is approaching completion. Residual foam volumes are still to be estimated and recorded. Estimation now has to be made on the basis of void surface, and height and contour of the foam. An aid to doing this quickly may be prepared on a card to be mounted in direct view of the operator. The card may show diagrams and an easily readable table of volumes corresponding to observed wall heights at 20% intervals of exposed liquid surface.

14. Obtaining foam data at 0-, 15-, 30- and 60-sec intervals is demanding but quite possible. In examining new compounds, parts at least of all the data have been found useful. The different curves reveal different characteristics of a degrading system. DFV-60 data have generally shown the closest parallelism in form of decay curve to surface tension behavior or acceptable analyses, working largely in nonionic areas. Were a single determination to be left out DFV-15 or DFV-30 usually would sacrifice least. If only two determinations were to be made one proposal would obtain DFV-5 and DFV-30 data. This saves some time but provides no assurance that the foam had first attained maximum volume before decay started. MFV and DFV-5 readings are about equally difficult to obtain.

ACKNOWLEDGMENT

R. M. Gerhold and the Procter and Gamble Company provided helpful discussions of foam generation test methods and the characteristics to be sought in a mechanized method. Wyandotte was able to build the machine first and it embodies ideas from both companies.

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[Received June 29, 1965—Accepted October 22, 1965]

Straight-Chain Alkylbenzenes: Structure and Performance Property Relations

III. Light-Duty Dishwashing Formulations[1]

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Abstract

A relationship between mixtures of straight-chain alkylbenzene sulfonates and their performances in light-duty dishwashing formulations has been established through studies of many pure isomers and isomer mixtures in both liquid and powder systems. The foam performance characteristics are shown to be directly related to carbon chain length, phenyl position, and water hardness in a readily calculable manner. Solubility studies on pure isomers are also reported.

Introduction

EARLIER REPORTS (1,2) from these laboratories established the relationship between the structure of straight-chain alkylbenzene sulfonates (LAS) and their performance in *heavy-duty* detergent systems. The performance characteristics of detergency and foam stability were shown to be directly related to carbon-chain length distribution and phenyl position. Appropriate formulae were given to determine the foam performance of mixed LAS systems. The optimum performers in heavy-duty systems were shown to be the internal (5, 6 and 7 phenyl) isomers of the C_{12}, C_{13} and C_{14} carbon-chain lengths. A partial study on light-duty powder system performance was also presented.

The powder system performance relationships were established in formulations where the alkylbenzene sulfonate was the sole organic active ingredient. This is not the case in a typical biodegradable light-duty liquid formulation utilizing alkylbenzene sulfonate, alcohol ether sulfate and fatty alkylolamide. In such a ternary system the determination of structural effects is much more complex. Maximum performance for this type of system was first developed in studies using a standard alkylbenzene sulfonate while varying the ether sulfate and alkylolamide. For the work described here, only the alkylbenzene sulfonate structure was varied; the ether sulfate and alkylolamide components were constant. There are no reports in the literature on the LAS structural relationships (both phenyl position and carbon-chain length) involved in the performance of light-duty liquid systems; this report will bear on that subject. Alcohol ether sulfate structural relationships have been reported (3).

Evaluation Techniques

Light-duty liquid foaming performance was evaluated in the formulation of interest by means of a miniature dishwashing procedure. This procedure was developed in our laboratory to fill two vital needs; reliable data from a small number of tests, and consumption of a minimum quantity of sample. This new method, which is to be described in a future publication, is a modification of a standard manual dishwashing test (4). It involves measuring the number of plates washed to a foam end-point under set conditions when the plates are carefully presoiled with exact amounts of a hydrogenated vegetable oil.

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TABLE I

Performance—LAS Isomers

Chain length	2 ø Isomer	Internal	Rating
	100 ppm		
C_{10}	0.99	0.97	equal
C_{11}	0.91	0.97	Int. > 2ø
C_{12}	0.85	1.05	Int. » 2ø
C_{13}	0.68	0.74	Int. > 2ø
C_{14}	0.41	0.49	Int. > 2ø
	250 ppm		
C_{10}	0.96	0.99	equal
C_{11}	0.88	0.93	Int. > 2ø
C_{12}	0.71	0.72	equal
C_{13}	0.44	0.49	Int. > 2ø
C_{14}	0.24	0.43	Int. > 2ø

Correlation studies have demonstrated that the range of replicate tests in this method is much narrower than in the standard manual dishwashing test. Individual results have much more significance in this new test, and even more meaningful data is gathered by averaging values of replicate tests. The performance of a given straight chain alkylbenzene sulfonate isomer is expressed as the ratio of the average of plates washed by the formulation containing the specific isomer to the plates washed by a control formula.

$$\text{Performance} = \frac{\text{Plates Washed LAS Formulation}}{\text{Plates Washed Control}}$$

A difference of 0.04 units is meaningful. The ratio is used as a mathematical convenience and only incidentally compares the performance of the sample of interest to that of the control formula. The light-duty liquid dishwashing formulations in which the straight-chain alkylbenzene sulfonate isomers were compared consisted of straight-chain alkylbenzene sulfonate, alcohol ether sulfate and alkylolamide, while the control formula was a nonbiodegradable standard consisting essentially of 18% branched dodecylbenzene sulfonate, 12% ethoxylated nonylphenol sulfate, and 5.5% fatty alkylolamide.

The study of a light-duty powder system was carried out on a "quid pro quo" direct comparison basis between straight- and branched-chain alkylbenzene sulfonates in order to correlate with our previously published data. The performance of a given isomer here is expressed as plates washed by the straight-chain isomer divided by plates washed by a standard branched dodecylbenzene sulfonate. The light-duty powder formulation was essentially 30–35% straight- or branched-chain alkylbenzene sulfonate and 65–70% sodium sulfate.

Discussion and Results

I. Foam Stability Studies in a Light-Duty Liquid Formulation

A. *Pure Isomers.* We have investigated the dishwashing performance of the 2-phenyl and internal isomer homologs of the C_{10}–C_{14} carbon-chain series. A typical internal isomer composition is illustrated by the mass-spectral analysis of the C_{12} compound which was 1.2% 2-phenyl, 3.4% 3-phenyl, 8.6% 4-phenyl, 37.1% 5-phenyl and 49.2% 6-phenyl. Preliminary studies on the effect of carbon-chain distribution of commercial straight-chain alkylbenzene sulfonates on performance were made in a typical light-duty liquid formula. It was evident that maximum performance resulted from a distribution composed mainly of C_{10}, C_{11} and C_{12} carbon chains. This report shows the relationship more clearly and defines the contribution of the structural components.

TABLE II

Performance—Variation with Water Hardness

	50 ppm	100 ppm	150 ppm	200 ppm	250 ppm	300 ppm
2ø C_{10}	1.06	0.99	1.00	0.97	0.96	1.00
Int. C_{12}	1.19	1.05	0.87	0.83	0.72	0.66

TABLE III

Performance—LAS Isomer Mixtures

Composition of LAS Used (Wt. %)	100 ppm Calc.	100 ppm Known	250 ppm Calc.	250 ppm Known
LAS A (100%)	0.99	1.00	0.93	0.95
LAS B (100%)	0.97	0.99	0.89	0.88
LAS C (100%)	0.98	0.97	0.86	0.88
Internal $C_{10,11,12,13}$ (10-30-50-10)	1.03	1.04	0.88	0.88
Internal $C_{10,11,12}$ (20-60-20)	1.03	1.04	0.99	0.97
Internal $C_{10,11,12}$ (30-40-30)	1.03	1.01	0.98	0.98
Internal $C_{11,12}$ (50-50)	1.05	1.00	0.92	0.96
2ø C_{12}, int. C_{12} (50-50)	0.99	0.99	0.81	0.77
2ø C_{10}, C_{12} (50-50)	0.95	0.94	0.93	0.93
2ø $C_{10,11,12}$ (30-40-30)	0.96	0.94	0.95	0.93
Internal $C_{11,13}$ (50-50)	0.90	0.90	0.81	0.84
2ø C_{12} (100%)	0.85	0.85	0.71	0.71
2ø $C_{10,11,12,13}$ (20-30-30-20)	0.90	0.85	......	......

Highest performance in the series of 2-phenyl isomers is observed at C_{10} in both 100 ppm and 250 ppm water hardnesses with the C_{11}–C_{14} homologs showing a gradual decline in performance. This is illustrated in Table I.

The internal phenyl isomer series shows the same downward progression from C_{10} in hard water (250 ppm). However, in soft water the performance goes through a maximum at C_{12} and the break in dishwashing performance between C_{12} and C_{13} is very pronounced —C_{13} washes about 10 plates fewer.

Comparing the performance of the 2-phenyl versus the internal isomer of any given chain length in Table I, it is evident that at 100 ppm the preferred type of isomer distribution is the internal one. At 250 ppm the internal isomer is also favored but the differences are not as pronounced as at the lower hardness level.

It should be noted that the foam performances of the pure isomers are substantially better at 100 ppm than at 250 ppm in the higher C_{12}–C_{14} chain lengths whereas in C_{10}–C_{11} they are equivalent. One isomer from each of these groups was chosen for more extensive examination of hardness-performance interactions. The performance of the 2-phenyl C_{10} and internal C_{12} isomers was studied over a wide range of water hardnesses from 50 ppm to 300 ppm. The results dramatically showed that the 2-phenyl C_{10} has virtually no performance-hardness interaction, whereas with the internal C_{12} a strong interaction exists, giving a much lower performance level at 300 ppm (about 50%) than at 50 ppm. This is illustrated in Table II.

The data in Tables I and II strongly indicate that for this particular light-duty liquid dishwashing formulation, a preponderance of the lower carbon-chain lengths (C_{10} and C_{11}) in the straight-chain alkylbenzene sulfonate is desirable for maximum performance over a wide hardness range.

B. *Mixtures of Isomers.* Our pure isomer performance studies have been extended to mixtures of pure carbon-chain isomers and to commercial carbon-chain isomer mixtures. In heavy-duty detergent systems, Rubinfeld, Emery and Cross (2) have shown that one can accurately predict the performance of a given mixed isomer-chain length alkylbenzene sulfonate by a summation of the performances of the individual isomers present. We were concerned whether any such relationship applied to light-duty liquid systems where a multicomponent active system is present as opposed to the mono-active alkylbenzene sulfonate system employed in heavy-duty detergent powders. Certain constant synergistic relationships were discovered by comparing simple summations of the pure isomer performances with the actual dishwashing of pure isomer mixtures in the same light-duty formula. Increased performance of the mixed isomers compared to their individual performance summations varied directly with water hardness. By including an empirical hardness-performance factor we have been able to derive an appropriate equation which will accurately predict the dishwashing performance of our typical multicomponent light-duty system using any mixture of straight-chain alkylbenzene sulfonate isomers. The equation is:

Performance of LAS Formulation =
(Σ % isomer $\times$ Isomer performance at given hardness)
+ (hardness in ppm $\times$ .0004).

Table III shows the calculated and known performances of some commercial straight-chain alkylbenzene sulfonates as well as pure isomer mixtures. Commercial alkylates were chosen from those with a molecular weight of close to 240 and a known carbon-chain distribution. The calculations for the commercial samples involved an estimation of performance for the 3 and 4 phenyl isomers since these were unavailable for characterization. It can be seen that the method can be applied to give a close approximation of performance over a widely diverse range of mixtures and performances.

The data in this table amply support the following propositions; that carbon chains of 10 and 11 members produce the best overall performance; that mixtures of internal isomers perform better than their 2-phenyl counterparts; and that carbon-chain distribution governs the performance variations shown in different water hardnesses.

II. Solubility Studies on Pure Isomers and Mixtures

Solubility data on the six isomers of the C_{12} alkylbenzene sulfonate series have been previously reported in the literature (5).

We have extended this work to include a number of the 2-phenyl and internal isomers of the C_{10}, C_{11}, C_{12} and C_{13} series as well as selected mixtures of these pure isomers. Cloud and clear points were determined on a micro scale for 15% solutions of the isomers which were desalted alkylbenzene sulfonate sodium salts. The results are shown in Table IV.

TABLE IV
Cloud-Clear Point Determinations
15% Solutions

LAS isomer or mixture	Cloud point	Clear point
2ø C_{10}	88F	94F
2ø C_{12}	95F	102F
Int. C_{11}	94F	96F
Int. C_{12}	180F	182F
Int. C_{13}	206F	210F
50-50 2ø C_{10}, Int. C_{12}	35F	......
50-50 Int. C_{11}, C_{12}	146F	150F
50-50 2ø C_{10}, C_{12}	72F	78F
C_{10}, 25% each 2, 3, 4, 5 ø	48F	51F
Commercial "D"	43F	46F
Commercial "E"	36F	......

From the data it appears that the solubility within a particular isomer series decreases with increasing carbon-chain length. This is much more marked in the internal isomer series than in the 2-phenyl where the homologs seem to group in a small range. The solubility relations at other concentrations were not studied because of limited samples.

Since solubility effects are very important in liquid formulations, it seemed that the better foaming properties of the internal isomers might be overshadowed by their poor solubility. To attempt to define how critical this would be in a commercial alkylbenzene sulfonate where different chain lengths are present as well as both types of isomers, we studied a 50-50 mixture of 2-phenyl C_{10} (cloud point 88F) and internal C_{12} (cloud point 180F). If the cloud point were a straight line function of the mixture with no interactions between the isomers, then the cloud point of the mixture should be about 134F. Indeed this was not the case; the cloud point was tremendously depressed to about 35F, substantially below that of either component. This effect was also observed in measurements on two different commercial straight-chain alkylbenzene sulfonates. A further experiment using a C_{10} homolog containing 25% each of the 2, 3, 4, 5 phenyl isomers resulted in a similarly low cloud point. On the other hand, a 50-50 mixture of pure internal 11 and 12 compounds showed a cloud point of 146F, almost half-way between the individual results. Again, a 50-50 mixture of 2-phenyl C_{10} and C_{12} had a lower cloud point (72F) than either of its components, but only to a relatively small degree. The cloud-clear points obtained by mixing carbon chains of the same phenyl isomer may possibly result from independent action of each carbon-chain isomer at its own concentration; e.g., 15% solution of 50-50 mixture acting like 7.5% solutions of each component. If this is the case, the material of lower solubility would be dominant in measuring cloud point. With mixtures of 2-phenyl and internal isomers, however, this cannot be true since then a 50-50 2ø C_{10} and internal C_{12} would have a cloud point close to that for 50-50 internal C_{11}, C_{12}. They in fact differ by more than one hundred degrees. There must then be a powerful solubility synergism between 2-phenyl and internal isomers in mixtures. A postulation of mutual solubility promotion among isomers of straight-chain phenyl-dodecane sulfonate is found in the literature (5). The possibility also exists that there is further synergistic action between different carbon-chain lengths of the same isomer, but this would be relatively minor in magnitude.

III. Foam Stability in a Light-Duty Powder Formulation

Data on foam stability performance (50 and 150 ppm) of various straight-chain alkylbenzene sulfonate isomers in a light-duty powder system have been previously reported by these laboratories (2). We have extend the scope of this work to include additional performance data at 100 ppm and 250 ppm. This study has indicated that the performance—hardness interaction is small for the C_{10} and C_{11} isomers of both types and much greater for the C_{12} and C_{13} isomers; the same result was shown for a multi-active light-duty liquid formulation in Tables I and II. However, whereas in the liquid system the changes with hardness were all in the direction of decreased foam performance, in the light-duty powder formulation both types of isomers of the C_{10} and C_{11} com-

TABLE V
Light-Duty Powder Plates Washed LAS/ABS

Isomer	50 ppm	100 ppm	150 ppm	250 ppm
2ø C_{10}	0.60	0.60	0.64	0.81
2ø C_{11}	0.92	0.94	0.96	1.12
2ø C_{12}	0.92	0.66	0.50	0.44
2ø C_{13}	0.87	0.32	0.14	0.19
Int. C_{10}	0.40	0.40	0.64	0.74
Int. C_{11}	0.92	......	0.96	......
Int. C_{12}	1.33	......	1.22	......
Int. C_{13}	1.07	0.90	0.88	0.33

pounds show improved performance with increased hardness. The opposite situation is found for the C_{12} and C_{13} isomers as is evident in Table V.

It is apparent from these data that there will be conflicting factors affecting the performance of mixtures of these isomers. For a given hardness, the 2-phenyl isomers reach maximum performance at C_{11}; then drop off. The internal isomers, however, peak at C_{12}. The overall best performance is found for the internal C_{12} isomer followed by both isomers of C_{11}. It should be noted that while the C_{10} homologs performed very well in a multi-active liquid system, their performance contribution is diminished in a mono-active light-duty powder. From a foam performance viewpoint, an ideal distribution for a straight-chain alkylbenzene sulfonate in this powder system would be a C_{11}–C_{12} mixture with a preponderance of the internal isomers.

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[Received July 26, 1965—Accepted October 22, 1965]

Phase Behavior of the Dimethyldodecyl Amine Oxide-H_2O System

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Abstract

An exploratory study of the aqueous system of dimethyldodecyl amine oxide (DDAO) revealed it to be an interesting and instructive surfactant system showing the unusual occurrence of at least 5 stable phases at room temperature—crystal (100—about 80% DDAO), neat (about 80–70%), viscous isotropic (70–65%), middle (65–35%) and fluid isotropic or nigre (35–0%) in order of decreasing DDAO content. In many respects the system resembles anionic detergent systems such as that of sodium palmitate, in which, however, viscous isotropic is not observed. The maximum temperatures of existence for crystal, neat and middle are, respectively, 116, 145 and 110C. Neat phase is soft and anisotropic, viscous isotropic is somewhat brittle and isotropic, middle is plastic and anisotropic. The mesomorphic phases are particularly well shown microscopically in "dried-down" samples under circular cover glasses. Middle and neat textures under the microscope are typical. At least four crystalline phases were recognized at various degrees of hydration.

Introduction

BECAUSE OF THEIR TECHNOLOGICAL importance and long availability, soaps and other anionic detergents have been subjected to phase study, and the classic aqueous sodium palmitate system is widely known (1). Familiar features of that system are the Krafft melting point near 65C, the two large mesomorphic regions—middle soap at higher and neat soap at lower H_2O contents, middle existing as high as 170C, neat up to 285C, and the curd or crystalline soap which, when anhydrous, passes through several phase states before becoming isotropic at about 300C.

A number of less detailed studies have been carried out on aqueous systems of nonionic detergents and other nonionic surface active compounds, with a wide variety of behavior appearing but normally reminiscent of that of sodium palmitate (2). Mesomorphic states are common. Occasionally middle phase is absent. Phases which are stiff but isotropic have been reported (3,4).

The present work concerns the aqueous system of dimethyldodecyl amine oxide (DDAO), a nonionic detergent of technological interest (5–9).

Experimental

Various preparations of DDAO were used for preliminary phase studies, all samples agreeing qualitatively with the final phase diagram. The principal preparation by A. O. Snoddy of this laboratory, showed the analyses of Table I. The sample which had been freeze-dried was used as such and accepted as 94.0% DDAO, 6.0% H_2O. From it the following main samples were prepared: (94.0), 89.0, 80.0, 75.0, 71.0, 67.0, 66.0, 61.0, 57.0, 47.0, 38.0, 30.0% DDAO. Any sample less than 30.0% DDAO was of fluid nigre phase at 25C and higher temperatures.

It was subsequently found that the DDAO could be dried substantially completely by refluxing in hexane with a Bidwell-Sterling moisture trap. The hexane solution was crystallized at 0C. The highest crystalline melting point obtained was 116C.

The main samples in 3 g amounts were sealed in 15 × 125 mm test tubes with a 2 mm constriction in the middle, through which homogenization was effected by centrifuging the sample back and forth. The samples were then observed between crossed polaroids at room temperature. The tubes were opened and samples introduced into thin-walled Pyrex capillaries for X-ray diffraction at 10 cm sample-to-film distance on a GE XRD-1 unit with CuKα radiation and 0.025 in. pinhole collimating system. Representative diffraction patterns were also recorded on a GE XRD-5 diffractometer with nickel-filtered CuKα radiation.

TABLE I

Analysis of DDAO

	Experiment (Av'ge.)	Theory	
		Anhydrous	(With 6.0% H_2O)
N_2 (Kjeldahl)	5.91%	6.11%	5.74%
H_2O (Karl Fischer)	5.3	0.0	6.0
Purity of alkyl (gas-liquid chromatography)			
C_{12}	94.5%		
C_{14}	3.7		
C_{16}	1.8		