Soap-Based Detergent Formulations: XV. Amino Esters of α-Sulfo Fatty Acids[1]

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ABSTRACT

Amphoteric surfactants were prepared either by direct esterification of α-sulfo fatty acids with various alkanolamines or by rearrangement of the corresponding alkanolamides of the α-sulfo fatty acids to the amino esters with the aid of aqueous hydrochloric acid. The α-sulfo fatty acid monoesters of diethanolamine could be prepared only via the rearrangement method. The amino esters in the C_{16}-C_{18} range possessed limited water solubility whereas α-sulfolaurate esters were soluble at room temperature. The amino esters were found to be stable to acid hydrolysis; however, they were generally not stable to alkali, by which they were either hydrolyzed or rearranged to the corresponding amide. Only the esters of isopropanolamine and diglycolamine were stable to alkali. Surface active properties of the esters were determined. The lime soap dispersant requirements of the compounds were slightly poorer than those of the corresponding amides. The compounds were good cotton detergents by themselves as well as in combination with soap and a silicate builder. The overall surface active properties of the amino esters were greatly inferior to those of the sulfobetaines previously reported. This indicates that an effective amphoteric lime soap dispersant should have its anionic group located at the very end of the molecule and the cationic group somewhat farther away, instead of the reverse.

INTRODUCTION

Amphoteric surfactants, particularly sulfobetaines, have been shown to possess excellent surface-active properties and function as extremely efficient lime soap dispersants (1,2). Such compounds have characteristic structures in which a sulfonate group is attached at one end of the molecule, and a quaternary ammonium group is inserted a few carbon atoms away from the sulfonate group as shown, for example, in the following structure:

$$\mathrm{RN^+(CH_3)_2CH_2CH_2CH_2SO_3^-}$$

where R represents a fat derived alkyl group.

It was of interest to determine whether a surfactant molecule that possessed a terminal cationic group and a nonterminal anionic sulfo group some distance away from the cationic site would show similar superior surface active properties. Accordingly, we synthesized a series of amino esters of α-sulfo fatty acids and determined their surface active properties.

α-Sulfo fatty acids and their esters and amides have been studied extensively in this laboratory (3-6) and were convenient starting materials for the synthesis of the compounds of this study. The amino esters were prepared by variants of two basic routes, direct esterification and rearrangement of the corresponding amide. The former route is illustrated by the acid catalyzed esterification of monoethanolamine:

$$\mathrm{RCH(SO_3)COOH + HOCH_2CH_2NH_2 \xrightarrow{[H]^+} RCH(SO_3^-)COOCH_2CH_2NH_3^+ + H_2O} \qquad \text{(I)}$$

The rearrangement of a diethanolamide of an α-sulfo fatty acid in the presence of an acid catalyst illustrates the other route:

$$\mathrm{RCH(SO_3H)CON(CH_2CH_2OH)_2 \xrightarrow{[H]^+} RCH(SO_3^-)COOCH_2CH_2N^+H_2CH_2CH_2OH} \qquad \text{(II)}$$

A quaternary ammonium type amphoteric was prepared by direct esterification of N,N-dimethylaminoethanol with an α-sulfo fatty acid, followed by methylation with dimethyl sulfate as shown in the following:

$$\mathrm{RCH(SO_3^-)COOCH_2CH_2N^+H(CH_3)_2 + (CH_3)_2SO_4 \longrightarrow RCH(SO_3^-)COOCH_2CH_2N^+(CH_3)_3 + CH_3OSO_3H} \qquad \text{(III)}$$

EXPERIMENTAL PROCEDURES

Materials

The α-sulfo fatty acids were obtained by direct SO_3 sulfonation of the fatty acids as described by Weil and coworkers (5). α-Sulfotallow fatty acid was prepared from the commercially available methyl ester (Bioterge TMS, Stepan Chemical Co., Northfield, IL). The methyl ester was purified as described by Smith et al. (6). A 10% aqueous solution of the methyl ester was then passed through an ion exchange column containing Dowex 50WX8 in the acid form. The ion exchanged solution was then evaporated to dryness on a steam bath. Complete hydrolysis occurred during this step, and the free diacid was obtained as a gelatinous mass. An IR spectrum of a sample of the neutralized acid showed no ester remaining.

Synthetic Procedures

All compounds of this study were synthesized by one of the three synthetic routes designated as A, B, or C. The route chosen for each compound is indicated on Table II.

(A) Direct esterification: The synthesis of the diglycolamine ester of α-sulfostearic acid is a typical example of the direct esterification procedure. Crude α-sulfostearic acid

TABLE I

Alkaline Hydrolysis or Rearrangement of Amino Esters of α-Sulfopalmitic Acid $C_{14}H_{29}CH(SO_3^-)COOR$ (after 1 hr at 100 C)

α-Sulfopalmitate of	Hydrolysis (%)	Conversion to amide (%)
$N^+H_3CH_2CH_2OH$	76	0
$N^+H_3CH_2CH_2CH_2OH$	0	100
$N^+H_3CH_2CH_2OCH_2CH_2OH$	0	0
$N^+H_3CH_2CHOHCH_3$	0	0
$N^+H_2(CH_2CH_2OH)_2$	10	60
$N^+H_2(CH_3)CH_2CH_2OH$	0	92
$N^+H(CH_3)_2CH_2CH_2OH$	36	0
$N^+(CH_3)_3CH_2CH_2OH$	80	0

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TABLE II

Physical and Surface Active Properties of α-Sulfo Fatty Esters $RCH(SO_3^-)COOR'$

R	R'	Method of preparation[a]	LSDR[b]	Krafft point (C)
$C_{10}H_{21}$	$CH_2CH_2N^+H_3$	A	11	1
$C_{14}H_{29}$		A	22	1
$C_{16}H_{31}$		A	20	1
tallow derived		A	25	--
$C_{10}H_{21}$	$CH_2CH_2CH_2N^+H_3$	A	10	--
$C_{14}H_{29}$		A	14	87.0
$C_{10}H_{21}$	$CH(CH_3)CH_2N^+H_3$	A	18	1
$C_{14}H_{29}$		A	14	85.0
$C_{16}H_{31}$		A	13	100
tallow derived		A	14	--
$C_{10}H_{21}$	$CH_2CH_2OCH_2CH_2N^+H_3$	A	28	1
$C_{14}H_{29}$		A	14	24.5
$C_{16}H_{31}$		A	13	62.1
tallow derived		A	15	--
$C_{10}H_{21}$	$CH_2CH_2N^+H_2CH_3$	B	10	--
$C_{14}H_{29}$		B	10	45.4
$C_{16}H_{31}$		B	8	59.6
tallow derived		B	8	--
$C_{10}H_{21}$	$CH_2CH_2N^+H(CH_3)_2$	A	27	--
$C_{14}H_{29}$		A	16	46.0
$C_{16}H_{31}$		A	14	100
$C_{14}H_{29}$	$CH_2CH_2N^+(CH_3)_3$	C	22	29.0
$C_{16}H_{31}$		C	18	42.0
$C_{16}H_{21}$	$CH_2CH_2N^+H_2CH_2CH_2OH$	B	14	26.0
$C_{14}H_{29}$		B	13	73.0
$C_{16}H_{31}$		B	9	81.6
tallow derived		B	9	--

[a] A = Direct esterification, B = rearrangement of alkanolamides, C = synthesis of quaternary compound.

[b] LSDR = Lime soap dispersant requirements.

(103.4 g, 0.284 mol), possessing a neutral equivalent of 164.4 (theoretical value 182.25), and diglycolamine (30 g, 0.284 mol) were added to benzene (600 ml), and the mixture was refluxed 8 hr through a Dean and Stark tube. Water separation ceased after that period of time, and IR spectra indicated complete esterification. The batch was evaporated to dryness, and the dry residue was dissolved in hot absolute alcohol (300 ml). The pH of the material was adjusted to 6 by the addition of a small amount of 5% sodium hydroxide solution. The suspended inorganic salts were removed by filtration, and distilled water (200 ml) was added to the filtrate. The filtrate was cooled to -25 C, and 96.3 g (74% yield) of ester were obtained by crystallization. The IR spectrum of the compound indicated absence of free carboxylate. Elemental analyses for C, H, N, and S were within 3% of the theoretical values. The ash content was 0.01%.

(B) Rearrangement of alkanolamides: The synthesis of the α-sulfostearate of N-methylethanolamine serves as an example of the rearrangement route. The N-methylethanolamide of α-sulfostearic acid was prepared as described by Smith et al. (6). The amide (26.4 g, 0.0545 mol) was refluxed 6 hr in 0.4 N hydrochloric acid (400 ml), at which time IR spectra indicated complete disappearance of amide. The solution was adjusted with sodium hydroxide to a pH of 6, evaporated to dryness, and finally dried in a vacuum oven at 60 C. The dry residue was dissolved in hot absolute alcohol (80 ml), the solution was filtered to remove suspended inorganic salt, and distilled water (55 ml) was added. The solution was chilled to -25 C, and the crystallized ester (24.5 g, 97.6% yield) was removed by filtration. Elemental analyses for C, H, S, and N were within 2% of theoretical values. IR spectra showed only ester carbonyl but no carboxylate ion or amide bands. Ash content 0.06%.

(C) Synthesis of quaternary amphoteric surfactant: The α-sulfostearate of N,N-dimethylaminoethanol was prepared by direct esterification as described above. The crystallized ester (20 g, 0.046 mol) was dissolved in carbon tetrachloride (200 ml), and dimethyl sulfate (6.4 g, 0.054 mol) was added. The mixture was heated 3 hr at 40-50 C, and the solution was evaporated to dryness. The residue was dissolved in hot absolute ethanol (80 ml), the solution neutralized with a 5% sodium hydroxide solution to pH 7, and inorganic salts removed by filtration. The filtrate, after addition of distilled water (50 ml), was allowed to crystallize at -25 C. The crystalline material was removed and recrystallized from a mixture of 60% ethanol and 40% water. There was obtained 15.8 g (77% yield) of the product containing 0.004% ash. The elemental analyses for C, H, N, and S were within 2% of the theoretical values.

Hydrolysis Studies

The different amino esters of α-sulfopalmitic acid were checked for stability to alkali in the following manner. A 0.01 mol sample of test surfactant in distilled water (40 ml) was refluxed with 2.0 N sodium hydroxide solution (10 ml). Aliquot samples were withdrawn initially and thereafter at 15 min intervals. The time intervals were increased to 1 hr in those cases where hydrolysis or rearrangement rates were fairly low. The aliquots were titrated with 0.1 N hydrochloric acid to a pH 3.6 end point, and the amounts of alkali consumed were calculated. The titrated samples were then neutralized to pH 8, carefully evaporated to dryness, and the residues examined by IR spectroscopy for unreacted ester, carboxylate ion, and alkanolamides. The relative amounts of these were estimated from the absorption intensities of the appropriate IR bands. The results are summarized in Table I.

The acid hydrolysis studies were carried out in an analogous fashion by refluxing a 0.01 mol sample of surfactant with 0.02 mol of hydrochloric acid. Aliquot samples were titrated with 0.1 N sodium hydroxide and examined by IR spectroscopy as outlined above. None of the esters hydrolyzed or rearranged under acid conditions.

Physical and Surface Active Properties

The Krafft points of 1% solutions of the surfactants were determined by a standard method and the lime soap dispersant requirements (LSDR) according to the method of Borghetty and Bergman (7). The data for the above physical measurements are given in Table II.

Detergency screening measurements were carried out in a Tergotometer at 120 F in water of 300 ppm hardness. Five 4-in. circles each of EMPA 100 standard soiled cotton (EMPA) (distributed by Testfabrics Inc., Middlesex, NJ), Testfabrics standard soiled cotton-polyester blend with permanent press finish (TF), and U.S. Testing Co. (Hoboken, NJ) soiled cotton (UST) were washed together in detergent solution (1 liter) for 20 min. A commercial phosphate built detergent was used as a control in all tests. To all test detergents there was added 1% of detergent grade carboxymethylcellulose to prevent soil redeposition. The lime soap dispersants were tested by themselves at concentrations of 0.04% (A) and 0.2% (B). Unbuilt soap-based detergent formulations (C) consisting of 75% tallow soap and 25% lime soap dispersant as well as previously developed (8) built formulations (D) of 65% tallow soap, 20% lime soap dispersant, and 15% sodium silicate (1 Na_2O:1.6 SiO_2) were tested at a total detergent concentration of 0.2%. The data obtained for A, B, C, and D for the N-methylethanolamine ester of α-sulfo tallow fatty acids are shown graphically in Figure 1. The detergency data for all amino esters of α-sulfopalmitic acid in formulations of type (D) described above are shown graphically in Figure 2. The detergency behavior of the α-sulfostearate and α-sulfotallowate is almost identical with that of α-sulfopalmitate, and the data for these two groups of surfactants are therefore omitted. The α-sulfolaurates are too low in mol wt to be good detergents by themselves or in combination with soap; thus, their detergencies are not reported.

DISCUSSION AND RESULTS

The direct esterification procedures used were conventional and straightforward. The rearrangement procedure represents a reversible reaction for the esters of secondary amine derivatives such as the esters of diethanolamine and N-methyl ethanolamine, e.g.:

$$\mathrm{RCH(SO_3^-)COOCH_2CH_2N^+H_2CH_2CH_2OH} \underset{[\mathrm{H}]^+}{\overset{[\mathrm{OH}]^-}{\rightleftharpoons}} \mathrm{RCH(SO_3^-)CON(CH_2CH_2OH)_2} \quad \text{(IV)}$$

This is borne out by the alkaline hydrolysis studies reported here and those of the acid hydrolysis of the alkanolamides of α-sulfo fatty acids reported previously (6). It was shown in the latter publication that secondary amides of α-sulfo fatty acids undergo rearrangement to the ester in the presence of hydrochloric acid. The synthetic procedure (B) reported here is based on that observation.

Unlike the corresponding amides of α-sulfo fatty acids, most of the esters are quite susceptible to attack by alkali, as shown in Table I. Only the esters of diglycolamine and isopropanolamine are alkali stable. The other six compounds undergo extensive hydrolysis, rearrangement to amide, or a combination of both. The stability of the monoisopropanolamine ester is somewhat surprising, as is the ready rearrangement of the 1-amino-3-propanol ester to the amide. The reversible rearrangement of the secondary amino derivatives to amide has been discussed above and in a previous publication (6).

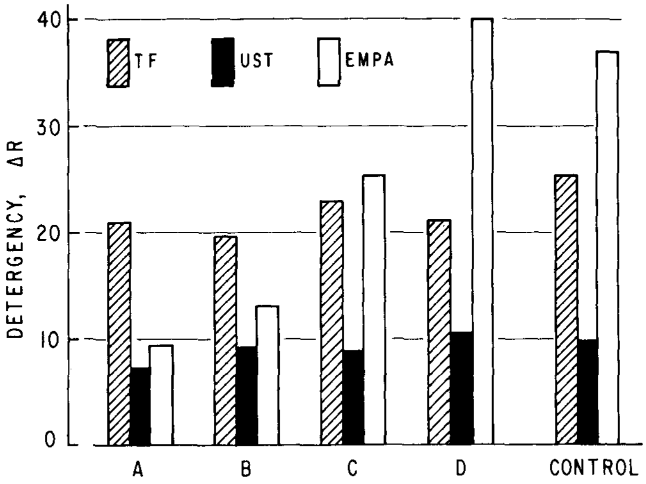

FIG. 1. Detergency of α-sulfotallowate of N-methylethanolamine as lime soap dispersing agent (LSDA). A, LSDA at 0.04%; B, LSDA at 0.2%; C, 75% tallow soap + 25% LSDA at 0.2%; D, 65% tallow soap + 20% LSDA + 15% sodium silicate (Na_2O:SiO_2 = 1:1.6) at 0.2%. All in 300 ppm hard water. TF = Testfabrics Inc. (Middlesex, NJ) soiled cotton-polyester blend cloth; UST = U.S. Testing Inc. (Hoboken, NJ) soiled cotton cloth; EMPA = EMPA 101 soiled cotton cloth (distributed by Testfabrics Inc.).

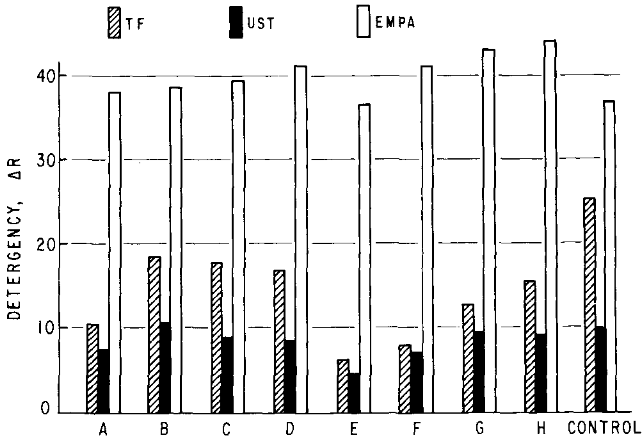

FIG. 2. Detergency of 0.2% solutions of ternary detergent formulations of 65% tallow soap, 20% α-sulfopalmitate lime soap dispersing agent, and 15% sodium silicate (Na_2O:SiO_2 = 1:1.6) in 300 ppm hard water. TF = Testfabrics Inc. (Middlesex, NJ) soiled cotton-polyester blend cloth; UST = U.S. Testing Inc. (Hoboken, NJ) soiled cotton cloth; EMPA = EMPA 101 soiled cotton cloth (distributed by Testfabrics Inc.). LSDA α-sulfopalmitates of: A, $HOCH_2CH_2N^+H_3$; B, $HOCH_2CH_2N^+H_2(CH_3)$; C, $HOCH_2CH_2N^+H(CH_3)_2$; D, $HOCH_2CH_2N^+(CH_3)_3$; E, $HOCH_2CH_2CH_2N^+H_3$; F, $HOCH(CH_3)CH_2N^+H_3$; G, $HOCH_2CH_2OCH_2CH_2N^+H_3$; H, $HOCH_2CH_2N^+H_2CH_2CH_2OH$.

The esters of monoethanolamine have lower Krafft points than the esters of the other amino alcohols. Although the laurates have Krafft points below room temperature, the palmitates become water soluble at or above room temperature, and some of the stearates are not soluble in boiling water. The analogous amides (6), on the other hand, have substantially lower Krafft points, with the exception of the monoethanolamides, whose Krafft points are substantially higher than those of the corresponding amino esters. Thus, both the esters and amides of monoethanolamine and α-sulfo fatty acids exhibit anomalous solubility behavior.

The lime soap dispersing ability of the amino esters is much poorer than that of the corresponding amides. The LSDR for the C_{16} and C_{18} amides range from 7 to 10, whereas those for the corresponding esters range from 9 to 22. The contrast between the sulfobetaines (1) and the amino esters is even more startling, with the former giving LSDR of 2-4. In fact, the sulfobetaines gave the lowest LSDR we have encountered. Because the amino esters are only fair lime soap dispersants in spite of their amphoteric structure, it is apparent that an efficient lime soap dispersing amphoteric surfactant should have its anionic function located at the end of the molecule and the cationic group some distance away toward the center of the molecule, instead of the reverse arrangement.

With respect to detergency performance, the amino esters differ very little from the analogous alkanolamides. An increase of concentration of surfactant by itself from 0.04% (Fig. 1, bars A) to 0.2% (Fig. 1, bars B) results in a slight increase of detergency on EMPA cloth. The binary formulation of amino ester and soap results in a substantial enhancement of EMPA detergency (bars C) but not of UST and only in a slight enhancement of that of the cotton-polyester blend TF. Addition of sodium silicate results in a ternary formulation D, whose EMPA detergency is greatly enhanced to surpass that of the control. A comparison of the detergency of ternary formulations of soap-silicate-amino esters is given in Figure 2. While all eight formulations wash EMPA cloth as well as or better than the control, only B, C, and D do reasonably well on TF cotton-polyester cloth. The control surpasses all formulations except B on UST cotton fabric. Thus, the ester of N-methylaminoethanol (B) emerges as the most effective compound of this series with respect to detergency of the ternary formulations. Interestingly, the detergency behavior of the corresponding alkanolamides (6) parallels that of the esters, and here, too, the derivative of N-methyl-aminoethanol surpasses all others of the series tested with respect to detergency.

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