Soap-Based Detergent Formulations: XII. Alternate Syntheses of Surface Active Sulfobetaines[1]

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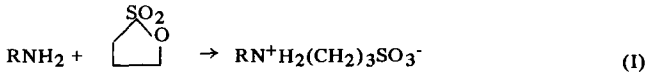
ABSTRACT

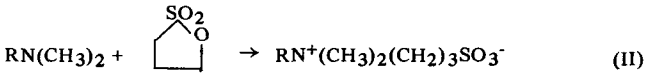
Sulfopropylated amphoteric surfactants, previously reported in this journal, displayed excellent surface active properties and were good detergents in combination with soap. New synthetic routes were investigated for the preparation of such types of compounds to provide a more economical process and eliminate the hazards due to propanesultone, which was used in the previously reported synthetic procedure. A series of 2-hydroxy-3-sulfopropyl amphoteric surfactants was prepared by reacting sodium 3-chloro-2-hydroxy-1-propanesulfonate (the addition product of sodium bisulfite to epichlorohydrin) with various primary fatty amines as well as with fat derived N,N-dimethylalkylamines. Quaternary sulfobetaines not possessing a hydroxyl group were obtained from tertiary amines by reaction with allyl chloride followed by bisulfite addition. The solubility behavior (Krafft points) of these compounds indicated that they were not identical with the sulfobetaines prepared with the aid of propanesultone. The secondary and quaternary ammonium compounds exhibited limited water solubility but were good lime soap dispersing agents. They displayed good detergency in combination with soap. The quaternary ammonium derivatives were particularly effective on cotton-polyester blend fabrics.

INTRODUCTION

Sulfopropylated amphoteric surfactants, previously prepared at this laboratory, displayed excellent surface active properties and were good detergents, particularly in combination with soap (1). These compounds were prepared in quantitative yields by reacting primary or tertiary fatty amines with 1,3-propanesultone.



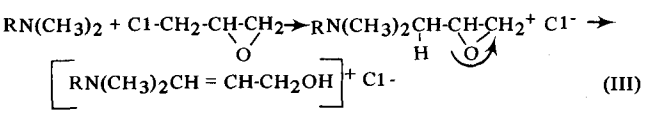
$$RNH_2 + \text{propanesultone} \rightarrow RN^+H_2(CH_2)_3SO_3^- \quad \text{(I)}$$



$$RN(CH_3)_2 + \text{propanesultone} \rightarrow RN^+(CH_3)_2(CH_2)_3SO_3^- \quad \text{(II)}$$

Because of the high price, relative unavailability, and hazardous nature of propanesultone, alternate synthetic routes were developed in this study in an effort to arrive at industrially utilizable sulfobetaines similar to the ones described above.

One alternate synthesis of sulfobetaines, a two step process involving the reaction of a fatty primary or tertiary amine with epichlorohydrin followed by sodium bisulfite treatment, did not appear feasible. Nikolaus (2) found that there was no practical way to obtain the expected secondary amine from the reaction of a fatty primary amine with epichlorohydrin. The reaction between an N-methyl fatty alkylamine and epichlorohydrin gave rise to a complex mixture of products. The analogous reaction with N,N-dimethyl-alkylamines, according to Nikolaus, resulted in a 60% yield of unsaturated quaternary ammonium compounds according to the following scheme:



$$RN(CH_3)_2 + Cl\text{-}CH_2\text{-}\underset{\underset{O}{\diagup\diagdown}}{CH}\text{-}CH_2 \rightarrow RN(CH_3)_2\overset{H}{\underset{}{CH}}\text{-}\underset{\underset{O}{\diagup\diagdown}}{CH}\text{-}CH_2^+\ Cl^- \rightarrow \left[RN(CH_3)_2CH = CH\text{-}CH_2OH\right]^+ Cl^- \quad \text{(III)}$$

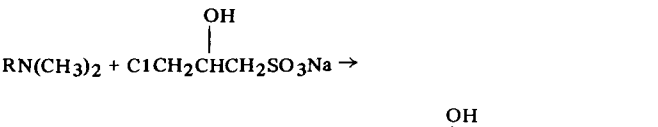
In contrast to this, in the patent literature (3), it is claimed that the addition of sodium bisulfite or sodium sulfite to the reaction product of epichlorohydrin with a long chain N,N-dimethylalkylamine gave rise to a mixture of the following two sulfobetaines:

A) $RN^+(CH_3)_2CH_2CHOHCH_2SO_3^-$

B) $RN^+(CH_3)_2CH(CH_2OH)CH_2SO_3^-$

The presence of the primary hydroxy substituted product B is difficult to explain, and it indicates that the reaction of epichlorohydrin with a fatty amine is a complex one which leads to a number of different products.

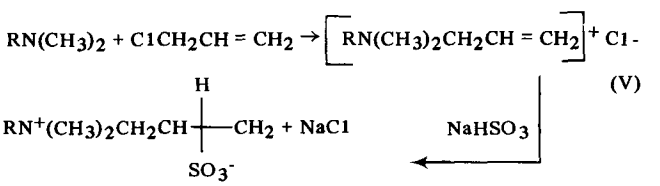
We found that the number of reaction products could be minimized by reversing the order of reaction. Addition of sodium bisulfite to epichlorohydrin proceeds via an ionic mechanism (4) to give 1-chloro-2-hydroxypropanesulfonate (5). Surface active agents were prepared in relatively poor yields by further reacting this intermediate with tertiary fatty amines (6,7) according to the following scheme:



$$RN(CH_3)_2 + ClCH_2\underset{\underset{OH}{|}}{CH}CH_2SO_3Na \rightarrow RN^+(CH_3)_2CH_2\underset{\underset{OH}{|}}{CH}CH_2SO_3^- + NaCl \quad \text{(IV)}$$

Nonsubstituted sulfopropyl derivatives similar to those prepared by the propanesultone route mentioned earlier in this study were also prepared in two steps through the reaction of fatty amines with allyl chloride followed by addition of sodium bisulfite. Bisulfite addition to olefins usually proceeds rather slowly, but in the presence of certain free radical initiators, the reaction proceeds faster and addition takes place in an anti-Markownikoff sense (8). The yields of the bisulfite adduct were increased by raising the level of the initiator such as a nitrate (9) or peroxides in combination with suitable organic solvents (10).

Accordingly, we synthesized a second series of sulfobetaines according to the following scheme:



$$RN(CH_3)_2 + ClCH_2CH = CH_2 \rightarrow \left[RN(CH_3)_2CH_2CH = CH_2\right]^+ Cl^- \quad \text{(V)}$$

$$RN^+(CH_3)_2CH_2CH(H)\text{-}CH_2 + NaCl \qquad NaHSO_3 \rightarrow SO_3^-$$

This sulfobetaine appeared to be the 2-sulfopropyl isomer or a mixture of what was presumed to be the 2-sulfopropyl and 3-sulfopropyl isomers, although we were not able to pinpoint the structure. The compounds of this series are referred to as "iso" sulfopropylated derivatives in the discussion below.

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

EXPERIMENTAL PROCEDURES

Materials

N,N-dimethyldodecylamine (Armeen DM12D), N,N-dimethyltetradecylamine (Armeen DM14D), N,N-dimethylhexadecylamine (Armeen DM16D), N,N-dimethyloctadecylamine (Armeen DM18D), N,N-dimethyl(hydrogenated tallow) (Armeen DMHTD), and tallowamine (Armeen T) were obtained from Armak Chemical Div., Akzona Inc. (Chicago, IL) and tallow from Wilson Martin Co. (Philadelphia, PA). Armeen T had the following composition by gas liquid chromatography (GLC) analysis: 2% $C_{14}H_{29}NH_2$, 24% $C_{16}H_{33}NH_2$, 46% $C_{18}H_{35}NH_2$, 28% $C_{18}H_{37}NH_2$; and tallow had the following composition: 3.2% myristic, 29.7% palmitic, 3.4% palmitoleic, 14.6% stearic, 46.8% oleic, 2.4% linoleic. Primary amines C_{12}, C_{16}, and C_{18} obtained from laboratory supply houses were better than 99% pure by GLC after redistillation. Propanesultone was purified by fractional distillation, bp 103-104 C/0.9 mm, n_D^{40} = 1.4515, and fp 31 C. (Exposure to propanesultone causes burns, and the material is known to cause cancer in animals.) N,N-dimethyl-1,3-propanediamine (Jefferson Chemical Co., Austin, TX) was redistilled at atmospheric pressure, bp 133 C.

Synthetic Procedures

Sodium 1-chloro-2-hydroxy-3-propanesulfonate: Epichlorohydrin (50 g, 0.540 mol) was gradually added to sodium bisulfite (64.7 g, 0.621 mol) and sodium sulfite (25.0 g, 0.199 mol) dissolved in 130 ml water. The reaction was exothermic, and temperature was maintained between 18-30 C with the aid of a cooling bath. The reaction product precipitated gradually, and the pH of the solution remained at 6. After agitation for 2 hr at room temperature, the reaction product was removed by filtration and dried, yielding 100.7 g (0.512 mol, 95% of theoretical) of the crude product. Elemental analyses were within 5% of theory, and the product was used in subsequent syntheses without further purification.

2-Hydroxy-3-sulfopropylamines

Sodium 2-hydroxy-3-sulfopropylalkylamines: Sodium 2-hydroxy-3-sulfopropyloctadecylamine was prepared by dissolving octadecylamine (6.9 g, 0.025 mol) and crude sodium 1-chloro-2-hydroxy-3-propanesulfonate (5.0 g) in 70 ml 70% aqueous ethanol, then refluxing the solution for 3 hr. The solution was cooled to 50 C and sodium carbonate (2.7 g, 0.025 mol) was added before refluxing again for another 11 hr. Insoluble inorganic salts were removed by filtration of the hot reaction mixture. The filtrate was cooled to room temperature and the crude product, which precipitated as a white crystalline powder, was isolated by filtration. Purification of the crude product was accomplished by first removing unreacted octadecylamine by Soxhlet extraction with benzene for 3 hr, followed by two crystallizations from 250 ml 70% aqueous ethanol at room temperature. Yield of purified sodium salt was 4.1 g (0.010 mol, 38% of theoretical) and was within experimental error for elemental analysis.

Sodium 2-hydroxy-3-sulfopropyltallowamine was prepared in a similar manner except that unreacted amine was extracted with petroleum ether (bp 63-70 C) from the reaction solution to which sufficient water had been added so that the product remained in solution at room temperature. The solvent was then carefully evaporated from the product. The product could not be separated from inorganic salts without fractionation and was evaluted without further purification. The product was a mixture of ca. 80% sodium salt of amphoteric surfactant, as indicated by lime soap dispersant requirement (LSDR) and 20% inorganic salts as determined by sulfated ash.

N-alkyl-N,N-dimethyl-1-ammonio-2-hydroxy-3-propanesulfonate: The preparation of N-dodecyl-N,N-dimethyl-1-ammonio-2-hydroxy-3-propanesulfonate is an example for the preparation of quaternary, zwitterionic compounds. N,N-dimethyldodecylamine (8.8 g, 0.041 mol) and sodium 1-chloro-2-hydroxy-3-propanesulfonate (8.1 g, 0.041 mol) were dissolved in 100 ml 70% aqueous ethanol and heated to reflux for 3 hr. The solution was then cooled to 50 C, sodium carbonate (4.4 g, 0.041 mol) was added, and the reaction mixture was refluxed for 6 hr. Unreacted amine was removed by extraction with 100 ml petroleum ether (bp 63-70 C), and the aqueous alcohol solution was evaporated to dryness. The residue was crystallized twice at 0 C from 100 ml absolute ethanol, and inorganic salts were removed as insolubles at room temperature. Seven g (0.020 mol, 48% theoretical) purified product was obtained and its elemental analysis agreed with theory within experimental error. The tallow derivative was prepared in a manner similar to that above, but was not purified by crystallization because this would alter the alkyl chain distribution of the product.

"Iso" Sulfopropylated Tertiary Amines

The dodecylammonio derivative was prepared by dissolving N,N-dimethyldodecylamine (21.3 g, 0.100 mol) in 300 ml absolute methanol followed by the addition of allyl chloride (11.5 g, 0.150 mol) (bp = 44.6 C). The mixture was heated to a gentle reflux for ca. 14 hr, at which time 98.5% of the amine had disappeared, as determined by titration of unreacted tertiary amine with 0.100 N HCl, using bromophenol blue as the indicator. The unreacted allyl chloride was removed by azeotropic distillation with methanol. The final volume of the reaction mixture was 70 ml.

N-dodecyl-N,N-dimethyl-3-ammoniopropanesulfonate was prepared by placing the above methanolic solution in a stainless steel pressure vessel together with a solution of sodium bisulfite (11.5 g, 0.11 mol) in 35 ml H_2O), and 0.25 g (0.001 mol) t-butylperbenzoate. Oxygen was removed from the reaction vessel by repeated flushing with nitrogen followed by evacuation under a slight vacuum. The vessel was then placed in boiling water for 7 hr followed by cooling to room temperature.

Completeness of reaction was determined by modification of the Cahn cationic tritration method (11) at pH 10 for residual unreacted quaternary ammonium compound. Direct titration of the quaternary ammonium compound with a standard solution of dodecanesulfonate (12) was not possible because of emulsion problems, so it was necessary to add a sample of the reaction mixture to a solution containing an excess of sodium dodecanesulfonate. The ammonium compound was determined indirectly by the titration of unreacted excess sodium dodecanesulfonate with a standardized solution of Hyamine 1322. The titration indicated the reaction to be 92% complete.

Purification of the N-dodecyl amphoteric surfactant was accomplished by evaporation of the solvent, followed by dissolution of the crude product in 300 ml absolute ethanol. The inorganic salts were removed as insolubles by filtration. The filtrate was again evaporated to dryness and the residue recrystallized from 300 ml petroleum ether (bp 63-70 C) containing 5% by volume absolute ethanol, at -30 C. The purified dodecyl amphoteric derivative was obtained in 24.2 g yield (0.072 mol, 72% theoretical) as a white crystalline powder whose elemental analysis agreed with theory within experimental error. It was necessary to recrystallize the analogous hydrogenated tallow derivative from absolute ethanol to obtain a purified product having an elemental analysis which agreed with theory within experimental limits.

N-(3-tallowamidopropyl)-N,N-dimethyl-3-ammonio-1-propanesulfonate: The tallowamide derivative was prepared

TABLE I

Solution Properties of Amphoteric Compounds

Amphoteric derivatives	Krafft point (C)	LSDR[a]	Calcium ion stability (ppm)
Secondary:			
2-hydroxy-3-sulfopropyl-			
$C_{12}H_{25}NHCH_2CH(OH)CH_2SO_3Na$	37	3	1187
$C_{16}H_{33}NHCH_2CH(OH)CH_2SO_3Na$	56	4	1068[c]
$C_{18}H_{37}NHCH_2CH(OH)CH_2SO_3Na$	[b]	3	253[c]
Tal[d]$NHCH_2CH(OH)CH_2SO_3Na$	< 0	7	626[c]
3-sulfopropyl-[e]			
$C_{12}H_{25}NHCH_2CH_2CH_2SO_3Na$	40	3	435
$C_{16}H_{33}NHCH_2CH_2CH_2SO_3Na$	58	4	221[c]
Tal[d]$NHCH_2CH_2CH_2SO_3Na$	[f]	4	1534
Quaternary:			
2-hydroxy-3-sulfopropyl-			
$C_{12}H_{25}N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	< 0	4	>1800
$C_{14}H_{29}N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	36	5	>1800
$C_{16}H_{33}N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	89	4	>1800[c]
$C_{18}H_{37}N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	[b]	5	>1800
HTal[g]$N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	[b]	5	>1800
3-sulfopropyl-[e]			
$C_{12}H_{25}N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$	< 0	4	>1800
$C_{16}H_{33}N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$	27	4	>1800
$C_{18}H_{37}N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$	88	3	[b]
HTal[g]$N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$	31	4	>1800
"iso"-sulfopropyl-			
$C_{12}H_{25}N^+(CH_3)_2C_3H_6SO_3^-$	< 0	4	>1800
$C_{14}H_{29}N^+(CH_3)_2C_3H_6SO_3^-$	< 0	3	>1800[c]
$C_{16}H_{33}N^+(CH_3)_2C_3H_6SO_3^-$	68	4	>1800[c]
HTal[g]$N^+(CH_3)_2C_3H_6SO_3$-h	[b]	6	>1800[c]
Tal[d]$CONHCH_2CH_2CH_2N^+(CH_3)_2C_3H_6SO_3$-h	< 0	5	>1800

[a]LSDR = Lime soap dispersant requirement.
[b]Insufficient solubility for measurement.
[c]Test was run above room temperature.
[d]Alkyl chain derived from tallow.
[e]Preparation same as ref. 1.
[f]Clear solution could not be obtained for this test.
[g]Alkyl chain derived from hydrogenated tallow.
[h]Compound contains ca. 90% active ingredient.

by melting tallow (1200 g, 1.40 mol) and adding N,N-dimethyl-1,3-propanediamine (460 g, 4.49 mol) with agitation. The reaction flask was stoppered and allowed to stand at room temperature for 4 days, at which time ca. 96 mol % conversion to amide was indicated by infrared absorbance.

Quaternization with allyl chloride and addition of sodium bisulfite was accomplished in the manner described above for the preceding dodecyl derivative, except that no thorough purification was attempted. However, some of the inorganic salts were removed as insolubles by filtration from absolute ethanol. The product contained about 90% active amphoteric surfactant based on completeness of amidation, quaternization, and bisulfite addition reactions as determined by infrared absorbance, titration of unquaternized amine, and sulfate ash, respectively.

Physical and Surface Active Properties

Methods for measuring surface active and physical properties such as calcium ion stability (13), Krafft point (14), LSDR according to the Borghetty and Bergman method (15), and detergency have been described previously (1). It was necessary to add sufficient ethanol to dissolve the more insoluble compounds for LSDR measurements. This did not, however, affect the LSDR because the same values were obtained for the compounds more soluble in water and aqueous ethanol solutions. Data obtained for Krafft point, LSDR, 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 0.2% of a binary mixture consisting of 75% tallow soap and 25% test compound. The last three columns give detergency 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). The detergency tests were performed on fabrics listed in footnote "a" of Table II.

RESULTS AND DISCUSSION

The data in Table I demonstrates the effect of chemical structure on solution properties, particularly between secondary and quaternary sulfopropyl amphoteric surfactants. The insertion of a hydroxyl group into the sulfopropyl chain had little effect on the Krafft points of the secondary amino compounds, but resulted in a marked increase of the Krafft point of the quaternary derivatives. The "iso" sulfopropylated quaternary ammonium compounds had substantially higher Krafft points than the analogous compounds prepared from propanesultone. Because both types of sulfopropylated derivatives gave identical elemental analysis and infrared spectra, the differences in Krafft points would indicate structural divergencies arising from the different synthetic routes employed. Thin layer chromatography studies indicated that the "iso" sulfopropylated derivative could not be clearly distinguished from the 3-sulfo derivative. We were unable to synthesize a sample of pure 2-sulfo derivative and therefore could not

TABLE II

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

Compound	Detergency, ΔR[a]					
	0.2% Binary			0.2% Ternary		
	EMPA	UST	TF	EMPA	UST	TF
$C_{12}H_{25}NHCH_2CH(OH)CH_2SO_3Na$	39	8	17	41	9	22
$C_{16}H_{33}NHCH_2CH(OH)CH_2SO_3Na$	31	6	5	44	7	8
$C_{18}H_{37}NHCH_2CH(OH)CH_2SO_3Na$	21	6	5	31	4	7
Tal[b]$NHCH_2CH(OH)CH_2SO_3Na$	35	7	10	41	7	10
$C_{12}H_{25}N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	35	13	32	41	12	23
$C_{14}H_{29}N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	30	12	33	41	13	25
$C_{16}H_{33}N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	23	12	28	41	14	28
$C_{18}H_{37}N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	21	9	20	36	14	28
HTal[c]$N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$	22	8	18	39	13	28
$C_{12}H_{25}N^+(CH_3)_2C_3H_6SO_3^-$[d]	24	10	17	29	10	15
$C_{14}H_{29}N^+(CH_3)_2C_3H_6SO_3^-$[d]	26	12	34	34	12	25
$C_{16}H_{33}N^+(CH_3)_2C_3H_6SO_3^-$[d]	18	12	31	32	13	23
HTal[c]$N^+(CH_3)_2C_3H_6SO_3^-$[d]	14	5	10	34	11	17
Tal[b]$CONH(CH_2)_3N^+(CH_3)_2C_3H_6SO_3^-$[d]	14	6	15	30	11	21
Control[e] at 0.2%				36	11	30

[a]Increase in reflectance after washing fabrics in the Tergotometer for 20 min. EMPA=EMPA 101 cotton (distributed by Testfabrics, Inc., Middlesex, NJ); UST=U.S. Testing Inc. (Hoboken, NJ), TF=Testfabrics cotton-polyester blend with a permanent press finish.

[b]Alkyl group derived from tallow.

[c]Alkyl group derived from hydrogenated tallow.

[d]"Iso"-sulfopropyl derivative.

[e]A leading commercial phosphate built detergent.

prove that the 2- and 3-sulfo derivatives had the same R_f values. Structural identification by nuclear magnetic resonance was complicated by the poor separation of the propyl methylene protons. Chemical shift reagents could not be used because of the poor solubility of these compounds in nonpolar solvents. Because bisulfite addition to olefins in the presence of free radical initiators proceeds via a free radical mechanism (8), one would expect the 3-sulfo derivative to form predominantly. We believe at this time that the "iso" sulfopropyl derivative is a mixture of the 2- and 3-sulfo derivatives; however, their structures have not been determined as yet.

The effect of the alkyl chain length on Krafft point was found to be much more pronounced for the quaternary than for the secondary amphoteric derivatives. Thus, a four carbon increase in chain length resulted in about a 20 C elevation of the Krafft point for the secondary amino compound, whereas an analogous two carbon chain length increase of the quaternary compounds resulted in an elevation of 53 C and 61 C for the 2-hydroxy-3-sulfopropyl and 3-sulfopropyl quaternary compounds as shown in Table I.

All amphoterics of this study were found to be good lime soap dispersants with LSDR values ranging from 3 to 7. The differences in structure of the test compounds obviously did not greatly affect LSDR. Calcium ion stability, on the other hand, was greatly affected by structure, with the secondary amino compounds giving values lower than the 1800 ppm $CaCO_3$ obtained for the quaternary compounds.

Detergency screening test results according to a previously described procedure (1) are summarized in Table II. As was noted previously (1), the secondary amino derivatives are generally inferior to the corresponding quaternary ammonium derivative on Testfabrics cotton-polyester blend fabric. This holds true both for binary soap-amphoteric formulations and ternary soap-amphoteric-silicate builder formulations. The somewhat poorer detergency data for the octadecyl derivatives is undoubtedly due to the poor solubility of these compounds. The tallow derivatives, which for the most part received no purification, also gave poorer detergency results and LSDR values. The presence of impurities is probably responsible for this behavior. The 2-hydroxyl group in the quaternary compounds causes enhancement of EMPA 101 cotton detergency for both binary and ternary mixtures. In fact, the ternary formulations with these 2-hydroxy substituted quaternary compounds performed as well as the control on all three fabrics.

The products of either alternate synthetic route are less soluble in water than the corresponding amphoterics prepared from propanesultone. Because of the good detergency data obtained, the 2-hydroxypropane sulfonate amphoterics offer the most promise as dispersants in soap-based detergents, and a suitable process for their synthesis is currently under investigation.

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