

All the processes discussed here remove significant amount of impurities other than ABS. They might, therefore, be used whether or not ABS were present. Most of the processes would, in fact, operate more efficiently if ABS were not present. Foaming is a possible exception. The synergistic action between small amount of ABS and other organic materials in waste water is, in many instances, very effective in producing stable foam. How strong the foaming tendency of waste water might be in the absence of the presently used ABS is not well known. A reduction in foamability would certainly be expected. This might be overcome partly by changes in the design of foaming equipment. It might also be possible to add small amount of foaming agents to produce a more stable foam.

Products and environmental patterns change with time. We cannot expect to tailor waste treatment for each new problem compound that comes along. Water reuse considerations will demand that only a very

low level of many contaminants be allowed to remain in water. We need an arsenal of highly efficient treatment methods to cope with all types of contaminants. There is no question that our technology can develop such methods. We must provide the treatment means if the clean water needed and demanded by the public is to be available.

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Performance of Straight-Chain Alkylbenzene Sulfonates (LAS) in Heavy-Duty Detergents

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Abstract

The foamability (dishwashing and washing machine) and detergency of LAS in heavy-duty detergents is directly compared with polypropylene ABS (PPABS) at various mol wt, conen, water hardnesses and temp. In every case a peak in performance is obtained in the C₁₁ to C₁₇ side chain range. The peak is shifted to lower mol wt as water hardness is increased, especially at low detergent conen. LAS opt performance is generally equal to PPABS, except in dishwashing foam in soft water. The LAS peaks, however, are shifted to ca. one carbon lower mol wt than the PPABS. Therefore, best over-all performance is obtained for LAS whose average mol wt corresponds to a 12.5 carbon side chain, whereas PPABS is best with an average 13.5 carbon side chain.

Dishwashing foamability is markedly different for the different isomers contained in LAS. When the phenyl group is attached to the middle of the alkyl chain, surprisingly high results are obtained. This dishwashing difference is great enough to be noticeable when the isomer distribution changes in whole products made using different alkylation catalysts. Detergency and washing machine foam are not affected enough to see differences between whole alkylates.

LAS solubility is greater than PPABS and is influenced by isomer distribution.

Introduction

THERE HAVE BEEN many reports on various aspects of the performance of detergents containing tetrapropylene ABS since it has been the most widely used synthetic anionic surfactant for many years. In the last few years the performance of some of the commercial polypropylene alkylates has been improved by

raising the average mol wt to equal about a 13.5 carbon side chain (1).

There have not been many reports on performance of LAS. Gray et al. (2,3) prepared several pure compounds and obtained wetting time, detergency and foam data. Baumgartner (4) prepared and tested a number of dodecylbenzene isomers. Koelbel and coworkers (5) reviewed the literature on the effect of structure on properties of a number of straight-chain and branched-chain alkylbenzene sulfonates and other anionics. Most of the data are on physical properties, such as surface tension and critical micelle concentration (CMC). Recently, Stanberry et al. (6) presented some data on performance of LAS vs. mol wt, but the LAS source was not specified and no direct comparison with polypropylene products was given.

Therefore, the question of how LAS performs in heavy-duty formulas in "practical-type" tests in direct comparison with PPABS has not previously been answered. The present report comes to bear on this question and on whether there is an opportunity to tailor straight-chain alkylbenzene sulfonates to obtain the superior properties of the higher mol wt polypropylene products. The dishwashing foam test is of particular interest because it was found to be a sensitive test for showing the improvement as mol wt was increased in the polypropylene case.

Unfortunately, polypropylene alkylbenzene sulfonate has become generally known simply as "ABS." Therefore, to avoid any confusion between materials and to emphasize the considerable difference between polypropylene and straight-chain products, we will refer to the latter as LAS, standing for linear alkylate sulfonate. The polypropylene product will be called PPABS.

Experimental

Preparation of Materials. The alkylbenzenes used in this work originated from several sources as summarized in Table I. They were batch sulfonated with

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TABLE I
 Material and Abbreviations

Description	Alkylate source	Abbreviation*
Tetrapropylene alkylbenzene sulfonate.....	Oronite Alkane 56	PPABS ₁₂
"Tridecyl" polypropylene alkylbenzene sulfonate.....	Oronite Alkane 60	PPABS _{13.5}
Sulfonates from narrow fractions of propylene alkylates.....	Distillation of laboratory prepared polypropylene alkylates	PPABS
Mixed secondary straight-chain alkylbenzene sulfonates.....	HF alkylation of α -olefins	Random LAS
Mixed secondary straight-chain alkylbenzene sulfonates with relatively high (30-85%) 2-phenyl content.....	AlCl ₃ alkylation of α -olefins	High 2-phenyl LAS
Single carbon straight-chain alkylbenzene sulfonates containing mostly 2-phenyl isomer.....	Distillation of HF/ α -olefin alkylate—highest boiling fraction	End Isomers
Single carbon straight-chain alkylbenzene sulfonates containing mostly 5-, 6-, 7-, 8-phenyl isomers.....	Distillation of HF/ α -olefin alkylate—lowest boiling fraction	Internal Isomers
Pure straight-chain alkylbenzene sulfonates.....	Grignard, dehydration, hydrogenation	e.g., 2-phenyl-C ₁₂

* Subscript numbers indicate the carbon number of the side chain.

oleum using a standard procedure (7). The PPABS₁₂ and PPABS_{13.5} are sulfonates from Alkanes 56 and 60, which are commercial products of the California Chemical Co. The "narrow fraction" PPABS samples are sulfonates of laboratory distillation fractions from wide range polypropylene alkylates. Each fraction contained 84-96% of a three-carbon spread in mol wt, with no single mol wt being more than 50% of the total, except for the 333 mol wt sulfonate which was 63% C₁₁ and the 348 mol wt sulfonate which was 76% C₁₂.

LAS of different mol wt were made by HF alkylation of α -olefins followed by sulfonation. Since a roughly random mixture of secondary alkylbenzenes is obtained by this procedure (8), these alkylates are called "random" LAS. The even-numbered α -olefins were obtained from Humphrey Wilkinson & Co. The odd-numbered were prepared by coupling the appropriate alkyl magnesium bromide with alkyl bromide. These olefins were at least 93% *n*-1-olefin. Some alkylates were prepared by AlCl₃ alkylation of α -olefins. This gives an alkylate which contains 30-35% 2-phenyl isomers (8); and the sulfonate, therefore, is called "high-2-phenyl" LAS.

Some of the random HF/1-olefin alkylates were carefully distilled (3-ft by 1-in. Penn State column with 20:1 reflux ratio at 10-mm Hg) into several fractions, thereby obtaining a partial separation of isomers. The lowest boiling fraction was rich (80-90%) in 5-, 6-, 7- and 8-phenyl isomers and the highest boiling fraction was rich (ca. 90%) in the 2-phenyl isomer. The former, sulfonated, is called "internal" isomers and the latter "end" isomers.

A number of pure straight-chain alkylates were

prepared by addition of the appropriate Grignard reagent (*n*-alkyl magnesium bromide) to a *n*-alkyl phenyl ketone, followed by dehydration over CuSO₄ and hydrogenation with CuCrO₄ catalyst. Specifically, a series of pure 2-phenylalkanes (C₁₀ to C₁₈) and centrally attached isomers (6-phenyldodecane, 7-phenyltetradecane, 8-phenylhexadecane) were prepared.

The single carbon random LAS, narrow fraction PPABS and pure compounds were desalted and deoiled in 70% ethanol before testing. Others were not. All samples were desalted and deoiled before running solubility tests.

Performance Testing. Detergency has been measured by washing carbon-containing soil from cotton swatches (Foster D. Snell) in a Terg-O-Tometer (Model BD-101, U.S. Testing Co.). Soil removal is measured in the usual way by reflectance (Photovolt Model 610 reflection meter), and the results are normalized by the use of two controls, one of which is picked to give a good cleaning job (6 on the scale) and the other a poor job (2 on the scale). In this way, periodic fluctuations in soil removal results are overcome.

Washing machine foamability has been obtained by averaging the observed height in inches after 2.5, 10, 15 and 20 min agitation in a twin-tub top-loading washing machine (Dexter type) containing twelve 16-in. x 37 in. 3-mil polyethylene sheets and 54 ppm of oleic acid.

The dishwashing test is basically similar to a number of published "practical" dishwashing tests (9,10). The detailed procedure was recently published by Spangler (11). The plates are soiled with 2 g of vegetable shortening (Crisco) containing a red dye and are washed until the foam disappears. The foam is originally generated by allowing water to run into the dish pan containing the test detergent from a height of 18 in.

Solubility data have been obtained by observing the temp at which a distilled water solution of the desalted, deoiled sodium sulfonate becomes clear when the temp is raised slowly (less than 1F/min).

Several heavy-duty formulas have been used in this work as shown in Table II. They are not intended to exactly duplicate any commercial products but are considered to roughly simulate them. The ingredients were mixed together just prior to each test.

Results and Discussion

Random LAS vs. PPABS. Results of detergency tests vs. mol wt are shown in Figures 1 and 2. The

 TABLE II
 Composition of Heavy-Duty Detergent Formulas

	35/40/5/1/19	17/3/50/5/1/24	28/31/5/0.8/35.2	25/40/7/1/19/8	17/2/3/45/5/1/19/8
Alkylbenzene sulfonate (LAS or PPABS).....	35	17	28	25	17
Lauric isopropanolamide.....		3			
Lauric ethanolamide.....					2
Sodium toluene sulfonate.....					3
Sodium tripolyphosphate.....	40	50	31	40	45
Sodium silicate.....	5	5	5	7	5
Sodium carboxymethyl-cellulose.....	1	1	0.8	1	1
Sodium sulfate.....	19	24	35.2	19	19
Water.....				8	8

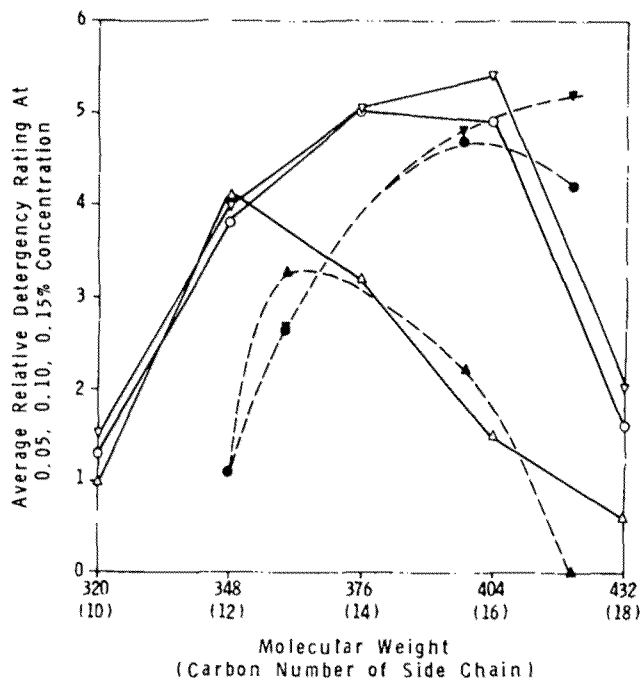


Fig. 1. Terg-O-Tometer detergency of LAS and PPABS vs. mol wt (no foam booster).

Formulation: 35/40/5/1/19;
Temp—120F; FDS soil

Hardness:
 ▽ 20 ppm ——— single carbon random LAS
 ○ 50 ppm ——— narrow fraction PPABS
 △ 180 ppm ——— narrow fraction PPABS

value plotted is the average of relative detergency ratings obtained at 0.05, 0.10 and 0.15% concn of the full formula. On this relative detergency rating scale, 5 to 6 roughly equals 50 to 65% soil removal and 1 to 2 roughly equals 20 to 30%. Some of the results shown are quite low in detergency because of the low detergent concn chosen for study. If one uses 0.2% or higher, almost all the sulfonates perform well; and therefore the differences tend to be obscured. (See, for example, Fig. 8.)

The general pattern for almost any detergent performance test (as opposed to some of the physical measurements) is for the property to go through a max when plotted against mol wt. This is seen for the detergency tests in Figures 1 and 2. Both the LAS and PPABS give about the same results, except that the LAS curves are shifted to lower mol wt by ca. 1 carbon.

Hardness has a drastic effect on both peak height and position when detergency is tested at these relatively low concn. The peak is shifted by ca. 3 carbons to lower mol wt at 180 ppm hardness for both LAS and PPABS. Most of the drop in performance comes from the high mol wt sulfonates giving values down in the -1 to +2 range at 0.05 and 0.10%. At 0.15% in 180 ppm hardness water, there is sufficient detergent to overcome the hardness and give relative detergency ratings around 5. (This kind of behavior can be seen in detail in Fig. 8.) Apparently, with high mol wt sulfonates (LAS or PPABS), the full detergency power of the surfactant is not obtained until enough phosphate has been added to sequester the hardness.

Figure 1 gives detergency in a simple formula containing no foam booster, whereas Figure 2 is for a formula containing 3% lauric isopropanolamide foam

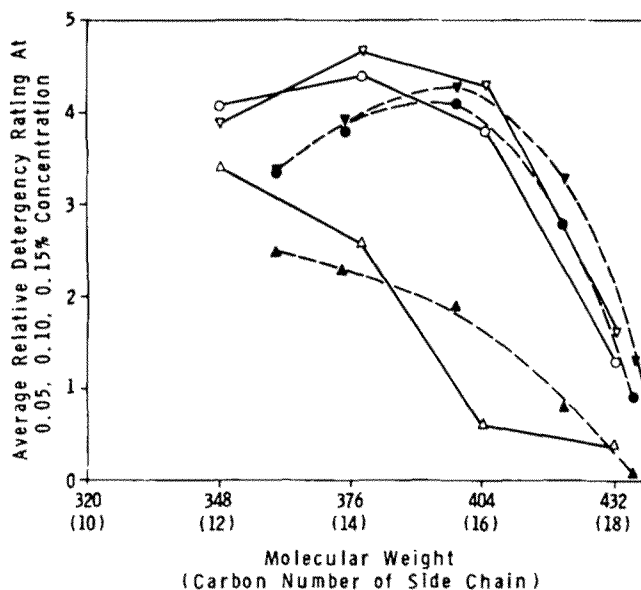


Fig. 2. Terg-O-Tometer detergency of LAS and PPABS vs. mol wt (with foam booster).

Formulation: 17/3/50/5/1/24;
Temp—120F; FDS soil

Hardness:
 ▽ 20 ppm ——— single carbon random LAS
 ○ 50 ppm ——— narrow fraction PPABS
 △ 180 ppm ——— narrow fraction PPABS

booster. The curves of Figure 2 are quite similar to Figure 1, except that they are a little flatter and show relatively better results at low mol wt, i.e., there is a shift in position of ca. 1 carbon.

Washing machine foam results are shown in Figure 3. The curves are very similar in shape and position to the detergency curves. The LAS peaks are at ca. 1 carbon lower mol wt than the PPABS peaks and hardness has a drastic effect for both LAS and PPABS.

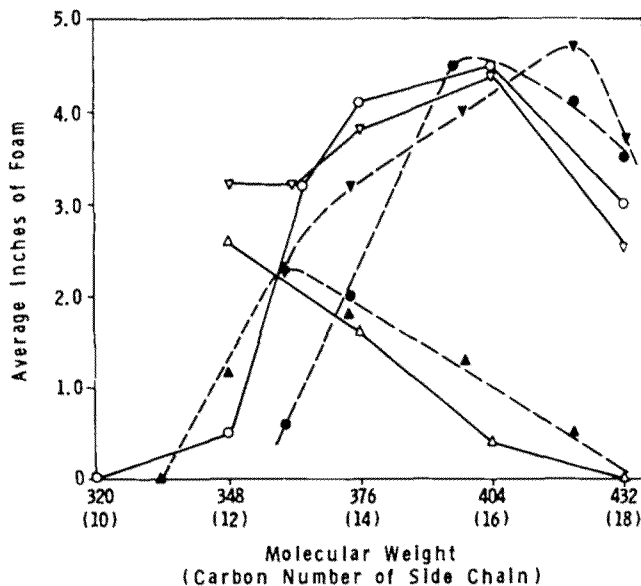


Fig. 3. Washing machine foam of LAS and PPABS vs. mol wt (no foam booster).

Formulation: 35/40/5/1/19;
Concn—0.07%; temp—120F

Hardness:
 ▽ 20 ppm ——— single carbon random LAS
 ○ 50 ppm ——— narrow fraction PPABS
 △ 180 ppm ——— narrow fraction PPABS

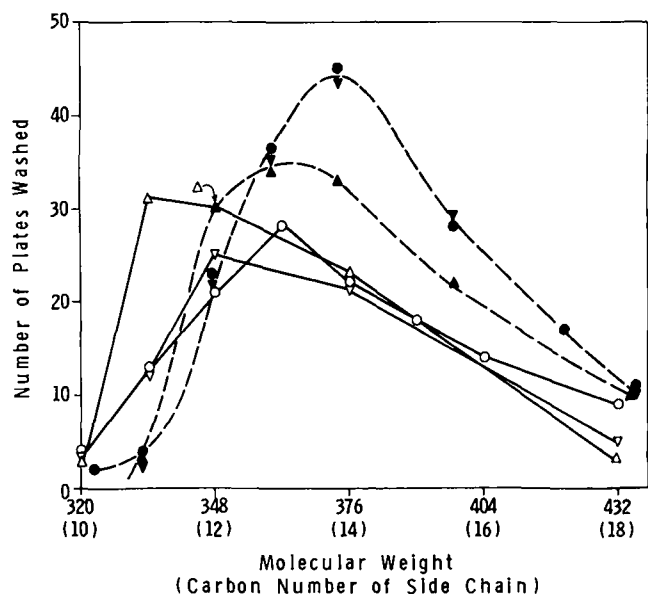


Fig. 4. Dishwashing foam of LAS and PPABS vs. mol wt (no foam booster).

Formulation: 35/40/5/1/19;
Concn—0.15%; temp—115F

Hardness:

- ▽ 20 ppm ——— single carbon random LAS
- 50 ppm - - - - narrow fraction PPABS
- △ 180 ppm

Dishwashing foam results are shown in Figures 4, 5 and 6. Again, we see typical peaks plotted against mol wt and the LAS peaks at ca. 1 carbon lower mol wt from the PPABS peaks. Here, however, the peak positions are at lower mol wt (in the C₁₁ to C₁₄ side chain range, whereas the detergency and washing machine foam peaks were generally in the C₁₃ to C₁₇ range). The effect of hardness is relatively small; the

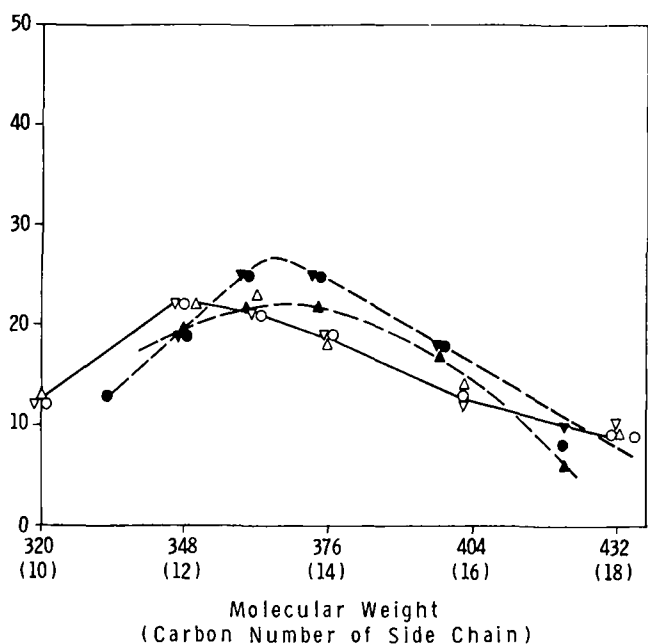


Fig. 5. Dishwashing foam of LAS and PPABS vs. mol wt (with foam booster).

Formulation: 17/3/50/5/1/24;
Concn—0.15%; temp—115F

Hardness:

- ▽ 20 ppm ——— single carbon random LAS
- 50 ppm - - - - narrow fraction PPABS
- △ 180 ppm

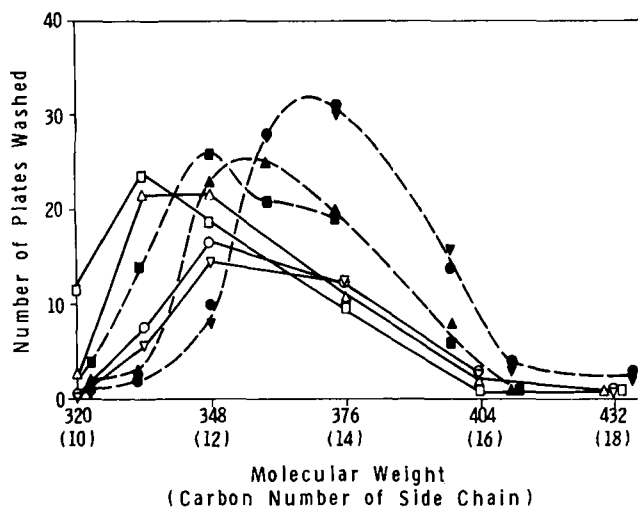


Fig. 6. Cold water dishwashing foam of LAS and PPABS vs. mol wt (no foam booster).

Formulation: 28/31/5/0.8/35.2;
Concn—0.15%; temp—80F

Hardness:

- ▽ 20 ppm ——— single carbon random LAS
- 50 ppm - - - - narrow fraction PPABS
- △ 180 ppm
- 300 ppm

peaks are shifted only 0 to 2 carbons to lower mol wt and the peak value only drops moderately for PPABS and actually rises slightly for LAS.

Figure 5 gives results for a foam booster formula. As before, the foam booster tends to flatten the curves, making the differences become less noticeable. Increasing hardness to 180 ppm has practically no effect. Dishwashing foam in cold water without foam

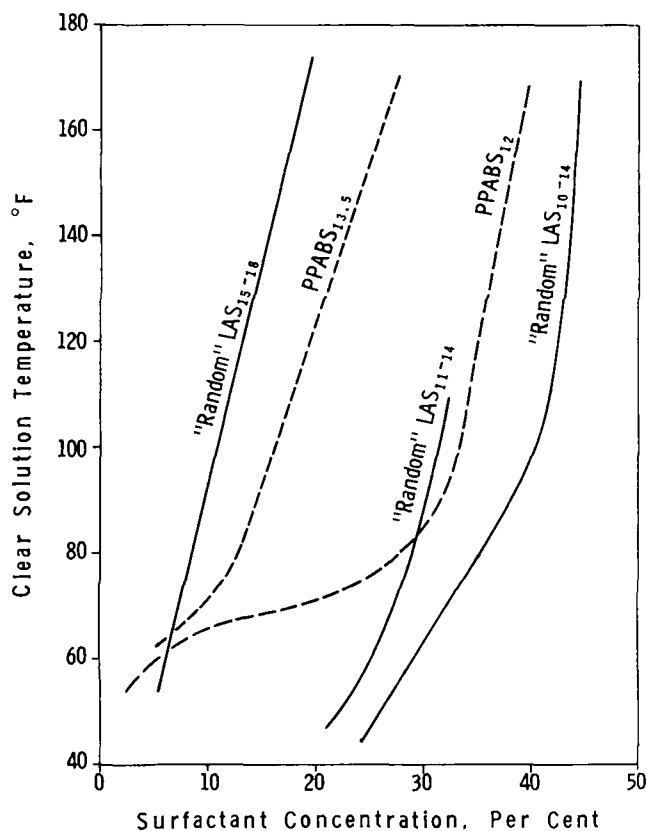


Fig. 7. Solubilities of random LAS vs. PPABS (sodium salts).

TABLE III
Summary of Performance Vs. Mol Wt for Random LAS and PPABS

	Hardness, ppm	Optimum performance peak				Performance at a fixed mol wt	
		PPABS		Random LAS		PPABS with Cis.5 side chain	Random LAS with Cis.5 side chain
		Side chain size	Value	Side chain size	Value		
Dishwashing foam, plates							
35/40/5/1/19 115F, 0.15%	20	14	45	12-14	25	43	24
	50	14	45	13	28	43	24
	180	12-14	35	11-12	31	34	28
17/3/50/5/1/24 115F, 0.15%							
	20	13-14	25	12-13	22	25	22
	50	13-14	25	12-13	22	25	22
	180	13-14	22	12-13	22	22	22
28/31/5/0.8/35 80F, 0.15%							
	20	13-14	32	12-13	15	31	15
	50	13-14	32	12-13	17	33	16
	180	12-13	26	11-12	22	22	20
	300	12-13	26	11-12	24	20	17
Washing machine foam, inches							
35/40/5/1/19 120F, 0.7%	20	16-17	4.7	14-16	4.4	3.0	3.2
	50	16-17	4.6	14-16	4.5	1.6	1.6
	180	13	2.3	~12	2.6	2.1	2.3
Terg-O-Tometer detergency, rel. det. rating							
35/40/5/1/19 120F, avg of 0.05, 0.10, 0.15%	20	16-17	5.2	14-16	5.4	3.4	4.2
	50	16-17	4.7	14-16	5.0	3.4	4.2
	180	13-14	3.3	12	4.1	3.2	3.9
17/3/50/5/1/24 120F, avg of 0.05, 0.10, 0.15%							
	20	15-16	4.3	13-15	4.7	3.7	4.1
	50	15-16	4.1	13-15	4.4	3.7	4.2
	180	~13	2.5	~12	3.4	2.4	3.2

booster is shown in Figure 6. These results are generally quite similar to those in Figure 4. The values are lower because a lower active formula was chosen. In this case, tests were run at 300 ppm hardness, as well as the usual 20, 50 and 180 ppm because in some foreign areas cold, very hard water is used. The results are only shifted slightly to lower mol wt compared with 180 ppm.

The most important difference between dishwashing foam and the other tests is that the random LAS max performance does not equal that for PPABS.

All the above data are summarized in Table III where the mol wt and value are tabulated for each of the performance peaks. Also, to obtain a better evaluation of a particular LAS versus a particular PPABS, values are shown for PPABS with a 13.5 carbon side chain and LAS with a 12.5 carbon side chain. These both appear to be the opt mol wt where the best com-

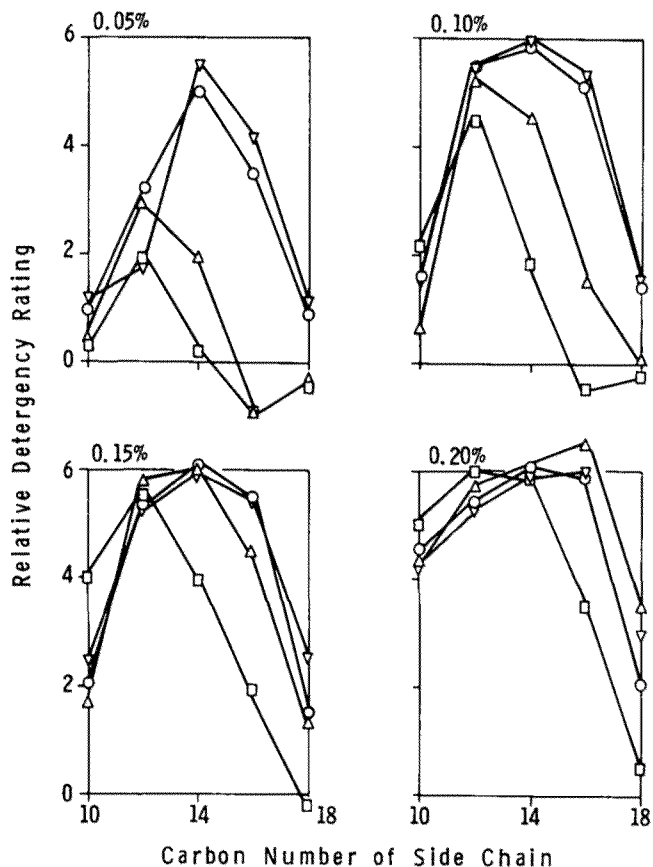


Fig. 8. Terg-O-Tometer detergency of pure 2-phenyl sulfonates.

Formula: 35/40/5/1/19; temp—120F; FDS soil

Hardness:
 ▽ 20 ppm △ 180 ppm
 ○ 50 ppm □ 300 ppm

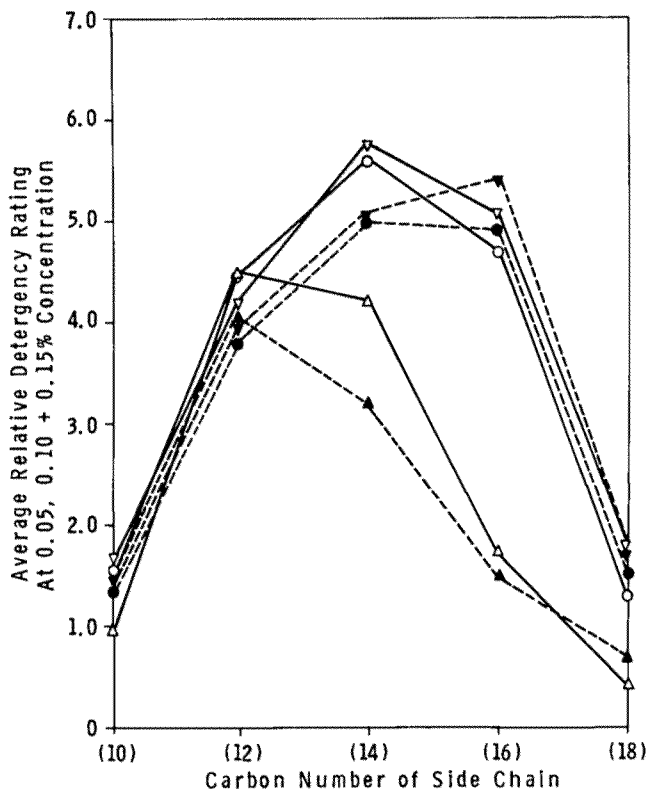


Fig. 9. Detergency of pure 2-phenyl sulfonates vs. random LAS.

Formula: 35/40/5/1/19; temp—120F; FDS soil

Hardness:
 ▽ 20 ppm ○ pure 2-phenyl sulfonates
 ○ 50 ppm △ random LAS
 △ 180 ppm

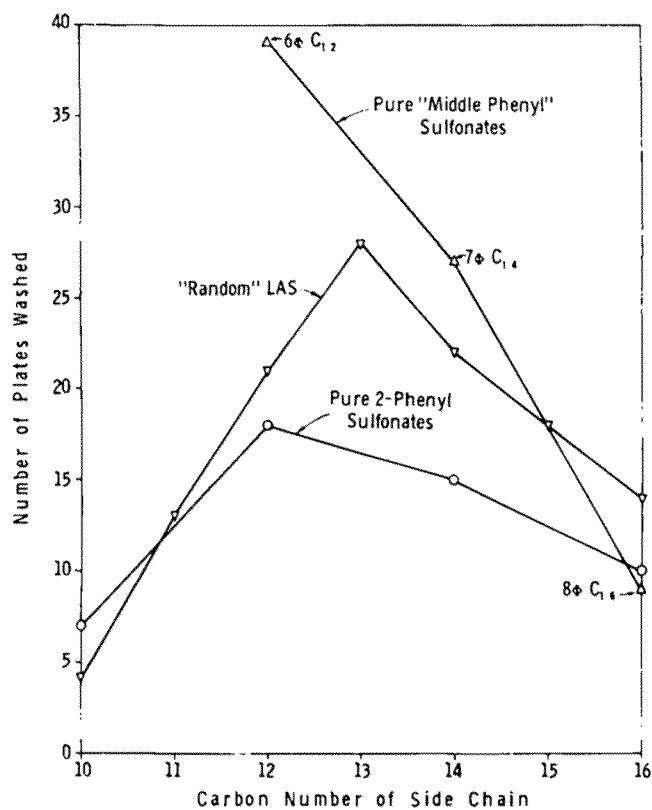


FIG. 10. Dishwashing foam of pure isomers and random LAS vs. mol wt.

Formulation: 35/40/5/1/19; hardness—50 ppm;
Concn—0.15%; temp—115F

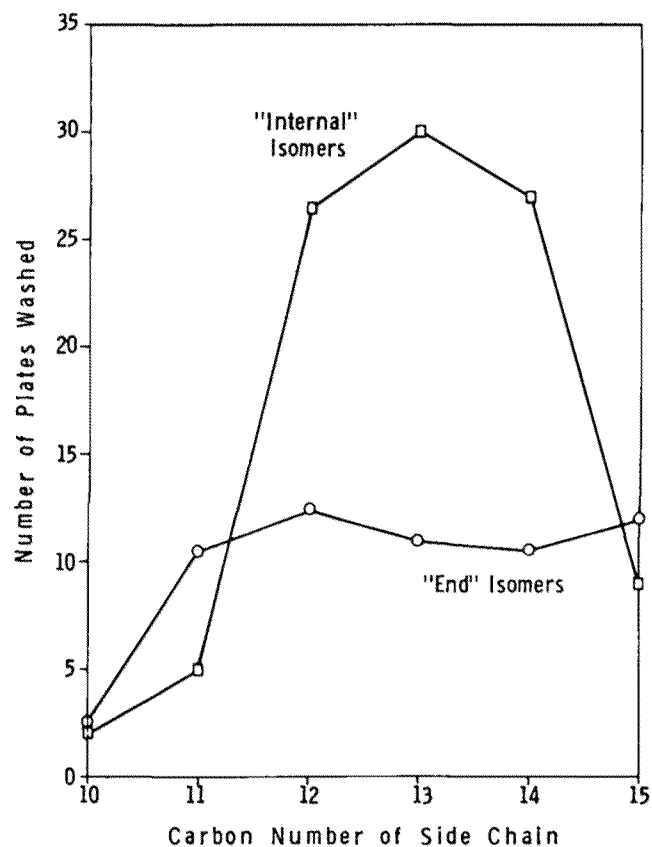


FIG. 11. Dishwashing foam of end and internal isomers vs. mol wt.

Formulation: 25/40/7/1/19/8; hardness—50 ppm;
Concn—0.15%; temp—115F

promise between performance in various tests is obtained. We often find with mixtures of homologues in the detergent range that a 4 carbon spread will show performance equal to its average mol wt. Therefore, 13.5 carbons for PPABS can be a C_{12} to C_{15} mixture of homologues like the commercial PPABS_{13.5}, as well as the C_{13} plus C_{14} mixture it implies. Similarly, $C_{12.5}$ for LAS can be a C_{11} to C_{14} mixture. This comparison shows again that, while random LAS is equal to or better than PPABS in detergency and washing machine foam, it is inferior in dishwashing foam.

The solubility of three wide-range random LAS samples is shown in Figure 7 in comparison with the commercial PPABS products. As expected, solubility decreases with increasing mol wt. Random LAS is generally more soluble than PPABS, especially at or below room temp. Even the high mol wt LAS₁₅₋₁₈ is almost as soluble as the PPABS_{13.5}, which is ca 3 carbons lower in mol wt. There is a noticeable difference between LAS₁₁₋₁₄ and LAS₁₀₋₁₄.

Performance of LAS Isomers. It is known that isomer distribution of LAS can vary with the alkylation catalyst employed (8). Previous investigators (2-5) had shown some differences in properties between LAS isomers, but there was no clear indication of how the isomers might behave in practical tests. For example, some earlier work in our own laboratories using the Ross-Miles foam test showed a little preference for the 2- and 3-phenyldodecane sulfonates over the 5- and 6-phenyl isomers, but the Ross-Miles test does not correlate well with formability in use (9). Therefore, the following work was undertaken.

One investigation involved synthesizing and testing a series of even-membered 2-phenylalkane sulfo-

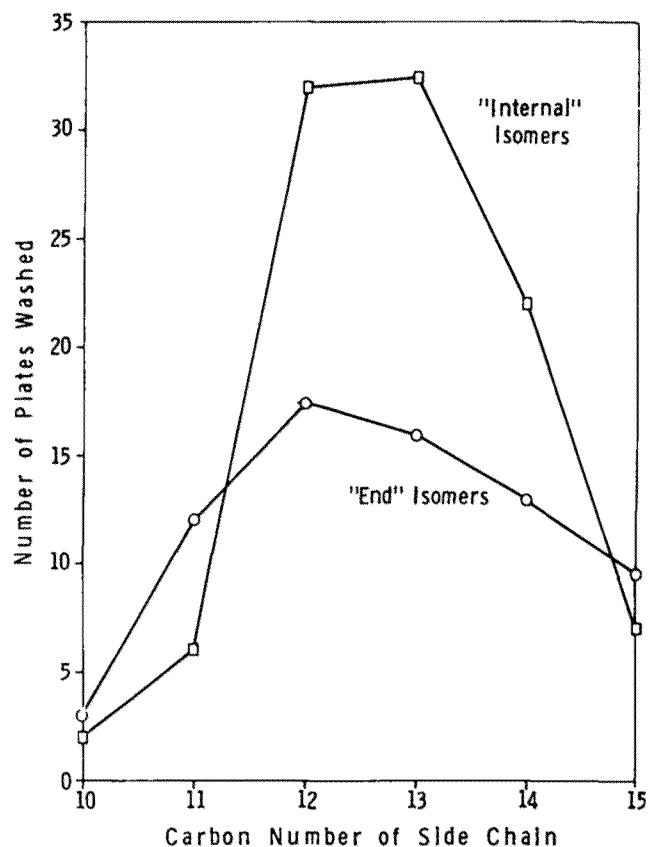


FIG. 12. Dishwashing foam of end and internal isomers vs. mol wt.

Formulation: 25/40/7/1/19/8; hardness—150 ppm;
Concn—0.15%; temp—115F

TABLE IV
Terg-O-Tometer Detergency of End Isomers Vs. Internal Isomers: Relative Detergency Rating, 120F, FDS Soil

Formula	35/40/5/1/19						17/3/50/5/1/24					
	50 ppm			180 ppm			50 ppm			180 ppm		
	0.05	0.10	0.15	0.05	0.10	0.15	0.05	0.10	0.15	0.05	0.10	0.15
C ₁₁ Internal	0.1	0.7	1.0	0.3	0.4	1.6	0.9	1.1	4.1	0.5	1.0	3.5
End	0.6	2.8	6.1	1.7	4.9	6.6	0.9	2.3	6.0	0.4	2.2	5.8
C ₁₂ Internal	0.6	2.1	5.0	0.2	3.9	6.1	1.1	3.7	4.7	0.3	2.6	5.9
End	1.2	4.7	5.0	1.7	4.5	5.0	1.5	5.1	5.9	1.6	3.9	6.1
C ₁₃ Internal	1.3	5.1	5.8	0.6	2.5	5.7	0.6	5.5	6.9	0	1.8	6.6
End	4.1	6.0	6.3	0.8	1.1	6.4	2.5	5.4	6.3	0.7	2.6	6.2
C ₁₄ Internal	1.1	4.9	5.4	1.2	1.6	5.8	3.5	5.3	5.7	-0.1	1.5	6.4
End	4.3	5.7	5.8	0.1	4.4	6.5	4.4	5.3	5.6	0.4	3.8	6.4
C ₁₅ Internal	0.8	1.3	5.2	-1.2	-1.0	1.0						
End	3.0	5.5	5.7	-1.4	0.8	3.8						
Whole LAS in 25/40/7/1/19/8 formula												
C ₁₁₋₁₄ random	0.7	5.3	5.9	0.2	2.7	6.0						
C ₁₁ high 2-phenyl	1.3	5.1	5.9	0.7	2.7	5.5						

nates. Terg-O-Tometer detergency for this series is shown in Figure 8 for each concn separately and in Figure 9 for the average of the 0.05, 0.10 and 0.15% concn. The random LAS data (Fig. 1) also are plotted in Figure 9 for comparison. The 2-phenyl sulfonates are marginally superior to the random LAS, but the difference is small and is not enough to be noticeable if the 2-phenyl content of a whole alkylate were only changed moderately, e.g., from 20% to 35%.

Dishwashing foam results for the 2-phenyl sulfonates are shown in Figure 10 in comparison with the random LAS and three pure compounds in which the phenyl group is attached to the middle of the alkyl chain. In this case, the 2-phenyl compounds are inferior to the random LAS; and, in agreement with that, the 6-phenyldodecane and 7-phenyltetradecane sulfonates are superior to it. The 6-phenyldodecane

value is unexpectedly high and is approaching the performance of the best PPABS.

Further information on isomer effects has been obtained by carefully distilling each of the random alkylates to yield a low boiling fraction containing 80-90% of the internal isomers (i.e., 5-, 6-phenyl, etc.) and a high boiling fraction containing ca. 90% 2-phenylalkane. After sulfonation, the former is called "internal" isomers and the latter "end" isomers. Dishwashing data for these materials are shown in Figure 11. (Note that the formula used in this case is similar to the previous one used but has a lower active content.) The same pattern seen in Figure 10 is evident, namely, that the end isomers gave relatively poor results, whereas the internal isomers at C₁₂, C₁₃ and C₁₄ gave exceptionally high values. (PPABS₁₂ washed 10 plates and PPABS_{13.5} 24 plates in this formula.)

Figure 12 shows data for these same sulfonates in hard water. One sees little change except to lower the C₁₄ internal isomers and to raise slightly both the end and internal C₁₂ and C₁₃ isomers. Dishwashing data for a foam booster formula are shown in Figure 13. The curves are very similar to Figure 12, except that the C₁₀ and C₁₁ results are improved by the foam booster.

Therefore, the big advantage of the C₁₂, C₁₃ and C₁₄ internal isomers exists under all the conditions tested; namely, in soft or hard water without foam booster and in soft water with foam booster. The 10- to 15-plate advantage of the internal isomers suggests that variations in the isomer distribution of whole alkylates should make a noticeable difference in dishwashing foamability.

Terg-O-Tometer detergency and washing machine foam results for the various end and internal sulfonates are shown in Tables IV and V. There is a marginal advantage to the end isomers in detergency (as there was in comparing the pure 2-phenylalkane sulfonates to the random LAS above) and in washing

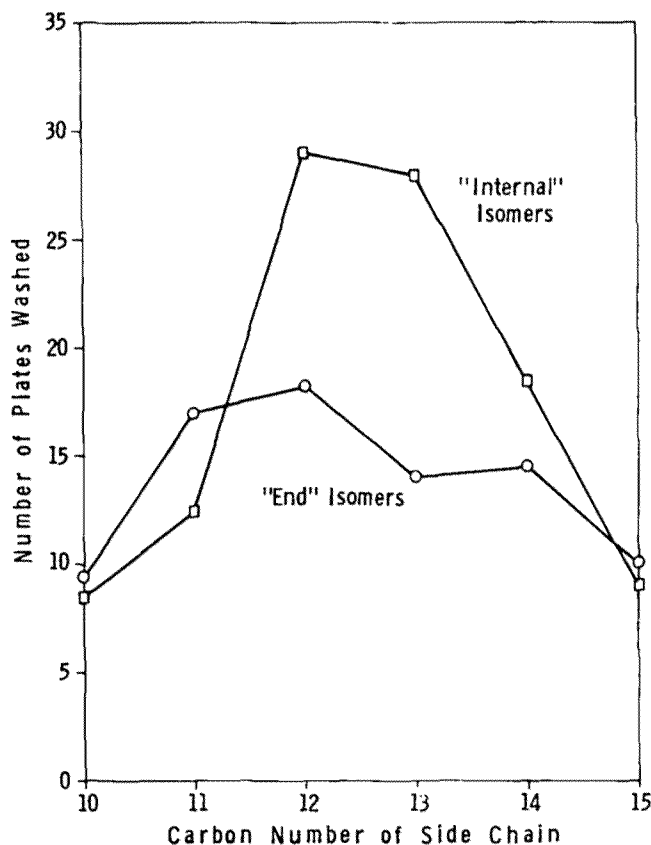


FIG. 13. Dishwashing foam of end and internal isomers vs. mol. wt.
Formulation: 17/2/3/45/5/1/19/8; hardness—50 ppm; Concn—0.15%; temp—115F

TABLE V
Washing Machine Foam of End Vs. Internal Isomers
Formula: 35/40/5/1/19
Concn: 0.075%; Temp: 120F

	Average foam height, inches		
	At following water hardness, ppm		
	20	50	180
C ₁₁ Internal	1.1	0	0
End	2.9	0	1.5
C ₁₂ Internal	3.6	0.5	1.8
End	5.3	3.2	1.5
C ₁₃ Internal	3.1	3.4	2.2
End	4.3	4.3	1.3
C ₁₄ Internal	5.4	5.6	1.5
End	6.1	5.8	1.2

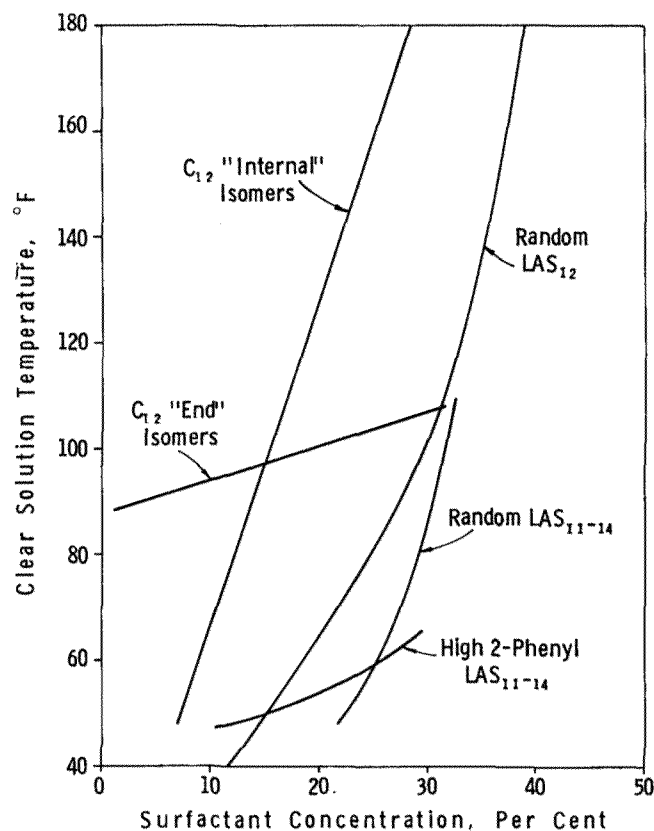


FIG. 14. Isomer effects on solubility (sodium salts).

machine foam, but the differences are not large enough to be noticeable in a wide-range product. For example, C_{11-14} random LAS and high 2-phenyl LAS whose 2-phenyl contents are ca. 18 and 32%, respectively, are compared in a 25/40/7/1/19/8 formula at the bottom of Table IV. There is no difference beyond experimental error between the two.

Solubility is also influenced by isomer distribution as shown in Figure 14. The C_{12} end isomers sulfonate has a very flat clear point curve reminiscent of a

number of pure straight-chain surfactants (12). (Pure 2-phenyldodecane sulfonate itself has a curve ca. 10°F higher.) The C_{12} internal isomers sulfonate which contains no 2-phenyl isomer has a very steep and straight clear point curve. The random C_{12} and C_{11-14} LAS which have low 2-phenyl contents (ca. 18%) are also steep but show a little tendency to curve over at low temp. The flattening out is quite pronounced with the high 2-phenyl LAS which contains about 32% 2-phenyl isomers. Therefore, increasing 2-phenyl content up to at least 32% increases room temp solubility.

LAS is basically equal to or better than PPABS, except in dishwashing foamability. The separate LAS isomers show a small advantage to the end attachment in detergency and washing machine foaming and a large advantage for the internal isomers in dishwashing foam tests. The latter effect appears large enough to be noticeable when the 2-phenyl content varies in commercial-type products.

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Straight-Chain Alkylbenzenes: Structure and Performance Property Relations

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Abstract

An intensive study of the mass spectral characteristics of straight-chain alkylbenzenes has been made in conjunction with their ultimate performance as sulfonates in heavy duty formulations. Two variables of the alkylates, carbon-chain length distribution (which fixes the mean mol wt) and phenyl position on the chain, have been successfully related to the observed dishwashing performances. Formulas are given which allow accurately predicting this performance criteria. The important role of phenyl position is illustrated by a detailed study of each phenyl isomer in the tetradecylbenzene series.

Introduction

THE MOST WIDELY USED SURFACTANT in household detergents for the past 10 years has been polypropylene tetramer branched alkylbenzene sulfonate, commonly known as ABS. Since World War II, the usage of ABS in the U.S. has grown to approx 560 million lb/year. Concurrent with increased use of ABS detergents, our laboratories investigated several hundred commercial polypropylene derived alkylates and were able to correlate performance characteristics with the mass spectrometric analyses.

Fundamentally this correlation depended on the observed molar distribution and also on a branching parameter, both derived from the mass spectral analysis of the alkylate prior to sulfonation. The degree of

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