Soap-Based Detergent Formulations: XVIII. Effect of Structure Variations on Surface-Active Properties of Sulfur Containing Amphoteric Surfactants¹

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ABSTRACT

Quaternary ammonium amphoteric surfactants have been found in the past to be excellent lime soap dispersing agents and detergents but exhibit unusual solubility behavior. In search of a relationship between chemical structure and surface-active properties, compounds having the following general formula were synthesized: $ZN^+(CH_3)_2(CH_2)_n X^-$, where Z is $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, or $C_{15}H_{31}CONHC_{3}H_{6}$, n is 2, 3, or 4 and X is SO_{3} or OSO3⁻. Tertiary amines were converted to sulfobetaines $(X = SO_3)$ by reaction with (a) butanesultone (n = 4), (b) propanesultone (n = 3), or (c) sodium 2-bromoethanesulfonate (n = 2). An alternate synthesis for the sulfoethylbetaines (n=2) involved the reaction of the tertiary amines with ethylene bromide, followed by treatment with sodium sulfite. All sulfated quaternary ammonium compounds (X = OSO_3^{-}) were synthesized by treatment of the tertiary amine with the appropriate chloroalcohol, followed by sulfation with chlorosulfonic acid. The sulfated quaternary ammonium amphoterics are stable to acid hydrolysis, and alkaline stability improves with increasing bridge chain length. Sulfoethyl amphoterics are less water soluble than sulfobutyl, which in turn are less soluble than sulfopropyl derivatives of the same alkyl chain length. For the most part, the sulfated amphoterics are insoluble but are solubilized by soap. The lime soap dispersing properties improve as the carbon chain bridge length increases for both the sulfates and sulfonates. Formulations of tallow soap, amphoteric surfactant, and sodium silicates gave good detergency in most cases.

INTRODUCTION

Quaternary ammonium sulfobetaine amphoteric surfactants have been shown to be excellent lime soap dispersing agents and to exhibit good detergency in combination with soap (1). (3-Sulfopropyl)dimethyl(alkyl)ammonium inner salts previously prepared at this laboratory (1) possess good surface-active properties. Because 1,3-propanesultone, an intermediate in their synthesis, has the disadvantages of commercial unavilability and hazardous properties, alternate syntheses of similar compounds have been investigated (2). Poor water solubility, as indicated by Krafft point, tends to limit the utility of such surfactants. The effect of the alkyl chain length on Krafft point was found to be much more pronounced for the quaternary (3-sulfopropyl) dimethyl(alkyl)ammonium inner salt and (2-hydroxypropyl)dimethyl(alkyl)ammonium inner salt than for their secondary amino analogs (1,2). Because small changes in the hydrophobic portion of the molecule have been shown to have a pronounced effect on surface-active properties and water solubility of the quaternary derivatives, it was important to determine the effects of changes in the hydrophilic portion of the molecules on solution and surfaceactive properties. Specifically, the effects due to the distance between the anionic and cationic sites and differences between analogous sulfonates and sulfates were investigated. Accordingly, compounds possessing the general structure $ZN^+(CH_3)_2$ $(CH_2)_nX^-$ were synthesized, where Z represents a fatty alkyl group or an N-(3-palmitamidopropyl) group, n is an integer varying from 2 to 4, and X is either a sulfonate or sulfate group.

The ethanesulfonate derivatives were prepared by either of the following two routes:

$$\begin{array}{l} \text{RN}(\text{CH}_3)_2 + \text{Br}\text{CH}_2\text{CH}_2\text{SO}_3\text{Na} \rightarrow \\ \\ \text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^- + \text{NaBr} \end{array}$$

or

 $\begin{array}{c|c} RN(CH_3)_2 + BrCH_2CH_2Br \rightarrow [RN(CH_3)_2CH_2CH_2Br]^+ Br^-\\ RN^+(CH_3)_2CH_2CH_2SO_3^- Na_2SO_3 \end{array}$

The latter method, published by Barnhurst (3), gives higher yields and is thus the preferred procedure. The propane and butanesulfonates were synthesized by direct reaction of the tertiary fatty amine with 1,3-propanesultone and 1,4-butanesultone in accordance with an earlier published method (1) for the preparation of sulfopropyl amphoteric compounds.

The N-ethyl and N-propyl sulfates of the series were prepared by quaternization of the tertiary amines by heating with ethylene chlorohydrin or 3-chloro-1-propanol, followed by sulfation with chlorosulfonic acid according to the following scheme:

 $\mathrm{RN}(\mathrm{CH}_3)_2 + \mathrm{C1}(\mathrm{CH}_2)_n\mathrm{OH} \rightarrow [\,\mathrm{RN}(\mathrm{CH}_3)_2(\mathrm{CH}_2)_n\mathrm{OH}\,]^+\mathrm{C1}^-$

$$I + HSO_3C1 \rightarrow \xrightarrow{NaOH} RN^+(CH_3)_2(CH_2)_nOSO_3^-$$

where n = 2 or 3

This procedure failed in the case of the analogous butyl sulfate derivatives because chlorobutanol is unstable upon standing or heating and decomposes to form tetrahydrofuran and hydrogen chloride. This problem was circumvented by initial sulfation of chlorobutanol with chlorosulfonic acid, a fast reaction taking place at low temperature, followed by quaternization according to the following scheme:

$$C1C_4H_8OH + HSO_3C1 \rightarrow \frac{NaOH}{C1C_4H_8OSO_3Na + NaC1}$$

 $C1C_4H_8OSO_3Na + RN(CH_3)_2 \rightarrow RN^+(CH_3)_2C_4H_8OSO_3^{-1}$

+ NaC1

EXPERIMENTAL PROCEDURES

Materials

N,N-dimethyldodecylamine (Armeen DM12D), N,Ndimethyltetradecylamine (Armeen DM14D), N,N-dimethylhexadecylamine (Armeen DM16D), and N,N-dimethyl-

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TABLE I

Hydrolytic Stability of Surface-Active Sulfates

	Half-life (min)		
Sulfates	0.05 N NaOH (at 100 C)	0.05 N HC1 (at 80 C)	
C ₁₆ H ₃₃ OSO ₃ Na	stablea	210 ^a	
$C_{14}H_{29}N^{+}(CH_{3})_{2}C_{2}H_{4}OSO_{3}^{-}$	26	stable	
C14H29N ⁺ (CH3)2C3H6OSO3 ⁻	stableb	stable	
RN ⁺ (CH ₃) ₂ C ₄ H ₈ OSO ₃ ⁻	stable	stable	
C ₁₅ H ₃₁ CONHC ₂ H ₄ OSO ₃ Na	83 ^c	8 3 ^c	
C15H31CONHC3H6OSO3Na	>500 ^c	180 ^c	

^aData from ref. 7.

b<10% Hydrolysis after 7 hr.

^cData from ref. 8.

octadecylamine (Armeen DM18D) were obtained through the courtesy of the Armak Chemical Division, Akzona Inc. (Chicago, IL). They were used after fractionation to give a purity of > 99% as indicated by gas liquid chromatographic analysis. Ethylene bromide, 2-chloroethanol, 3-chloropropanol, propylene chlorohydrin, and 1,3-propanesultone were obtained from laboratory supply houses. (Exposure to 1,3-propanesultone causes burns and the material is known to cause cancer in animals.) The intermediate N(N',N'dimethylaminopropyl) palmitamide was prepared as previously cited (1).

Synthetic Procedures

Synthesis of N-(2-sulfoethyl) derivatives: Preparation of (2-sulfoethyl)dimethyl(hexadecyl) ammonium inner salt is cited as an example for preparation of the ethanesulfonate derivatives. N-hexadecyl-N,N-dimethylamine (21.2 g, 0.079 mol) was added to a reaction flask containing ethylene bromide (142.5 g, 0.758 mol) and heated to 50 C for 6 hr. When a sample of the crude product was titrated for free amine with 0.1 N NC1 using bromophenol blue as the indicator, no free amine was found to be present. Unreacted ethylene bromide was removed by distillation at 36-38 C/43-49 mm, and the crude residue was crystallized twice from 250 ml absolute ethanol at -30 C. The product, a white crystalline solid, was found to be free of fatty amine hydrobromide when titrated with 0.1 N NaOH using phenolphthalein indicator. Yield of pure product was 26.3 g (0.058 mol, 73% theoretical); it had the expected elemental analysis.

(2-Bromoethyl)dimethyl(hexadecyl) ammonium bromide (23.1 g, 0.051 mol) was added to a reaction flask containing sodium sulfite (10.7 g, 0.085 mol) dissolved in 100 ml distilled water. The reaction mixture was refluxed for 8 hr, after which the water was removed from the crude product on the steam bath. The crude product was stirred in 250 ml boiling 95% ethanol, and the insoluble inorganic salts were removed by filtration. The product crystallized at room temperature and was recrystallized from 400 ml 65% ethanol. Pure product, 11.6 g (0.031 mol, 62% theoretical), was recovered at room temperature; it had the expected elemental analysis. The N-dodecyl and N-tetradecyl homologs of the above were synthesized in a similar fashion and were obtained in about the same yields. Likewise, the N-palmitamidopropyl homolog of the above was prepared from N-(N,N-dimethylaminopropyl) palmitamide (1) in an analogous fashion and in similar yields.

Synthesis of N-(3-sulfopropyl) derivatives: All compounds of this group were prepared by reaction between 1,3-propanesultone and the appropriate tertiary amine as described previously by Parris et al. (1).

Synthesis of N-(4-sulfobutyl) derivatives: The inter-

mediate 1,4-butanesultone (bp 105 C/1.8 mm) was prepared by the methods described by Snoddy (4) and Helberger and Lantermann (5). However, the work-up procedures of the latter was found to be the most efficient.

(4-Sulfobutyl)dimethyl(octadecyl) ammonium inner salt is cited as a typical synthesis for the N-(4-sulfobutyl) derivatives. 1,4-Butanesultone (6.8 g, 0.050 mol) was added dropwise to N-octadecyl-N,N-dimethylamine (14.9 g, 0.050 mol) dissolved in 50 ml dichloroethane at room temperature, and the reaction mixture was refluxed for 4 hr. After cooling to 50 C, 100 ml acetone was added and 16.9 g (.039 mol, 78% theoretical) of precipitated product was recovered by filtration at room temperature.

Synthesis of N-(2-sulfatoethyl) derivatives: The synthesis of (2-sulfatoethyl)dimethyl(3-palmitamidopropyl) ammonium inner salt is cited as a typical preparation for N-(2-sulfatoethyl) derivatives. N-3-palmitamidopropyl-N,N-dimethylamine (18.4 g, 0.054 mol) was added to a reaction flask containing freshly distilled ethylene chlorohydrin (8.7 g, 0.109 mol), and the mixture was heated to 80-85 C for 5 hr. Thereafter, no free amine was found after titration with 0.1 N HCl using bromophenol blue as the indicator. Petroleum ether, 100 ml (bp 63-70 C), was added to the reaction mixture and sufficient chloroform was added to dissolve the product at the boiling point. Thus, 17.9 g (0.043 mol, 79% theoretical) of pure product was collected by filtration at -30 C; it gave the expected elemental analysis. (2-Hydroxyethyl)dimethyl(3-palmitamidopropyl) ammonium chloride (13.3 g, 0.032 mol) was dissolved in 100 ml chloroform, and the solution was chilled to -30 C. Chlorosulfonic acid (5.2 g, 0.045 mol) was then added dropwise to the solution, and the temperature was permitted to rise to 15 C. The mixture was allowed to stir at room temperature for 1 hr, then chilled to -30 C. Cold absolute ethanol (100 ml) was added to the reaction mixture, which was chilled again to -30 C, and precipitated solids were removed by filtration. The filtrate was made slightly alkaline with 17.4 ml 18 N NaOH. Insolubles formed during neutralization were removed by filtration and the desired product crystallized from the filtrate at -30 C. This product, 6.6 g (0.011 mol, 34% theoretical), had the expected elemental analysis.

Synthesis of N-(3-sulfatopropyl) derivatives: The compounds of this series were all prepared in a manner analogous to the synthesis of the preceding N-(2-sulfatoethyl) derivatives, except that 3-chloro-1-propanol was used in place of the ethylene chlorohydrin in the quaternization step. Typically, the intermediate (3-hydroxypropyl)dimethyl-(hexadecyl) ammonium chloride was isolated in a 72% yield, and after sulfation a 51% overall yield of product was obtained.

Synthesis of N-(2-sulfatopropyl) derivatives: (2-Sulfatopropyl)dimethyl(hexadecyl) ammonium inner salt was prepared in a manner similar to that of the N-(2-sulfatoethyl) derivatives, except that the time for the reaction between the amine and propylene chlorohydrin was 24 hr. The intermediate (2-hydroxypropyl)dimethyl(hexadecyl) ammonium chloride was isolated in 78% yield, and after sulfation a 60% overall yield of amphoteric sulfate was obtained.

Synthesis of N-(4-sulfatobutyl) derivatives: The intermediate 4-chloro-1-butanol was prepared by the method of Starr and Hixon (6) in a high degree of purity. First, 4chloro-1-butanol (49.1 g, 0.452 mol) was dissolved in 100 ml chloroform and chilled to -30 C, and chlorosulfonic acid (69.3 g, 0.595 mol) was added dropwise over 30 min as the temperature increased to 11 C. The mixture was stirred for 1 hr as the reaction temperature rose to 23 C. After chilling the mixture to -30 C, 150 ml cold methanol was added, followed by neutralization with 36 ml 18 N sodium hydroxide. The neutral product was then heated to reflux, and inorganic salts were removed as insolubles by filtration of the hot solution. The crude product was obtained after

filtration at -30 C and was recrystallized from 500 ml 97% aqueous ethanol. Thus, 29.0 g (0.134 mol, 30% theoretical) of pure product was isolated after filtration at 0 C; it had the expected elemental analysis. The synthesis of (4-sulfatobutyl)dimethyl(hexadecyl) ammonium inner salt is cited as a typical preparation for N-(4-sulfatobutyl) derivatives. N-Hexadecyl-N,N-dimethylamine (7.7 g, 0.029 mol) was added to 100 ml 90% aqueous butanol containing sodium 4-chloro-1-butanesulfate (6.0 g, 0.029 mol) and brought to reflux. The formation of fatty amine hydrochloride due to hydrolysis of the intermediate and disappearance of fatty amine was followed by titration with strong base and strong acid, respectively. The reaction was stopped after 43 hr when the rate of formation of fatty amine hydrochloride exceeded that of the disappearance of fatty amine. At this point, 7% of the fatty amine was present as the hydrochloride and 18% was unreacted. The solvent was removed on a rotary evaporator at 50 C and the residue dissolved in aqueous ethanol. The pH was adjusted to 10 with NaOH, and unreacted amine was removed from the crude product by extraction with petroleum ether (bp 63-70 C). The product was crystallized at -30 C, dried and recrystallized from 50 ml n-propanol and 3.0 g (0.009 mol, 33% theoretical) pure product was isolated at 0 C having the expected elemental analysis.

Hydrolysis Studies

Stability of the amphoteric compounds to equimolar amounts of sodium hydroxide at 100 C or hydrochloric acid at 80 C was determined according to the method of Weil et al. (7). The results for the sulfates are listed in Table I, along with corresponding data for an alkanesulfate (7) and sulfated alkanolamides (8) for comparison. The sulfonates were found to be hydrolytically stable, so that data for them were omitted.

Physical and Surface-Active Properties

Solution properties such as Krafft points and lime soap dispersant requirements (LSDR) were measured according to accepted methods (9,10). Some ethanol was added to help dissolve insoluble compounds for the LSDR test. The ethanol did not affect the LSDR, inasmuch as the same results were obtained for a water soluble compound run in aqueous ethanol as well as in water alone. Detergency was determined as described in a previous publication (1).

Data obtained for Krafft point and LSDR are listed in Table II. Detergency data for ternary detergent formulations consisting of 65% tallow soap, 20% amphoteric surfactant, and 15% sodium silicate ($Na_2O:SiO_2 = 1:1.6$) at 120 F and 300 ppm water hardness are shown in Table III. See footnote of Table III for the soiled test fabrics used.

RESULTS AND DISCUSSION

The synthetic procedures described above are fairly straightforward. The low yields are primarily due to losses incurred during purification. The amphoteric sulfates of this study were examined for hydrolytic stability under acid and alkaline conditions and compared for stabilitywith a sulfated fatty alcohol as well as with two sulfated alkanolamides of a fatty acid, as shown in Table I. The length of the carbon chain bridge between the anionic and cationic sites affects hydrolytic stability. Only the twocarbon bridged material is susceptible to alkaline hydrolysis, whereas the three-carbon atom bridged compound is much more stable and the four-carbon bridged amphoteric sulfate is completely stable. This parallels the hydrolytic stability of the sulfated alkanolamides (8), where hydrolytic stability was increased substantially as the bridging between amide and sulfate groups was increased from two

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Solution Properties of Amphoteric Derivatives

	Krafft point (1%, C)	LSDR ^a (%)
Sulfonates		
Sulfoethyl, RN ⁺ (CH3) ₂ C ₂ H4SO ₃ ⁻		
$R = C_{12}H_{25}$	71	4 ^b
C14H29-	82	46
C16H33-	с	6 ^b
C ₁₅ H ₃₁ CONH(CH ₂) ₃ -	60	4
Sulfopropyl ^d , RN ⁺ (CH ₃) ₂ C ₃ H ₆ SO ₃ ⁻		
$R = C_{12}H_{25}$	<0 ^e	4
C16H33-	27 ^e	4
C ₁₈ H ₃₇ .	88 ^e	3p
C ₁₅ H ₃₁ CONH(CH ₂) ₃ -	<0	2
Sulfobutyl, RN ⁺ (CH ₃) ₂ C ₄ H ₈ SO ₃ ⁻		
$R = C_{16}H_{33}$	36	3
C ₁₈ H ₃₇ -	63	3p
C ₁₅ H ₃₁ CONH(CH ₂) ₃ -	24	2
Sulfates		
Sulfatoethyl, RN ⁺ (CH ₃) ₂ C ₂ H ₄ OSO ₃ ⁻		
$R = C_{14}H_{29}$	с	4 ^b
C ₁₆ H ₃₃ -	с	4b
C ₁₅ H ₃₁ CONH(CH ₂) ₃ . ^f	60	5
Sulfatopropyl, RN ⁺ (CH ₃) ₂ C ₃ H ₆ OSO ₃	-	
$R = C_{14}H_{29}$	с	3b
C16H33-	с	4 ^b
C ₁₅ H ₃₁ CONH(CH ₂) ₃ -	с	30
Sulfatobutyl, RN ⁺ (CH ₃) ₂ C ₄ H ₈ OSO ₃ ⁻		
$R = C_{12}H_{25}$ -f	с	3p
C ₁₆ H ₃₃ -	c	2 ^b
C1 = H31CONH(CH2)3-	c	2 ^b

^aLSDR = lime soap dispersant requirement.

^bAlcohol required to make lime soap dispersing agent solution.

 $c_{Krafft point} > 90 C.$

^dPreparation same as ref. 1.

^eKrafft points taken from ref. 2.

^fProduct contained small amount of inorganic salts.

to three carbon atoms. In contrast to these amphoteric sulfates, fatty alcohol sulfates are stable to alkaline but not acid hydrolysis. All of the amphoteric sulfonates in this study were stable to acid and alkaline hydrolysis under the same conditions.

The solution properties, as shown in Table II, indicate that the sulfonates are more water soluble, i.e., have lower Krafft points, than the analogous sulfates. The insertion of an amido group brings about a lowering of the Krafft point, as was noted in an earlier publication (1). Lengthening of the carbon bridge has a marked effect on the Krafft point. As the bridge of the sulfonates is lengthened from two to three carbon atoms, the Krafft point is lowered, but then in most cases it is raised again as the bridge length is increased to four carbon atoms. This is contrary to the findings of Hikota (11) for sodium sulfoethyl, sulfopropyl, and sulfobutyl esters of fatty acids. He found that, as the carbon bridge length increased between the sulfonate and ester groups, the Krafft points decreased steadily. In our case, however, we are dealing with a separation of ionic charges, which may account for the difference in solubility behavior.

The quaternary ammonium amphoteric surfactants exhibit unusual solubility in terms of Krafft point variation with increasing length of the fatty alkyl chain, as shown in Figure 1. Curves for the secondary amine derivatives and for the sulfopropylated quaternary amphoterics with and

TABLE III

Detergency of	Ternary	Formu	ulations	of Soap,
Amphoteric S	Surfactan	t, and	Sodium	Silicate

	Detergency ^a (% control) 0.2% Ternary		
Test compounds	EMPA	UST	TF
Sulfobetaines			
RN^{+} (CH ₃) ₂ C ₂ H ₄ SO ₃ ⁻			
$R = C_{12}H_{25}$	100	92	69
C14H29-	95	92	50
C ₁₆ H ₃₃ -	63	50	12
C ₁₅ H ₃₁ CONHC ₃ H ₆ -	97	108	100
RN ⁺ (CH ₃) ₂ C ₃ H ₆ SO ₃ ⁻			
$R = C_{12}H_{25}$	100	92	65
C ₁₆ H ₃₃ -	100	108	92
C18H37-	86	116	119
C ₁₅ H ₃₁ CONHC ₃ H ₆ -	80	100	92
RN^+ (CH ₃) ₂ C ₄ H ₈ SO ₃ ⁻			
$R = C_{16}H_{33}$ -	100	108	108
C ₁₈ H ₃₇ -	100	108	96
C ₁₅ H ₃₁ CONHC ₃ H ₆ -	100	108	81
Sulfatobetaines			
RN ⁺ (CH ₃) ₂ C ₂ H ₄ OSO ₃ ⁻			
$R = C_{14}H_{29}$	95	108	104
C16H33-	91	108	119
C ₁₅ H ₃₁ CONHC ₃ H ₆ -	89	108	96
RN^+ (CH ₃) ₂ C ₃ H ₆ OSO ₃ ⁻			
$R = C_{14}H_{29}$ -	103	100	92
C16H33-	97	83	54
C ₁₅ H ₃₁ CONC ₃ H ₆ -	91	116	96
RN^+ (CH ₃) ₂ C ₄ H ₈ OSO ₃ ⁻			
$R = C_{16}H_{33}$	100	108	104
C ₁₅ H ₃₁ CONHC ₃ H ₆ -	106	108	92
Control at 0.2% ^b	100	100	100

^aDetergency was measured as increase in reflectance (ΔR) after washing EMPA 101 Cotton (EMPA) (distributed by Testfabrics Inc., Middlesex, NJ), U.S. Testing Cotton (UST) (Hoboken, NJ), and Testfabrics cotton-polyester blend with a permanent press finish (TF) in the Tergotometer for 20 min at 120 F and 300 ppm water hardness. ΔR of the control was adjusted to 100.

^bA leading commercial phosphate-built detergent.

without a hydroxyl group in the bridge section of the molecule are included in Figure 1 from a previous publication (2) for comparison. It can be seen that the Krafft points of the sulfopropylated amphoterics with or without the hydroxyl substituent rise very steeply with increasing fatty alkyl chain length. The slope for the sulfobutylated amphoteric is less steep, whereas that for the sulfoethyl amphoterics is much less steep and almost the same as that for the two curves for the secondary amine derivatives.

It was also noted that branching of the bridge did not improve water solubility. Thus, the sulfated N-(2-hydroxyethyl)-, N-(2-hydroxypropyl)- and N-(3-hydroxypropyl derivatives were all water insoluble. Only by inserting an amido group into the molecule were we able to produce a water soluble sulfated amphoteric surfactant.

Although many compounds of this study were water insoluble, their surface-active properties such as lime soap dispersing ability and detergency could be determined because soap solubilizes the surfactants in water. Addition of alcohol also aids water solubility. The lime soap dispersing properties of all compounds of this study were excellent, as shown in Table II, even those of the water insoluble



FIG. 1. Krafft points for secondary and quaternary sulfonates. aKrafft points taken from ref. 2.

amphoterics which first had to be solubilized with alcohol. As noted earlier (2), we see here again that the LSDR is improved by the insertion of an amido group. The LSDR also decreases as the carbon chain bridge is lengthened.

The detergency of the compounds of this study was determined for ternary mixtures of 65% tallow soap, 20% amphoteric surfactant, and 15% sodium silicate (Na2- $O:SiO_2 = 1:1.6$) and tabulated in Table III. The detergency of all ternary mixtures containing amphoterics in the tallow range was excellent and equalled or surpassed that of a commercial high phosphate-built detergent in most cases. The poorer detergency obtained for the N-(2-sulfoethyl) derivatives in ternary formulation is probably due to their poor water solubility compared to that of the other sulfonates. Detergency was improved by insertion of an amido group or by shortening the hydrophobic alkyl chain length of the N-(2-sulfoethyl) derivatives. It would appear that, in the sulfonate as well as in the sulfate series, detergency improved somewhat with increasing length of the carbon atom bridge.

Zwitterionic quaternary ammonium sulfates are excellent lime soap dispersants and detergents in combination with soap. The LSDR improves as the carbon chain bridge length increases. The amphoteric sulfates are stable to acid hydrolysis, and stability to alkali improves with increasing bridge chain length. In general, the sulfonates were more water soluble than the sulfates; however, the nature of the anionic group did not otherwise affect the surface-active properties.

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