

## SURFACTANTS AND DETERGENTS TECHNICAL

**Detergency Performance Comparison Between LAS  
and ABS Using Calcium Sulfonate Precipitation  
Boundary Diagrams**

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## Technical

### ❖ Detergency Performance Comparison Between LAS and ABS Using Calcium Sulfonate Precipitation Boundary Diagrams<sup>1</sup>

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#### ABSTRACT

Detergency performance comparisons of dodecyl-type LAS and ABS show that at typical conditions for countries in Latin America, Africa, the Middle East and Southeast Asia, LAS gives better cleaning performance than ABS. The differences in carbon chain distribution between dodecyl-type LAS and ABS account for some of the improvement in performance. An additional factor is the solubility of the calcium sulfonate salts. At high use level wash conditions, LAS is less hardness-sensitive than ABS. This increase in  $\text{Ca}^{+2}$  tolerance by LAS can result in improved cost/performance of HDP formulations.

#### INTRODUCTION

Roughly 20 years have passed since detergent manufacturers in the U.S. made the switch from nonbiodegradable, branched-chain alkylbenzene sulfonate (ABS) to biodegradable linear alkylbenzene sulfonate (LAS). While that switch was motivated primarily by concern about environmental pollution, it certainly was also advantageous that under U.S. washing conditions the detergency performance of LAS was

equivalent to or better than ABS. Within a very short time, LAS replaced ABS in U.S. household detergent products. Today LAS remains the largest volume synthetic detergent active in the world (1,2).

Branched-chain ABS continues to be used in many parts of the world, including Latin America, Southeast Asia, Africa and the Middle East. Most of this ABS is of the C12 average molecular weight type. During the last decade, environmental concern has motivated several countries in these areas to enact legislation requiring the use of biodegradable surfactants. The most recent country to make this decision has been Thailand (3). The trend away from ABS is expected to continue in the future. However, in these countries, environmental concerns will be weighed carefully against the importance of maintaining good cost/performance efficiency of detergent products. Detergent manufacturers are understandably concerned that under their typical washing conditions, the switch from ABS to LAS will not cause any decrease in cleaning efficiency. The purpose for this study was to evaluate the detergency performance differences between dodecyl LAS and ABS and to provide a model to explain why these differences occur.

<sup>1</sup> Presented at the AOCS meeting in Dallas, TX, in May 1984.

## EXPERIMENTAL

The pertinent analytical data for the commercial dodecyl type LAS and ABS sample used in this study are given in Table I.

The calcium/surfactant mixtures used to define the precipitation boundary diagrams were prepared using the LAS and ABS material (as described above but desalted) and reagent grade  $\text{CaCl}_2$ . Observations of turbidity were taken after 24 hr using a .5 MW HeNe laser (Spectra Physics) together with a dark background sample observation box. Mixtures were judged to be clear if at observation angle of

TABLE I

Analytical Data for Commercial Dodecyl Type LAS and ABS

	LAS	ABS
Active	49.3	52.3
Salt	.5	1.4
Oil	1.3	.6
Typical homolog distribution		
C10	6.2	6.3
C11	31.3	14.9
C12	36.3	60.0
C13	25.2	13.4
C14	1.0	3.3
C15	—	2.1
Average molecular weight	344	348

$90^\circ$  to the incident laser beam, no red line, indicative of the red HeNe laser beam's path, was observed. Mixtures were judged to be turbid if cloudiness or precipitate was plainly visible or if the red line indicating the laser beam's path was visible at the  $90^\circ$  observation angle.

Detergency tests were run using a modification of Conoco CTS Lab Method No. 303-74 which is similar to ASTM Method No. D3050-75. The modification involved a 30-min delay at the start of each detergency run to allow the surfactant and  $\text{Ca}^{+2}$  to approach equilibrium. Such long soaking times are not uncommon in areas where laundry washing is done primarily by hand.

## RESULTS AND DISCUSSION

Detergency studies of commercial C12-type LAS and ABS samples show, over a broad range of water hardness and use concentrations, that LAS generally gives better cleaning performance than ABS. These results are shown in Figures 1 and 2 for sebum soil on cotton cloth at ambient temperature (75 F) washing conditions typical for Latin America. Part of this detergency difference can be attributed to the different carbon chain distributions of the two products shown in Table I. With LAS, the linear alkyl chain length distribution can be controlled by distillation of normal paraffins to give the best performance. With ABS, the branched alkyl side chain is based on a refinery product which is less easily controlled. Homolog studies show that under most washing conditions, the C12 and higher carbon chain lengths give the optimum performance for LAS for both foam and detergency (Figs. 3 and 4) (4). In contrast, the optimum detergency and foam performance for ABS occur at the C13 and higher carbon chain lengths (Fig. 4 and Table II). However, most of the ABS produced throughout the world is of the C12 type, presumably due to economic and processing considerations.

But carbon chain distribution does not entirely account for the observed detergency performance difference. At the high use level, high hardness, cold water conditions typical for washing laundry by hand, C12 LAS appears to be less

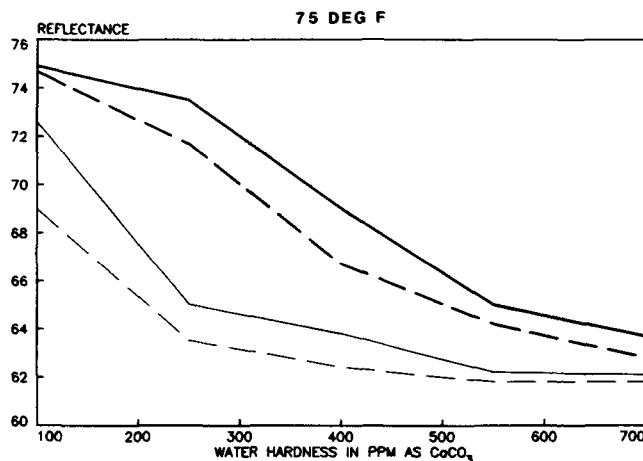


FIG. 1. Detergency at Latin American conditions on cotton sebum. 2.5% active/3.5% STPP/10% silicate/2% CMC. —, .1% LAS; ----, .1% ABS; — — —, .2% LAS, and - · - · -, .2% ABS.

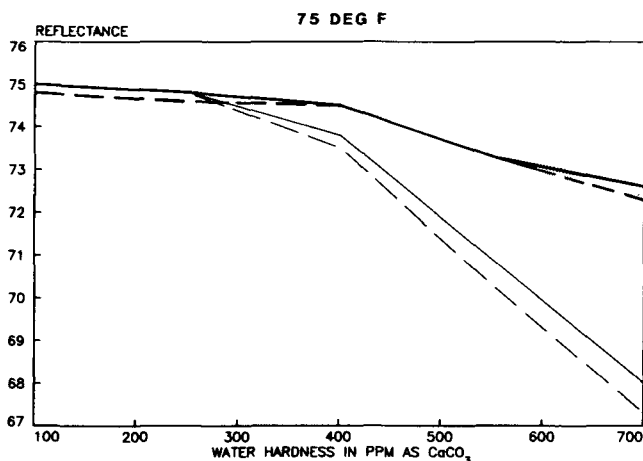


FIG. 2. Detergency at Latin American conditions on cotton sebum. 2.5% active/3.5% STPP/10% silicate/2% CMC. —, .3% LAS; ----, .3% ABS; — — —, .4% LAS, and - · - · -, .4% ABS.

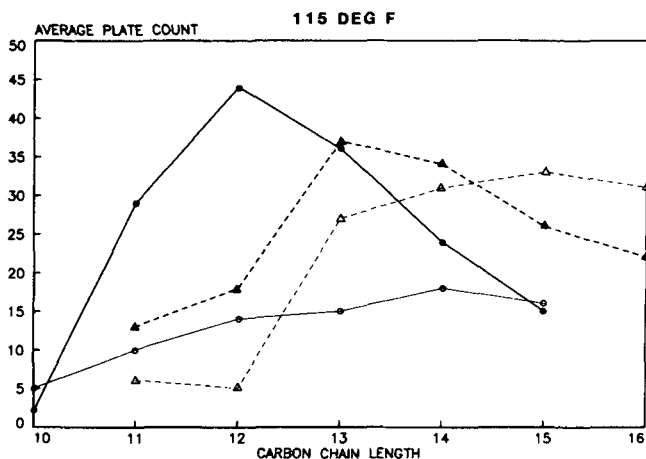


FIG. 3. LAS vs ABS homolog dishwashing study. 2% sulfonate/50% STPP, 0.125% conc., 115 F.  $\Delta$ - $\Delta$ - $\Delta$ , ABS 300 ppm hardness;  $\triangle$ - $\triangle$ - $\triangle$ , ABS 50 ppm hardness;  $\bullet$ - $\bullet$ - $\bullet$ , LAS 300 ppm hardness, and  $\circ$ - $\circ$ - $\circ$ , LAS 50 ppm hardness.

sensitive to water hardness than C12 ABS. The effect of reducing STPP in a 17% active HDP formulation is shown in Figures 5 and 6. That may seem somewhat of a surprise because, due to the structural differences between a linear and a branched hydrophobic group, one might expect the

## DETERGENCY PERFORMANCE COMPARISON

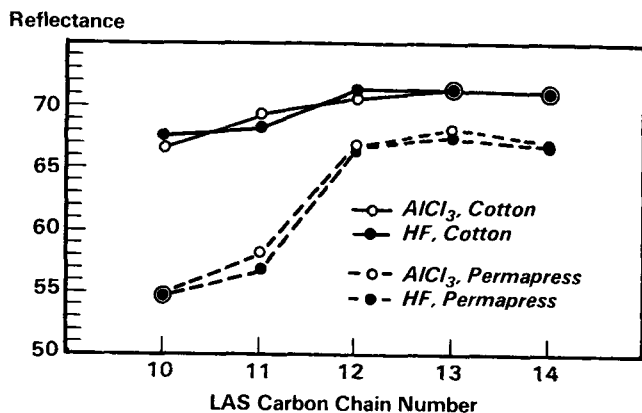


FIG. 4. HF and AICI<sub>3</sub> LAS homolog detergency. 100 F, .15% conc., sebum, 150 ppm hardness. 16% LAS/30% STPP/10% silicate.

TABLE II

Detergency Performance of Branched Chain ABS<sup>a</sup> 120 F, 0.2% Conc., 20% Active/50% STPP/5% Silicate/1% CMC

High hardness level (ppm)	Relative detergency ratings for various carbon chain lengths		
	C12	C13	C14
50	6.0	7.6	7.5
300	5.0	6.1	6.7

<sup>a</sup>C12 and C14 are individual homologs; C13 is a blend.

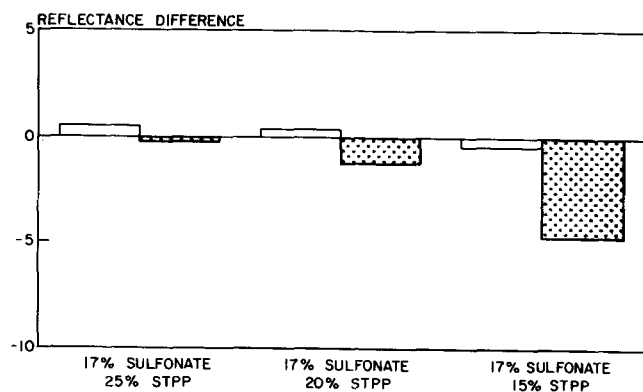


FIG. 5. Detergency performance relative to 20% ABS/25% STPP. Sebum oil, cotton, 25 C, 0.25% conc., 100 ppm water hardness. □, LAS; ▨, ABS.

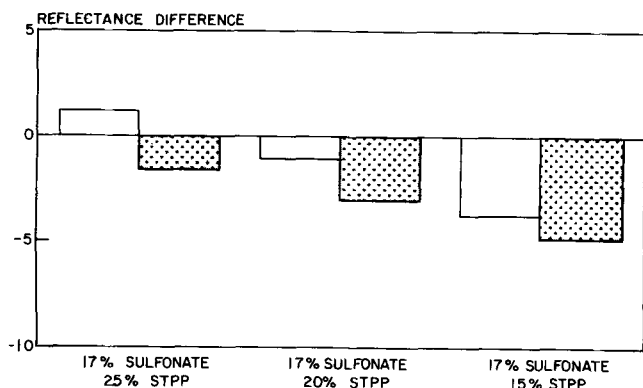


FIG. 6. Detergency performance relative to 20% ABS/25% STPP. Sebum soil, cotton, 25 C, 0.25% conc., 200 ppm water hardness. □, LAS; ▨, ABS.

Ca(LAS)<sub>2</sub>K<sub>sp</sub> to be smaller than the Ca(ABS)<sub>2</sub>K<sub>sp</sub>. This apparent inconsistency between detergency performance and calcium sulfonate solubility can be resolved and understood by the use of a calcium precipitation boundary diagram.

These diagrams provide much useful information about surfactant interaction with Ca<sup>2+</sup>, including estimates of CMC and K<sub>sp</sub> values as well as some information on the interaction of Ca<sup>2+</sup> ions with micelles. A number of articles have appeared in the literature during the last several years addressing the subject of precipitation boundary diagrams for Ca<sup>2+</sup> salts of anionic surfactants (5-8). This diagram is essentially a phase diagram for an anionic surfactant as a function of Ca<sup>2+</sup> concentration. It is drawn on a log-log plot of anionic surfactant concentration versus Ca<sup>2+</sup> concentration. The precipitation boundary is the locus of points at which one observed the onset of precipitation.

A generalized diagram of the boundary is shown in Figure 7. The line segment SPL, or surfactant precipitation line, represents the solubility limit of surfactant monomers in the presence of Ca<sup>2+</sup>. It is a straight line given by the equation (7):

$$\log [\text{Surf}^-] = -\frac{1}{2} \log [\text{Ca}^{+2}] + \frac{1}{2} \log K_{sp} \quad [1]$$

where K<sub>sp</sub> is the solubility product for Ca(Surf)<sub>2</sub>. The factor of -1/2 for the slope comes in because there are two surfactant anions per Ca<sup>2+</sup> cation.

The line segment SML, or surfactant micellization line, shows how the CMC of the surfactant changes with Ca<sup>2+</sup> concentration. It is given by the equation (7):

$$\log \text{CMC} = a - b \log [\text{Ca}^{+2}] \quad [2]$$

where a and b are empirically determined constants.

The curved segment MSL is the micelle saturation line. Above this boundary, as surfactant concentration increases, precipitated calcium surfactant is resolubilized by the micelles. Another way to look at it is that the Ca<sup>2+</sup> ions are electrostatically bound onto the exterior of the micelles, and this boundary represents the Ca<sup>2+</sup> saturation limit of the micelles. Below this line, Ca(Surf)<sub>2</sub> precipitates out of solution. This equation for this curve is a complex expression which includes the total concentration of calcium present, either as ions or precipitate, the degree of association of Ca<sup>2+</sup> with the micelles, and the CMC, which varies with Ca<sup>2+</sup> concentration (7).

The precipitation boundary, consisting of line segments MSL and SPL, divides the graph into regions of clear solutions and cloudy mixtures. Below the line segments SML and SPL, only surfactant monomers are present in solution. Above line segments SML and MSL, both micelles and

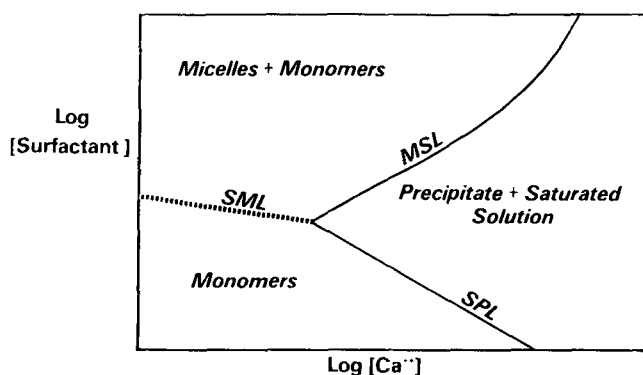


FIG. 7. Generalized calcium sulfonate precipitation boundary diagram.

monomers are present. In the region between MSL and SPL, saturated solution exists in equilibrium with the precipitate of the calcium salt of the surfactant.

The precipitation boundary diagrams for typical commercial C12-type LAS and ABS are shown in Figures 8 and 9. Figure 8 shows the diagrams for LAS and ABS in pure water, while Figure 9 shows the diagrams for both sulfonates in the presence of .01 M Na<sub>2</sub>SO<sub>4</sub>. Estimates of the CMC values for LAS and ABS in the presence of Ca<sup>2+</sup> can be taken from the concentration where the apex of the boundary occurs. As expected, the ABS has a higher CMC than LAS and a larger K<sub>sp</sub> value for the calcium sulfonate salt, as shown in Table III. In the presence of the .01 M Na<sub>2</sub>SO<sub>4</sub>, the CMC's for both surfactants are decreased. Also, the apparent K<sub>sp</sub> values increase due to the lowering effect that ionic strength has on the activities of the dissolved surfactant species (9).

At low use concentrations (less than 10<sup>-3</sup> M), LAS is

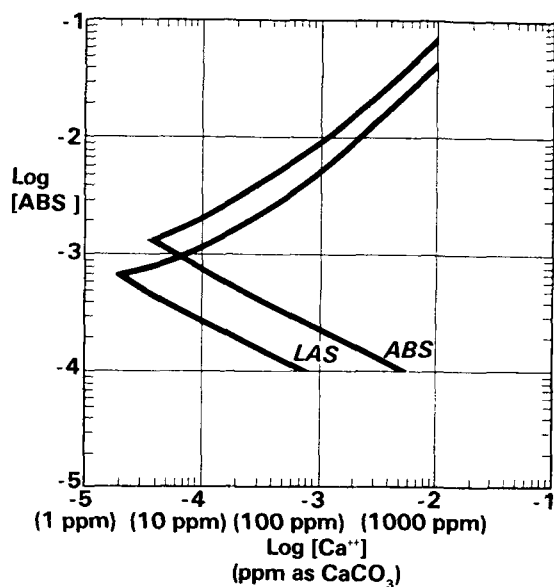


FIG. 8. Ca(ABS)<sub>2</sub> precipitation boundary diagrams for dodecyl LAS and branched chain ABS.

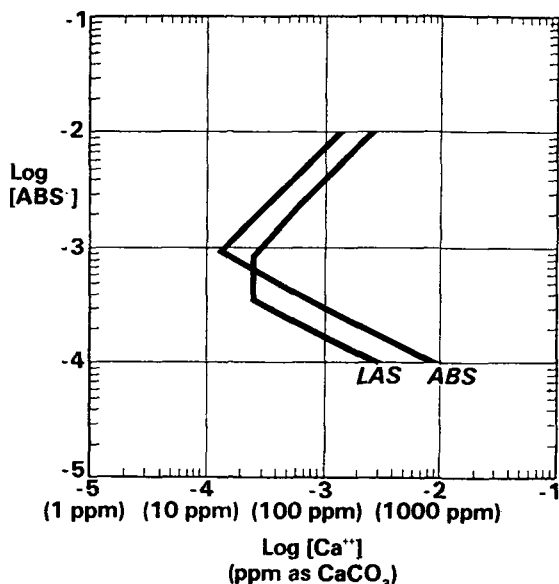


FIG. 9. Ca(ABS)<sub>2</sub> precipitation boundary diagrams for dodecyl LAS and branched chain ABS, .01 M Na<sub>2</sub>SO<sub>4</sub>.

more sensitive to hardness, as the precipitation diagrams show. However, in the concentration region of interest for hand laundry conditions (0.05 to 0.15 weight % or 1.0 × 10<sup>-3</sup> to 3.0 × 10<sup>-3</sup> M active), the LAS precipitation boundary shows a greater tolerance to Ca<sup>2+</sup> ions than the ABS, as indicated by the positioning of the boundaries.

To verify that this hardness sensitivity difference correlated to actual performance differences, Terg-O-Tometer detergency studies were run comparing the intrinsic cleaning performance of the surfactants alone (no builder) in the presence of fixed levels of Ca<sup>2+</sup>. The results are shown in Figures 10 and 11 plotted as the Y reflectance of LAS minus the Y reflectance of ABS versus initial concentration. As can be seen in the diagram, the difference between LAS

TABLE III

Estimated Values for Apparent CMC and K<sub>sp</sub> for Dodecyl LAS and ABS from Figures 8 and 9

	No salt		.01 M Na <sub>2</sub> SO <sub>4</sub>	
	CMC	K <sub>sp</sub>	CMC	K <sub>sp</sub>
LAS	7.0 × 10 <sup>-4</sup> M	8.1 × 10 <sup>-12</sup>	3.4 × 10 <sup>-4</sup> M	2.7 × 10 <sup>-11</sup>
ABS	1.3 × 10 <sup>-3</sup> M	5.1 × 10 <sup>-11</sup>	9.0 × 10 <sup>-4</sup> M	9.3 × 10 <sup>-11</sup>

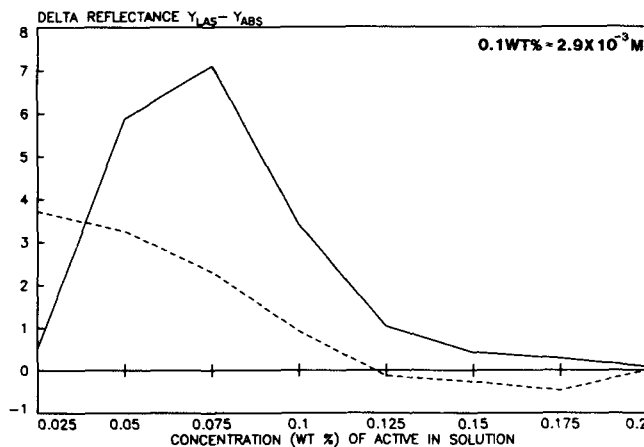


FIG. 10. Detergency study of calcium sulfonate (LAS vs ABS). Hardness (Ca<sup>2+</sup>) 20 ppm; 75 F. —, sebum cotton; ---, sebum permanent press.

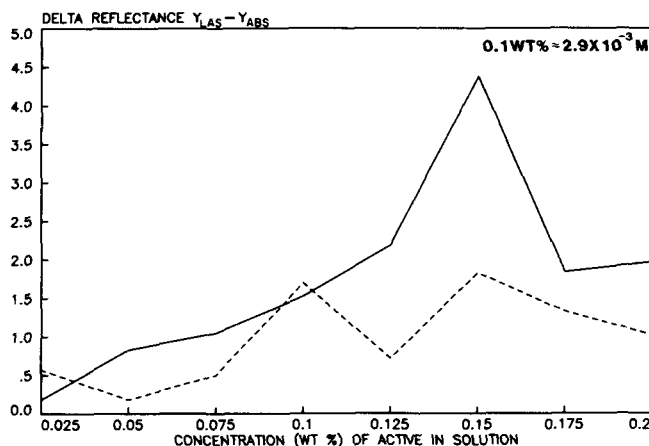


FIG. 11. Detergency study of calcium sulfonate (LAS vs ABS). Hardness (Ca<sup>2+</sup>) 200 ppm; 75 F. —, sebum cotton; ---, sebum permanent press.

## DETERGENCY PERFORMANCE COMPARISON

performance and ABS performance does not change uniformly as initial surfactant concentration is gradually increased. The  $\Delta$  reflectance maximum at the low hardness level corresponds roughly to the concentration range in which the LAS precipitation boundary is crossed, while the ABS precipitation boundary has yet to be crossed.

At 200 ppm  $\text{Ca}^{+2}$ , the position of the  $\Delta$  reflectance maximum appears to occur at the surfactant concentration below both the LAS and ABS boundaries. A slightly different approach is needed to explain the position of this  $\Delta$  reflectance maximum. Figure 12 shows a family of curves generated by the expression  $10Y = 2(10^X + C)$ . This mathematical expression (a derivation of which is given in the appendix) is based solely on mass balance and the assumption that one  $\text{Ca}^{+2}$  precipitates out with low surfactant monomers. These curves roughly predict how solution concentrations change as the anionic surfactant precipitates with  $\text{Ca}^{+2}$ . A mixture of surfactant and  $\text{Ca}^{+2}$  inside the boundary will undergo changes in solution concentration by following along the curve passing through (or nearest to) the point marking the initial concentrations of surfactant and  $\text{Ca}^{+2}$ . Equilibrium is reached (precipitation stops) at the intersection of the precipitation boundary with the particular curve corresponding to the initial concentrations of species.

Figure 13 shows an overlay of the curves, the boundary diagrams and the concentration ranges for which large differences in detergency performance occur. Overlaying the family of curves onto the precipitation diagram (Fig. 13), it can be seen that the  $\Delta$  reflectance maximum at 200 ppm  $\text{Ca}^{+2}$  and 0.15% surfactant corresponds to a region where the decrease in  $\text{LAS}^-$  concentration is slight because of the close proximity of the LAS boundary, while the decrease in  $\text{ABS}^-$  concentration is very large.

Detergency studies also were run on similar systems containing 0.01 M  $\text{Na}_2\text{SO}_4$  to correlate intrinsic cleaning performance with the precipitation diagram shown in Figure 9. The results of these studies are shown in Figures 14, 15 and 16. The detergency data at 30 ppm residual hardness (Fig. 14) does show a large detergency difference in the concentration range predicted by the diagram. At the higher hardness levels (Figs. 15 and 16), detergency differences favoring LAS do occur, but they are at the low concentration range corresponding to the lower part of the boundary. It appears

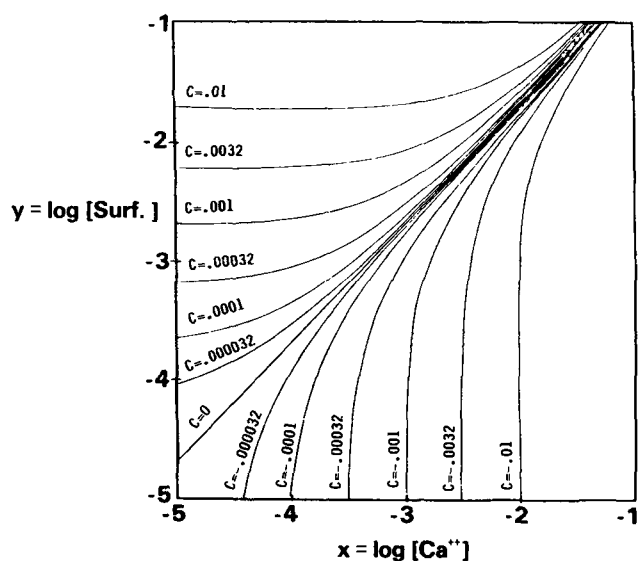


FIG. 12. Family of curves generated by the expression  $10Y = 2 \cdot 10^X + 2C$ .

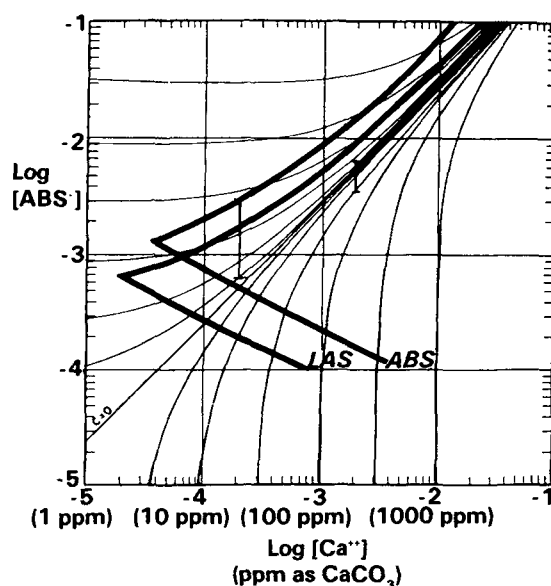


FIG. 13.  $\text{Ca}(\text{ABS})_2$  precipitation boundary diagrams for dodecyl LAS and branched chain ABS.

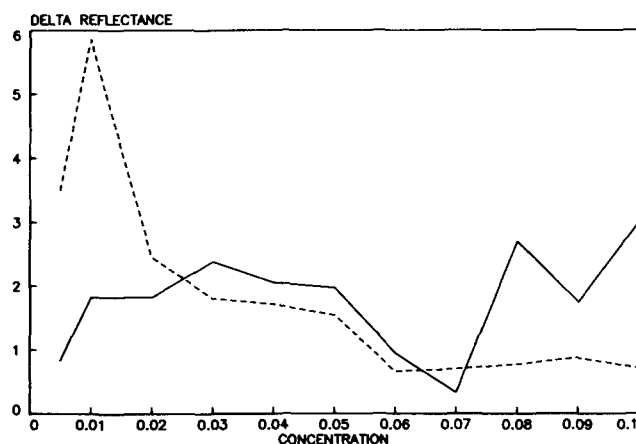


FIG. 14. Detergency reflectance difference (LAS vs ABS). 75 F, 30 ppm,  $(\text{Ca}^{++})$ , sebum, .01 M  $\text{Na}_2\text{SO}_4$ . —, cotton; ---, permanent press.

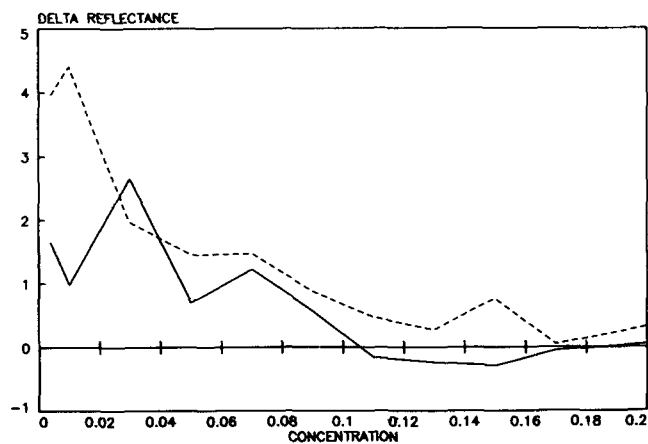


FIG. 15. Detergency reflectance difference (LAS vs ABS). 75 F, 70 ppm,  $(\text{Ca}^{++})$ , sebum, .01 M  $\text{Na}_2\text{SO}_4$ . —, cotton; ---, permanent press.

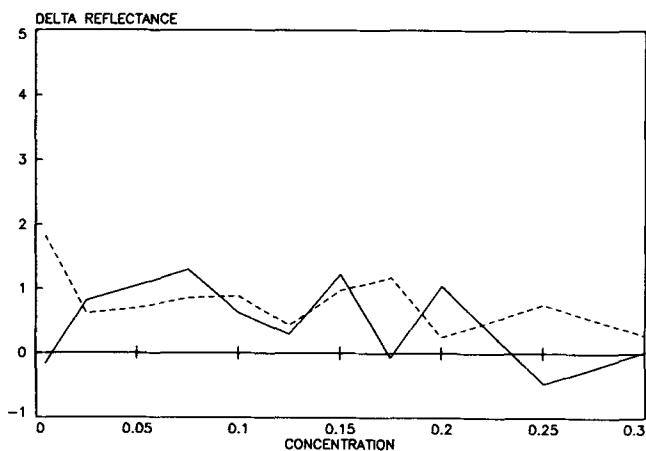


FIG. 16. Detergency reflectance difference (LAS vs ABS). 75 F, 200 ppm,  $(Ca^{+2})$ , sebum, .01 M  $Na_2SO_4$ . —, cotton; ---, permanent press.

that at low concentrations of 50 to 500 ppm surfactant, where efficiency of surfactant adsorption at interfaces is important, better detergency is seen at the onset of formation of  $Ca(LAS)_2$ , particularly on permanent press cloth.

In general, this increased tolerance for  $Ca^{+2}$  by LAS at high use concentration and increased cleaning efficiency at low concentrations can be translated to either a performance advantage or a formulation cost savings. For example, at an 0.4% use level, an HDP containing 35% LAS can tolerate about 40 ppm more hardness than ABS. That 40 ppm hardness corresponds on a sequestration basis to about 4% STPP in the formulation. Thus, at high use levels, LAS-based laundry powers can be formulated with slightly less STPP without suffering any loss of cleaning performance. The reason for this is the better hardness tolerance of LAS compared to ABS at the high use concentrations typical for hand wash laundry conditions.

## APPENDIX

### Derivation of the Expression $10^Y = 2(10^X + C)$

$$y = \log [ABS^-] = 0.434 \ln [ABS^-] \text{ or } [ABS^-] = e^{2.303Y} = 10^Y$$

$$x = \log [Ca^{+2}] = 0.434 \ln [Ca^{+2}] \quad [Ca^{+2}] = e^{2.303X} = 10^X$$

$$\frac{dy}{dx} = \frac{d(\log[ABS^-])}{d(\log[Ca^{+2}])} = \frac{0.434 d \ln [ABS^-]}{0.434 d \ln [Ca^{+2}]} = \frac{[Ca^{+2}] d [ABS^-]}{[ABS^-] d [Ca^{+2}]}$$

Here it is assumed that  $d[ABS^-]/d[Ca^{+2}] = 2$ , because two  $ABS^-$  ions combine with one  $Ca^{+2}$  ion in the precipitation process.

$$\frac{dy}{dx} = \frac{2[Ca^{+2}]}{[ABS^-]} = 2 \frac{e^{2.303X}}{e^{2.303Y}}$$

The solution to this differential equation proceeds by sepa-

ration of variables and integrating.

$$e^{2.303Y} dy = 2 e^{2.303X} dx$$

$$\int e^{2.303Y} dy = 2 \int e^{2.303X} dx$$

$$e^{2.303Y} = 2 e^{2.303X} + 2C \text{ (where } 2C \text{ is the integration constant)}$$

or in base 10,

$$10^Y = 2 \cdot 10^X + 2C$$

The constant C determines which ion is present in excess.

$$\text{Where } C = 0, 10^Y = 2 \cdot 10^X \text{ or } [ABS^-] = 2 [Ca^{+2}]$$

Thus,  $C = 0$  is the line of stoichiometric equivalence. Elsewhere,

$$2C = 10^Y - 2 \cdot 10^X \text{ and}$$

$$C = 1/2 [ABS^-] - [Ca^{+2}]$$

If  $C > 0$ , then there is excess  $[ABS^-]$ .

If  $C < 0$ , then there is excess  $[Ca^{+2}]$ .

This family of curves roughly predicts how solution concentration changes as an anionic surfactant precipitates with  $Ca^{+2}$ . It is believed to be accurate for the lower part (the  $K_{sp}$  side) of a precipitation diagram. Along the upper part of the boundary, however, it is known that  $Ca^{+2}$  interacts with the micelles that are present. This will change the combination ratio of  $ABS^-$  with  $Ca^{+2}$ . Instead of  $d[ABS^-]/d[Ca^{+2}] = 2$  for the precipitation of  $ABS^-$  with  $Ca^{+2}$ , it will be something different. It will appear that  $d[ABS^-]/d[Ca^{+2}]$  is less than 2. This will have the effect of causing the curves for  $C > 0$  to bend more sharply toward the upper part of the precipitation boundary.

## ACKNOWLEDGMENT

Dr. Kang Yang of Conoco Inc. helped with the derivation given in the appendix.

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