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SURFACTANTS AND DETERGENTS TECHNICAL

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Technical

♣Interactions Between LAS and Nonionic Surfactants[1]

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ABSTRACT

Physicochemical interactions between linear alkylbenzene sulfonate (LAS) and various linear alcohol nonionics (NI) have been investigated. The effect of adding nonionic to LAS on critical micelle concentration (cmc), surface tension, water hardness sensitivity and detergency performance depends on both hydrophobe and hydrophile structure. The addition of low levels of a lauryl range-high EO nonionic surfactant significantly lowers cmc and causes the formation of micelles containing predominantly nonionic molecules. These mixed micelles improve hard water performance by acting as a sink for LAS and free calcium. Nonionic surfactant enhances LAS hard water performance by preventing the loss of LAS via $Ca(LAS)_2$ precipitation, not by its own soil removal capabilities. Nonionic surfactant acts as a micelle promotion agent, while LAS remains responsible for surface and interfacial properties.

INTRODUCTION

Linear Alkylbenzene Sulfonate (LAS) is the most commonly used surfactant active for laundry powders throughout the world. In comparison with other actives, LAS offers superior processability and cost/performance (1). However, in underbuilt products, or at less than recommended use levels, LAS performance is diminished in the presence of high levels of water hardness ions.

Nonionic (NI) surfactants are more difficult to process and generally are more expensive, but the fact that they are less sensitive to water hardness makes them attractive as potential additives to LAS systems.

This study examined the effects on detergency, water hardness sensitivity and surfactant properties of adding nonionic surfactant to LAS. The purpose of this work was to investigate the interaction between LAS and nonionic surfactants, and to determine how this interaction affects performance, especially detergency performance at high water hardness conditions. Results show that LAS hard water detergency is improved through the addition of low levels of a high EO nonionic surfactant. Detergency improvement appears to be the result of several factors associated with LAS/NI surfactant interactions, including reduced CMC, lower monomer concentration, reduced free calcium concentration, and $Ca(LAS)_2$ solubilization.

EXPERIMENTAL

Detergency Testing

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

Detergent formulations consisted of 15% surfactant, 25% sodium tripolyphosphate (STPP), 10% soluble silicate and 35% sodium sulfate. Formulations were tested using typical U.S. wash conditions (Table I). To simplify the correlation of performance test results with physical property measurements, water hardness consisted of Ca^{+2} only (no Mg^{+2}).

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[1] Presented at the AOCS meeting in May 1984 in Dallas, Texas.

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)
Water hardness	Ca^{+2} only (as ppm $CaCO_3$)
Number of soiled cloths (3 by 4½ inch)	6 (3 cotton and 3 perma press)
Number of unsoiled cloths (as ballast)	3 (cotton)
Soil	Sebum[a]
Cloth	Cotton,[b] permanent press[c]
Formulation use level	0.15%
Test procedures	Conoco CRS Lab Method 303-74[d]
Reflectance measuring device	Gardner (Model XL20) Colorimeter

[a] Spangler sebum (6).

[b] Test Fabrics S/419.

[c] 65% Dacron/35% cotton with a permanent press finish (Test Fabrics S/7406).

[d] Similar to ASTM Standards, Part 30, 465-466 (1977).

TABLE II

Surfactants Used in Study

LAS

Dodecylbenzene sulfonate-commercial C_{12} (average) LAS (low 2-phenyl isomer type)

Nonionics	Alcohol[a] blend	% EO	Moles EO
810-40	42% C_8/58% C_{10}	40	2.2
810-60	42% C_8/58% C_{10}	60	5
1214-40	55% C_{12}/45% C_{14}	40	3
1214-60	55% C_{12}/45% C_{14}	60	6.7
1214-70	55% C_{12}/45% C_{14}	70	10.6
1214-80	55% C_{12}/45% C_{14}	80	18
1618-40	59% C_{16}/41% C_{18}	40	3.8
1618-60	59% C_{16}/41% C_{18}	60	8.6
1618-70	59% C_{16}/41% C_{18}	70	13.4
1618-80	59% C_{16}/41% C_{18}	80	23

[a] Linear primary carbon chain.

Calcium Precipitation Titrations

Calcium titrations were performed to determine the concentration of calcium required to cloud solutions of detergent formulations. Test solutions were prepared by diluting each detergent formulation (nonbuilt) to a 0.15% use level. Each solution contained 0.01 M Na_2SO_4 to provide the same level of ionic strength observed in the wash liquors of typical laundry powders. The pH of each solution was adjusted to approximately 9 with NaOH. Solutions were equilibrated in a 100 ± 1 F water bath prior to titration. Aliquots (0.2 ml) of 0.05 M $CaCl_2$ were added to each solution. Solutions then were mixed and placed back in a water bath. After 10 min, each solution was checked for turbidity using a helium-neon laser (Septra Physics, Model 155) as a detection aid. This titration procedure was repeated on each solution until turbidity was detected. All tests were performed in duplicate.

For solutions having low calcium sensitivity, aliquots of 0.25 M $CaCl_2$ were added in order to keep the total volume of calcium solution added to a minimum.

Calcium sensitivity was calculated as follows:

$$\text{Calcium sensitivity} = \frac{X \cdot V_X}{V + V_X}$$

where X = concentration of calcium solution (in ppm as $CaCO_3$); V_X = minimum volume of calcium solution required to cloud solution, and V = initial volume of solution (100 ml).

CMC Measurements

Critical Micelle Concentration (cmc) measurements were obtained using a Spinning Drop Tensiometer (Univerity of Texas, Model 300). Measurements were made at 100 F (38 C) and 0 ppm water hardness. Test solutions contained 0.01 M Na_2SO_4 to approximate the ionic strength of a typical laundry powder.

Surfactants

The surfactants employed in this study are listed in Table II.

RESULTS AND DISCUSSION

Detergency Studies

Detergency tests were performed on 15% LAS and several 12% LAS/3% nonionic formulations. Nonionics varying in carbon-chain length and ethylene oxide (EO) content were used.

Figure 1 compares the detergency performance (reflectance) of LAS versus LAS/NI blends as a function of water hardness (Ca^{+2}). Each nonionic surfactant tested contained a different alcohol carbon-chain length with 60% EO. As shown, detergency performance of all formulations decreases significantly with increasing water hardness. On sebum-soiled permanent press cloth (Fig. 1A), the all-LAS

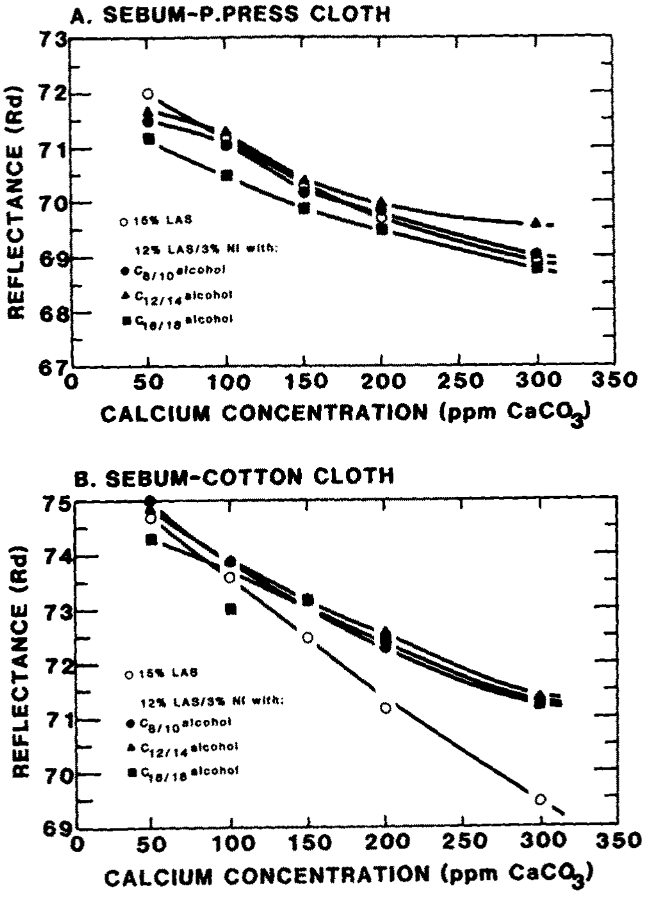


FIG. 1. Detergency performance of LAS versus LAS/NI blends (containing nonionics varying in carbon-chain length with 60% EO) as a function of water hardness (Ca^{+2}). Test conditions—100 F, 0.15% use level. Formulations contained dodecyl LAS, 25% STPP, 10% silicate and 35% sodium sulfate.

formulation gives the best performance at 50 ppm hardness. Between 100 and 200 ppm, the all-LAS formulation and the LAS/NI formulations containing 1214-60 and 810-60 nonionics are statistically equal. At 300 ppm, the LAS/NI blend containing 1214-60 NI shows superior performance. The LAS/1618-60 NI combination shows the poorest performance at all hardness levels.

On sebum soiled cotton cloth (Fig. 1B), the addition of NI to LAS clearly improves performance at higher water hardness levels. An LAS/NI blend containing 1214-60 and 810-60 nonionics gives the best overall performance. The LAS/NI blend containing 1618-60 NI also performs well at water hardness levels above 100 ppm, but under low free hardness conditions (at a 0.15% use level, 25% phosphate sequesters approximately 100 ppm Ca^{+2}), its performance drops below that of the all-LAS formulation.

Overall, detergency results from the above studies indicate that a $C_{12/14}$ hydrophobe is the optimum for the nonionic chain length in an LAS/NI blend.

The effect of ethylene oxide content on LAS/NI detergency is shown in Figure 2. As shown, LAS is compared to several LAS/NI blends containing $C_{12/14}$ nonionics with 40, 60, 70 and 80% EO. On sebum-soiled permanent press, the LAS formulation is best at water hardness levels up to 150 ppm. At 200 and 300 ppm, LAS/NI blends containing nonionics with 60, 70 and 80% EO are superior. Although the LAS/1214-80 NI formulation performs well at 200 and 300 ppm, its detergency at 50 and 100 ppm is poorer than the all-LAS formulation. Performance of the LAS/1214-40 NI formulation is poorer than LAS alone at all hardness levels above 50 ppm.

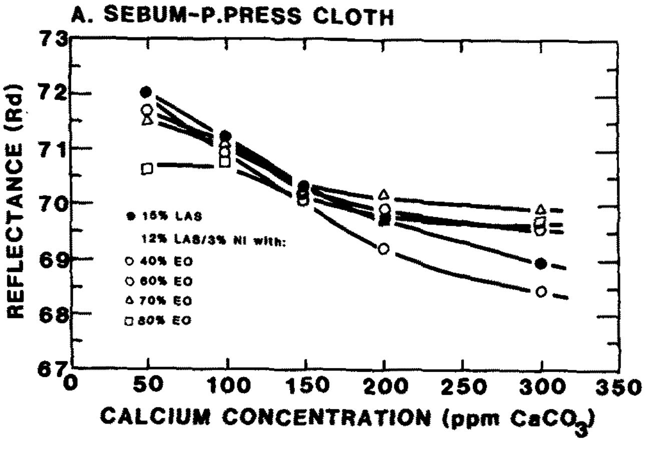
On sebum-soiled cotton (Fig. 2B), LAS/NI blends containing nonionic surfactants with 60, 70 and 80% EO clearly give better detergency in comparison to LAS at hardnesses above 50 ppm. Overall, nonionics with 70% or 80% EO are best. Again, the LAS/NI formulation containing 1214-40 NI shows the poorest performance.

Based upon these detergency data, optimum detergency is obtained with an LAS/NI blend where the nonionic consists of a lauryl-range alcohol blend with 70% EO.

Once the identity of the optimum nonionic cosurfactant was determined, additional tests were performed to ascertain the optimum LAS/NI ratio. Detergency as a function of LAS/NI ratio is shown in Figure 3. On sebum-soiled permanent press (Fig. 3A), LAS as the sole surfactant gives better detergency performance than does 1214-70 NI at all three hardness levels. At 50 ppm, performance actually is reduced by adding nonionic to LAS. At 150 and 250 ppm, blends of the two surfactants appear to give a synergistic effect. The magnitude of this synergism increases with increasing water hardness.

On sebum-soiled cotton (Fig. 3B), little difference is seen among formulations at 50 or 150 ppm. At very high water hardness levels, the addition of nonionic enhances LAS performance.

The optimum LAS/NI ratio depends on water hardness. It also depend on builder type and use level, because these parameters ultimately determine the level of free hardness. Detergency results also show that the optimum LAS/NI blend depends on cloth type. On permanent press cloth (at high-water hardness), optimum detergency is obtained with a 13/2 or 12/3 LAS/NI formulation. On cotton cloth, little performance difference is seen except for very high water hardness conditions.



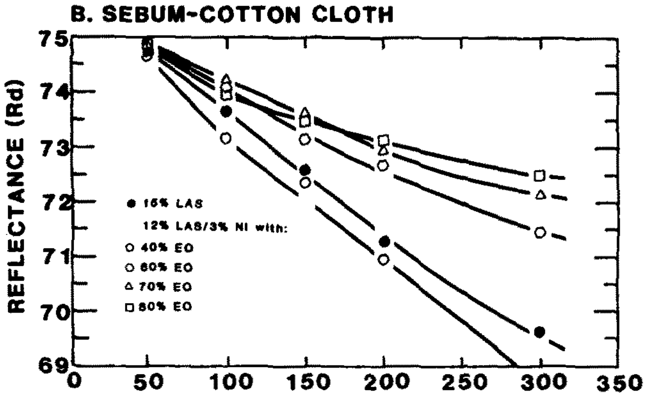
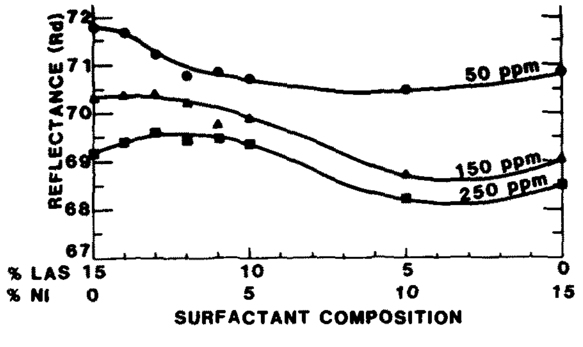


FIG. 2. Detergency performance of LAS versus LAS/NI blends (containing nonionics varying in ethylene oxide content having a constant $C_{12/14}$ carbon-chain length) as a function of water hardness (Ca^{+2}). Test conditions—100 F, 0.15% use level. Formulations contained dodecyl LAS, 25% STPP, 10% silicate and 35% sodium sulfate.



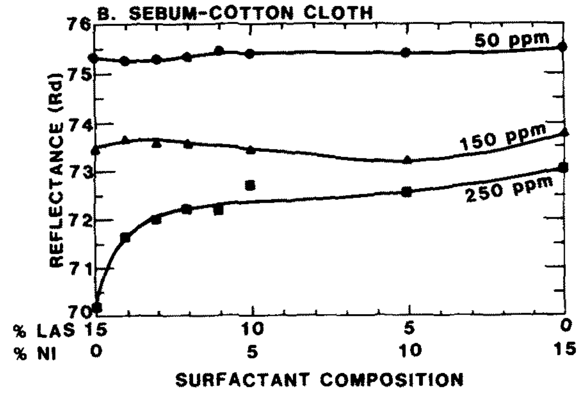


FIG. 3. Detergency performance as a function of LAS/NI ratio at 50, 150 and 250 ppm water hardness (Ca^{+2}). Test condtions—100 F, 0.15% use level. Formulations contained dodecyl LAS, 1214-70 nonionic, 25% STPP, 10% silicate and 35% sodium sulfate.

These detergency tests indicate LAS detergency performance is modified by the addition of nonionic surfactant. Whether performance is improved or diminished depends on the composition (carbon-chain length and EO content) of the nonionic and the water hardness level. Results show that the addition of nonionic surfactant can be beneficial (at high water hardness) or detrimental (at low water hardness). The effect of adding nonionic surfactant to LAS also would depend on other factors, such as LAS molecular weight, wash temperature and soil type.

Calcium Sensitivity

Detergency performance is inversely related to water hardness, as demonstrated in Figures 1, 2 and 3. This is the result of (i) interaction of hardness ions with soil and (ii) loss of surfactant (especially anionics) via formation of insoluble complexes with hardness ions. The improvement in LAS detergency observed at high water hardness with the addition of nonionic is likely related to a decrease in hardness sensitivity.

Experiments were performed to determine the relative hardness sensitivities of 12% LAS/3% NI mixtures as a function of nonionic carbon-chain length and EO content. Figure 4 shows the amount of free calcium required to cloud various LAS/NI blends (at a 0.15% use level) as a function of nonionic carbon chain length and EO content (moles). For example, a solution of 12% LAS/3% 1214-80 (at 0.15% with a 0.1 M Na_2SO_4) required more than 200 ppm calcium (as $CaCO_3$) to form insoluble $Ca(LAS)_2$. As shown, hardness sensitivity is reduced as EO content of the nonionic is increased. Nonionic carbon chain length appears to have little effect. Relative to LAS alone (55-ppm Ca^{+2} to cloud), LAS/NI blends containing 1214-70, 1214-80, 1618-60, 1618-70 and 1618-80 nonionics give decreased calcium sensitivity. In contrast, the addition of 810-40, 810-60, 1214-40 and 1618-40 nonionics increase hardness sensitivity. In the case of the 40% ethoxylate/LAS blends, the observed turbidity may in fact be ethoxylate (normally insoluble in water) coming out of solution due to a change in the solubilization properties of the micelle. These data correlate fairly well with detergency data, indicating that the addition of nonionic affects LAS detergency by modifying hardness sensitivity. The fact that detergency testing does not show 1618-80 NI to perform best (in an LAS/NI blend) suggests that an optimum in detergency exists which does not appear in the titration data indicating that other factors (surfactant solubility, fabric adsorption, etc.) may also be involved.

The effect of LAS/NI ratio on calcium sensitivity is shown in Figure 5. Hardness sensitivity decreases rapidly as nonionic is substituted for LAS. The nonlinear relationship between nonionic content (or LAS content) and calcium sensitivity would be expected based on the K_{sp} of $Ca(LAS)_2$.

$$K_{sp} = [Ca^{+2}][LAS^{-}]^2$$

The dotted line in Figure 5 shows how the calcium concentration required to precipitate $Ca(LAS)_2$ is affected by lowering LAS concentration. It is based on the apparent K_{sp} observed with the all-LAS formulation as total active level is decreased and assumes $Ca(LAS)_2$ behaves as a simple salt. The fact that the observed relationship between LAS/NI composition and hardness sensitivity differs greatly from the theoretical K_{sp} curve indicates that the LAS and nonionic surfactants themselves interact.

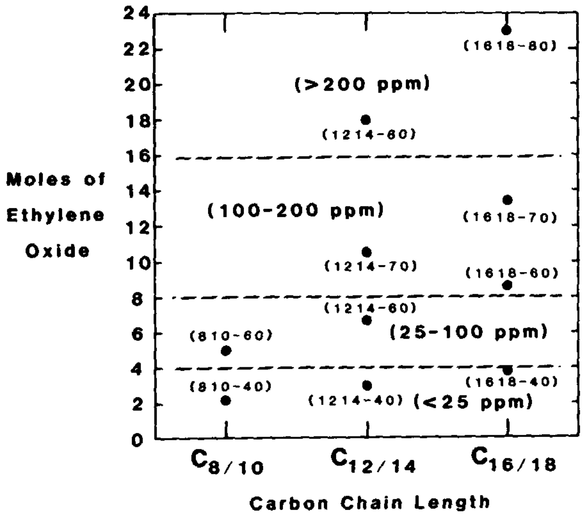


FIG. 4. Hardness sensitivity (concentration of calcium [ppm $CaCO_3$] required to cloud 12% LAS/3% NI solutions) as a function of nonionic carbon-chain length and ethylene oxide content. Test conditions—100 F, 0.15% use level, with dodecyl LAS. Test solutions also contained 0.1 M Na_2SO_4 to buffer ionic strength.

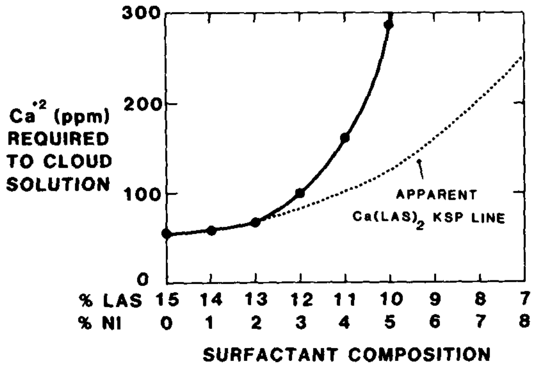


FIG. 5. Hardness sensitivity (concentration of calcium [ppm $CaCO_3$] required to cloud LAS/NI solutions) as a function of LAS/NI ratio. Test conditions—100 F, 0.15% use level, with dodecyl LAS and 1214-70 nonionic.

Surfactant Interaction

A decrease in LAS-hardness sensitivity beyond what would be expected based on $Ca(LAS)_2$ solubility alone suggests that a change in micellar properties has occurred. In order to examine what changes do occur, surface tension measurements were made as a function of concentration (Gibbs' Plots) to determine the critical micelle concentrations (cmc) of dodecyl LAS, 1214-70 NI and two LAS/NI blends. Figure 6 shows cmc as a function of mole fraction of nonionic in the LAS/NI solutions. As shown 1214-70 NI has a lower cmc than dodecyl LAS. Theoretically, if there is no LAS/NI interaction, the cmc's of LAS/NI blends would fall on a tie line (dotted line) between the pure surfactants themselves. However, LAS/NI blends give cmc values well below the theoretical tie line, indicating that the LAS and NI surfactants interact synergistically and form mixed micelles.

If the mixed micelle were ideal, the cmc values would fall on the dotted line predicted by the relationship:

$$\frac{1}{C_{12}^{M}} = \frac{\alpha}{C_{1}^{M}} + \frac{1-\alpha}{C_{2}^{M}}$$

where C_{12}^{M} = cmc for the mixed micelle system of Surfactant 1 and Surfactant 2; C_{1}^{M} = cmc of Surfactant 1; C_{2}^{M} = cmc of Surfactant 2, and α = Mole fraction of Surfactant 1.

However, the combination of LAS and nonionic shows considerable deviation from the ideal. Consequently, the

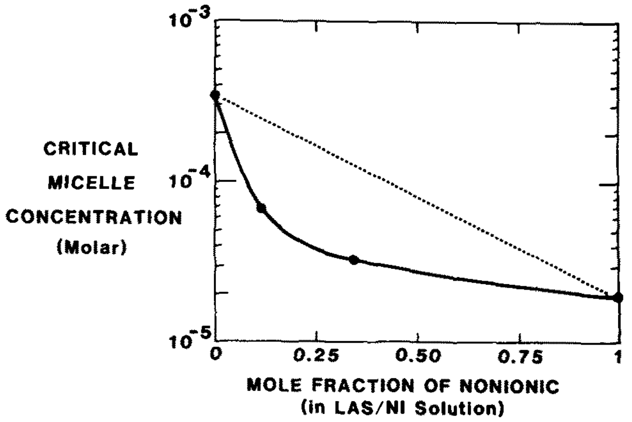


FIG. 6. Critical micelle concentration versus mole fraction of nonionic in LAS/NI solution, at 100 F using dodecyl LAS and 1214-70 nonionic.

data must be treated in the manner previously described by Rosen and Hua (2,3). Using their treatment, the actual micellar participation (in mole fraction) of each surfactant can be determined using the following equation:

$$\frac{(X_1^M)^2 \ \ln \dfrac{C_{12}^M \alpha}{C_1^M X_1^M}}{(1 - X_1^M)^2 \ \ln \dfrac{C_{12}^M (1 - \alpha)}{C_2^M (1 - X_1^M)}} = 1$$

where X_1^M = Mole fraction of Surfactant 1 in micelle.

This equation was solved iteratively for X_1^M using the experimentally determined cmc values for LAS (Surfactant 1), NI (Surfactant 2) and the 12% LAS/3% NI blend. The X_1^M value was calculated to be 0.41. This indicates that although the molar ratio of LAS to nonionic in the total system is greater than 8 to 1, the composition of the mixed micelle is closer to 1 to 1.5 (1 LAS to 1.5 nonionic). In this system, the micelle actually may be viewed as a nonionic based micelle into which LAS has been incorporated.

From the above model, it is possible to understand why the presence of a small amount of nonionic mixed with LAS results in such a dramatic shift in overall calcium sensitivity. Formation of nonionic-based micelles incorporating LAS causes a reduction in free LAS monomer concentration. The micelles themselves also act as a sink for free calcium through counter-ion binding, which in effect lowers free Ca^{+2} concentration. A reduction in both the free LAS monomer concentration and the free calcium concentration reduces the amount of $Ca(LAS)_2$ formed in solution. In addition, a LAS/NI blend is better able to solubilize $Ca(LAS)_2$ than is straight LAS because it (i) has a lower cmc, so solubilization can occur at lower overall concentrations, and (ii) has less ionic interactions among the polar head groups in the micellar structure. The presence of nonionic in the micelle also acts to disrupt ordering of the $Ca(LAS)_2$ species which helps prevent crystal formation (e.g., precipitation). In other words, nonionic acts as a micelle promotion agent which ultimately provides calcium protection for LAS.

The role of each surfactant in detergency performance also can be determined from the Gibbs' plots. The surface excess adsorption values for LAS/NI blends up to a 1:1 (by weight) LAS:NI ratio were found to be equal to the surface excess adsorption value of LAS alone. This indicates that the surface properties (interfacial properties) of the LAS/NI system are not significantly different from those of LAS alone. Apparently, while nonionic prefers to be in micellar form, LAS prefers to be drawn to interfaces. LAS continues as the active surfactant responsible for interfacial and detergency properties, and nonionic acts as a micelle promotion agent which provides hardness protection for the LAS.

The data presented above indicate a strong molecular interaction between LAS and 1214-70 nonionic surfactants. The magnitude of this interaction can be quantified according to Rosen (2,3) and Rubingh (4) using the following equation:

$$\beta^M = \frac{\ln C_{12}^M/(C_1^M X_1^M)}{(1 - X_1^M)^2}$$

where β^M = Surfactant interaction parameter between Surfactant 1 and Surfactant 2.

Using the cmc data from the 12% LAS/3% 1214-70 NI nonionic system, β^M was calculated to be −2.12. Although this value is somewhat less than values (approximately −4) reported for other anionic and nonionic surfactants (2,3,5) it does indicate molecular interaction occurs.

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