Soap-Based Detergent Formulations: XIV. Amphoteric Derivatives of Alkylbenzenesulfonamides[1]

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ABSTRACT

Surface active amphoteric derivatives were prepared from alkylbenzenesulfonyl chlorides. Industrial detergent alkylates, as well as benzene and pure 1-phenylalkanes whose side chains ranged from C_1 to C_{12}, were used as starting materials in this study of chemical structure-physical property relationships. The alkylbenzenes were first converted into the corresponding alkylbenzenesulfonyl chlorides with chlorosulfonic acid, and the sulfonyl chlorides were further treated with N,N-dimethyl-1,3-diaminopropane or N,N-bis-(2-hydroxyethyl)-1,3-diaminopropane. The reaction products were quaternized with propanesultone to produce amphoteric surfactants in high yields. The N,N-dimethyl derivatives of pure phenylalkanes were white crystalline powders, whereas the N,N-bis-(2-hydroxyethyl) derivatives were light brown, tacky, and amorphous in character. Krafft points, lime soap dispersing requirement, surface tension, wetting ability, and calcium ion stability were determined. The commercial detergent alkylate derivatives showed good detergency by themselves as well as in formulations with soap or with soap and silicate builder. Good lime soap dispersing properties were observed with compounds possessing a side chain of at least 4 carbon atoms.

INTRODUCTION

Amphoteric surfactants, particularly the so-called sulfobetaines, which contain both a quaternary ammonium group and a sulfonate group in the same zwitterionic structure, have been shown to be unusually effective lime soap dispersants (1,2). The lime soap dispersant requirements (LSDR) for sulfobetaines containing an amido group in the general structure $RCONHCH_2CH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$ were somewhat lower than those for the corresponding simple sulfobetaines of the structure $RN^+(CH_3)_2CH_2CH_2CH_2SO_3^-$. The surface active properties of sulfobetaines containing a sulfonamido group have not been investigated so far.

Alkylbenzenesulfonic acids are readily accessible, and anionic surfactants prepared from various alkylbenzenesulfonamides have been shown to be good lime soap dispersants and detergents (3). Thus, it was of interest to prepare amphoteric surfactants derived from alkylbenzenesulfonamides of different alkyl chain lengths and to determine their surface active properties such as detergency and lime soap dispersing ability.

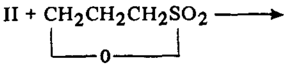
Two types of amphoterics were prepared according to the following schemes:

$$R\text{-}\langle O\rangle + 2HSO_3Cl \longrightarrow R\text{-}\langle O\rangle\text{-}SO_2Cl + HCl + H_2SO_4$$

(I)

$$I + H_2NCH_2CH_2CH_2N(CH_3)_2 \longrightarrow$$
$$R\text{-}\langle O\rangle\text{-}SO_2NHCH_2CH_2CH_2N(CH_3)_2$$

(II)



$$II + \underbrace{CH_2CH_2CH_2SO_2}_{O} \longrightarrow$$

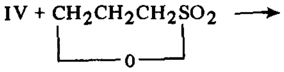
$$R\text{-}\langle O\rangle\text{-}SO_2NHCH_2CH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$$

(III) Type A Amphoteric

and in an analogous fashion;

$$I + H_2NCH_2CH_2CH_2N(CH_2CH_2OH)_2 \longrightarrow$$
$$R\text{-}\langle O\rangle\text{-}SO_2NHCH_2CH_2CH_2N(CH_2CH_2OH)_2$$

(IV)



$$IV + \underbrace{CH_2CH_2CH_2SO_2}_{O} \longrightarrow$$

$$R\text{-}\langle O\rangle\text{-}SO_2NHCH_2CH_2CH_2N^+(CH_2CH_2OH)_2CH_2CH_2CH_2SO_3^-$$

(V) Type B Amphoteric

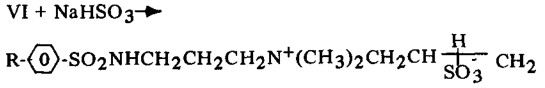
In this study, model compounds were prepared from benzene, alkylbenzenes ranging from toluene to 1-phenyldodecane, as well as from various commercial linear alkylbenzenes. The bis-N,N-(2-hydroxyethyl) derivatives (Type B) were prepared because it was surmised that the increased hydrophilic bulk of such structures might further enhance the lime soap dispersing ability. This, indeed, was found to be the case.

Because of the unavailability and potential hazard connected with the use of propanesultone, we also prepared Type A sulfobetaines by the following alternate route (4):

$$II + CH_2{=}CHCH_2Cl$$
$$\longrightarrow [R\text{-}\langle O\rangle\text{-}SO_2NHCH_2CH_2CH_2N(CH_3)_2CH_2CH{=}CH_2]^+Cl^-$$

(VI)

$$VI + NaHSO_3 \longrightarrow$$



$$R\text{-}\langle O\rangle\text{-}SO_2NHCH_2CH_2CH_2N^+(CH_3)_2CH_2CH\overset{H}{\underset{SO_3}{\mp}}CH_2$$

(VII)

This product cannot be clearly established and is presumed to be a mixture of the N(2-sulfopropyl) and N(3-sulfopropyl) derivatives.

EXPERIMENTAL PROCEDURES

Materials

Commercial grade dodecylbenzenes were supplied by Continental Oil Co., New York, NY (Nalkylene 500, mol wt 236), and Monsanto Co., St. Louis, MO (Alkylate 215, mol wt 236; Alkylate 225, mol wt 243; and Alkylate 230L, mol wt 261). N,N-Dimethyl-1,3-diaminopropane and N,N-bis-(2-hydroxyethyl)-1,3-diaminopropane were supplied by Jefferson Chemical Co. (Houston, TX). Phenylalkanes of 96% or better purity were obtained from Aldrich Chemical Co. (Milwaukee, WI).

Synthesis of Type A Amphoteric Surfactants

All sulfonyl chlorides were prepared according to a pre-

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[1] Presented at the AOCS Fall Meeting, Philadelphia, September 1974.

TABLE I

Surface Active Properties of $RC_6H_4SO_2NH(CH_2)_3{}^+N(CH_3)_2(CH_2)_3SO_3{}^-$ (Type A)

R Group	LSDR[a]	Krafft point[b]	Surface tension of 0.1% solution (dynes/cm)	Draves wetting time of 0.1% solution (sec)
From pure phenyl alkanes				
H (Benzene)	>100	< 1	69.7	>300
Methyl	>100	< 1	69.3	>300
Ethyl	80	< 1	61.8	>300
n-Butyl	7	< 1	44.3	>300
Sec-Butyl	>100	< 1	42.1	>300
Hexyl	4	32	36.0	43
Heptyl	3	50	36.4	30
Octyl	3	65	35.0	29
Decyl	2	76	34.2	49
Dodecyl	2	>97	34.3	68
Dodecyl + allyl Chloride + bisulfite	3	>97	30.7	88
From commercial detergent alkylates				
Nalkylene 500	3	–	26.6	14
Alkylate 215	3	–	27.4	40
Alkylate 225	3	–	27.8	11
Alkylate 230L	3	–	27.6	26
Nalkylene 500 + allyl Chloride + bisulfite	3	–	27.7	45

[a] LSDR = Lime soap dispersant requirement. Grams of agent required to maintain dispersion of lime soap curd from 100 g of sodium oleate (5).

[b] Krafft point is temperature C at which a 1% dispersion becomes clear on gradual heating.

viously published procedure (3). The following serves as an example of the preparation of a typical N,N-dimethyl derivative. A solution of crude dodecylbenzenesulfonyl chloride (I) was prepared from 25.0 g (0.105 moles) of a commercial detergent alkylate (Nalkylene 500), 27.8 g (0.24 moles) of chlorosulfonic acid, and 50 ml 1,2-dichloroethane. The solution of sulfonyl chloride was poured into a beaker containing 5 g of powdered anhydrous sodium carbonate in order to remove acidic material such as hydrogen chloride, sulfuric acid, excess chlorosulfonic acid, and alkylbenzenesulfonic acid. The resulting slurry was stirred for 10 min and was then filtered through a coarse fritted disc filter. The solution of crude sulfonyl chloride was used in the subsequent Schotten-Baumann reaction without further purification.

N,N-Dimethyl-1,3-diaminopropane (13 g, 0.13 moles) was dissolved in 200 ml 1,2-dichloroethane and cooled to 8 C. The previously prepared dodecylbenzenesulfonyl chloride (I) solution was then added dropwise to the amine over a 30 min period. Stirring a room temperature was continued for 4 hr. The resulting crude amine hydrochloride solution was poured into 100 ml of a 10% sodium carbonate solution, and the mixture was stirred for 20 min. The aqueous solution was separated and discarded and the dichloroethane solution was then dried azeotropically by refluxing through a Dean-Stark trap. An aliquot of this solution was evaporated to dryness at 70 C under a vacuum (25 mm Hg) to remove solvent and unreacted diamine. To provide a basis for propanesultone addition, the aliquot residue was analyzed and found to contain 95% amine by titration with standard acid. The tertiary amine (II) solution was cooled to room temperature, and propanesultone (14.1 g, 0.116 moles) was added dropwise. Propanesultone should be handled with care because it has been found to be carcinogenic to test animals upon ingestion. The stirred solution was subsequently heated to 85 C for 4 hr. Upon evaporation of the solvent, an amber waxy product (III) was recovered in a 90% crude yield. This product could not be recrystallized.

The Type A compounds derived from pure phenylalkanes were recrystallized from 70% ethanol as white crystalline powders in 50-80% yields. The elemental analyses for C, H, S, and N agreed well with theoretical values. The derivatives from commercial detergent alkylates were used in crude form in the evaluation tests that follow.

Synthesis of Isomeric Type A Amphoteric Surfactant

The dichloroethane solution of the sulfonamide (II) derived from Nalkylene 500 was evaporated to dryness, and 41.5 g (0.105 moles) of the crude sulfonamide residue was dissolved in 300 ml methanol. Allyl chloride, 12.2 g (0.16 moles) was then added and the mixture was refluxed for a period of 14 hr. Excess methanol and allyl chloride were removed by vacuum distillation at 65 C (25 mm Hg). Titration with standard acid indicated that 95% of the amine had reacted. The quaternary ammonium compound (VI), dissolved in 50 ml methanol, was placed in a 100 ml Parr Pressure Apparatus. Sodium bisulfite (11.8 g, 0.13 moles) and t-butylperbenzoate (0.7 g, 0.0036 moles), catalyst, in 30 ml distilled water were added to the apparatus. The reagents were caused to react at 96 C for 7 hr at 20 lb pressure. The product was evaporated to dryness and subsequently dissolved in alcohol to remove inorganic salt by filtration. A yield of 39.2 g (72%) of an amorphous crude product (VII) was obtained after the solvent had been evaporated. The product could not be recrystallized, and was thus used in crude form for subsequent physical tests.

The derivative of pure 1-phenyldodecane, obtained in 69% yield, was readily recrystallized and gave the expected analyses for C,H, S, and N.

Synthesis of Type B Amphoteric Surfactants

The synthesis of the derivative of a commercial detergent alkylate (Nalkylene 500) is characteristic for that of all of the Type B amphoteric surfactants of this study.

N,N-bis-(2-Hydroxyethyl)-1,3-diaminopropane (20.7 g, 0.126 moles) was dissolved in 200 ml 1,2-dichloroethane and chilled to 8 C. A solution of dodecylbenzenesulfonyl chloride (I) in dichloroethane was prepared as described above and was added dropwise over a 30 min period. The reactants were stirred for 4 hr at 25 C. The product was poured into 100 ml of a 10% sodium carbonate solution, and the mixture was stirred for 20 min. The aqueous layer was drawn off and discarded. The dichloroethane solution of the amide (IV) was dried azeotropically and cooled to 25 C. Propanesultone (14.0 g, 0.116 moles) was added dropwise, and the stirred reaction mixture was refluxed for 4 hr. The crude amphoteric (V), an amorphous waxy solid,

TABLE II

Surface Active Properties of $RC_6H_4SO_2NH(CH_2)_3{}^+N(C_2H_4OH)_2(CH_2)_3SO_3{}^-$ (Type B)

R Group	LSDR[a]	Surface tension of 0.1% solution (dynes/cm)	Draves wetting time of 0.1% solution (sec)
From pure phenyl alkanes			
H (Benzene)	37.5	44.5	>300
Methyl	15	41.1	>300
Ethyl	15	39.7	>300
n-Butyl	6	38.6	>300
Sec-Butyl	45	34.2	>300
Hexyl	4	32.0	56
Heptyl	3	31.9	28
Octyl	3	31.1	68
Decyl	2	31.1	105
Dodecyl	2	33.8	232
From commercial dodecyl benzene			
Nalkylene 500	2	28.1	29
Alkylate 215	3	27.5	22
Alkylate 225	3	27.8	72
Alkylate 230L	3	27.9	140

[a]LSDR = Lime soap dispersant requirement.

was obtained on evaporation of solvent.

It was not possible to recrystallize any of the N,N-bis-(2-hydroxyethyl) derivatives, even those derived from pure 1-phenylalkanes.

Physical and Surface Active Properties

LSDR were determined according to the method of Borghetty and Bergman (5). Krafft points, calcium ion stabilities (6), wetting speed (7), and surface tension were measured by standard methods. The data are listed in Table I for Type A compounds and in Table II for Type B compounds. LSDR for both types of plotted in Figure 1.

Detergency measurements were carried out in 300 ppm hard water in the Tergotometer at 120 F with 3 types of test soiled cloths, EMPA 101 cotton (EMPA, St. Gallen, Switzerland, US Testing Company cotton (Hoboken, NJ) (UST), and Testfabrics (Middlesex, NJ) polyester-cotton blend with permanent press finish (TF). The tests were carried out as described in a previous publication by Weil and Coworkers (8). Solutions of 0.2% detergent in 300 ppm hard water were prepared of ternary mixtures containing 65% tallow soap, 20% lime soap dispersant, and 15% sodium silicate ($Na_2O:SiO_2$ = 1:1.6). The detergency data for the Type A lime soap dispersants are shown in Figure 2 and those for Type B dispersants in Figure 3.

The detergency behavior of the commercial detergent alkylate derivatives was studied by measuring detergency of 0.2% solutions of the surfactants alone, 0.2% solutions of binary mixtures containing 75% tallow soap and 25% surfactant, and finally 0.2% solutions of ternary mixtures of 65% soap, 15% sodium silicate, and 20% surfactant. The detergency data for the above are given in Table III. A leading commercial phosphate built detergent was used as a control in all detergency tests.

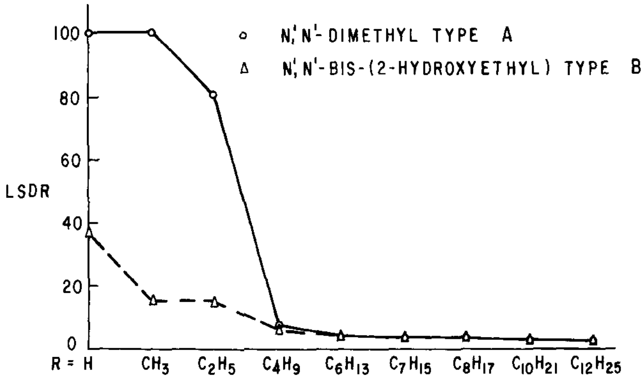

FIG. 1. Lime soap dispersant requirements of amphoteric surfactants.

RESULTS AND DISCUSSION

The synthetic procedures described above were found to be straightforward ones and were not complicated by side reactions. Thus, good yields were obtained in all cases, and even compounds which could not be purified by recrystallization such as all the Type B compounds and the detergent alkylate derivatives of Type A possessed excellent surface active properties. This indicates absence of large amounts of impurities.

The Krafft points of the Type A compounds prepared from pure phenylalkanes are given in Table I. Since the Type B compounds and the Type A detergent alkylate derivatives could not be purified, Krafft points for these compounds were not determined. The Type A compounds prepared from pure phenylalkanes exhibit a very sharp rise of Krafft point with increasing mol wt. This behavior appears to be characteristic for quaternary amphoteric surfactants (4). The Krafft points for a homologous series of anionic surfactant rises more gradually with increasing mol wt (3). The solubility behavior of the compounds of this study is influenced by pH. At a pH of 10, all compounds were sufficiently water soluble for determinations of surface active properties.

Optimum wetting ability is attained at C_7-C_8 side chain length for both types of compounds. The overall structure of the compounds of this study with its polar group at the end of the molecule is not a favorable one for good wetting properties. The improved wetting ability and surface tension lowering observed with the detergent alkylate derivatives can probably be attributed to branching of the alkyl side chains of these compounds.

The amphoterics of this study, like most amphoteric surfactants, are insensitive to calcium ions with all calcium ion stability values in excess of 1800 ppm as $CaCO_3$.

The washing tests of the ternary mixtures prepared with soap, sodium silicate, and the various amphoterics derived from pure phenylalkanes show clearly (Fig. 2 and 3) that the amphoterics with less than 7 carbon atoms in the alkyl side chain do not contribute significantly to detergency. The phenyldodecane derivatives of both Types A and B give the best detergency of the ternary formulations, and the detergency behavior (ΔR) values for the C_{12} side chain Type A derivative exceed those for the control detergent on the EMPA and UST cloths. Generally, the Type B deriva-

TABLE III

Detergency Behavior (ΔR) of Amphoterics Derived from Detergent Alkylates

Starting material for amphoteric	0.2%			0.2% Binary[a]			0.2% Ternary[b]		
	EMPA[c]	UST[c]	TF[c]	EMPA	UST	TF	EMPA	UST	TF
Type A									
Nalkylene 500	38	15	32	38	12	29	45	13	25
Alkylate 215	38	15	24	39	8	26	44	13	26
Alkylate 225	37	14	28	39	10	26	44	14	25
Alkylate 230L	30	9	23	36	8	26	36	12	19
Type B									
Nalkylene 500	41	14	35	41	13	27	43	13	24
Alkylate 215	44	14	35	44	13	25	45	13	27
Alkylate 225	41	13	35	41	13	25	42	14	27
Alkylate 230L	39	11	29	39	13	25	41	13	26
Control[d]							43	13	31

[a] A formulation of 75% tallow soap and 25% amphoteric surfactant.

[b] A formulation of 65% tallow soap, 20% amphoteric surfactant, and 15% sodium silicate ($Na_2O:SiO_2$ = 1:1.6).

[c] EMPA = EMPA 101 cotton; UST = US Testing Co. cotton; TF = Test fabrics polyester-cotton blend with permanent press finish.

[d] A leading commercial high phosphate-built detergent.

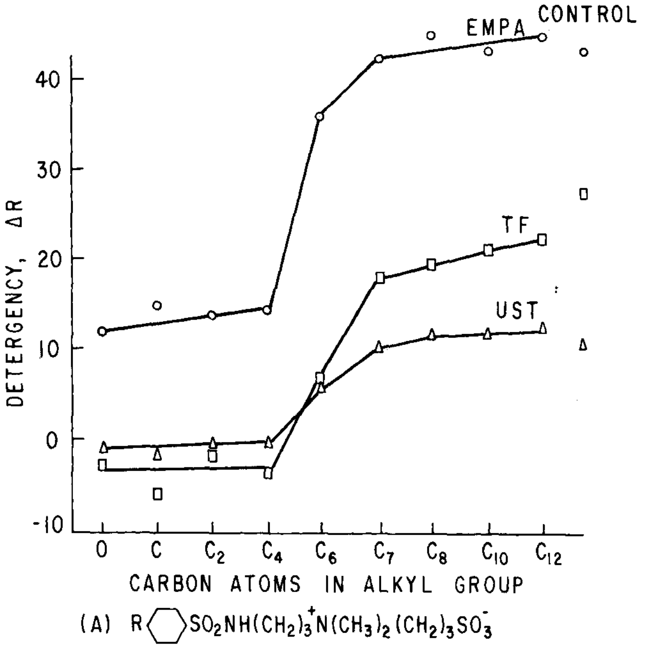

FIG. 2. Detergency of ternary detergent formulations containing Type A amphoterics. Control = a leading commercial phosphate-built detergent. EMPA = EMPA 101 cotton; TF = Testfabrics polyester-cotton blend with permanent press finish; UST = US Testing Co. cotton.

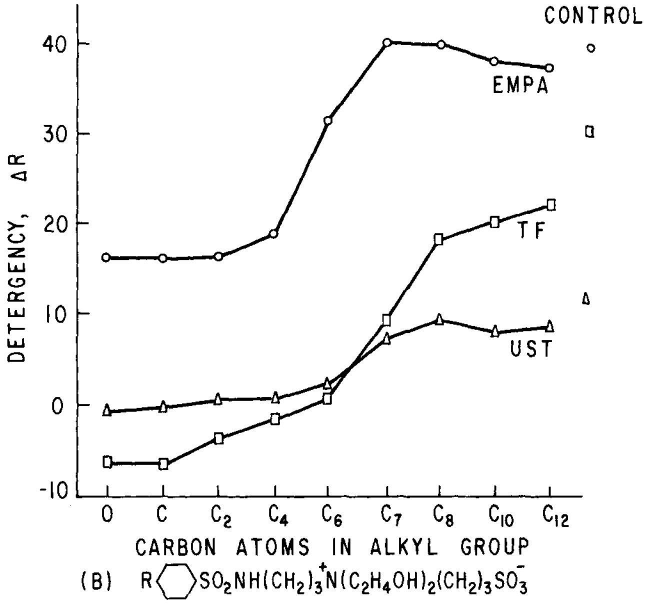

FIG. 3. Detergency of ternary detergent formulations containing Type B amphoterics. Control = a leading commercial phosphate-built detergent. EMPA = EMPA 101 cotton; TF = Testfabrics polyester-cotton blend with permanent press finish; UST = US Testing Co. Cotton.

tives are slightly inferior in detergency to the analogous Type A derivatives.

The detergency behavior of the amphoterics derived from the commercial detergent alkylates differs significantly from that of the pure phenylalkane derivatives. As is shown in Table III, the Type B derivatives by themselves and in binary mixtures are superior in detergency to Type A. In ternary mixtures both types are about equally effective and closely approach the detergency of the control. Differences between the Nalkylene 500, Alkylate 215, and Alkylate 225 derivatives are not significant. Alkylate 230L, whose average mol wt corresponds to that of tridecylbenzene, apparently possesses too high a mol wt so that its amphoteric derivatives are slightly inferior in detergency to the other detergent alkylate derivatives.

The LSDR of both series are shown in Figure 1. Both types of amphoterics are excellent lime soap dispersants when the alkyl chain is at least 4 carbons in length. Since butylbenzene is not normally sufficiently large to serve as the hydrophobic group of a surfactant molecule, it must be assumed that the carbon atoms between the sulfonamido group and the sulfonate group also contribute some hydrophobicity. The behavior of the benzene, toluene, and ethylbenzene derivatives is even more interesting. While the Type A derivatives of these 3 hydrocarbons did not function as lime soap dispersants, the Type B derivatives were surprisingly effective. The LSDR of the benzene derivative slightly surpasses that of 40 for linear alkylbenzenesulfonate, and the LSDR for the toluene and ethylbenzene derivatives approach those for the methyl esters of α-sulfo fatty acids (9). Thus, the 2 hydroxyethyl groups on the quaternary nitrogen atom exert a substantial effect on the LSDR of the lower mol wt derivatives.

A comparison between the detergency and LSDR of this study shows again that detergency and lime soap dispersing ability are unrelated surface active properties. While the hydroxyethyl groups of some Type B compounds enhanced lime soap dispersing ability, they imparied detergency of ternary mixtures containing the higher molecular Type B compounds. Likewise, the C_2-C_6 side chain Type B compounds, while offering good lime soap dispersing ability, do not contribute adequately to detergency. In soap-based detergent systems, lime soap dispersing ability is a prerequisite for good detergency; however, the detergency behavior of the dispersant itself and absence of detergency antagonism to soap, such as was observed in the case of nonionic surfactants (8), determines washing effectiveness.

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L.H. Scroggins and A.S. Kravitz performed elemental analyses.

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