Performance and Properties of Nonionic Surfactants from Linear Secondary Alcohols

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Abstract

Surfactants based on the linear secondary alcohols provide a new source of biodegradable detergents. The nonionic surfactants of these alcohols are discussed in relationship to their surfactant properties and performance in detergent formulations. The performance properties in detergent formulations are defined by the results of detergency and foam stability tests. The surfactant properties presented are viscosity, surface tension, wetting and alkaline color stability.

The above properties of the nonionic surfactants from the linear secondary alcohols have been compared to the properties of the less degradable nonylphenol nonionics and to the nonionic surfactants from the linear alkylphenol, oxo alcohol and Ziegler alcohol hydrophobes.

Introduction

IT HAS BEEN SHOWN in previously published work (1, 2,3) that a degradable surfactant can be obtained when the hydrophobic portion of the molecule is linear. There are several methods available for obtaining this linear hydrophobe including the manufacture of the linear secondary alcohol, the linear alkylphenol, the oxo alcohol from the linear α-olefin and the primary alcohol from the Ziegler process. The experimental work presented in this paper illustrates the performance of the nonionic surfactants from linear secondary alcohols and provides a comparison of these properties with those of the nonionic surfactants from other linear hydrophobes.

Experimental

1. *Surfactant Description.* The secondary alcohols were prepared from linear paraffins separated by a molecular sieve process from the kerosene fraction of petroleum. These alcohols contain no primary hydroxyl groups and the secondary hydroxyl groups are distributed at random along the hydrophobe with no particular isomer predominating. The linear secondary alcohol adducts are marketed as the TERGITOL® nonionic 15-S series of surfactants. This trade name completely describes the nature of the surfactant. The 15 is derived by dropping the first digit of each number describing the alcohol distribution. The 15 then refers to the C_{11-15} alcohols. The S means secondary or soft with the number following the S identifying the average number of moles of ethylene oxide. For example, TERGITOL 15-S-9 contains an average of nine moles of ethylene oxide, and has an alcohol mol wt distribution of C_{11}, C_{12}, C_{13}, C_{14}, C_{15} and C_{16} in the ratio of 15 : 21 : 23 : 18 : 15 : 8.

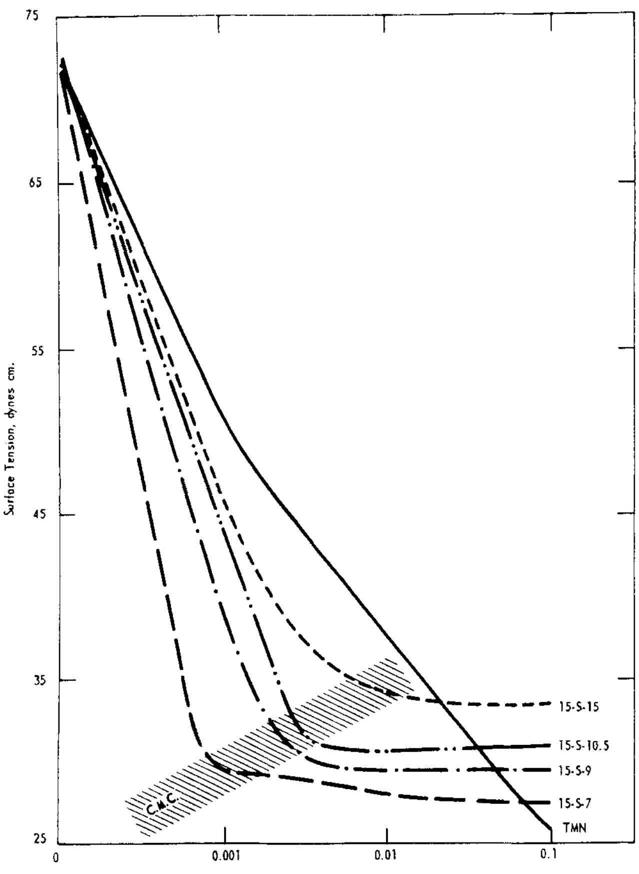

FIG. 1. Surface tension values at 25C for the nonionic surfactants from the TERGITOL 15-S-Series.

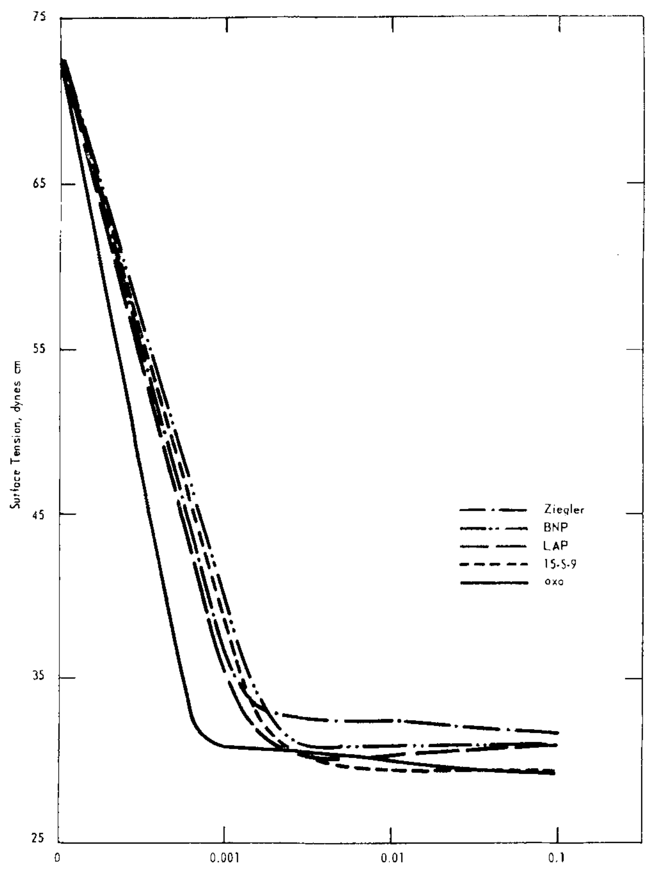

FIG. 2. Surface tension values for selected nonionic surfactants at 25C.

TABLE I
Wetting Properties of Nonionic Surfactants at 25C

Nonionic surfactant from	Cloud point °C	Wetting properties			
		Wetting time, sec			20-Sec wetting concn, %
		0.2%	0.1%	0.05%	
TERGITOL 15-S-7	35	2.4	5.5	19.6	0.049
TERGITOL 15-S-9	64	3.6	12.3	27.8	0.070
TERGITOL 15-S-10.5	76	6.6	14.6	37.9	0.078
TERGITOL 15-S-15	100	29.0	56.6	75.1	>0.2
BNP	63	3.6	8.4	24.1	0.055
TERGITOL TMN	36	....	3.2	15.6	0.049
Ziegler	64	60.4	98.9	202.6	>0.2
oxo	65	16.4	27.1	53.0	0.150
LAP	56	4.7	11.4	26.9	0.062

The nonionic surfactants evaluated for comparison purposes were prepared from the following hydrophobes. The Ziegler (4) alcohol was a mixture of C_{14}, C_{16} and C_{18} in the ratio of 40 : 40 : 20. The oxo alcohol from a linear α-olefin (5) was a mixture of C_{14} and C_{16} in a 50 : 50 ratio. The linear alkylphenol (LAP) was prepared from the linear paraffins separated from kerosene using the molecular sieve process. The surfactant from the branched chain nonylphenol (BNP) was TERGITOL nonionic NPX.

2. *Surface Evaluation.*

A. *Surface Tension and Critical Micelle Concentration.* Surfactant solutions were prepared with redistilled water, and surface tension measurements were made at 25C by the du Nouy Ring Method using an Instron Tensile Tester (6,7). The critical micelle concn (cmc) were approximated from the surface tension versus concn curves.

B. *Wetting.* The wetting properties of the surfactants were measured at 25C by the Draves-Clarkson method (8) using 5 g cotton skeins. In this test, the wetting rates were determined at four surfactant concn: 0.2, 0.1, 0.05 and 0.025 wt/per cent. From these data, a plot of concn versus wetting time was made and the 20 sec wetting concn was determined. It was by the 20 sec wetting concn that the surfactants were compared.

C. *Alkaline Color Stability.* The color stability of the surfactants adsorbed on sodium hydroxide and sodium ortho silicate was measured for periods up to 10 days. In this test, a mixture of one part surfactant to nine parts alkaline base was prepared and stored in sealed glass containers for the duration of the test. Discoloration was measured visually and given a relative color ranking of 1-5; one representing no color change or white, while five indicated a dark brown or red-brown color.

D. *Viscosity and Gel Properties.* The test solutions were prepared and allowed to age for 24 hr before viscosities of aqueous surfactant solutions were measured at 25C using Cannon-Fenske viscometers. The concn range in which

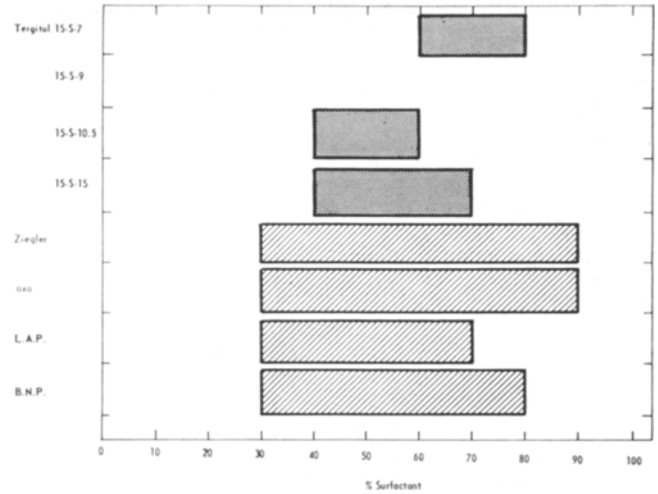

FIG. 3. Gel range characteristics of nonionic surfactants at 25C.

the surfactants formed gels was determined visually after the sample had been allowed to age 24 hr.

E. *Detergency and Foam Properties.* Detergency properties of the nonionic surfactants were determined employing a Terg-O-Tometer with U.S. Testing and F. D. Snell soiled cotton fabric. The pertinent test conditions and the detergent formulation are shown below:

Formulation	Parts by wt
Nonionic surfactants	12.0
Sodium tripolyphosphate	40.0
Sodium meta silicate pentahydrate	10.0
Sodium carboxymethyl cellulose	1.0
Sodium sulfate	37.0

Terg-O-Tometer conditions	
Detergent concentration	0.2%
Wash temp	120F, (49C)
Wash cycle	15 min
Agitation	100 rpm
Water hardness	50, 150 ppm as $CaCO_3$

The Ross-Miles Foam Test (9) was used to compare the foam properties of the various nonionic surfactants. This test was run at 120F with 0.2% of the nonionic surfactant.

Discussion

1. *Properties of the Nonionic Surfactants.*

A. *Surface Tension.* Two of the classical criteria by which a surface-active agent is classified are ability to reduce surface tension and critical micelle concentration. Figure 1 illustrates the surface tension vs. concn curves for a series of ethylene oxide adducts of the sec-

TABLE II
Alkaline Color Stability of Nonionic Surfactants; Storage on Sodium Hydroxide/Sodium Ortho Silicate

Nonionic surfactant from	Cloud point °C	Initial	1 Hr	5 Hr	1 Day	2 Days	3 Days	4 Days	10 Days
TERGITOL 15-S-7	35	1/1	2/1	2/1	2/1	2/1	2/1	2/1	3/1
TERGITOL 15-S-9	64	1/1	1/1	1/1	1/1	2/1	2/1	2/1	2/1
TERGITOL 15-S-10.5	76	1/1	1/1	1/1	1/1	1/1	1/1	2/1	2/2
TERGITOL 15-S-15	100	1/1	1/1	1/1	3/1	3/1	2/1	2/1	3/1
BNP	63	1/1	2/1	2/1	4/1	4/1	4/1	4/1	4/1
Ziegler	64	1/1	4/2	4/2	5/3	5/3	5/3	5/3	5/3
oxo	65	1/1	2/2	4/2	4/2	4/3	4/3	4/3	4/3
LAP	56	1/1	2/1	2/1	2/1	2/1	2/1	2/1	3/1

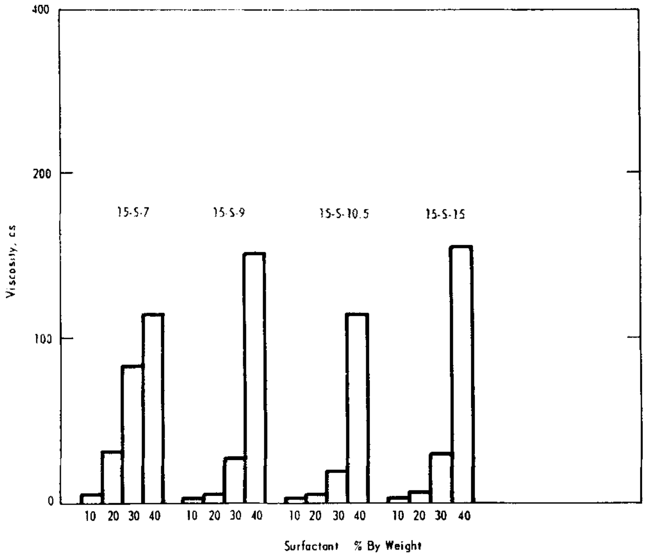

FIG. 4. Viscosity of aqueous solutions of the TERGITOL 15-S series.

ondary alcohols: the TERGITOL nonionic 15-S surfactants and TERGITOL nonionic TMN, a secondary alcohol derived from 2,6,8-trimethyl-4-nonanol. This figure compares the surfactants in the 15-S series, and shows that as the ethylene oxide concn of the hydrophil increases, surfactant effectiveness in reducing surface tension decreases, and the cmc increases. Figure 1 also compares the secondary alcohol surfactants of comparable cloud points, i.e., 15-S-7 and TMN, which show surface tension values of 27.5 and 26.0 dynes/cm, respectively, at 0.1% concn. The corresponding cmc for these two surfactants are 0.001 and 0.1%. These data illustrate some of the differences between a branched chain and linear secondary alcohol nonionic surfactant.

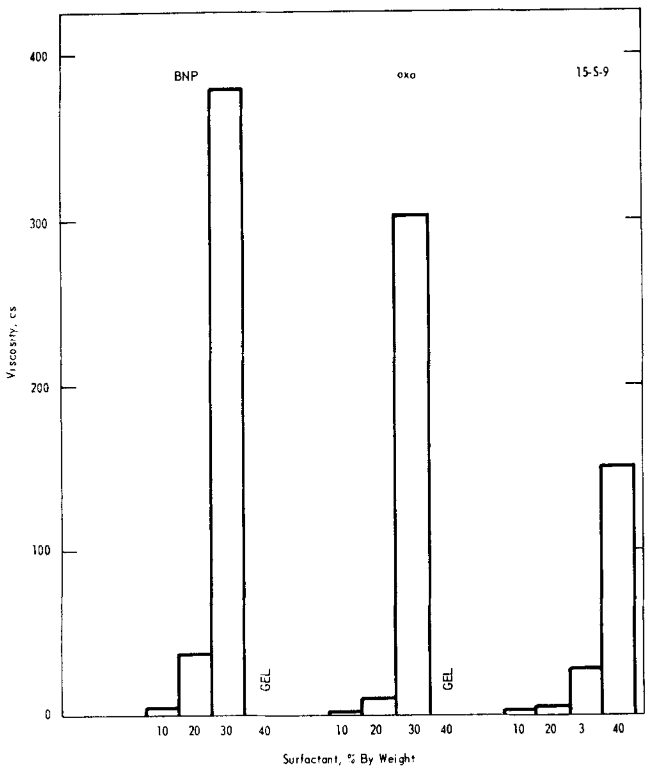

FIG. 5. Viscosity of aqueous solutions of selected nonionic surfactants at 25C.

TABLE III
Effect of Hydrophobe Length on Detergency for Nonionic Surfactants from the Secondary Alcohols

Surfactant hydrophobe	Cloud point °C	Detergency, percentage soil removal					
		U.S. Testing fabric		F. D. Snell fabric		EMPA fabric	
		50 ppm	150 ppm	50 ppm	150 ppm	50 ppm	150 ppm
C_{12}	55	28	26	22	20	61	60
C_{14}	55	27	29	23	25	60	61
C_{16}	55	30	31	25	24	61	64

The data in Figure 2 illustrate the surface tension vs. concn curves for the various nonionic surfactants of comparable cloud point. 15-S-9 has a minimum surface tension value of 29.4 dynes/cm. By comparison, the minimum values for the oxo, Ziegler, linear alkylphenol and branched chain nonylphenol nonionics are 29.3, 33.1, 30.2 and 30.6 dynes/cm, respectively. The cmc of 15-S-9 and the branched and linear alkylphenol nonionics is approx 0.005%, while the surfactants from the oxo and Ziegler alcohols have an approx cmc of 0.001 and 0.005%.

B. *Wetting Properties.* Table I lists the results of the Draves-Clarkson wetting tests at 25C. The 15-S series of surfactants was evaluated and the results show that wetting efficiency decreases as the cloud point of the surfactants increases. The wetting rates for two nonionic surfactants from branched chain hydrophobes are also shown in this table. TMN, which is used in many applications for its excellent wetting characteristics, is compared to 15-S-7 and their wetting properties are shown to be equal. TERGITOL nonionic NPX is seen to be a slightly more effective wetting agent than the 15-S-9. A final comparison available from this table shows the relative wetting characteristics of the surfactants prepared from linear hydrophobes. The nonionic surfactants from the linear alkylphenol and 15-S-9 have similar wetting effectiveness while the nonionics from the oxo and Ziegler alcohols are considerably less effective.

The wetting properties of the 15-S surfactants suggest their use in textile applications, metal cleaning formulations, agricultural sprays and in other areas where good wetting performance is essential.

C. *Alkaline Color Stability.* Table II lists the results of the alkaline color stability tests for periods through ten days. In each case, two numbers are reported. The top number represents the results of the test using sodium hydroxide and the bottom number, sodium ortho silicate. From this table, it can be seen that when tested with sodium hydroxide, the 15-S series discolors less on aging than the

TABLE IV
Effect of Ethylene Oxide on Detergency for the Nonionic Surfactants from the TERGITOL 15-S Series

Cloud point °C	Detergency, percentage soil removal			
	U.S. Testing Co. fabric		F. D. Snell fabric	
	50 ppm	150 ppm	50 ppm	150 ppm
41	27	27	20	19
46	31	28	20	20
57	29	28	18	22
60	27	29	20	19
64	28	27	21	20
71	27	28	23	21

TABLE V
Detergency Characteristics of Nonionic Surfactants

Nonionic surfactant from	Cloud point °C	Detergency, percentage soil removal			
		U.S. Testing fabric		F. D. Snell fabric	
		50 ppm	150 ppm	50 ppm	150 ppm
TERGITOL 15-S	64	28	27	21	20
BNP	63	27	26	24	24
LAP	56	26	26	24	24
oxo	65	28	27	23	25
Ziegler	64	27	27	22	23

surfactants from the other linear hydrophobes and the branched chain nonylphenol. When tested with sodium ortho silicate, the relative ranking of the nonionic surfactants is similar to that obtained on sodium hydroxide with the exception that the linear alkylphenol nonionic performs as well as the entire 15-S series. The color change of all surfactants is less intense on sodium ortho silicate than on sodium hydroxide.

These test results suggest that the 15-S surfactants are of use in alkaline paint strippers, drain cleaners, metal cleaners and other products for the chemical specialty and industrial detergent industries where dry alkaline products are formulated to include a nonionic surfactant.

D. *Viscosity and Gel Characteristics of Aqueous Solutions of Surfactants.* The viscosity characteristics of concd aqueous solutions will vary depending on surfactant type, concn and solution temp. It is known that the branched chain nonylphenol nonionics will form gels at certain ratios of water to surfactant and the formation of this gel is of concern when a concd solution of nonionic is desired, or when this formulation is encountered during the preparation of a detergent.

In Figure 3, the shaded blocks depict the concn range in which a gel is formed. The data in this figure show that the surfactants from the 15-S series have a much narrower gel range than do the surfactants from the linear hydrophobes. Whereas this sample of 15-S-9 shows no tendency to gel, the surfactants from the other hydrophobes are gels in the concn range of 30–70 or 30–90%.

In Figure 4 the viscosities of 10–40% solutions of the 15-S nonionic surfactant are shown. Figure 5 compares the viscosities of solutions of 15-S-9 and the nonionic surfactants from the branched chain nonylphenol and the oxo alcohol. The data from this test indicate that the viscosities of solutions of the secondary alcohol surfactants are much lower than the viscosities of the other nonionic surfactants tested.

Results of other tests indicate the secondary alcohols have essentially identical lime soap dispersing powers to the surfactants from the linear and branched chain hydrophobes and have less cloud point depression in the presence of electrolytes than the branched chain nonylphenols.

2. *Performance Evaluation of the Nonionic Surfactants.* The most pressing need for biodegradable surfactants is in household detergents. Because of this need, the nonionic surfactants from the secondary alcohols have initially been evaluated for their performance characteristics in simulated household detergent products. The following data considers the foaming and detergency characteristics of the 15-S nonionics and compares their performance with the oxo, Ziegler, linear alkylphenol and branched chain nonylphenol nonionics. As far as possible, the comparisons among surfactants were made using similar cloud point nonionics.

TABLE VI
Foam Characteristics of the Nonionic Surfactants at 120F

Surfactant	Cloud point °C	Ross-Miles foam test mm of foam	
		Initial	5 min
TERGITOL 15-S-9	64	165.0	25.0
BNP	63	157.5	40.0
oxo	65	111.0	17.5
Ziegler	64	121.0	10.7
LAP	56	164.0	16.0

In the initial screening of the nonionics from the secondary alcohols, the effect of varying the hydrophobe length of the surfactant on detergency properties was studied. To accomplish this, a series of refined alcohols from C_{12} to C_{16} and their ethylene oxide adducts were specially prepared by the Research and Development Dept. These tests provided the basic information by which the preferred alcohol blends could be chosen. The results are shown in Table III. Three types of standard soil fabrics were included in this evaluation as it has been noted in previous testing that the test results of one fabric are not always conclusive. From these results, it is seen that as hydrophobe length increases from C_{12} to C_{16}, there is a trend for detergency values to increase. This would indicate a general trend for detergency to improve as the surfactant hydrophobe length increases. However, these differences are small.

The variation in performance resulting from a change in ethylene oxide content of the surfactant is shown in Table IV for the 15-S series of nonionics. These data show that no well defined performance trend can be detected with increasing cloud point in the range of 41–76C.

A comparison of the detergency performance of 15-S-9 was made with surfactants from the several linear hydrophobes and the branched chain nonylphenol in a built detergent formulation. Table V shows the comparison of these surfactants. The results of these tests indicate that there is little difference in performance among the various surfactants.

The foam values for the nonionics described in the detergency tests have been determined by the Ross-Miles Foam Test and are shown in Table VI. These results show that 15-S-9, the linear alkylphenol and the branched chain nonylphenol surfactants have equivalent foam while the nonionics from the oxo and Ziegler alcohols have lower initial foam values.

In summary, the data presented show the nonionics from the 15-S series to have excellent surface tension and wetting properties, unique viscosity and gel range characteristics and improved alkaline color stability properties. In the performance tests, these surfactants have detergency and foam performance equivalent to the other products tested. The performance of the secondary alcohol ethoxylate surfactants in the tests discussed indicate that they have outstanding properties and suggest that the use of these materials should be considered in household detergents and a wide variety of other surfactants applications.

ACKNOWLEDGMENTS

Preparation of samples by R. C. Myerly and J. N. Rector. Physical property and performance data by the Misses M. E. Turney and R. E. Johnston; Mrs. G. M. Weigel; and H. T. Zika.

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[Received June 17, 1964—Accepted September 9, 1964]

Fish Bioassays of Linear Alkylate Sulfonates (LAS) and Intermediate Biodegradation Products

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Abstract

Linear alkylate sulfonates (LAS) are relatively toxic to fish when tested under static conditions by standard bioassay techniques, the median tolerance limit (TL_m) being around 3 mg/liter and 0.6 mg/liter for the C_{12} and C_{14} homologs, respectively. However, these materials are so readily degraded by bacterial attack that bluegill fingerlings live with no trouble in effluents from laboratory continuous flow activated sludge units being fed 100 mg/liter or more of either product. No effects on the fish were noticeable in exposures of 96 hr or more, except for slight alterations in the microscopic appearance of the gill tissue. Thus, the removal of the LAS by biodegradation is paralleled by the removal of toxicity and there is no indication that toxic intermediates accumulate during the biodegradation process. This conclusion is substantiated by the observation of a much lower degree of toxicity (TL_m 75 mg/liter) for sulfophenylundecanoic acid disodium salt (mixed isomers), synthesized as a model of an intermediate degradation product. Characterization, gas chromatography and methylene blue analysis of this product are also discussed.

Introduction

THE DETERGENT INDUSTRY of the U.S. has announced that it is discontinuing the production of tetrapropylene derived alkylbenzene sulfonates (ABS) and replacing them with the more biodegradable linear alkylate sulfonate (LAS) (1). This new product is ABS in which the alkyl groups are straight chains, readily attacked by bacteria. In contrast, tetrapropylene ABS is a mixture characterized by highly branched alkyl groups, and about one-quarter to one-third of it is quite resistant to bacterial attack because of unfavorably compact alkyl structure (2). This has sometimes resulted in objectionable foaming in rivers and ground waters upon contamination with sewage (3), which has in turn provided the incentive for the expenditure of a large amount of capital in the construction of the new manfacturing facilities required for the LAS raw materials.

LAS, like its predecessor tetrapropylene ABS, exhibits a very low degree of toxicity to mammals (4). Again like tetrapropylene ABS, LAS is significantly toxic to fish, with median tolerance limit (TL_m, 50% survival) values lying in the region of 1–10 mg/liter for 24–96 hr exposure. The comprehensive studies of Hirsch have shown very interesting correlations between the fish TL_m and the structure of the LAS components, and that some of these components are significantly more toxic than tetrapropylene ABS when tested under the same conditions (5).

Nevertheless, the use of LAS in detergent formulations need not constitute any added threat to the nation's fish life; in fact, it may be that a still greater margin of safety will result. The present concn of ABS found in our rivers are for the most part below 1 mg/liter (6) and have been judged to be no particular hazard to fish life (7). Since LAS is destroyed more rapidly and more completely by biodegradation than the current tetrapropylene ABS (8), it is to be expected that the concn in rivers will be much lower than at present, with a correspondingly lower hazard.

This expected lower hazard in contingent not only upon more rapid degradation of LAS, but also upon intermediate degradation products of LAS being no more toxic than LAS itself. The relatively low toxicity of the intermediates is implicit in the work of Herbert et al. (9) and of Niemitz and Pestlin (10), who found that the ABS remaining after partial degradation of either tetrapropylene or straight chain ABS was less toxic than the original. The solutions which they examined would of course also contain intermediate products originating from that portion of the ABS which had already degraded.

The present experiments involved determination of a) fish TL_m of C_{12} and C_{14} LAS in standard reference water, b) effects on the fish of effluents from continuous activated sludge units fed up to several hundred times these TL_m concn, c) toxicity of C_{14} LAS in activated sludge effluents, and d) TL_m of sulfophenylundecanoic acid disodium salt (mixed isomers), a probable intermediate biodegradation product of LAS, in standard reference water. Our results suggest that no complications relating to fish toxicity should arise when the detergent industry changes from tetrapropylene ABS to LAS.

Materials and Methods

C_{12} and C_{14} Linear Alkylate Sulfonate (C_{12} LAS and C_{14} LAS). These samples were prepared by alkylation of benzene with alpha-dodecene (Aldrich D22160) and alpha-tetradecene (Aldrich T980) respectively, using $AlCl_3$ catalyst. The monoalkylbenzenes were isolated by fractional distillation and comprised mixtures of all possible secondary isomers: 2-,3-,4-,5- and 6-phenyldodecane in one case and 2-,3-, 4-,5-,6- and 7-phenyltetradecane in the other, in proportions decreasing somewhat from the 2-phenyl to the