Formulating Characteristics of High and Low 2-Phenyl Linear Alkylbenzene Sulfonates in Liquid Detergents[1]

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Detergent range linear alkylbenzene (LAB) currently is manufactured by two different processes, using either aluminum chloride or hydrogen fluoride as the alkylation catalyst. The alkylates from the two processes are not exactly the same. Furthermore, the properties of the linear alkylbenzene sulfonate (LAS) surfactants made by sulfonation of the LABs also differ. Because LAS is used in most types of detergent products, it is important to know how the properties of each type of LAS differ. This paper compares the formulating characteristics (such as viscosity, solubility and foaming) of high and low 2-phenyl LAS in some typical household cleaning product formulations. It is concluded that the two types of LAS should not be used interchangeably without first checking carefully all the physical properties required in a product.

Currently, two processes are used for the manufacture of detergent range linear alkylbenzene (LAB). The alkylate presently most used for linear alkylbenzene sulfonates (LAS) in household detergents is that manufactured using hydrogen fluoride as the alkylation catalyst. Until the early 1980's, the aluminum chloride process dominated. This changed in 1982 when a major plant using the aluminum chloride process was put on stand-by status and a new hydrogen fluoride LAB plant went on-stream. The properties of the LAS surfactants obtained from these two alkylates are not the same. Because LAS is the "workhorse" surfactant of the detergents industry, produced in greater volume than any other surfactant and used in most types of detergent products, it is important that detergent manufacturers know how the properties of LAS obtained from each type of LAB differ.

BACKGROUND

In the U.S. most LAB is produced by alkylating benzene with olefins using hydrogen fluoride catalyst or monochloroparaffins using aluminum chloride catalyst. A little less than two-thirds of it is the hydrogen fluoride type (1). Most of the alkylate used in liquid products is probably of the aluminum chloride type; the situation is just the reverse in powders. In Europe the HF type also predominates, and European LAB and LAB sulfonic acid reach our shores sporadically.

Alkylation of benzene.

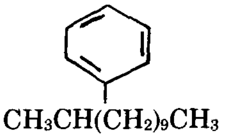
$$\text{(i) Olefin} + \text{Benzene} \xrightarrow{\text{HF}} \text{Alkylbenzene}$$

$$\text{(ii) Monochloroparaffin} + \text{Benzene} \xrightarrow{\text{AlCl}_3} \text{Alkylbenzene} + \text{Hydrochloric Acid}$$

Olson has discussed the mechanism of these reactions (2).

One of the major manufacturing differences between the two processes shown is that the aluminum chloride-catalyzed process produces hydrochloric acid as a by-product and, therefore, is more corrosive to equipment than the hydrogen fluoride-catalyzed process. The HF process also is said to have a higher degree of conversion, but it produces a slightly darker colored aklylate. It appears that the HF process is more economical and that producers are now moving toward it.

In any case, the two alkylbenzenes obtained are not the same. They differ in isomer distribution, with the phenyl group being distributed differently along the paraffin chain. The greatest difference is in the amount of 2-phenyl isomer formed as shown for a hypothetical dodecylbenzene:



$CH_3CH(CH_2)_9CH_3$

25-30% from $AlCl_3$ catalyst

15-20% from HF catalyst

2-Phenyldodecane

The $AlCl_3$ catalyzed process gives rise to about 25-30% of the 2-phenyl isomer with the amounts of 3, 4, 5 and 6-phenyl isomer decreasing steadily from about 22% to 15%, respectively. The HF process gives an LAB with about 15-20% of the 2-phenyl isomer distributed fairly evenly among the secondary carbon atoms (3). The alkylates obtained from the $AlCl_3$ and HF processes are, therefore, commonly referred to as high and low 2-phenyl LAB, respectively, as are the LAS's. These differences in 2-phenyl content markedly affect formulating properties of LAS in liquid detergents, particularly solubility and viscosity, as will be shown later.

Matheson and Matson (3) investigated the effect of phenyl isomer distribution and carbon chain length on foam, dishwashing and detergency of individual C_{10} through C_{14} alkylbenzene sulfonates. They found the most important factor in performance to be chain length and that high and low 2-phenyl LAS of the same carbon number perform essentially the same. They suggest that $AlCl_3$ and HF LAS can be used interchangeably. They did not report the physical properties of their test formulations.

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Sweeny and Olson (4) have shown detergency (Terg-o-Tometer, carbon-containing soil on cotton fabric) differences between pure 2-phenyl isomers and HF LAS to be insignificant. However, pure 2-phenyl LAS was inferior to HF LAS in a dishwashing foam test. Distillation of an HF alkylate into a mixture of lower boiling isomers (5- and 6-phenyl) and higher boiling isomers (ca. 90% 2-phenyl), and subsequent sulfonation led to "internal" and "end" LAS, respectively. The "internal" LAS isomers gave superior dishwashing performance in soft and hard water. Terg-o-Tometer and washing machine foam results showed only a marginal advantage for the "end" isomers. Their general conclusions were that the 2-phenyl isomer has a small advantage in detergency and wash machine foam, and the internal isomers have a large advantage for dishwashing foam. In this study all the formulations tested were phosphate/silicate built powders.

Rubenfeld and Cross (5) have suggested that for light duty liquids 15-25% 2-phenyl isomer is optimum and that for heavy-duty formulations less than 20% is desirable.

Baumgartner (6) has shown that detersive ability is best for the 3-phenyl isomer (Launder-O-Meter, lampblack/petrolatum soil on cotton fabric). Tjepkema, Paulis and Huiser (7) also studied the properties of the pure isomers and found that of the five phenyldodecane sulfonates, those with the phenyl group near the center of the alkane chain were better foamers and wetters. They also reported that the isomers "exhibit remarkable differencs" in water solubility. For mixtures of 2- and 6-phenyl LAS, a solubility maximum occurs with 30-40% of the 2-phenyl isomer.

It also has been reported that if the phenyl group is near the end of the alkyl chain, biodegradation is easier, and if near the middle, detergency is better (8).

The literature shows that differences in detergency and foam performance do, indeed, exist between individual isomers. On the other hand, it is not clear whether there are differences of practical significance between commercial high and low 2-phenyl LAS.

OBJECTIVES

The purpose of this work was to compare the formulating properties of high and low 2-phenyl LAS made from commercially available LAB by the aluminum chloride and hydrogen fluoride process. We were interested in properties important in formulating liquid detergents such as clarity, viscosity and physical stability of formulated products. Some foam studies were done in addition to surface tension and wetting measurements. We include here results on sodium, triethanolammonium and ammonium LAS because they are the most commonly used. Detergency testing was not included. As shown earlier, the literature might cause one to expect some performance differences. Up to now, no one has reported on the equally important formulating properties of LAS obtained from commercially available high and low 2-phenyl LAB.

EXPERIMENTAL

Sulfonation of LAB. Samples of commercial high and low 2-phenyl alkylate were sulfonated using Stepan's patented thin film air/SO_3 process. The high 2-phenyl LAB contained 29.4% of the 2-phenyl isomer and the low 14.0% (Table 1). The analyses of the LAS acids obtained are shown in Table 2. The analyses were similar and so, in a general way, any differences in properties observed could reasonably be attributed to differences in 2-phenyl isomer content of the LAB used. The low 2-phenyl acid did have a lower free oil content, and all things being equal it might be predicted from this that solubility in water would be greater than the high 2-phenyl material. Most of the effects observed were contrary to this, and so it appears that the lower 2-phenyl content overwhelmed the expected effect if there was one.

TABLE 1

Properties of Commercial Alkylates

	High 2-phenyl[a]	Low 2-phenyl[b]
Appearance	clear, colorless liquid	clear, colorless liquid
Molecular weight	236	236
Carbon chain length	11.6	11.3
2-Phenyl isomer, %[c]	29.4	14.0
Homolog distribution[c]		
C_9 and less		1
C_{10}	15	16
C_{11}	42	42
C_{12}	33	40
C_{13}	10	1
C_{14} and greater		—

[a] Vista Nalkylene N-500.
[b] Monsanto Alkylate A-215.
[c] By analysis. Other values from manufacturers' literature.

TABLE 2

Alkylbenzene Sulfonic Acids

	High 2-Phenyl	Low 2-Phenyl
LAB process catalyst	$AlCl_3$	HF
2-Phenyl isomer, %	29	14
Molecular weight	316	316
Solubility (1% in D.I. water)	clear	clear
Active, %	96.4	96.5
H_2SO_4, %	1.4	1.3
Free oil, %	2.3	1.6
Viscosity (cps @ 25 C)	1150	1300

Preparation of LAS salts. Sodium, triethanolammonium and ammonium LAS salts were prepared by adding the LAS acid to an equimolar amount of the appropriate base in deionized water. The final pH was kept between 7 and 8.

MATERIALS AND METHODS

The linear alkylbenzenes (LAB) used were commercially available from Monsanto Industrial Chemicals

Co. (Alkylate A-215, low 2-phenyl) and Vista Chemical Co. (Nalkylene N-500, high 2-phenyl). The sodium xylene sulfonate (SXS) used was Stepanate® X; fatty alkanolamide (FAA) was Ninol® 128 Extra, a coconut super diethanolamide; alcohol ethoxy sulfate (AES) was Steol® CS-460, a sodium coconut range alcohol 3-mole ethoxysulfate; all commercially available from the Stepan Company. Water used in preparing all solutions was deionized unless stated otherwise.

Surface tension measurements were made using a

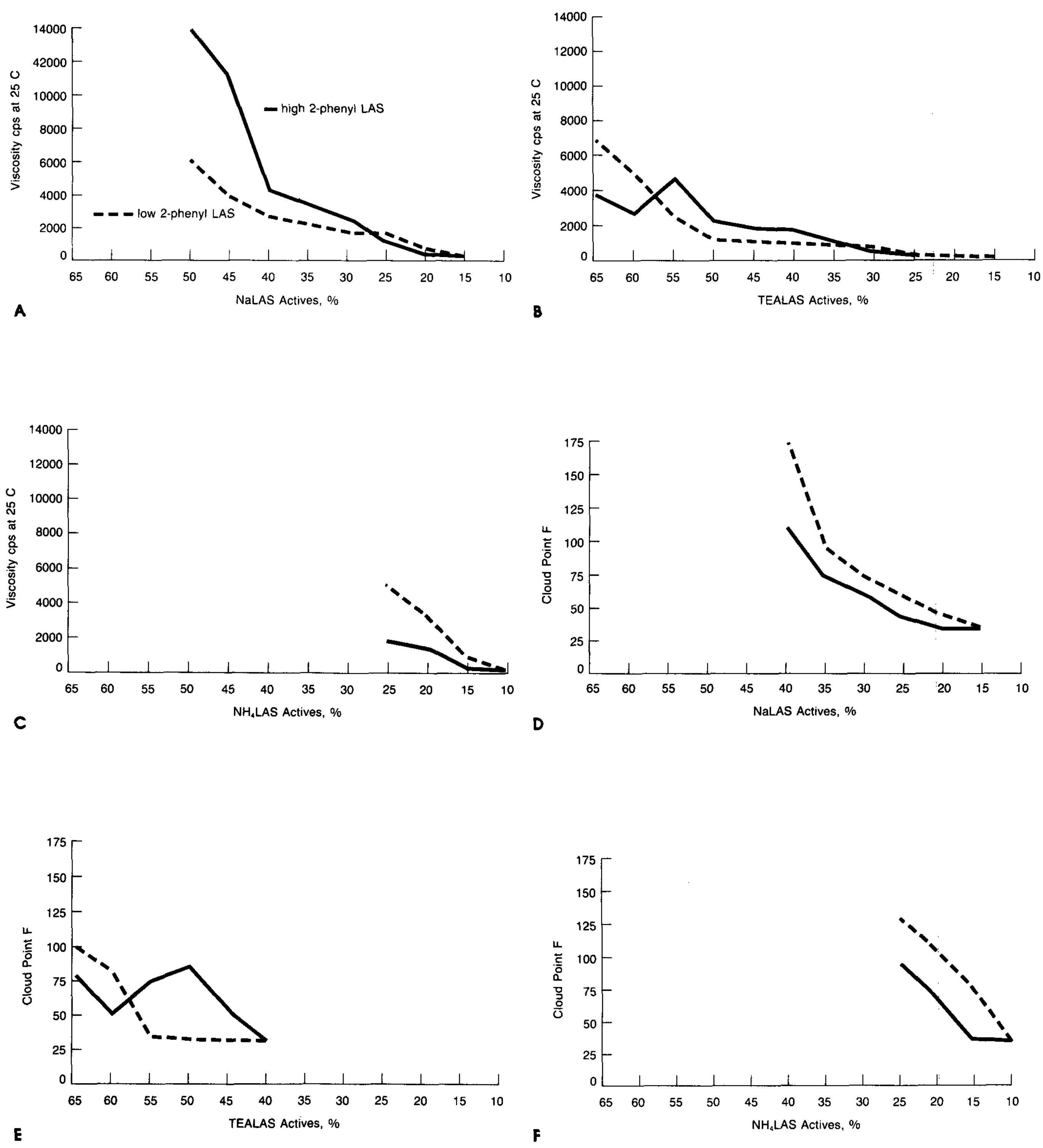

FIG. 1. Viscosity and cloud point as functions of concentration. Throughout this paper solid lines are used for high 2-phenyl LAS and broken lines for low 2-phenyl LAS.

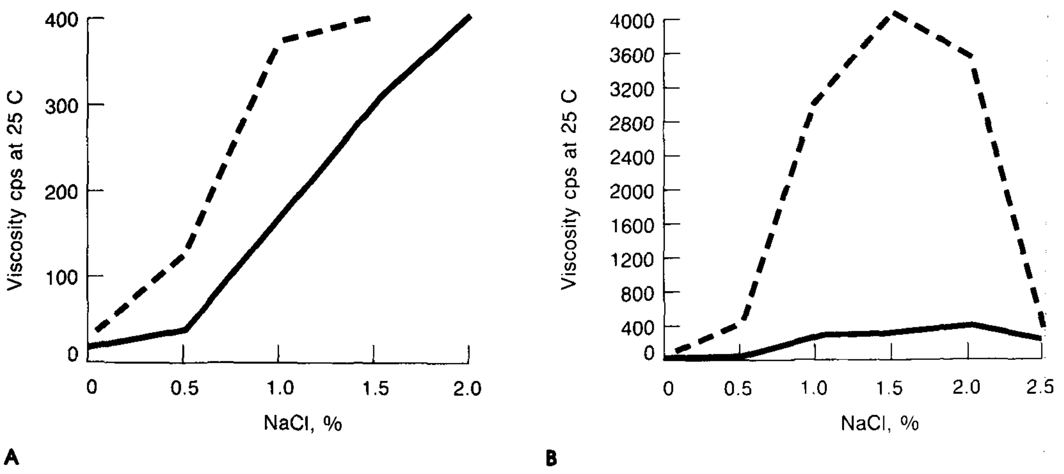

FIG. 2. Effect of salt on viscosity of (A) 15% NaLAS and (B) 10% NH_4LAS.

du Nouy tensiometer according to ASTM D 1331-56 (9). No corrections were made, so the values reported should be compared only relative to one another. Wetting times were determined using the Draves technique according to ASTM D 2281-68 (10). Foam heights were measured using the Ross-Miles technique according to ASTM D 1173-53 (11). Viscosity measurements were all made at 25 C using a Brookfield LVF viscometer.

RESULTS AND DISCUSSION

Viscosity. The viscosity of sodium, triethanolammonium and ammonium LAS as a function of active surfactant concentration is shown in Figures 1A-1C. At equal actives, the ammonium LAS gave the highest viscosity, followed by sodium LAS and then triethanolammonium LAS exhibiting the lowest viscosity. This was generally true for both high and low 2-phenyl LAS.

The high and low 2-phenyl LAS's had quite different viscosity properties for each cation. For sodium, the high 2-phenyl LAS gave significantly higher viscosities. For example, at 50% active, high 2-phenyl NaLAS had a viscosity of 14,000 cps, whereas the low 2-phenyl material was 6,000 cps. The viscosity picture for NH_4LAS was just the opposite, with high 2-phenyl giving lower values. Viscosities at concentrations greater than 25% are not reported for the ammonium salts because of a tendency to gel. The low 2-phenyl TEALAS gave lower viscosities at concentrations less than around 55%. The viscosity differences were most apparent at concentrations higher than 35% active surfactant. At less than 35%, the differences seemed slight.

Cloud points. As a measure of solubility, the cloud points of the surfactant solutions were determined. The results are shown in Figures 1D-1F. These were the temperatures at which the solutions became cloudy upon cooling. As indicated by cloud point, the high 2-phenyl NaLAS and NH_4LAS are more soluble than low 2-phenyl. At 75 F the solubility of the low 2-phenyl NaLAS is roughly only 75-80% that of the high 2-phenyl LAS. Below about 55% active, the situation with the TEA salt is just the opposite, with the high 2-phenyl being much less soluble than low.

The low 2-phenyl NaLAS has a considerably higher cloud point at relatively high actives levels (greater

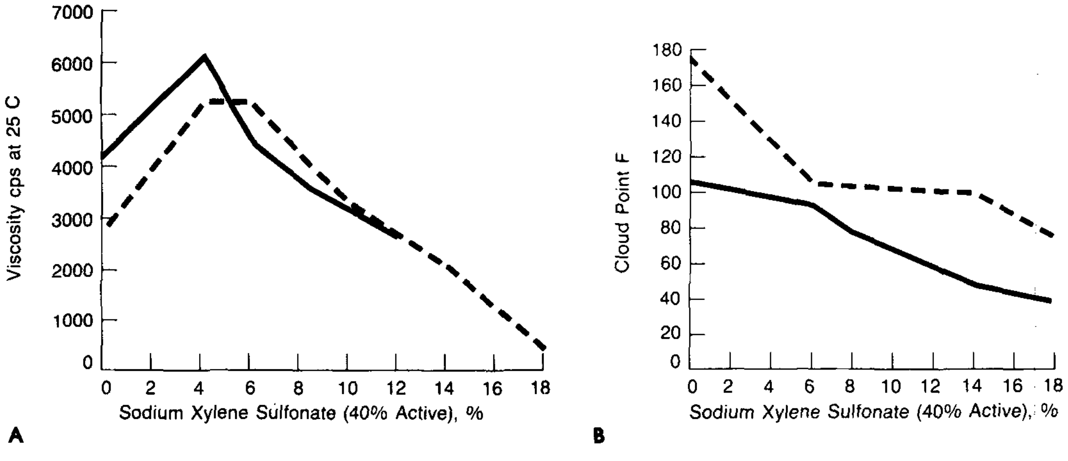

FIG. 3. Effect of SXS on (A) viscosity and (B) clarity of 40% NaLAS.

than 15%). This presents a particular problem when one considers that the viscosity of the low 2-phenyl LAS is, in addition, lower than high 2-phenyl. This is a formulating problem, because the addition of hydrotrope to lower the cloud point would likely result in viscosities less than desired. This difficulty is illustrated in one of the example formulations described later.

Effect of salt on viscosity. The effect of salt addition on the viscosity of high and low 2-phenyl LAS solutions was also determined. Both types of LAS responded in a similar fashion for sodium and triethanolammonium cations. Here, at 15% actives, the viscosity increased with salt addition (Fig. 2A). The low 2-phenyl LAS gave higher viscosities. The ammonium low 2-phenyl LAS gave viscosities much higher than could be achieved with the high 2-phenyl LAS (Fig. 2B). The difference is rather dramatic.

Effect of hydrotrope on viscosity and cloud point. The effect of the hydrotrope sodium xylene sulfonate (SXS, 40%) on the viscosity and cloud point of 40% active high and low 2-phenyl NaLAS is shown in Figures 3A and 3B. Quite a large amount of hydrotrope (more than 18%) was required to make the low 2-phenyl LAS clear at 40% actives whereas the high 2-phenyl remained clear at room temperature with about only half as much hydrotrope. The effect of urea and ethanol on viscosity and cloud points was also determined. Urea had only a slight effect on viscosity but was useful in lowering cloud point. Ethanol was effective in lowering viscosity but was not as good as sodium xylene sulfonate in reducing cloud point. In all of these experiments, the solubility of the low 2-phenyl LAS was always significantly less than that of high 2-phenyl under the same conditions.

Viscosity, cloud point and foaming of high and low 2-phenyl LAS blends with FAA and AES. High and low 2-phenyl NaLAS was blended with a fatty alkanolamide (FAA) at ratios of 100% LAS, to 80% LAS:20% FAA active surfactant maintaining total actives constant at 30%. The viscosity and cloud point of the blends obtained are shown in Figures 4A and 4B. As might have been expected from the data already presented, lower viscosities and higher cloud points were obtained using low 2-phenyl LAS. There was not much difference in foaming (Ross-Miles) between the high and low 2-phenyl blends (Fig. 4C). No attempts were made to adjust the properties of these blends using salts or hydrotropes.

Blends of 100% LAS to 50% LAS:50% sodium alcohol ethoxysulfate (AES) showed trends similar to those obtained with FAA except at the 50/50 LAS/AES ratio where the high 2-phenyl foamed more.

Surfactant properties. Sodium high 2-phenyl LAS gave better surface tension reduction than low 2-phenyl (Fig. 5A). This may be due to the higher C_{13} LAS content of the product. For the TEA sulfonate, low 2-phenyl gave lower values; no major differences were apparent with ammonium salts.

Wetting times were less for the low 2-phenyl NaLAS (Fig. 5B) and the same for ammonium and TEA. This was in agreement with what was expected from the literature (better wetting with the phenyl sulfonate group in the middle of the alkyl chain).

The high 2-phenyl sodium and TEA sulfonates

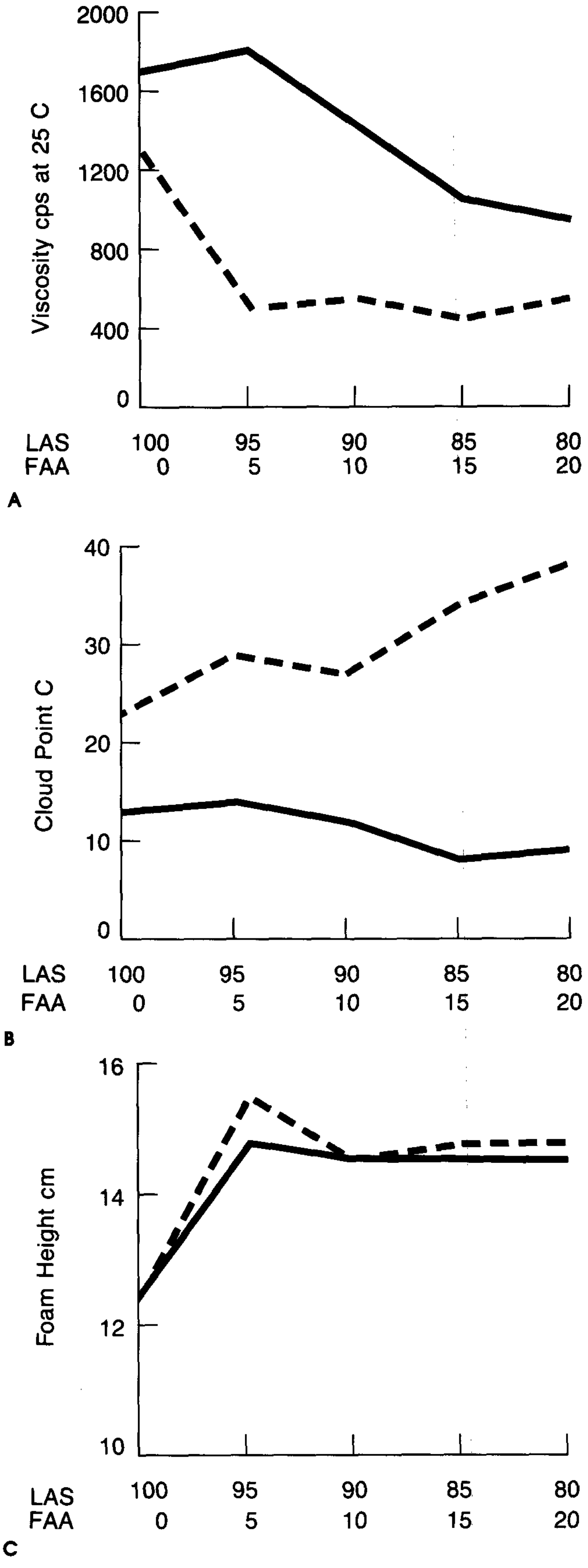

FIG. 4. Effect of LAS/FAA ratio on (A) viscosity and (B) cloud point of 30% total concentration solutions and (C) foam height at 0.1% total concentration.

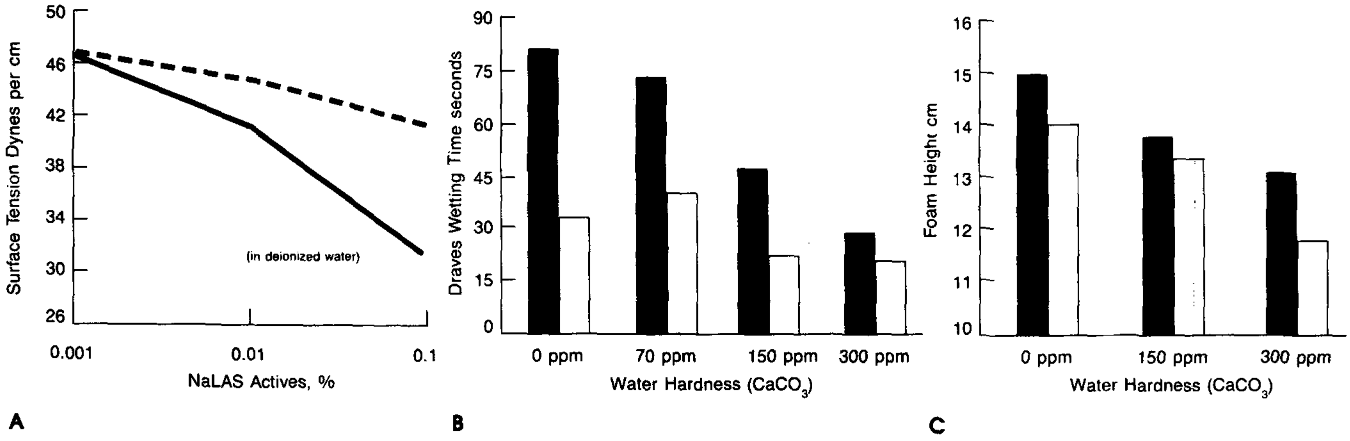

FIG. 5. Surface active properties. In these graphs, the solid bars represent high 2-phenyl LAS and the open bars represent low 2-phenyl LAS. A, surface tension; B, Draves wetting times, 0.025% NaLAS (at 0.1%, all wetting times were the same); and C, foam height, 0.1% NaLAS (both were cloudy at 150 and 300 ppm hardness).

TABLE 3

High Actives Dishwash

Ingredients	% by wt
NaLAS	25.0
NaAES	5.3
SXS	2.6
Coco DEA	3.3
Water	63.8
	100.0

	Low 2-phenyl	High 2-phenyl
Viscosity, cps	385	354
Cloud point	44 F	36 F
Freeze-thaw	pass	pass
Appearance	clear & fluid	clear & fluid

The addition of 0.8% additional SXS brought the cloud point of the low 2-phenyl formulation down to less than 36 F.

TABLE 4

Economy Dishwash

Ingredients	% by wt
NaLAS	9.00
Coco DEA	2.37
NaCl	0.81
Water	87.82
	100.00

	Low 2-phenyl	High 2-phenyl
Viscosity, cps	220	191
Cloud point	70 F	34 F
Freeze-thaw	fail	pass
Appearance	cloudy, unstable	clear

Reducing the salt content of the low 2-phenyl blend made it acceptable.

TABLE 5

Liquid Laundry Detergent

Ingredients	% by wt
TEALAS	5.7
Nonionic[a]	20.0
TEA	1.0
3A-Alcohol	5.0
Water	68.3
	100.0

	Low 2-phenyl	High 2-phenyl
Viscosity, cps	280	260
Cloud point	39 F	39 F
Freeze-thaw	pass	pass
Appearance	water-white liquid	water-white liquid

Both low 2-phenyl and high 2-phenyl acceptable.

[a] Nonylphenol (8 mol E.O.) ethoxylate.

TABLE 6

Liquid Laundry Detergent

Ingredients	% by wt
NaLAS	14.4
Nonionic[a]	44.0
SXS	2.0
3A-Alcohol	5.0
Water	34.6
	100.0

	Low 2-phenyl	High 2-phenyl
Viscosity, cps	220	196
Cloud point	48 F	50 F
Freeze-thaw	fail	fail
Appearance	light yellow liquid	light yellow liquid

The high 2-phenyl formulation failed on the third freeze-thaw cycle, the low 2-phenyl on the second. The addition of 0.8% additional SXS caused both formulations to pass three freeze-thaw cycles.

[a] Nonylphenol (10 moles E.O.) ethoxylate.

TABLE 7

Hard Surface Cleaner

Ingredients	% by wt
NaLAS	2.0
Coco DEA	10.0
SXS	3.6
STPP	5.0
Water	79.4
	100.0

	Low 2-phenyl	High 2-phenyl
Viscosity, cps	106	116
Cloud point	37 F	40 F
Freeze-thaw	fail	pass
Appearance	clear, light yellow	clear, light yellow

The addition of 0.4% additional SXS caused the low 2-phenyl formulation to pass three freeze-thaw cycles with little change in viscosity.

foam somewhat more than low 2-phenyl (Fig. 5C). There were no major differences between the high and low 2-phenyl NH_4 LAS's.

Properties of typical household formulations based on high and low 2-phenyl NaLAS. In order to compare the practical consequences of using NaLAS with high or low 2-phenyl isomer content, simple formulations typical of various household cleaning products were made up, each using either high or low 2-phenyl LAS. These formulations ranged from dishwashing and laundry liquids to floor cleaners. The physical properties of the blends were determined and compared. If the properties were different, an adjustment to the formulation judged to have the poorer properties was made to try and make them equal. In most cases this amounted to adding hydrotrope to the low 2-phenyl blend in order to improve clarity and freeze-thaw stability. The formulations tested and results obtained are shown in Tables 3 through 7.

A premium type of dishwashing formulation containing 25% NaLAS exhibited only a slightly higher cloud point for low 2-phenyl compared to high 2-phenyl LAS, 44 and less than 36 F, respectively. The addition of less than 1% active sodium xylene sulfonate also brought the higher cloud point blend down to less than 36 F. Somewhat unexpectedly, an economy type dishwashing liquid (about 10% active) showed major deficiencies for the low 2-phenyl-derived blend (Table 4) with a cloudy product beginning to separate at room temperature. However, simply decreasing the salt content in the formulation made it acceptable.

There were no major differences in a 26% total actives HDL (Table 5), but a 60% actives blend (Table 6) suggested a poorer freeze-thaw stability for low 2-phenyl LAS. Again, addition of a small amount of SXS eliminated the differences.

A general purpose cleaner (Table 7) containing 5% STPP required less than 1% SXS (active) to get the acceptable freeze-thaw stability with low 2-phenyl LAS.

The formulating properties of high and low 2-phenyl LAS are not the same. They should not be used interchangeably without first carefully checking the physical properties required of a product. The solubility of sodium and ammonium low 2-phenyl LAS can often be less than that of high 2-phenyl, causing cloudy or hazy mixtures. The situation is just the reverse for triethanolammonium LAS. This probably can be improved by using hydrotrope. Viscosities of solutions of the various salts of high and low 2-phenyl LAS are not the same but do not appear as significant as the solubility differences.

In the early to mid 1960's the detergents chemist had to learn to use linear alkylbenzene sulfonates as the branched tetrapropylene alkylbenzene sulfonates came into disfavor for household detergents because of slower biodegradability. More recently, the main differences in formulating with various LAS's were due to their molecular weight. Differences in the alkylate manufacturing processes, however, have resulted in LAS's with very different properties even though they may have the same molecular weight. It appears now, therefore, that the selection of alkylbenzene sulfonate surfactants will become more complicated as phenyl isomer distribution will have to be taken into account.

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