Soap Based Detergent Formulations. V. Amphoteric Lime Soap Dispersing Agents[1]

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ABSTRACT

A series of amphoteric surfactants was prepared by the reaction of 1,3-propanesultone with fat derived primary amines, N-methylalkylamines, N,N-dimethylalkylamines, and N-acyl-N′,N′-dimethyl-1,3-propanediamines. Both mono- and disulfopropylated derivatives of the primary amines were synthesized. All compounds were found to be excellent lime soap dispersing agents. The quaternary sulfobetaines were found to possess the best detergency properties both by themselves and when formulated with tallow soap with or without sodium silicate builder. The detergency performance of such formulations is ca. the same as that of a commercial phosphate-built detergent.

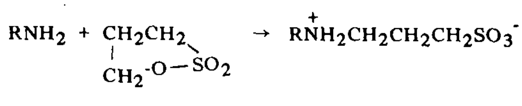
INTRODUCTION

In recent publications (1,2), the use of anionic lime soap dispersing agents (lsda) in conjunction with tallow soap was described. It was found that the detergency performance of soap in hard water was improved substantially by adding lsda. Lime soap precipitate was kept in suspension through both washing and rinsing cycles. The detergency of the mixture approached that of a phosphate built detergent in hard water. Further enhancement of detergency was attained by the addition of a suitable inorganic builder, such as a glassy sodium silicate, so that formulations were obtained whose detergency performance in hard and soft water was equal to that of commercial phosphate built detergents.

Nonionic surfactants also were found to be highly efficient lsda (3) with a lime soap dispersant requirement as low as 2%. However, tallow soap formulated with nonionics showed poor hard water detergency. This might have been due to the excessive bulk of the hydrophilic portion of the nonionic molecule which caused the combined detergent to take on the surface properties of the nonionic.

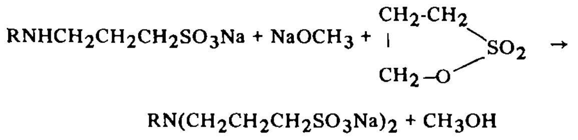
Because of the known high degree of compatibility of amphoteric surfactants (4) with anionic or cationic surfactants, we investigated the suitability of amphoterics as lsda in soap-based detergent systems. The reaction of 1,3-propanesultone with nucleophilic sites on aliphatic compounds, such as fatty alcohols, fatty amides, and fatty acids, has been shown in a previous publication by Parris, et al., (5) to proceed readily to yield various anionic surfactants, some of which showed good lime soap dispersing characteristics.

In the present study fatty primary amines were brought into reaction with 1,3-propanesultone, according to the following scheme:



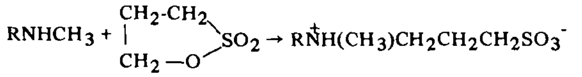
$$RNH_2 + CH_2CH_2CH_2\text{-}O\text{-}SO_2 \rightarrow R\overset{+}{N}H_2CH_2CH_2CH_2SO_3^-$$

This reaction was described by Hirai, et al., (6) and Suga and coworkers (7). The sodium salt of the monosulfopropylated primary amine could react with yet another mole of propanesultone in the presence of sodium methoxide to form the corresponding disulfopropylated compound.



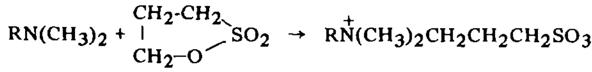
$$RNHCH_2CH_2CH_2SO_3Na + NaOCH_3 + CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_2 \rightarrow RN(CH_2CH_2CH_2SO_3Na)_2 + CH_3OH$$

A monosulfopropylated derivative was readily derived from an N-methylalkylamine.



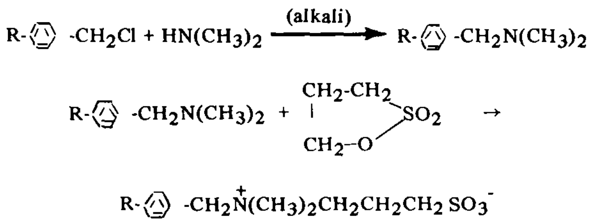
$$RNHCH_3 + CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_2 \rightarrow R\overset{+}{N}H(CH_3)CH_2CH_2CH_2SO_3^-$$

Similarly N,N-dimethylalkylamines could be converted to the quaternary sulfobetaines.

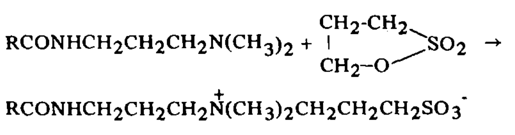


$$RN(CH_3)_2 + CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_2 \rightarrow R\overset{+}{N}(CH_3)_2CH_2CH_2CH_2SO_3^-$$

Linfield, et al., (4) described the synthesis and some of the surface active properties of sulfobetaines; and, in a more recent patent by Ernst (8), the synthesis and lime soap dispersing properties of this type of amphoteric surfactant were discussed. The excellent lime soap dispersant and detergent properties of a related type of sulfobetaine derived from an alkylbenzene were shown in a patent by Hirst (9) who synthesized the following type of surfactant:



Since N,N-dimethyl-1,3-propanediamine has become an article of commerce, it was also logical to study the surface active properties of the quaternized N-acyl derivatives of this material. The reaction of 1,3-propanesultone with this type of amidoamine proceeded about as readily as that with the fatty N,N-dimethylalkylamine.



$$RCONHCH_2CH_2CH_2N(CH_3)_2 + CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_2 \rightarrow RCONHCH_2CH_2CH_2\overset{+}{N}(CH_3)_2CH_2CH_2CH_2SO_3^-$$

In this investigation we tried to correlate surface active properties with the chemical structure of the various sulfopropylated fatty amines. The detergency behavior of these surfactants upon incorporation into the ternary detergent system, soap-builder-lsda, was of particular interest in view of similar research carried out at this laboratory on anionic lime soap dispersing agents (1,2).

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TABLE I

Solution Properties of Amphoteric Compounds

Compound	KP[a]	LSDR[b]	Surface tension[c]	Calcium ion stability[d]
$C12H_{25}NHC_3H_6SO_3Na$	40	3	e	435
$C_{16}H_{33}NHC_3H_6SO_3Na$	58	4	e	e
Tal[f]$NHC_3H_6SO_3Na$	e	4	—	e
$C_{16}H_{33}NH(CH_3)C_3H_6SO_3Na$	17	3	34	>1800
$C_{12}H_{25}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	<0	4	38	>1800
$C_{16}H_{33}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	27	4	35	>1800
$C_{18}H_{37}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	e	e	e	e
HTal[g]$\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	31	4	—	>1800
$C_{16}H_{33}N(C_3H_6SO_3Na)_2$	<0	3	46	>1800
$C_{18}H_{37}N(C_3H_6SO_3Na)_2$	<0	3	47	>1800
HTal[g]$N(C_3H_6SO_3Na)_2$	<0	3	---	>1800
$C_{11}H_{23}CONHC_3H_6\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$[h]	<0	3	30	
$C_{15}H_{31}CONHC_3H_6\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	<0	2	36	

[a] KP is temperature C at which a 1% solution becomes clear on gradual heating (12).

[b] LSDR = lime soap dispersant requirement. Grams of agent required to maintain dispersion of lime soap curd from 100 g of sodium oleate (11).

[c] Surface tension, dynes/cm, of 0.1% solution determined by the du Noüy method at 25 C.

[d] Calcium ion stability as ppm $CaCO_3$ tolerance (13).

[e] Insufficient solubility for measurement.

[f] Alkyl chain derived from tallow.

[g] Alkyl chain derived from hydrogenated tallow.

[h] Not purified.

EXPERIMENTAL PROCEDURES

Materials

N,N-Dimethyldodecylamine (Armeen DM12D), N,N-dimethylhexadecylamine (Armeen DM16D), N,N-dimethyloctadecylamine (Armeen DM18D), N,N-dimethyl hydrogenated tallowamine (Armeed DMHTD), hydrogenated tallowamine (Armeen HTD), and tallowamine (Armeen T) were obtained through the courtesy of the Armak Chemical Division, Akzona Inc., Chicago, Ill. The latter amine was found by gas liquid chromatographic (GLC) analysis to have the following composition: 2% $C_{14}H_{29}NH_2$, 24% $C_{16}H_{33}NH_2$, 46% $C_{18}H_{35}NH_2$, and 28% $C_{18}H_{37}NH_2$. Redistillation of the primary C_{12}, C_{16}, and C_{18} amines which were obtained from laboratory supply houses resulted in amines of greater than 99% purity according to GLC analyses. N-Methylhexadecylamine, mp 35-36 C, was prepared reducing N-methylpalmitamide with lithium aluminum hydride, according to the procedure of Foglia and Maerker (10). It was purified by recrystallization from petroleum ether. Propanesultone was purified by fractional distillation. The fraction boiling at 103-104 C/0.9 mm was collected, n^{40}_D = 1.4515, fp 31 C. N,N-Dimethyl-1,3-propanediamine (Jefferson Chemical Co., Austin, Texas) was redistilled at atmospheric pressure, and the fraction boiling at 133 C was collected.

N,N-Dimethylaminopropylamides

N(N′,N′-Dimethylaminopropyl)palmitamide was prepared by heating 54.1 g (0.200 mole) methyl palmitate with 24.5 g (0.220 mole) N,N-dimethyl-1,3-propanediamine in the presence of 0.46 g (0.020 mole) metallic sodium at 125-128 C for 40 min. The byproduct methanol distilled off rapidly during this period. The crude material was taken up in a boiling mixture of some petroleum ether (bp 63-70 C) and 250 ml absolute ethanol; insolubles were filtered from the boiling solution, and 38.6 g (.113 moles) product was crystallized at -30 C, mp 60.1-60.6 C. The composition of this compound was confirmed by elemental analysis. N(N′,N′-Dimethylaminopropyl)lauramide was prepared in a similar manner; but, due to its greater solubility in petroleum ether and other solvents, purification by crystallization was not successful.

Propane Sultone Reactions

Sodium N-3-sulfopropylakylamines: The preparation of N-hexadecyl-3-aminopropanesulfonic acid, sodium salt, is cited here as an example for the preparation of a monosulfopropylated primary amine derivative. A solution of 24.2 g (0.1 mole) of hexadecylamine in 125 ml of 1,2-dichloroethane was treated with 12.2 g (0.1 mole) of molten 1,3-propanesultone by dropwise addition for 10 min, followed by refluxing for 1 hr. Chlorinated solvent was removed by vacuum evaporation, and the residue was crystallized from 1200 ml absolute ethanol at room temperature to yield 29.0 g (.08 mole, 80% theoretical) of the inner salt form of the product. Recrystallization of the product from 800 ml of ethanol containing 0.089 equivalents of sodium hydroxide yielded 25.6 g (0.071 mole, 71% theoretical) of the sodium salt. The composition of the inner salt, as well as of the sodium salt, was confirmed by C, H, N, S, and Na elemental analyses.

N-(bis-3-sulfopropyl)alkylamines, disodium salt: The preparation of a disulfopropylated amine is illustrated by the preparation of N-(*bis*-3-sulfopropyl)hexadecylamine, disodium salt. To a solution of 10.0 g (0.041 mole) of n-hexadecylamine in 270 ml of freshly distilled toluene, there was added dropwise 5.1 g (0.041 mole) propanesultone. The reaction mixture was agitated vigorously; and the temperature was held at 60 C during the addition, and the reaction mixture then was refluxed for 1 1/2 hr. After cooling down to 60 C, 4.4 g (0.082 mole) sodium methoxide was added and the resulting methanol distilled off as an azeotrope with 130 ml toluene. After recooling to 60 C, 5.1 g (0.041 mole) propanesultone was added dropwise, and, thereafter, the mixture was refluxed for 2

TABLE II

Detergency Evaluation of Amphoterics at 120 F and 300 ppm Water Hardness

Compound	Detergency, ΔR^a								
	0.05% Amphoteric			0.2% Binary[b]			0.2% Ternary[c]		
	EMPA	UST	TF	EMPA	UST	TF	EMPA	UST	TF
$C_{12}H_{25}NHC_3H_6SO_3Na$	8	4	7	24	8	22	29	9	23
$C_{16}H_{33}NHC_3H_6SO_3Na$	8	3	5	12	4	8	18	4	10
$Tal^dNHC_3H_6SO_3Na$	5	2	7	12	3	5	18	3	6
$C_{16}H_{33}N(CH_3)C_3H_6SO_3Na$				14	6	21	24	6	18
$C_{16}H_{33}N(C_3H_6SO_3Na)_2$	14	9	12	29	8	14	34	9	12
$C_{18}H_{37}N(C_3H_6SO_3Na)_2$	13	9	11	30	8	15	30	8	14
$HTal^eN(C_3H_6SO_3Na)_2$	11	9	13	28	8	15	30	8	15
$C_{12}H_{25}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	10	5	8	31	12	22	33	8	15
$C_{16}H_{33}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	18	14	24	24	12	29	34	13	27
$C_{18}H_{37}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	7	13	25	17	11	25	27	13	26
$HTal^e\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	9	12	25	22	11	27	34	13	25
$C_{11}H_{23}CONHC_3H_6\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	9	4	7	26	8	11	24	4	7
$C_{16}H_{33}CONHC_3H_6\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	11	13	27	24	14	28	30	11	23
Control[f] at 0.2%				37	11	25			

[a] Increase in reflectance after washing Empa 101 cotton (EMPA), U.S. Testing cotton (UST), and Testfabrics Cotton – polyester blend with a permanent press finish (TF) in the tergotometer for 20 min.

[b] Binary mixture:0.05% lime soap dispersing agent + 0.15% tallow soap with 0.002% CMC.

[c] Ternary mixture:0.04% lime soap dispersing agent + 0.13% tallow soap + 0.03% sodium silicate (SiO_2/Na_2O = 1.6) with 0.002% CMC.

[d] Alkyl group derived from tallow.

[e] Alkyl group derived from hydrogenated tallow.

[f] A leading commercial phosphate built detergent.

1/2 hr.

A crude yield of 19.1 g was obtained by precipitation from the solution through the addition of 200 ml acetone. Recrystallization from 600 ml 85% ethanol at room temperature yielded 10.5 g (0.020 moles, 48% theoretical) of a product having the expected analysis for C, H, N, Na, and S.

Sodium N-methyl-N-(3-sulfopropyl)hexadecylamine: This was prepared from N-methylhexadecylamine by the same procedure as described above for the monosulfopropylated primary amine, and it gave the expected elemental analysis for C, H, N, S, and Na.

N-alkyl-N,N-dimethyl-3-ammonio-1-propanesulfonate: The preparation of N-hexadecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate is cited as an example for the preparation of quaternary, zwitterionic compounds. A solution of 27.0 g (0.100 mole) N,N-dimethylhexadecylamine in 75 ml 1,2-dichloroethane was heated to 50 C, and 12.2 g (0.100 mole) propanesultone was added dropwise with stirring for 30 min, maintaining the temperature at 50 C which required occasional cooling, since the reaction was exothermic. The reaction mixture then was refluxed for 30 min after the addition had been completed. The reaction mixture was cooled to 40 C, and 38.2 g (.0975 mole) crude product was precipitated by the addition of 300 ml acetone. After two recrystallizations from 95% ethanol, there was obtained 29.5 g (.0753 mole, 75% theoretical) product having the correct elemental analyses for C, H, N, and S.

N-(3-palmitamidopropyl)N,N-dimethyl-3-ammonio-1-propanesulfonate was prepared by causing propanesultone to react with N-(3-palmitamidopropyl) -N,N-dimethylamine in the same manner as described above for the sulfopropylation of an alkyldimethylamine. Purification of this compound was accomplished by first adding sufficient 18 N sodium hydroxide to the alcoholic solution of the crude sulfobetaine to raise the pH to 11-12. The fatty acid, present as an impurity in the product, thus was converted to the insoluble sodium soap which was removed by filtration. The filtrate was then neutralized with 1 N aqueous hydrochloric acid to pH 6. After crystallization from the alcoholic solution, the sulfobetaine was obtained in a 48% yield, and it gave the expected elemental analyses for C, H, N, and S.

Physical and Surface Active Properties

Methods for measuring surface active and physical properties, such as calcium ion stability, Krafft point, lime soap dispersant requirement (lsdr) (according to the Borghetty and Bergman method [11]) and detergency, have been described previously (1,2,3,5). Data obtained for Krafft point, lsdr, surface tension, by the du Noüy method, and calcium ion stability are listed in Table I. Table II lists detergency screening data at 120 F and 300 ppm water hardness. The first three columns show detergency of the amphoteric compounds by themselves at 0.05%. The next three columns show detergency of 0.2% binary mixture consisting of 75% tallow soap and 25% test compound. Finally the last three columns give detergency data for 0.2% of a ternary mixture of 65% tallow soap, 20% test compound, and 15% sodium silicate ($Na_2O:SiO_2$ = 1:1.6).

Neutralization curves were obtained for the disodium salt of the disulfopropylated hexadecylamine, as well as for the quaternary N,N-dimethylhexadecylammoniopropanesulfonate. Since the latter does not form an isolable sodium salt, one equivalent of sodium hydroxide was added to an aqueous solution of the purified neutral sulfobetaine prior to titration. Both compounds were then titrated with standard hydrochloric acid and the pH was measured after each incremental addition of acid. The resulting data were plotted as shown in Figure 1.

RESULTS AND DISCUSSION

The chemical structure of the sulfopropylated amines described above has a profound influence upon their water

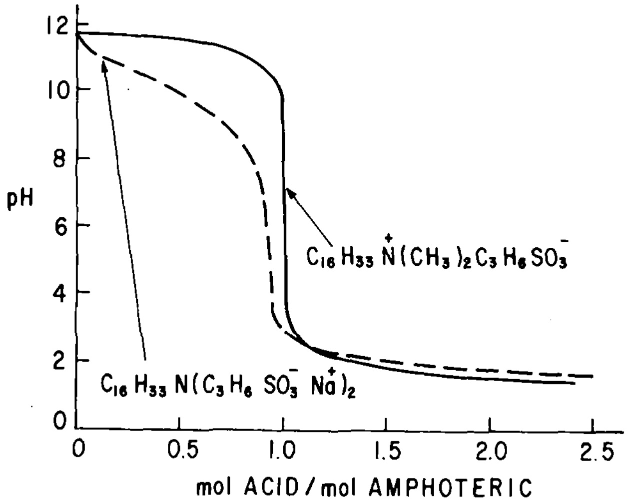

FIG. 1. Neutralization curves for $C_{16}H_{33}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$ and $C_{16}H_{33}N(C_3H_6SO_3^-Na^+)_2$, pH vs. moles HCl added per mole amphoteric.

solubility characteristics in terms of Krafft points as shown in Table I. The sodium salts of the monosulfopropylated primary amines had the highest Krafft points of the entire series studied, and the tallow derivative did not completely dissolve even at 100 C. These compounds in the zwitterionic form were always water insoluble. As expected, Krafft points increased with increasing mol wt of monosulfopropylated primary amines. The introduction of an N-methyl group into the molecule resulted in a sharply lowered Krafft point and hence greater water solubility. The disulfopropylation of the primary amines, as might be expected from the introduction of yet another hydrophilic group, lowered the Krafft point to such an extent that all compounds of this class of surfactants studied dissolved in water even at 0 C.

The sulfobetaines obtained by quaternization of N,N-dimethylakylamines with propane sultone had somewhat lower Krafft points than those of the monosulfopropylated primary amines but higher than those of the analogous disulfopropylated compounds. None of the compounds of this study melted below 190 C.

All compounds of this study, except the monosulfopropylated primary amines, were found to have calcium ion stability (13) in excess of 1800 ppm, expressed as $CaCO_3$. The tertiary and quaternary amines were more surface active than the disulfopropylamines as indicated by their low surface tension. All compounds were highly effective lime soap dispersing agents, with lsdr values of 2-4.

To determine possible buffering effects and isoelectric points, neutralization curves shown in Figure 1 were obtained for the disulfopropylated primary amine derivative, as well as for the monosulfopropylated N,N-dimethyl fatty amino derivative. Because of poor water solubility of the monosulfopropylated primary fatty amine, its titration curve could not be obtained. The curve for the quaternary amphoteric $C_{16}H_{33}\overset{+}{N}(CH_3)_2CH_2CH_2CH_2SO_3^-$ as expected looks like the neutralization curve of strong base with a strong acid, and the isoelectric point is close to 7.0. On the other hand, the curve for the tertiary amino compound $C_{16}H_{33}N(CH_2CH_2CH_2SO_3Na)_2$ shows the effect of a weaker base, and the isoelectric point lies near 5.2. The buffering effect of this compound on the acid side would make it less desirable for incorporation into alkaline soap-based formulations.

The detergency data shown in Table II were obtained in a Tergotometer and, thus, represent no more than laboratory screening tests. We believe, however, that comparisons, especially between members of a homologous series, have considerable significance. Since the basic goal of this research was the development of a phosphate-free detergent, a commercial household detergent containing ca. 50% sodium tripolyphosphate was used as a control in these studies.

The detergency of the amphoterics by themselves is generally poor at a concentration of 0.05%. The fatty sulfobetaines appear to be the best detergents in this series both by themselves or combined in binary or ternary mixtures. In all cases the detergency of the individual compounds at 0.05% was increased when 0.15% tallow soap was added, as shown by a comparison between the 0.05% amphoteric columns and the 0.2% binary columns in Table II. The replacement of 15% of the binary mixture by a glassy silicate resulted in almost every case in a further enhancement of the detergency. The best amphoteric lime soap dispersant of this series from a detergency viewpoint appears to be the tallow derived sulfobetaine. The ternary mixture prepared with this material gave a detergency performance close to that of a leading commercial phosphate detergent.

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