Soap-Based Detergent Formulations: VI. Alkylaryl Sulfonamide Derivatives as Lime Soap Dispersing Agents[1]

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ABSTRACT

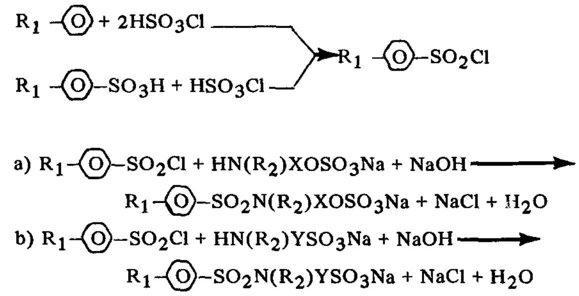
Alkylbenzenes, such as industrial detergent alkylates, as well as pure 1-phenylalkanes whose side chain lengths varied C_8-C_{12}, were converted into the corresponding alkylbenzenesulfonyl chlorides with chlorosulfonic acid. Surface active sulfonamides were obtained from the reaction of the sulfonyl chlorides with various low mol wt aminosulfonic acids, such as N-methyltaurine, or with aminoalkyl esters of sulfuric acid, such as 2-aminoethyl hydrogen sulfate. The hydrolytic stability of the resulting surface active sulfonamide derivatives was investigated. As expected, the sulfonates were quite resistant to acid or alkaline hydrolysis, while the sulfates were more susceptible to hydrolysis. Hydrolytic stability of the sulfonamides was compared with that of the analogous fatty acid amide sulfactants. All of the compounds were excellent lime soap dispersing agents giving Borhetty-Bergman values of 4-10. The compounds were evaluated for detergency either alone or formulated either with tallow soap or with tallow soap and sodium silicate (Na_2O/SiO_2 ratio of 1:1.6). The derivatives of the pure hydrocarbons which gave the best overall detergency were those of 1-phenyldecane and 1-phenyldodecane, whereas those of 1-phenyloctane exhibited poor detergency. This ranking was observed when the compounds were tested alone as well as when formulated. The sulfonamide derivatives of the detergent alkylate type of alkylbenzenes exhibited excellent detergency characteristics and showed substantial potentiation of detergency when mixed with soap or with a soap-sodium silicate blend. The detergency performance of some of these formulated detergents was equal to that of a commercial household detergent used as a control.

INTRODUCTION

In previous publications from this laboratory (1, 2) on the subject of soap-based laundry detergents, emphasis was placed upon the study of fat-derived lime soap dispersing agents (LSDA). In the present study, it will be shown that LSDA of petrochemical origin, such as sulfonamide derivatives of various alkylbenzenes, can serve equally well as effective LSDA which can be formulated readily with tallow soap and a glassy silicate builder to give detergents that equal the performance of conventional phosphate-built commercial detergents in Tergotometer screening tests.

In a recent publication (3), the excellent detergency properties of sulfate esters of sulfonates of alkylbenzene sulfonamide surfactants were described. Molecules of the type $R{-}\!\bigcirc\!{-}SO_2NHCH_2CH_2OSO_3Na$ or $R{-}\!\bigcirc\!{-}SO_2N(CH_3){-}CH_2CH_2SO_3Na$ possessed the required hydrophilic bulk for an LSDA (4). Since such compounds are somewhat analogous to the sulfated fatty acid alkanolamides $RCONHCH_2CH_2OSO_3Na$ or N-methyltaurine amides of fatty acids $RCON(CH_3)$-$CH_2CH_2SO_3Na$ whose usefulness as LSDA in soap-based detergents has been reported (1, 2), the suitability of the sulfonamides for this study was investigated as LSDA in such soap-based formulations.

The sulfonamides were prepared from pure 1-phenylalkanes, as well as from ceommercial detergent alkylates. Commercial alkylbenzenesulfonic acids (whose sodium salts, known as LAS, are the workhorse of the detergent industry) also could have served as starting materials for the synthesis. All compounds of this study were prepared according to the following general scheme:



R_1 stands for a long linear alkyl chain; R_2 for H or CH_3; X for $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH_2CH_2-$ or $-CH_2CH_2OCH_2CH_2-$ groups; and Y for $-CH_2CH_2-$.

As in previous publications from this laboratory, we attempted to correlate various surface active properties with the chemical structure of the LSDA. The detergency behavior of the system tallow soap-LSDA-sodium silicate was studied in some detail because of its relevance to the problem of development of a phosphate-free detergent.

EXPERIMENTAL PROCEDURES

Materials

Commercial grade dodecylbenzenes were supplied by Continental Oil Co., (Nalkylene 500, mol wt 236) and Monsanto Co., St. Louis, Mo. (Alkylate 215, mol wt 236; Alkylate 225, mol wt 243; and Alkylate 230-L, mol wt 261). Linear dodecylbenzenesulfonic acid (Ultrawet 99LS, mol wt 317) was received from Arco Chemical Co., Philadelphia, Pa. 1-Phenyloctane, 1-phenyldecane and 1-phenyldodecane were purchased from Aldrich Chemical Co., Milwaukee, Wis. Diglycolamine was supplied by Jefferson Chemical Co., Houston, Tex.

Preparation of Aminoalkyl Hydrogen Sulfates

Aminoethyl hydrogen sulfate, amino-n-propyl hydrogen sulfate, aminoisopropyl hydrogen sulfate, aminoethoxyethyl hydrogen sulfate, and methyl aminoethyl hydrogen sulfate were prepared according to the method of Rollins and Calderwood (4), as illustrated by the following. Sulfuric acid (335.8 g, 3.4 moles) was chilled to 8 C with 170 g ice, and 236 g (3.2 moles) 3-amino-1-propanol then was added dropwise. The solution was heated gradually under vacuum to a temperature of 125 C. After cooling, the crude product was crystallized from 1700 ml 50% ethanol. The yield of white, crystalline 3-aminopropyl hydrogen sulfate was 448 g (93%).

Preparation of Alkylaryl Sulfonyl Chloride

Dodecylbenzenesulfonyl chloride was prepared from dodecylbenzene as follows: 50.4 g (0.205 moles) dodecylbenzene (Nalkylene 500) was dissolved in 50 ml dichloroethane. Chlorosulfonic acid (56.5 g, 0.485 moles) was

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added slowly at 10 C. The solution was transferred to a separatory funnel and allowed to stand overnight. The next morning, the lower layer which contained most of the by-product sulfuric acid (18.4 g) was drawn off. The solution of crude sulfonyl chloride (upper layer) was used in the Schotten-Baumann reaction described below, without further purification (2).

Dodecylbenzenesulfonic acid (53.5 g, 0.169 moles) was dissolved in 50 ml dichloroethane, and 19.7 g (0.169 moles) chlorosulfonic acid was added slowly at 13 C. The resulting solution was placed in a separatory funnel and the by-product sulfuric acid allowed to settle out overnight. The solution of crude sulfonyl chloride was used in subsequent reactions without further purification.

Synthesis of Sulfonamide Surfactants

The sulfonamides were prepared via the Schotten-Baumann reaction as illustrated by the following example.

The synthetic procedure of Linfield, et al., (3) was modified by replacement of the solvent dimethyl sulfoxide by 1-methyl-2-pyrrolidinone which was effective at a much lower concentration. Sodium hydroxide (27 g, 0.66 moles) was dissolved in 125 ml distilled water and cooled to room temperature. Aminoethyl hydrogen sulfate (30 g, 0.21 moles) and 5 ml 1-methyl-2-pyrrolidinone then were added. The entire solution of crude dodecylbenzenesulfonyl chloride in dichloroethane, as obtained above, was added dropwise to the alkaline solution of aminoethyl hydrogen sulfate with vigorous stirring. Ca. 1 hr after completion of the addition, the reaction mass became viscous and the pH dropped to 8. Occasionally the pH dropped to 6 so that additional sodium hydroxide was required to bring the pH back to 8. Dichloroethane (10 ml) and 30 ml isopropanol then were added, and the reaction mass was heated to 60 C. The material was transferred to a separatory funnel, and the lower layer containing mainly inorganic salts and water was discarded. The upper layer containing the product was concentrated on a steam bath and dried to constant wt in a vacuum oven. The product dried to a yellow spongy mass weighing 90.6 g. The active anionic surfactant content of the solution was determined by titration with a standardized Hyamine 1622 (Rohm and Haas Co., Philadelphia, Pa.) solution using dichlorofluorescein as indicator (5). The product contained 94.5% active ingredient corresponding to a 89.5% yield, basis dodecylbenzene.

Rate of Sulfonamide Formation

A series of experiments was conducted to determine the rate of formation of sodium dodecylbenzenesulfonamidoethyl sulfate under different emulsification conditions. Four different runs were carried out. The first one, represented by curve a of Figure 1, corresponds to the reaction carried out as described above, except that 5 g preformed sulfonamide from a previous run was added. Curve b represents a run carried out after the addition of 5 ml 1-methyl-2-pyrrolidinone. Curve c corresponds to a reaction carried out without any additives, and finally curve d represents a run without additives, wherein emulsification was achieved with the aid of an ultrasonic transducer (Lab-Line Labsonic System). A 10 ml aliquot was withdrawn every 30 min (every 15 min for curve d) and analyzed for anionic surfactant content by cationic titration (5).

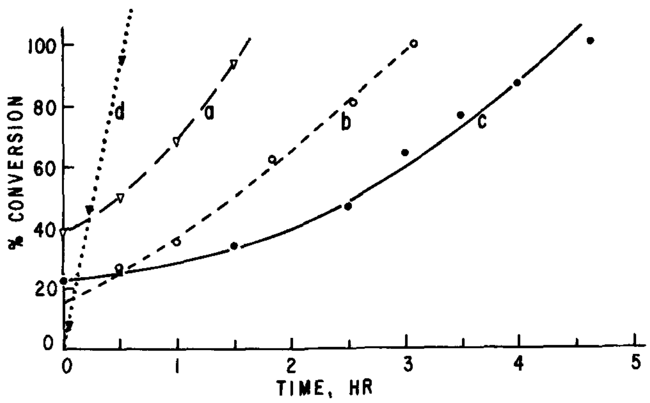

FIG. 1. Reaction time required for dodecylbenzenesulfonamido ethyl sulfate formation under variojs conditions. Curve a: 5% preformed product added, curve b: 5 g 1-methyl-2-pyrrolidinone added, curve c: no additives, and curve d: no additives, ultrasonic agitation.

Purification of Amides

The sulfonamides prepared from commercial alkylbenzenes (detergent alkylates) were used without further purification, since it was found that these substances were soluble in water, as well as in common organic solvents and, thus, could not be recrystallized. The derivatives of the pure 1-phenylalkanes were recrystallized from hot 95% ethanol. The recrystallized surfactants were found to be over 95% pure by Hyamine 1622 titration, and the purity was confirmed by elemental analyses. The structure of these compounds was confirmed by NMR spectroscopy as outlined in a previous publication (3).

The degree of purity of the detergent alkylate derivatives was improved, and their tackiness was reduced by the elimination of 1-methyl-2-pyrrolidinone from the Schotten-Baumann reaction mixture.

Hydrolysis Studies

Acid hydrolysis was measured in 100 ml distilled water

TABLE I

Hydrolytic Stability of Sulfonamide Surfactants and Analogous Carboxylic Amide Surfactants under Acid and Alkaline Conditions

Chemical structure of lime soap dispersing agent	Percent hydrolysis after 1 hr	
	Alkaline (100 C)	Acid (80 C)
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2OSO_3Na$	57	20
$C_{17}H_{35}CONHCH_2CH_2OSO_3Na$	38	37
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2CH_2OSO_3Na$	2	4
$C_{15}H_{31}CONHCH_2CH_2CH_2OSO_3Na$	9	16
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH(CH_3)OSO_3Na$	57	22
$C_{17}H_{35}CONHCH_2CH(CH_3)OSO_3Na$	32	39
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2OCH_2CH_2OSO_3Na$	12	10
$C_{17}H_{35}CONHCH_2CH_2OCH_2CH_2OSO_3Na$	0.5	14
$C_{10}H_{21}C_6H_4SO_2N(CH_3)CH_2CH_2OSO_3Na$	42	16
$C_{17}H_{35}CON(CH_3)CH_2CH_2OSO_3Na$	>98	71
$C_{10}H_{21}C_6H_4SO_2N(CH_3)CH_2CH_2SO_3Na$	too small to measure	
$C_{17}H_{35}CON(CH_3)CH_2CH_2SO_3Na$	too small to measure	

TABLE II

Surface Active Properties of Sulfonamides Derived from Commercial Starting Materials

Chemical structure of lime soap dispersing agent	Lime soap dispersant requirement	Surface tension of 0.1% solution in dynes/cm	Draves wetting speed of 0.1% solution in sec	Ca^{++} ion stability in ppm of $CaCO_3$
$R^a-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	7	33.8	8.9	>1800
$R^a-C_6H_4-SO_2NHCH_2CH(CH_3)OSO_3Na$	7	33.9	8.6	1180
$R^a-C_6H_4-SO_2NHCH_2CH_2CH_2OSO_3Na$	6	33.5	9.3	1100
$R^a-C_6H_4-SO_2NHCH_2CH_2OCH_2CH_2OSO_3Na$	4	31.8	11.6	>1800
$R^a-C_6H_4-SO_2NHCH_2CH_2SO_3Na$	8	33.7	7.0	1400
$R^a-C_6H_4-SO_2N(CH_3)CH_2CH_2SO_3Na$	9	34.3	7.5	1220
$R^b-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	7	32.4	7.3	610
$R^c-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	7	32.0	6.7	645
$R^d-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	7	30.8	16.5	1155
$R^e-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	6	32.2	6.3	>1800

[a] Side chain corresponds to that of Nalkylene 500 (Continental Oil Co.).
[b] Side chain corresponds to that of Alkylate 215 (Monsanto Co.).
[c] Side chain corresponds to that of Alkylate 225 (Monsanto Co.).
[d] Side chain corresponds to that of Alkylate 230-L (Monsanto Co.).
[e] Side chain corresponds to that of Ultrawet 99LS (Arco Chem. Co.).

solutions containing 0.005 moles HCl and 0.005 moles sulfonamide surfactant. The temperature was maintained at 80 C; a 10 ml aliquot was withdrawn after 1 hr. The samples were titrated with 0.1 N NaOH using phenolphthalein indicator. The extent of hydrolysis was estimated from the increase in acidity.

Alkaline hydrolysis was measured at 100 C in 100 ml distilled water solutions containing 0.005 moles NaOH and 0.005 moles sulfonamide surfactant. A 10 ml aliquot was withdrawn after 1 hr and titrated with 0.1 N HCl using phenolphthalein indicator. The extent of hydrolysis was measured in terms of decreased alkalinity of the solution. The hydrolysis data for compounds prepared from the pure 1-phenyldecane are tabulated in Table I. Since hydrolysis under milder alkaline conditions is important in formulated detergents, the stability of the sulfated sulfonamide of ethanolamine was determined at a pH of 10.5 obtained with a buffered sodium orthophosphate solution. Under these conditions, the content of anionic surfactant, as determined by cationic titration, remained unchanged after 4 hr at 100 C.

Physical and Surface Active Properties

Lime soap dispersant requirement (LSDR) was determined according to the method of Borghetty and Bergman (6). Krafft point, calcium ion stability (7), wetting speed (8), surface tension, and critical micelle concentration (9) were measured by standard methods. The data are listed in Table II for compounds prepared from commercial alkylbenzenes and Table III for compounds from pure 1-phenylalkanes.

Detergency measurements were carried out in the Tergotometer at 120 F. Three types of test soils were used, namely U.S. Testing Co. cotton (UST), Testfabrics cotton-

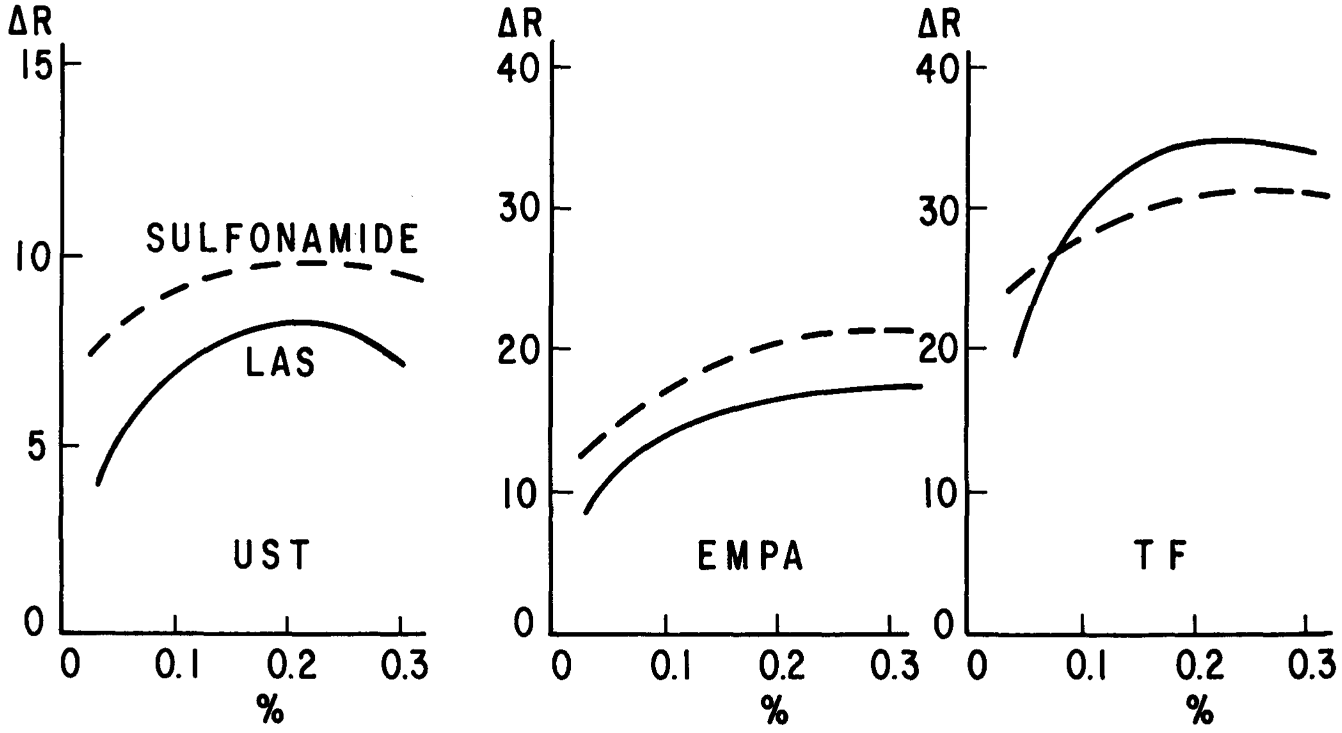

FIG. 2. Detergency behavior of alkylbenzenesulfonic and sulfated alkylbenzene sulfonamide of ethanolamine at 120 C and 300 ppm water hardness. Reflectance increase (ΔR) at various concentrations of surfactants. Test cloths: EMPA 101 cotton (EMPA), U.S. Testing Co. cotton (UST), and Testfabrics, Inc., cotton-polyester blend with permanent press finish (TF).

polyester blend with permanent press finish (TF), and EMPA 101 cotton (EMPA). The tests were carried out as described in a previous publication by Weil and coworkers (10). A detergency profile for one sulfonamide LSDA, the sodium salt of the alkylbenzene sulfonamide (derived from Nalkylene 500) of 2-aminoethyl hydrogen sulfate, was obtained by testing the compound by itself at 50, 150, and 300 ppm water hardnesses and at concentrations of 0.05, 0.1, 0.2, and 0.3%. A similar profile also was obtained for a commercial linear alkylbenzenesulfonate (LAS). The data for 300 ppm water hardness and the three test cloths (EMPA, UST, TF) are represented graphically in Figure 2.

All compounds were evaluated by a simple screening method at 300 ppm water hardness and at 120 F. The test solutions were as follows: test LSDA at 0.2%, binary mixture of .15% soap + 0.05% LSDA, and ternary mixture of 0.13% soap + 0.04% LSDA + 0.03% sodium silicate ($Na_2O:SiO_2 = 1:1.6$).

The data are reported in Table IV for compounds from commercial dodecylbenzenes and Table V for those derived from pure 1-phenylalkanes.

The sulfonamide derivatives of one of the commercial detergent alkylates (Nalkylene 500) were subjected to a more extensive formulation and detergency evaluation study. Formulations were prepared consisting of binary blends of sulfonamide and tallow soap in soap:LSDA ratios of 90:10, 85:15, 80:20, and 75:25. Ternary formulations were obtained by adding various increments of sodium silicate ($Na_2O:SiO_2 = 1:1.6$) to the above binary mixtures. Since differences between different sulfonamide surfactants were slight, only the detergency data for the formulated N-methyltaurine sulfonamide prepared from Nalkylene 500 were recorded in Table VI.

RESULTS AND DISCUSSION

The previously reported synthetic procedure (3) was modified to improve yield and shorten reaction time. The sulfonyl chloride in dichloroethane was quite hydrophobic so that there was little contact between the solvent and aqueous layers of the Schotten-Baumann reaction mixture, resulting in a slow reaction rate. This situation could be remedied by the use of a mutual solvent, such as dimethylsulfoxide (DMSO), as reported or 1-methyl-2-pyrrolidinone which we found to be more effective. It was found in this study that a purer sulfonamide and an even faster reaction time were achieved through the use of a small amount of seed of a previously prepared batch of the same sulfonamide which acted as an emulsifying agent for the two phase reaction mixture. Figure 1 clearly shows that the reaction will go to completion with the aid of seed material in ca. one-third the time required to achieve the same conversion without seed, while the addition of 1-methyl-2-pyrrolidinone cuts the reaction time ca. in half. The shortest reaction time, however, was obtained not with either a cosolvent or seed, but with an ultrasonic transducer. Presumably the ultrasonic energy input reduced the oil droplet size, thus greatly increasing the area of contact between the oil and water phases.

We found that the use of sodium carbonate as an acid scavenger in place of sodium hydroxide offered no advantage, and we were not successful in carrying out conversion to sulfonamide in the presence of sodium bicarbonate. The use of this alkali, as well as the nonstoichiometric proportions of reactants, reported by Langguth and coworkers (11) may account for the unusually poor detergency performance observed by them.

Since the LSDA of this study contained a sulfonamide group and most of them contained a hydrolyzable sulfate ester group as well, the hydrolytic stability of the compounds was an important aspect of this study. The reaction mechanism and the nature of the hydrolysis products

TABLE III

Surface Active Properties of Sulfonamides Derived from Pure Phenylalkanes

Chemical structure of lime soap dispersing agent	Lime soap dispersant requirement	Krafft point C	Ca^{++} ion stability in ppm $CaCO_3$	Surface tension of 0.1% solution in dynes/cm	Draves wetting time of 0.1% solution in sec	Critical micelle concentration in millimoles/1
$C_8H_{17}C_6H_4SO_2NHCH_2CH_2OSO_3Na$	8	14	>1800	38.6	7.2	0.356
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2OSO_3Na$	9	20.5	>1800	37.8	13.2	0.101
$C_{12}H_{25}C_6H_4SO_2NHCH_2CH_2OSO_3Na$	9	24	>1800	37.0	18.6	0.0254
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2CH_2OSO_3Na$	7	<1	>1800	40.0	10.9	0.0737
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH(CH_3)OSO_3Na$	9	<1	>1800	37.3	15.2	0.0841
$C_{10}H_{21}C_6H_4SO_2N(CH_3)CH_2CH_2OSO_3Na$	6	29	>1800	38.6	16.3	0.0719
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2OCH_2CH_2OSO_3Na$	3	<1	>1800	36.3	20.3	0.0671
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2SO_3Na$	9	26	>1800	37.6	10.8	0.0732
$C_{10}H_{21}C_6H_4SO_2N(CH_3)CH_2CH_2SO_3Na$	7	<1	930	38.2	15.5	0.0596

TABLE IV

Detergent Properties of Sulfonamides Derived from Commercial Starting Materials

Chemical structure of lime soap dispersing agent (LSDA)	Detergency (ΔR) at 120 F and 300 ppm water hardness								
	LSDA at $0.2\%^a$			Binary mixture of 0.15% soap + 0.05% LSDA			Ternary mixture of 0.13% soap + 0.04 % LSDA + 0.03% sodium silicate		
	EMPA	UST	TF	EMPA	UST	TF	EMPA	UST	TF
$R^a-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	21.9	12.3	25.2	32.2	8.4	19.6	31.5	6.6	14.9
$R^a-C_6H_4-SO_2NHCH_2CH(CH_3)OSO_3Na$	22.2	13.2	25.5	27.4	8.9	18.1	32.5	6.3	17.2
$R^a-C_6H_4-SO_2NHCH_2CH_2CH_2OSO_3Na$	21.5	11.6	25.6	30.4	8.9	18.7	32.5	7.1	20.2
$R^a-C_6H_4-SO_2NHCH_2CH_2OCH_2CH_2OSO_3Na$	16.1	12.0	26.6	27.4	9.4	19.4	27.6	7.2	11.9
$R^a-C_6H_4-SO_2NHCH_2CH_2SO_3Na$	26.5	12.3	26.5	30.9	9.3	20.9	32.7	6.1	16.1
$R^a-C_6H_4-SO_2(N(CH_3)CH_2CH_2SO_3Na$	18.7	12.1	26.0	30.7	10.0	20.8	34.3	8.1	19.5
$R^b-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	21.2	12.6	31.5	32.6	8.1	19.4	32.9	5.5	12.6
$R^c-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	19.5	12.3	34.0	32.8	7.4	19.2	34.3	6.8	14.0
$R^d-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	15.1	10.8	33.3	30.7	6.8	18.8	32.3	11.0	22.2
$R^e-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$	29.2	10.7	24.2	25.3	11.8	24.3	27.0	9.6	19.7
Commercial control							34.5	11.6	24.6

[a] EMPA = EMPA 101 cotton, UST = U.S. Testing Co. cotton, and TF = Testfabrics, Inc., cotton-polyester blend with permanent press finish.

[b] Side chain corresponds to that of Nalkylene 500 (Continental Oil Co.).

[c] Side chain corresponds to that of Alkylate 215 (Monsanto Co.).

[d] Side chain corresponds to that of Alkylate 225 (Monsanto Co.).

[e] Side chain corresponds to that of Alkylate 230-L (Monsanto Co.).

[f] Side chain corresponds to that of Ultrawet 99LS (Arco Chem. Co.).

formed were not investigated. The data shown in Table I show percent hydrolysis in terms of acid generated or alkali consumed during hydrolysis. In a few instances, we also checked the hydrolysis data obtained for some of the sulfates against the loss of anionic activity as determined by Hyamine 1622 titration and found good agreement between the two. Because of this agreement, the cationic titrations were not continued, and the results are not reported here.

The new compounds were compared with each other and with analogous fatty amide derivatives reported in previous publications (12-14). Table I shows the data obtained for acid and alkaline hydrolysis at temperatures corresponding to those used in the previous publications (12-14). As expected, the benzene sulfonamide of N-methyltaurine, like the fatty amide of this compound, was extremely resistant to hydrolysis. The sulfated benzenesulfonamides of ethanolamine, isopropanolamine, and diglycolamine were more stable to acid hydrolysis but less stable to alkaline hydrolysis than the corresponding fatty acid amides. The sulfated benzene sulfonamide of 3-hydroxy-1-propylamine was more stable to hydrolysis under both conditions than the analogous fatty acid amide; and, in the case of the benzene sulfonamide of sulfated N-methyl-ethanolamine, the stability of this compound compared with the analogous fatty amide was even more striking. This would suggest that the hydrolysis mechanism for the two types of amides is probably not the same. Since the sulfated benzene sulfonamide of ethanolamine was found to be stable to hydrolysis at a pH of 10.5, it is reasonable to assume that this compound can be compounded safely into mildly alkaline detergent formulations.

Our investigation of the surface active properties of the LSDA of this series was more extensive in the case of the 1-phenylalkane derivatives which could be purified by recrystallization and by necessity rather limited in the case of the derivatives of commercial detergent alkylates which are mixtures of homoglogs and isomers; thus, purification of the latter would not serve any useful purpose. The surface active properties of these compounds, as shown in Table II, are quite similar regardless of origin of the commercial alkylbenzene or the nature of the substituent anionic group attached to the sulfonamide nitrogen. LSDR varied typically between 6-9; only the sulfated diglycolamide showed a lower value. The surface tension measurements and wetting speeds were all found to be of the same order of magnitude. The calcium ion stability data, on the other hand, showed discrepancies which could be explained readily. This holds particularly true for the sulfated ethanolamides derived from the three Alkylates where the calcium ion stability increases with increasing mol wt. A possible explanation is the presence of impurities, since we were unable to purify these compounds. This assumption is borne out by the analogous data for the pure 1-phenylalkane derivatives shown in Table III. These compounds were purified by recrystallization and except for the N-methyltaurine derivative showed a calcium ion stability of greater than 1800 ppm.

The pure hydrocarbon derivatives, like the detergent alkylate derivatives, exhibited LSDR between 6-9, except for the sulfated diglycolamide derivative which again had a lower value. As in the case of the detergent alkylate derivatives, the pure phenylalkane derivatives do not differ greatly from each other with respect to surface tension and wetting speed. The critical micelle concentration (cmc) data show the expected decrease as the alkyl side chain is lengthened from C_8 to C_{12}. Within the C_{10} series, however, the cmc is affected slightly by the nature of the substituent on the benzene sulfonamido nitrogen atom. It also was found that the sulfonates have a lower cmc than the analogous sulfates.

Various aspects of detergency were investigated. Since a recent publication (11) indicated that the sulfated benzene sulfonamide of ethanolamine was inferior to LAS and that "the performance findings would not justify further development effort with this new surfactant," we wanted to ascertain the performance of this compound by itself in comparison with LAS. Therefore, a detergency profile for these two surfactants was determined. The performance pattern at the three hardnesses was found to be very similar. Thus, only the performance at the highest hardness of 300 ppm is shown here in Figure 2. The curves clearly show the benzenesulfonamide to be slightly superior to LAS on the two cotton cloths, whereas LAS is slightly

TABLE V

Detergent Properties of Sulfonamides Derived from Pure Phenylalkanes

	Detergency (ΔR) at 120 F and 300 ppm water hardness								
	LSDA at 0.2%[a]			Binary mixture of 0.15% soap Binary mixture of			Ternary mixture of 0.13% soap + 0.04% LSDA + 0.03% sodium silicate		
Chemical structure of lime soap dispersing agent (LSDA)	EMPA	UST	TF	EMPA	UST	TF	EMPA	UST	TF
$C_8H_{17}C_6H_4SO_2NHCH_2CH_2OSO_3Na$	15.2	7.4	16.3	17.4	3.4	1.4	14.4	0.6	−4.7
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2OSO_3Na$	19.8	10.3	23.6	32.1	11.2	19.1	34.3	6.9	12.4
$C_{12}H_{25}C_6H_4SO_2NHCH_2CH_2OSO_3Na$	19.3	10.7	30.8	31.3	11.5	21.4	33.9	10.3	20.0
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2CH_2OSO_3Na$	23.2	10.1	20.2	35.5	10.8	20.9	34.5	7.5	15.3
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH(CH_3)OSO_3Na$	16.8	9.2	21.8	33.6	10.1	19.5	33.1	6.5	11.9
$C_{10}H_{21}C_6H_4SO_2N(CH_3)CH_2CH_2OSO_3Na$	17.5	11.1	27,8	30.3	14.2	20.9	32.6	10.9	18.7
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2OCH_2CH_2OSO_3Na$	14.0	9.2	22.3	26.2	9.2	16.9	27.5	5.6	10.8
$C_{10}H_{21}C_6H_4SO_2NHCH_2CH_2SO_3Na$	17.2	10.5	27.6	32.8	10.4	19.2	33.1	6.9	12.3
$C_{10}H_{21}C_6H_4SO_2N(CH_3)CH_2CH_2SO_3Na$	14.6	9.5	29.2	31.2	10.9	18.2	33.5	7.3	14.8
Commercial control							34.5	11.6	24.6

[a] EMPA = EMPA 101 cotton, UST = U.S. Testing Co. cotton, and TF = Testfabric, Inc., cotton-polyester blend with permanent press finish.

superior on the cotton-polyester blend. It was, therefore, concluded that the sulfonamide was not inherently inferior to LAS.

In subsequent Tergotometer screening tests, the benzenesulfonamide surfactants were evaluated uncompounded, compounded with tallow soap, and finally with the tallow soap and sodium silicate (Tables IV and V). A leading commercial phosphate-built detergent served as the control for all tests. A certain pattern can be observed in both tables. Regardless of the structure of the LSDA, the detergency with EMPA was increased substantially by substituting 75% LSDA by tallow soap, and the inclusion of the silicate usually enhanced the detergency slightly. The detergency on U.S. Testing and Testfabrics cloths showed a successive decrease as the LSDA was replaced partially by soap and, in turn, as part of that binary mixture was replaced by sodium silicate. In fact, on Testfabrics cloth, the detergency of the LSDA by themselves surpassed that of the control. These trends reflect, of course, some bias due to the nature of the artificial soil. However, for the most part, they are characteristic of the benzenesulfonamide LSDA themselves. Previously published work (2) indicated that other types of LSDA did not follow the above patterns.

The nature of the substituent group on the sulfonamido nitrogen atom appeared to have no effect upon detergency with the exception of the diglycolamide derivatives which showed inferior detergency. Conceivably, the great hydrophilic bulk of the diglycolamides rendered them the most highly effective LSDA of this series, but the bulk was excessive for good detergency. The length and undoubtedly the structure of the alkyl side chain appeared to have the greatest influence upon detergency. This is shown most clearly in the case of the Alkylate derivatives in Table IV where detergency improved substantially with a slight increase in length of the alkyl chain and in Table V where detergency improved dramatically as the side chain is lengthened from C_8 to C_{10}. A further increase from C_{10} to C_{12}, however, did not result in greatly enhanced detergency with EMPA cloth but resulted in improved detergency of the ternary mixture on U.S. Testing and Testfabrics cloths. The detergency of the ternary formulation containing the Alkylate 230-L derivative as the LSDA (Table IV), as well as that containing the pure sulfated

TABLE VI

Detergency Behavior of Formulations of Tallow Soap, Alkylbenzene Sulfonamide of N-Methyltaurine, and Sodium Silicate ($Na_2O:SiO_2$ = 1:1.6)

	Detergency (ΔR) of 0.2% solutions[a]		
Composition of formulation	EMPA	UST	TF
90% soap + 10% lime soap dispersing agent (LSDA)	27.1	3.6	4.1
81% soap + 9% LSDA + 10% sodium silicate	31.1	4.6	10.1
77% soap + 8% LSDA + 15% sodium silicate	28.4	3.2	7.8
72% soap + 8% LSDA + 20% sodium silicate	28.7	3.6	7.8
85% soap + 15% LSDA	29.7	5.8	8.8
76% soap + 13% LSDA + 10% sodium silicate	36.1	7.6	16.3
72% soap + 13% LSDA + 15% sodium silicate	33.7	7.3	14.5
68% soap + 12% LSDA + 20% sodium silicate	32.9	5.5	14.8
80% soap + 20% LSDA	27.5	8.1	16.4
72% soap + 18% LSDA + 10% sodium silicate	34.2	9.3	15.9
68% soap + 17% LSDA + 15% sodium silicate	33.5	6.7	16.3
64% soap + 16% LSDA + 20% sodium silicate	38.0	7.2	16.8
75% soap + 25% LSDA	30.7	10.0	20.8
68% soap + 22% LSDA + 10% sodium silicate	34.3	9.5	17.0
64% soap + 21% LSDA + 15% sodium silicate	34.3	8.1	19.5
60% soap + 20% LSDA + 20% sodium silicate	31.8	6.3	17.2
Commercial control	34.5	11.6	24.6

[a] EMPA = EMPA 101 cotton, UST = U.S. Testing Co. cotton, and TF = Testfabrics, Inc., cotton-polyester blend with permanent press finish.

dodecylbenzenesulfonamide of ethanolamine as the LSDA (Table V), exhibited a detergency performance almost equal to that of the control.

Because of the promising results obtained in the above detergency screening tests, a more detailed formulation and evaluation study was undertaken with the LSDA derived from Nalkylene 500. Since, as mentioned above, the different substituents on the sulfonamido nitrogen atom had little effect upon detergency, only the results obtained with the sulfonamide of N-methyltaurine are shown in Table VI. The EMPA detergency of the binary soap-LSDA mixture was enhanced by the incorporation of 10-15% sodium silicate. Higher silicate levels did not cause additional enhancement of detergency. However the addition of 10% silicate aided slightly in the U.S. Testing cotton detergency. The addition of silicate to the formulation appeared to have little enhancing effect upon Testfabrics detergency except in the case of the two highest soap/LSDA ratios of 90/10 and 85/15 where some enhancement due to the addition of silicate could be observed. It would appear that a soap/LSDA ratio of 75/25 is required for the best detergency and that a 10-15% addition of sodium silicate will further enhance performance on EMPA cotton. On the whole, the component ratio of formulations containing the sulfonamides appears to be not quite as critical as in the case of other anionic LSDA discussed in earlier publications (1, 2).

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