts to improve hardness tolerance is best applied to nonbuilt laundry liquids.

## Cosurfactants as Micelle Promotion Agents

The addition of surfactants also can be effective in improving the hard-water performance of LAS. However, in comparison to increasing ionic strength, the effect of adding a

cosurfactant is complicated by interactions which can occur between the cosurfactant itself and other species in solution. For example, Figures 4-6 show the effectiveness of adding a nonionic (NI) surfactant with a high ethylene oxide (EO) content. As shown, the addition of 1214-70 ( $C_{12}$  alcohol w/70% EO) nonionic surfactant significantly reduces cmc, increases hard-water tolerance and improves hard-water detergency. In contrast, nonionic surfactants with a low EO content are ineffective, and can even be detrimental to detergency performance (3). These trends are the result of two sets of interactions:

1. LAS and nonionic surfactants interact to produce the nonlinear decrease in cmc observed when NI is substituted for LAS (Fig. 4). It is this interaction that produces a sub-

stantial reduction in cmc with only a small amount of nonionic surfactant.

2. A greater EO content increases the ability of the surfactant to interact with (and solubilize)  $Ca/Mg(LAS)_2$ . Other studies suggest that this effect is the result of either an adsorption/dispersion mechanism (4) or due to a direct interaction between the metal complexes and the EO chain (5).

Although nonionic surfactants containing a high EO content are not normally recommended for detergency applications, keep in mind that the purpose of the cosurfactant is to lower cmc and promote the interactions discussed above. The addition of cosurfactants to improve hard-water performance is much more versatile than simply

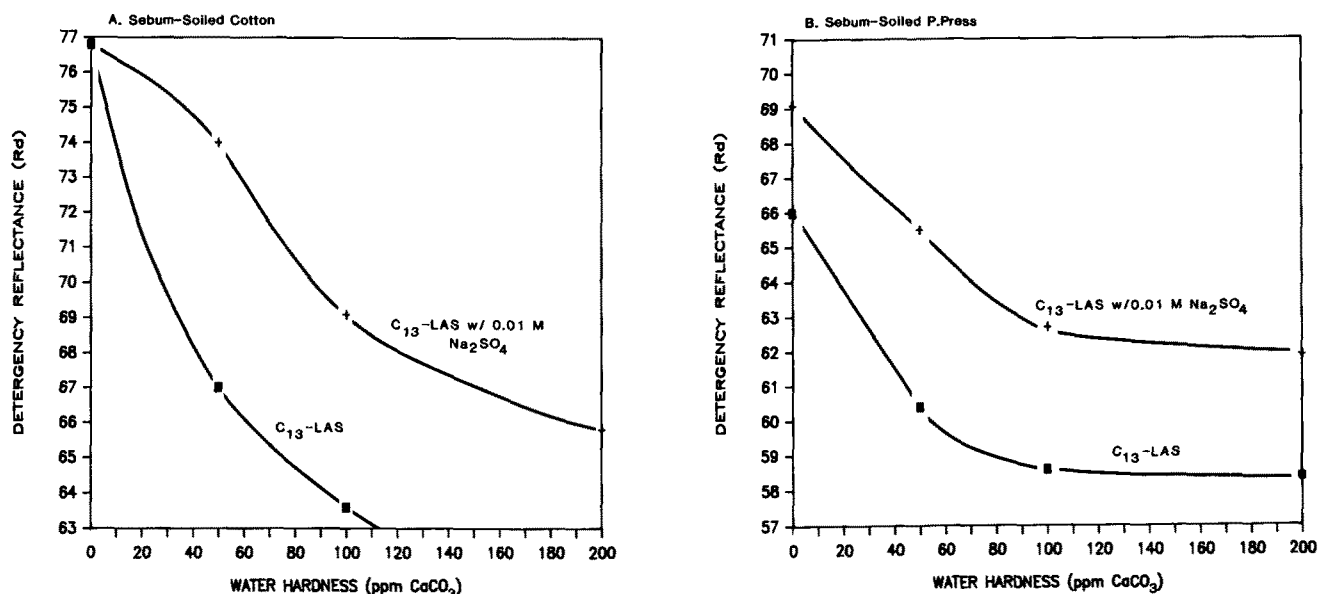


FIG. 3. Detergency performance of tridecyl LAS with 0.00, 0.01 and 0.05 M  $Na_2SO_4$  as a function of water hardness (4:1  $Ca^{2+}/Mg^{2+}$ ) on sebum-soiled cotton (A) and sebum-soiled p.press (B) cloths. Test formulations contained 15% LAS and 10% soluble silicate (to buffer pH).

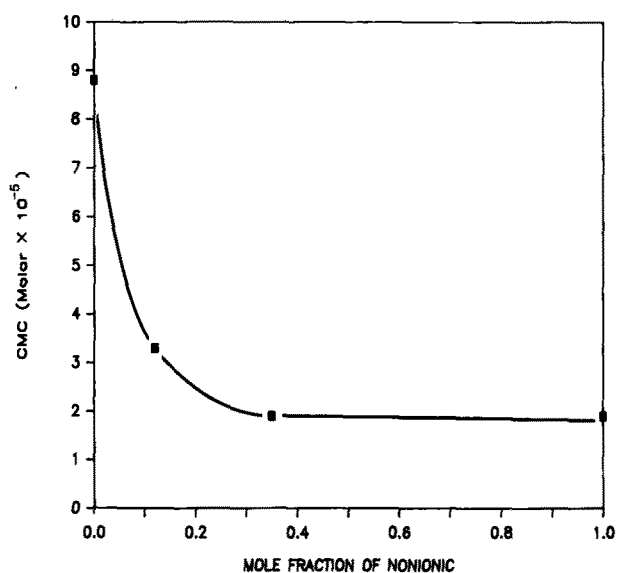


FIG. 4. Critical micelle concentration versus mole fraction of nonionic in LAS/NI solution using tridecyl LAS and 1214-70 nonionic surfactants (at 100 F with 0.01 M  $Na_2SO_4$ ).

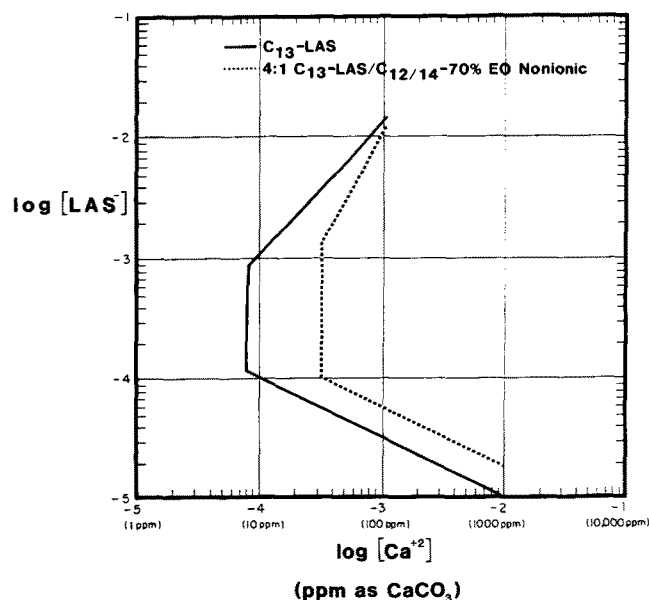


FIG. 5. Precipitation boundary diagrams comparing the  $Ca^{2+}$ -tolerance of tridecyl LAS and a 4:1 blend of tridecyl LAS and 1214-70 nonionic surfactants.

## MICELLE PROMOTION AGENTS

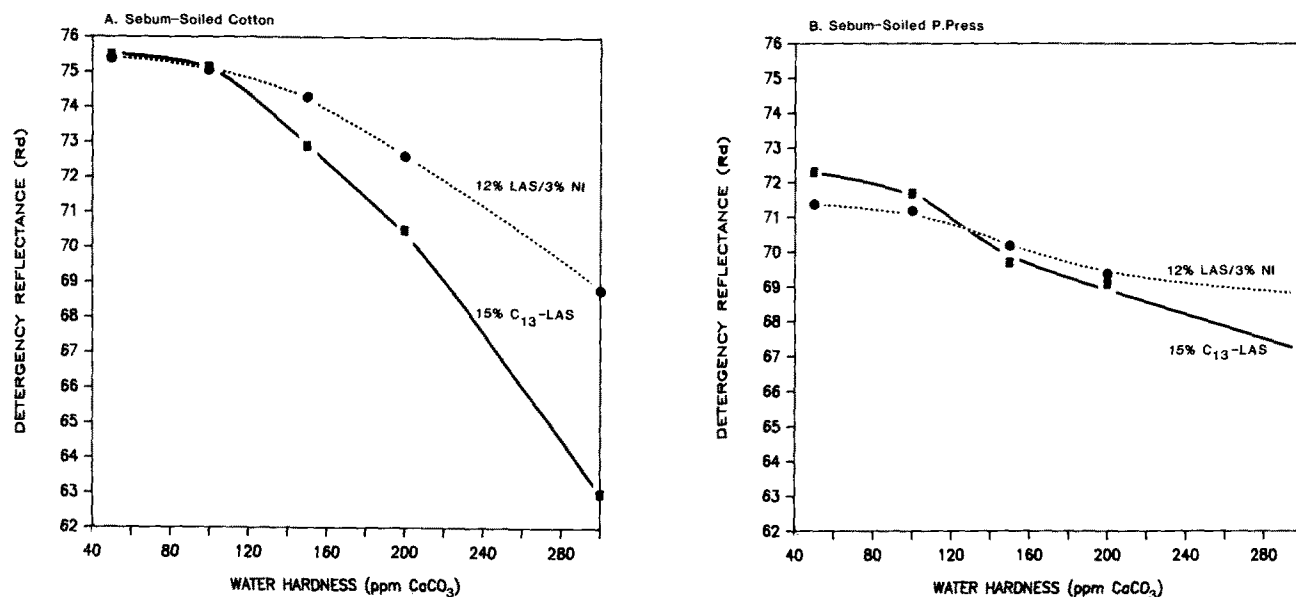


FIG. 6. Detergency performance of 15% LAS and 12% LAS/3% NI as a function of water hardness ( $\text{Ca}^{2+}$  only) on sebum soiled cotton (A) and sebum-soiled p.press (B) cloths using tridecyl LAS and 1214-70 NI surfactants. All test formulations contained 35% sodium sulfate, 25% sodium tripolyphosphate 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 $\text{Ca}(\text{LAS})_2$ <sup>1</sup>

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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.

<sup>1</sup> Presented at the AOCS meeting in Philadelphia, May 1985.

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  $\text{CaCO}_3$ . 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  $\text{CaCO}_3$  was prepared.

The presence of micelles was detected by using a  $1 \times 10^{-4}$  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