Soap Based Detergent Formulation: XXIV. Sulfobetaine Derivatives of Fatty Amides[1]

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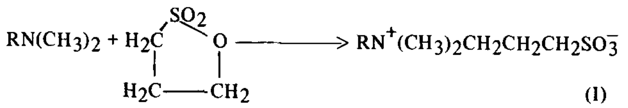
ABSTRACT AND SUMMARY

Sulfobetaines were prepared from the reaction of fatty acids, fatty acid methyl esters or fatty glycerides with N,N-dimethyl-1,3-propanediamine to form an aminoamide which could be allowed to react further with either sodium 3-chloro-2-hydroxy-1-propanesulfonate (from epichlorohydrin and sodium bisulfite) or with allyl chloride followed by addition of sodium bisulfite to form sulfobetaines. The conditions for the reaction between aminoamide and sodium 3-chloro-2-hydroxy-1-propanesulfonate were studied in an effort to minimize the extent of hydrolysis of the 3-chloro-compound and thus increase the yield of desired compound. Investigation of the quaternization of the aminoamide with allyl chloride showed that this reaction proceeded readily at pressures above atmospheric. The addition of sodium bisulfite to the resulting allyl quaternary ammonium compound took place readily in the presence of certain free radical initiators. Solution properties and detergency performance of the compounds are reported. Detergency of ternary formulations of soap, glassy silicate builder, and the above sulfobetaines was the same as that obtained with ternary formulations containing the analogous sulfobetaines obtained from the reaction of propanesultone with the aminoamide. We have developed a synthetic scheme for fatty amido sulfobetaines that requires no purification, avoids the use of carcinogenic 1,3-propanesultone and expensive fatty tertiary amines, and produces detergents that perform as well as the previously described purified sulfobetaines [Parris et al., JAOCS 50:509 (1973); Parris et al., Ibid. 53:60 (1976)].

INTRODUCTION

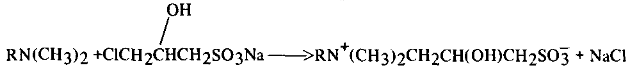
Sulfopropylated quaternary ammonium amphoteric surfactants have been prepared from the reaction of fatty tertiary amines and 1,3-propanesultone according to the following scheme (I).



(I)

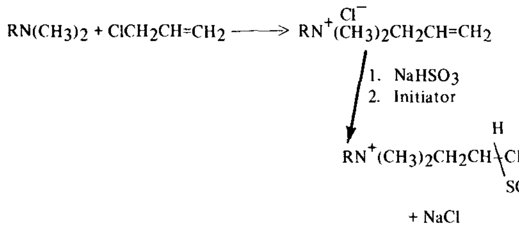
where R = alkyl, alkylbenzyl

The syntheses of nonaromatic (1,2) and aromatic (3) derivatives are described in the literature, where their evaluations as lime soap dispersants are also discussed. The nonaromatic compounds exhibited good surface active properties and were formulated into excellent detergents in combination with soap. However, because of the hazardous nature of propanesultone, its high cost, and its commercial unavailability, alternative syntheses were investigated (4,6), as shown in Schemes II and III, to give compounds structurally similar to the original amphoteric.



$$RN(CH_3)_2 + ClCH_2\overset{OH}{C}HCH_2SO_3Na \longrightarrow RN^+(CH_3)_2CH_2CH(OH)CH_2SO_3^- + NaCl$$

(II)



$$RN(CH_3)_2 + ClCH_2CH{=}CH_2 \longrightarrow R\overset{+}{N}\overset{Cl^-}{(}CH_3)_2CH_2CH{=}CH_2 \xrightarrow[2.\ Initiator]{1.\ NaHSO_3} RN^+(CH_3)_2CH_2CH(H)CH_2SO_3^- + NaCl$$

(III)

Poor yields and the relatively high cost of fatty tertiary amines make commercial utilization of such materials unattractive.

The use of fatty tertiary amines is avoided by reacting N,N-dimethyl-1,3-propanediamine directly with either a fatty acid, a fatty acid methyl ester, or a fatty glyceride, according to the following scheme for the fatty acid.

$$RCO_2H + H_2NC_3H_6N(CH_3)_2 \longrightarrow RCONHC_3H_6N(CH_3)_2 + H_2O \qquad (IV)$$

Quaternization of the resulting aminoamide was achieved with an aqueous solution of sodium 3-chloro-2-hydroxy-1-propanesulfonate which need not be purified. The pH of the reaction was controlled so that sodium-3-chloro-2-hydroxy-1-propanesulfonate underwent a minimal amount of aklaline hydrolysis, and thus more of it was available for reaction.

Optimum conditions were determined for the quaternization of the aminoamide with allyl chloride, followed by addition of sodium bisulfite, in analogy to scheme III. Use of several free radical initiators and exclusion of oxygen were important facets of the bisulfite addition step that were investigated. The product of the addition reaction was believed to be a mixture of the 2- and 3-sulfopropylated derivatives, and hence is referred to in this study as "iso"-sulfopropylated derivatives (6).

The (2-hydroxy-3-sulfopropyl) and ("iso"-sulfopropyl) dimethyl (3-tallowamidopropyl) ammonium inner salts were both prepared in a manner simulating industrial practice, i.e., at a minimum cost and without purification.

EXPERIMENTAL PROCEDURES

Materials

Fatty acids were obtained from laboratory supply houses. The methyl esters of the purified fatty acids were found to have a purity in excess of 99% by gas liquid chromatography (GLC). Tallow was obtained from the Wilson Martin Company (Philadelphia, PA). N,N-dimethyl-1,3-propanediamine (Jefferson Chemical Company, Austin, TX) was redistilled at atmospheric pressure, bp 133 C. Epichlorohydrin and allyl chloride were obtained from Aldrich Chemical Company, Incorporated, (Milwaukee, WI) and both were redistilled at atmospheric pressures. "Vazo" 52 was supplied by E.I. DuPont de Nemours and Company (Wilmington, DE).

Synthetic Procedures

Amides of N,N-dimethyl-1,3-propanediamine: Amides of N,N-dimethyl-1,3-propanediamine were prepared in a manner similar to the previously described reactions of N,N-dimethyl-1,3-propane diamine with fatty acid (5), or

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[1] Presented at the AOCS Meeting, Chicago, September 1976.

from the reaction of the methyl ester of fatty acid (1) or tallow (6) with the above diamine.

Sodium 3-chloro-2-hydroxy-1-propanesulfonate: Sodium bisulfite (46.7 g, 0.449 mole) was dissolved in 130 ml water followed by the addition of sodium hydroxide (5.8 g, 0.144 mole). Epichlorohydrin (31.3 g, 0.336 mole) was added dropwise to the solution and the resulting exothermic reaction was maintained by cooling to 20-25 C. The product gradually precipitated out of solution, and reaction was complete after 1-1/2 hr. An additional 100 ml water was added to dissolve the product, and the final concentration was 1.20 M (determined by the absence of sodium bisulfite iodometrically and assuming quantitative conversion). The solution was used in subsequent reactions without further purification.

(2-Hydroxy-3-sulfopropyl) dimethyl (3-amidopropyl) ammonium inner salt: The preparation of (2-hydroxy-3-sulfopropyl) dimethyl (3-stearamidopropyl) ammonium inner salt is cited as a typical example for the preparation of quaternary zwitterionic compounds. To N,N-dimethyl-3(N-stearamido) propylamine (18.4 g, 0.050 mole) dissolved in 100 ml isopropanol was added (42 ml, 0.050 mole) of 1.20 M sodium 3-chloro-2-hydroxy-1-propanesulfonate solution prepared above. After a 3 hr reflux period, the reaction was 48 mole % complete as indicated by acid-base titration of aminoamide hydrochloride and unreacted free aminoamide. An additional (22 ml, 0.026 mole) of the sulfonate solution was added to the reaction mixture and the latter was allowed to reflux again for 3 hr. The mixture was cooled, sodium carbonate (0.6 g, 0.006 mole) was added to neutralize the aminoamide hydrochloride, and the mixture was allowed to reflux for 3 hr.

Unreacted aminoamide, 1.3 g, was removed by extraction with petroleum ether (bp 63-70 C) and the aqueous phase was evaporated to dryness. Inorganic salts were removed as insolubles after the crude residue had been dissolved in 200 ml absolute ethanol, and the product was isolated by crystallization at 0 C. The pure product (15.6 g, 0.031 mole, 62% of theoretical) was obtained after recrystallization from 200 ml absolute ethanol. Results of elemental analysis agreed with those expected for the proposed structure.

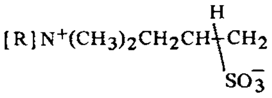
(2-Hydroxy-3-sulfopropyl) dimethyl (3-tallowamidopropyl) ammonium inner salt was prepared in a manner similar to that for the pure stearamidopropyl derivative except that in order to simulate industrial practice, no attempt was made to purify the product, and a solution containing 58% solids and 45% active ingredient according to a previously described method (6) was obtained.

("Iso"-sulfopropyl) dimethyl (3-amidopropyl) ammonium inner salt: Pure ("iso"-sulfopropyl) dimethyl (3-palmitamidopropyl) ammonium inner salt was prepared by the same method as described for the simple N-alkyl inner salt (6).

The preparation of ("iso"-sulfopropyl) dimethyl (3-tallowamidopropyl) ammonium inner salt was modified for practical application by determining optimum reaction conditions without purification of product. Allyl chloride (62 g, 0.81 mole) was added to a stainless steel pressure vessel containing N,N-dimethyl-3(N-tallowamido)propylamine (276 g, 0.77 mole) dissolved in 200 ml isopropanol, and the vessel was flushed with nitrogen. The reaction mixture was heated to a temperature of 110-120 C, resulting in a pressure of 31 psi. After 1 hr, the reaction was more than 98% complete, as indicated by titration for free aminoamide and by cationic titration of the resulting allyl quaternary ammonium intermediate against a linear alkyl benzene sulfonate standard as described earlier (6). Unreacted allyl chloride was removed under vacuum at room temperature and 15 mm after 1 hr. The alcoholic solution, containing the quaternary ammonium compound, was flushed with nitrogen and to it were added sodium bisulfite (99.5 g, 0.85 mole) dissolved in 200 ml oxygen-free water followed by 2,2′azobis-(2,4-dimethylvaleronitrile) (Vazo 52, duPont) (1.92 g, 0.008 mole). The reaction mixture was heated to 70 C in a nitrogen atmosphere and at atmospheric pressure for 3 hr. The product was obtained as a slurry containing 56% solids and 50% active ingredient as determined by a previously described method (6).

TABLE I

Solution Properties of Amphoteric Surfactants

Sulfobetaines	Krafft point (1% soln., C)	LSDR[a]
$[R]N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$ (2-hydroxy-3-sulfopropyl)		
$[C_{11}H_{23}CONHC_3H_6\text{-}]$	<0	3
$[C_{13}H_{27}CONHC_3H_6\text{-}]$	<0	2
$[C_{15}H_{31}CONHC_3H_6\text{-}]$	b	2[c]
$[C_{17}H_{35}CONHC_3H_6\text{-}]$	b	4[c]
$[C_{12}H_{25}\text{-}]$[d]	<0	4
$[C_{14}H_{29}\text{-}]$[d]	36	5
 $[R]N^+(CH_3)_2CH_2\overset{H}{C}H\text{-}CH_2SO_3^-$ ("iso"-sulfopropyl)		
$[C_{15}H_{31}CONHC_3H_6\text{-}]$	16	2
$[C_{16}H_{33}\text{-}]$[d]	68	4

[a] LSDR = lime soap dispersant requirement.

[b] Krafft point >90 C.

[c] Alcohol required to make lime soap dispersing agent solution.

[d] Data from reference (6).

(3-Sulfopropyl) dimethyl (3-tallowamidopropyl) ammonium inner salt (TASB): TASB was prepared from the reaction of propanesultone with tallowamidoamine by a previously described method (1).

Physical and Surface-Active Properties

Solution properties such as Krafft point and lime soap dispersent requirements (LSDR) were measured according to standard methods (7,8). Some ethanol was added to help dissolve insoluble compounds for the LSDR test. The addition of ethanol did not affect the LSDR, inasmuch as the same results were obtained for a water soluble reference compound dissolved either in aqueous ethanol or in water alone. Detergency was determined as described in a previous publication (1).

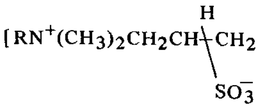
Data obtained for Krafft point and LSDR are listed in Table I. Detergency data for ternary detergent formulations consisting of 65% tallow soap, 20% amphoteric surfactant, and 15% sodium silicate ($Na_2:SiO_2 = 1:1.6$) at 120 F and 300 ppm water hardness are shown in Table II. Detergency was measured as difference in light reflectance (ΔR) of the test clothes before and after washing. Two controls were used. The first one was the above ternary formulation in which the amphoteric lime soap dispersant was the tallowamido sulfobetaine prepared with propanesultone (TASB). The second control was a leading commercial detergent containing about 50% sodium tripolyphosphate. All detergency data in Table II are expressed as percentages of the detergency of the two controls.

RESULTS AND DISCUSSION

Optimum conditions for the syntheses of the 2-hydroxy-3-sulfopropyl and "iso"-sulfopropyl derivatives of fatty amides were determined. The yields of the purified

TABLE II

Detergency of Ternary Formulation of Soap, Amphoteric Surfactant, and Sodium Silicate

	Detergency[a] (0.2% Ternary)					
Test compounds	Normalized to TASB control[b]			Normalized to high phosphate control[c]		
$[R]N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$ (2-hydroxy-3-sulfopropyl)	EMPA	UST	TF	EMPA	UST	TF
$[C_{11}H_{13}CONHC_3H_6\text{-}]$	55	86	94	75	66	
$[C_{13}H_{27}CONHC_3H_6\text{-}]$	115	82	114	94	113	86
$[C_{15}H_{31}CONHC_3H_6\text{-}]$	108	109	114	88	150	93
$[C_{17}H_{35}CONHC_3H_6\text{-}]$	92	118	127	75	150	86
$[TalCONHC_3H_6\text{-}]$	96	118	123	78	163	97
 $[RN^+(CH_3)_2CH_2\underset{SO_3^-}{\overset{H}{CH}}CH_2$ ("iso"-sulpropyl)						
$[C_{15}H_{31}CONHC_3H_6\text{-}]$	100	100	114	81	138	86
$[TalCONHC_3H_6\text{-}]$	96	100	96	78	138	72
TASB (formulated 0.2%)	100	100	100	81	138	76
Control (at 0.2%)	123	73	132	100	100	100

[a] Detergency was measured as increase in reflectance (ΔR) after washing EMPA 101 Cotton (EMPA) (distributed by Testfabrics Inc., Middlesex, NJ), US. Texting 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 and TASB was adjusted to 100.

[b] Prepared from propanesultone. Reference (1).

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

2-hydroxy-3-sulfopropyl derivatives of the fatty amides were 25% higher than those obtained for the corresponding alkyl-amine derivatives (6). This was achieved by controlling the pH of the quaternization reaction at 8-9 and thus minimizing the amount of hydrolysis of the intermediate sodium 3-chloro-2-hydroxy-1-propanesulfonate. The first step of the synthesis of the "iso" compounds, quaternization of the aminoamide with allyl chloride, proceeded more readily at 110-120 C and 30-35 psi than at atmospheric pressures. On the other hand, pressure above atmospheric was not necessary for the addition of sodium bisulfite to the allyl quaternary ammonium chloride intermediate. The tallow derivatives of both types of compounds were prepared as solutions containing 45-50% active ingredient. This assay is based on completeness of amidation, quaternization, and bisulfite addition reactions as described previously. Although this assay method is indirect and not an entirely reliable analytical method for determining active ingredient content, a more reliable method has not as yet been developed.

Water solubility of the aminoamide derivatives is better than that of the simple fatty amide derivatives (Table I). Both the 2-hydroxy-3-sulfopropyl and "iso"-sulfopropyl aminoamides have lower Krafft points and are therefore more water soluble than their alkyl analogs. In addition, the Krafft point increases more rapidly with increasing hydrophobic chain length for the aminoamides than for the amine derivatives. For example, an increase of two carbons in the hydrophobic chain for the fatty amine derivatives results in a Krafft point increase of ca. 36 C, whereas for an analogous increase in the carbon chain for the aminoamide derivatives the Krafft point rise is greater than 90 C. The aminoamide derivatives are also better lime soap dispersing agents than the analogous alkylamine derivatives, as indicated by their lower LSDR values.

Detergency screening data are listed in Table II. The ternary formulations of the 2-hydroxy-3-sulfopropyl and "iso"-sulfopropyl derivatives, in the tallow range, performed as well as a control formulated with TASB. Even the first two compounds in the coconut oil range performed well on the cotton fabrics. A similar comparison with the high phosphate control shows that both types of test compounds did not perform as well as the phosphate control for EMPA and TF but performed much better than the control for UST fabrics.

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