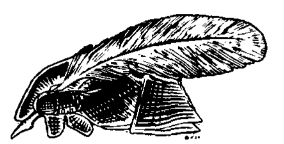
SD&C Technical



Soap-based Detergent Formulations: XXI. Amphoteric Derivatives of Fatty Amides of Aminoethylethanolamine[1]

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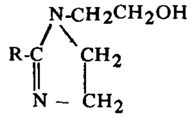
ABSTRACT

Amides and 2-alkyl-N-(2-hydroxyethyl)-imidazolines were converted into various types of sulfated or sulfonated amphoteric lime soap dispersants. The alkylimidazolines could be readily hydrolyzed to give amidoamines. The cyclized amphoteric surfactants were generally superior in detergency and lime soap dispersing ability to analogous surfactants derived from amidoamines. Some of the cyclized surfactants, when formulated with soap and silicate builder, washed about as well under the test conditions as a control containing 50% sodium tripolyphosphate.

INTRODUCTION

Previous publications have shown that certain types of amphoteric surfactants such as the sulfobetaines are highly efficient lime soap dispersants that function well in soap-based detergent formulations (1-4). Since fatty derivatives of N-(2-aminoethyl)-ethanolamine, particularly the N-(2-hydroxyethyl)-imidazolines derived from fatty acids, have been commercially available for several decades, it would appear that sulfobetaines derived from such imidazolines might prove to be useful and industrially feasible lime soap dispersants. There exists a substantial body of patent literature dealing with various methods of condensation of fatty acids with ethylenediamine or with aminoethylethanolamine. Chwala prepared 2-alkylimidazolines via the reaction of ethylenediamine with fatty acids, and subsequent treatment with ethylene oxide or propylene oxide gave the N-(2-hydroxyethyl)-derivatives (5). The commercial availability of aminoethylethanolamine subsequently led to the direct condensation of fatty acids with this amine to give the N-(2-hydroxyethyl)-imidazoline in one step (6,7), and this procedure is in industrial use today. Discoloration of such imidazolines is prevented by the addition of various borohydrides to the reaction mixture (8).

The reaction proceeds in two steps, amidation first, followed by ring closure to give compound (I):

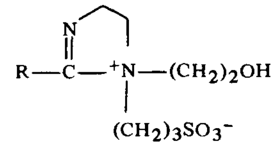


(I)

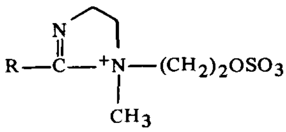
The reaction is not quite as straightforward as indicated in this scheme, since some diamide (9) and tertiary amide are also formed as by-products which are incapable of cyclization. If the methyl ester of a fatty acid is used in place of fatty acid in the above reaction in the presence of an alkaline catalyst, the tertiary amide is the major reaction product according to Chakrabarti (10). The cyclization step of the above reaction scheme is reversible, and the secondary amide II can be obtained by hydrolysis of the imidazoline I according to Bergman and Hansen (11). The imidazolines can be treated with monochloroacetic acid to yield betaines according to several patents granted to Mannheimer, and a variety of such products are produced today under the Miranol trade name (11).

In previous studies we have found that sulfated or sulfonated quaternary ammonium compounds are more suitable than betaines as lime soap dispersants. Accordingly, in this study several series of sulfated or sulfonated imidazolines derivatives and derivatives of the uncyclized amides were synthesized, and their surface-active properties were evaluated.

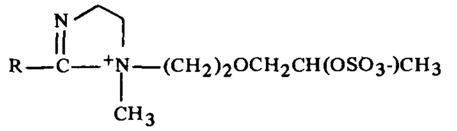
The three types of surfactants prepared from the imidazolines were the following:



Type I-A

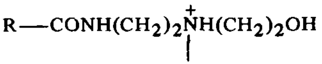


Type I-B



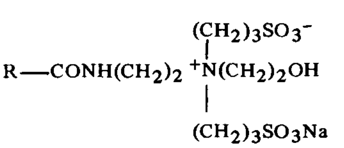
Type I-C

Reaction of the amidoamine II, obtained from I by hydrolysis, with either one or two moles of 1,3-propanesultone gave Types II-A and II-D amphoterics having the following structures:



$$R\text{—}CONH(CH_2)_2\overset{+}{N}H(CH_2)_2OH \quad (N\text{—}(CH_2)_3SO_3^-)$$

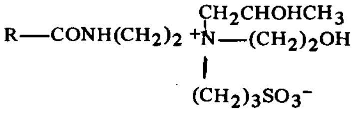
Type II-A



$$R\text{—}CONH(CH_2)_2\,{}^{+}\underset{(CH_2)_3SO_3Na}{\overset{(CH_2)_3SO_3^-}{N}}(CH_2)_2OH$$

Type II-D

Oxypropylation of the amidoamine II followed by quaternization with 1,3-propanesultone gave Type II-E surfactant possessing the structure:



$$R\text{—}CONH(CH_2)_2\,{}^{+}\underset{(CH_2)_3SO_3^-}{\overset{CH_2CHOHCH_3}{N}}\text{—}(CH_2)_2OH$$

Type II-E

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[1] Presented at the AOCS Meeting, New Orleans, May 1976.

EXPERIMENTAL PROCEDURES

Materials

Fatty acids were commercial grades purified so that their purities, as determined by gas liquid chromatography of their methyl esters, exceeded 98.9%. Stearic acid obtained from Humko Sheffield Chemical Division, Memphis, TN, after crystallization from acetone had a purity of 98.9%. Palmitic, myristic, and lauric acids all obtained from Ashland Chemical Co., Columbus, OH, after distillation had purities of 99.9%. Oleic acid obtained from Applied Science Laboratories, Inc., State College, PA, had a purity of 99% and was used as is, as was aminoethylethanolamine obtained from Carbide and Carbon Co., New York, NY. Amine analysis for secondary and primary amine gave the theoretical value 9.60 meq/g by the method described below. Reagent grade dimethyl sulfate was supplied by Matheson Coleman and Bell, Rutherford, NJ. Propanesultone obtained from Eastman Kodak Co., Rochester, NY, was distilled, and a center cut (bp 147 C at 0.25 mm) was used. Propylene oxide also obtained from Eastman Kodak Co., Rochester, NY, was used as is. Tallow hydroxyethylimidazoline obtained from Mona Industries, Inc., Patterson, NJ, was used without purification.

Synthetic Procedures

Synthesis of alkylimidazoline (I): Palmitic acid (50.5 g, 0.197 mole) was heated with aminoethylethanolamine (22.6 g, 0.217 mole) at 80-120 C for 1 hr and then at 120-130 C for 5 hr. The temperature was increased to 146 C during 2 hr, and cyclization was completed at 180-190 C in 4 hr. A reduced pressure of 2 mm was maintained throughout the entire heating period. Amine analysis (methodology described below) showed a total amine content of 2.83 meq/g: 0.02 meq/g of primary amine, 0.06 meq/g of secondary amine, and 2.75 meq/g or tertiary amine (theoretical 3.08 meq/g). The product was used in subsequent syntheses without purification. The alkylimidazolines derived from lauric, myristic, stearic, and oleic fatty acids were prepared in an analogous manner.

Synthesis of type I-A surfactants: The following synthetic procedure is typical for the preparation of all members of this type of surfactant. 1,3-Propanesultone[2] (25.2 g, 0.2063 mole) was added dropwise to the palmitic acid-derived imidazoline (I) (63.9 g, 0.197 mole) dissolved in 200 ml of dry 1,2-dichloroethane maintained at 50 C. The product was crystallized from a mixture of ethanol and 1,2-dichloroethane at 30 C and recrystallized from aqueous alcohol to obtain 82.0 g (93.2% yield) of the desired product.

Synthesis of type I-B surfactants: The following procedures is characteristic for the synthesis of all compounds of this type.

Dimethyl sulfate (14.7 g, 0.116 mole) was added dropwise to a stirred solution of the palmitic acid-derived imidazoline (I) 38 g, 0.111 mole) in 120 ml dry 1,2-dichloroethane, while the temperature was maintained at 40-50 C. After the solution had stood overnight at room temperature, insoluble material was separated by filtration. This precipitate proved to be water insoluble and was discarded. Aqueous alcohol was added to the filtrate, the pH of which was adjusted to 8.6 with 6N sodium hydroxide, and the solution was evaporated to dryness. After removal of inorganic salts the product was crystallized from aqueous alcohol to obtain 18.6 g (86.9% yield) of the desired product.

Synthesis of type I-C surfactant: The palmitic acid-derived imidazoline (I) (48.5 g, 0.149 mole) dissolved in 200 ml dry dichloroethane was quaternized with dimethyl sulfate (19.8 g, 0.157 mole) as described above for type I-B. The reaction product was evaporated to dryness, and the residue was dissolved in 200 ml t-butyl alcohol in which sodium metal (0.6 g, .026 mole) had been dissolved. Propylene oxide (10.3 g, 0.177 mole) was added, and the material was heated at reflux for 4 hr, evaporated to dryness, and the residue dried in the vacuum oven at 70 C. The residue was dissolved in 200 ml of dry 1,2-dichloroethane. Chlorosulfonic acid (18.3 g, 0.157 mole) was added dropwise over a period of 20 min to the stirred reaction mixture maintained at 10-15 C. The product was allowed to come to room temperature, was heated briefly to 40 C, and was cooled to 10 C. Then 100 ml of 60% aqueous ethanol was added, and the solution was adjusted to pH 8.5 with 6 N sodium hydroxide. After removal of inorganic salts and crystallization from aqueous alcohol, 59.2 g of the desired product (83% of theoretical) was obtained.

Synthesis of amidoamine (II): The palmitic acid-derived imidazoline (I) (63.9 g) in 200 ml 90% ethanol was heated at reflux 1.3 hr. The amide was isolated bycrystallization at 0 C to yield 64.2 g of product (95.2% of theoretical). The IR spectrum showed the expected N-H stretch, an O-H stretch at 3290 cm^{-1} and 3260 cm^{-1}, amide-1 at 1650 cm^{-1}, N-H bend at 1568 cm^{-1}, and absence of adsorption at 1610-1622 cm^{-1} which, if present, would indicate unreacted imidazoline. Titration of the product for amine content gave 2.6 meq/g of secondary amine (theoretical value 2.92 meq/g), 0.06 meq/g tertiary amine, and 0.02 meq/g primary amine.

Synthesis of type II-A surfactant: Propanesultone (9.0 g, 0.0735 mole) was added dropwise to a stirred solution of palmitic acid-derived amidoamine II (24 g, 0.07 mole) in 100 ml 1,2-dichloroethane while the temperature was maintained at 30-40 C. The reaction was completed at 50 C during 1 hr and the product was isolated by crystallization from a mixture of ethanol and 1,2-dichloroethane. After recrystallization from aqueous alcohol, 28.5 g (87.2% yield) of the desired product was obtained.

Synthesis of type II-B surfactant: The reaction of palmitic acid-derived amidoamine II (24 g, 0.07 mole) with a roughly equimolar amount of 1,3-propanesultone was carried out as described under type II-A above, except that 100 ml of t-butyl alcohol was used as solvent. Upon completion of the reaction, 100 ml of t-butyl alcohol, in which sodium metal (1.9 g, 0.083 mole) had been dissolved, was added. Propanesultone (9 g, 0.074 mole) was added dropwise to the stirred reaction mixture at 40-50 C, which was heated at that temperature for another hour. After removal of inorganic salts and recrystallization from aqueous alcohol, the yield of the desired product was 35.8 g (83,4% of the theoretical).

Synthesis of type II-C surfactant: Propylene oxide (3.4 g, 0.058 mole), was heated at reflux for 5 hr with amidoamine II derived from palmitic acid (18.2 g, 0.053 mole) in 100 ml of t-butyl alcohol. The reaction mixture was cooled to room temperature, and propanesultone (6.8 g, 0.056 mole) was added dropwise to the stirred mass during a period of 6 min. The reaction was exothermic, and the temperature was maintained at 50 C. After the addition, the product was kept at 40-50 C for another hour. After removal of inorganic salts and crystallization from aqueous alcohol, the yield of the desired product was 23.5 g (84.5% of theoretical).

Analytical Procedure for Amine Content

An HCl-isopropanol titrant (ca. 0.2 N) was prepared and standardized against standard NaOH. Toal amine content

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[2] 1,3-Propanesultone has been reported to be carcinogenic to animals and therefore extreme caution should be exercised in handling this material.

TABLE I

Surface-Active Peoperties of Amphteric Surfactants

				Detergency % ΔR in 300 ppm hard water[a]											
		Krafft pt.		Formulation A			Formulation B			Formulation C			Formulation D		
Type	Origin	°C	LSDR	EMPA	TF	UST	EMPA	TF	UST	EMPA	TF	UST	EMPA	TF	UST
I-A	Lauric	<1	4	34	48	39	13	29	22	0	33	0	0	37	0
	Myristic	<1	6	90	68	80	50	64	49	35	59	45	33	87	40
	Palmitic	43	7	87	89	155	77	80	133	84	122	117	97	100	133
	Stearic	52	10	55	61	70	44	26	54	34	57	32	44	86	52
	Oleic	<1	3	87	89	155	74	78	122	84	119	1221	94	94	94
	Tallow[b]	<1	4	24	13	199	19	18	12	77	82	98	80	93	84
I-B	Palmitic	<99	6	59	73	80	59	70	80	65	87	80	97	91	90
I-C	Palmitic	<1	9	66	63	68	34	26	31	6	28	14	30	41	39
	Stearic	<1	11	60	49	60	28	20	25	6	25	15	30	40	35
II-A	Palmitic	38	6	38	26	18	34	26	31	5	29	14	30	41	39
II-D	Palmitic	<1	7	87	88	111	64	77	122	64	103	64	80	88	64
II-E	Palmitic	<1	8	37	35	31	19	27	23	6	36	18	16	43	21
	Stearic	<1	14	42	45	34	19	32	27	10	30	24	30	50	30

[a] Formulation A = 0.2% conc. of the test compound, Formulation B = 0.04% conc. of the test compound, Formulation C = 0.2% soln. of a blend of 75% tallow soap and 25% test compound, and Formulation D = 0.2% soln. of a blend of 65% tallow soap, 20% test compound, and 15% of a glassy silicate (1 Na_2O:1.6 SiO_2).

[b] Prepared from commercial tallow imidazoline.

was determined by titration of the sample dissolved in neutral isopropanol using bromophenol blue as indicator. Treatment of a sample with an excess of phenyl isothiocyanate (12) followed by titration gave the tertiary amine content. Treatment with an excess of salicylaldehyde (13) followed by titration gave the sum of secondary and tertiary amine contents. The primary and secondary amine contents can then be calculated from the above titrations.

Alkaline Stability Studies

The amphoteric surfactants derived from compounds I and II were submitted to alkaline stability study. Each 0.01 mole sample was heated at reflux with 100 ml of 0.02 N aqueous sodium hydroxide for 7 hr. Samples were withdrawn at fixed intervals and titrated with 0.1 N hydrochloric acid to phenolphthalein endpoint. The compounds were recovered following this treatment and their IR spectra were observed in order to determine whether a change had occurred.

Acid Stability Studies

An analogous series of experiments was carried out in which 0.01 mole samples of surfactants were heated at reflux with 0.02 mole of aqueous hydrochloric acid for 7 hr.

Physical and Surface-Active Properties

The Krafft point was measured by gradually heating a 1% dispersion of the test compound until a clear solution was obtained. The Krafft point data are shown in Table I.

The lime soap dispersant requirements (LSDR) was measured according to the method of Borghetty and Bergman (14). The LSDR data are given in the table.

Detergency screening measurements were carried out in a Tergotometer at 120 F in water of 300 ppm hardness as described previously (3). Five 4-in. circles each of EMPA-101 cotton, Test-fabrics cotton polyester blend with permanent press finish (TF), and U.S. Testing Co. soiled cotton (UST) were washed together in 1 liter detergent solution for 20 min. A commercial detergent containing 50% phosphate was used as a control. The detergency was calculated as % ΔR, the percentage of detergency with respect to that of an 0.2 g solution of the control according to the following equation:

$$\% \Delta R = \frac{R_{Ta} - R_b}{R_{Ca} - R_b} \times 100$$

where R_{Ta} is the light reflectance of the cloth after washing in the test detergent, R_b is the reflectance before washing, and R_{Ca} is the reflectance after washing with control detergent.

The detergency tests were carried out on four different formulations for each test compound. Formulation A is the test compound by itself at 0.2% concentration; formulation B is the test compound by itself at a concentration of 0.04%; formulation C is a 0.2% solution of a blend of 75% tallow soap and 25% test compound; and formulation D is a 0.2% solution of a blend of 65% tallow soap, 20% test compound, and 15% of a glassy silicate (1 Na_2O:1.6 SiO_2). The detergency data are summarized in the table.

RESULTS AND DISCUSSION

The synthesis of the imidazoline I is always accompanied by the formation of some by-product. Rapid heating of the fatty acid and the aminoethylethanolamine to 180 C appears to accelerate diamide formation, as has been previously observed (9). The amine analyses of the imidazolines of this study indicate a diamide content of 8-10%. When a methyl ester was used in place of the fatty acid, little reaction with the amine took place unless an alkaline catalyst such as sodium methoxide was added. Under these conditions over 40% of diamide was formed. It thus appears that the alkali-catalyzed reaction with a methyl ester might be a good synthetic route to the diamide.

The uncyclized amidoamine II is prepared most suitably by hydrolysis of the imidazoline I according to the procedure of Bergman and Hansen (11). This approach is preferred over the direct synthesis of the amide I by heating the reactants to 130-150 C which invariably gives rise to a mixture of imidazoline, diamide, unreacted starting materials, as well as the desired monoamide.

The amphoteric surfactants prepared from I or II were obtained by conventional methods. The sulfated quaternized imidazoline I-B proved to be extremely susceptible to acid and alkaline hydrolysis. Under alkaline and acid conditions it was completely hydrolyzed after a 15 min reflux period. The type I-C amphoteric, a sulfated oxypropylated imidazoline, was stable to alkaline hydrolysis but hydrolyzed to the extent of 20% after 7 hr under the conditions of acid hydrolysis described above. The four remaining types of surfactants of this study were unaffected by acid or alkali. This indicates not only that sulfonates do not hydrolyze readily, as was expected, but that the imidazoline ring after quaternization is very stable, whereas the unquaternized imidazoline hydrolyzes readily, as indicated by the conversion of the cyclized compound I to the amidoamine II.

Further evidence of the hydrolytic stability of the surfactants was obtained by observing the IR spectra of the test samples recovered after treatment with acid or alkali. The characteristic IR adsorption of the imidazoline-derived surfactants at 1610-1622 cm^{-1} and that of the amide-derived surfactants at 1650 cm^{-1} was unaffected in all cases.

The surface-active properties of the surfactants are shown in the table. The type I-B surfactant, where the anionic and cationic groups are separated by a two carbon bridge, is water insoluble (high Krafft point); whereas all the other compounds, which have at least a three carbon bridge, are much more water soluble. This same solubility behavior has been observed in previous studies on sulfobetaines (4). The LSDR values for this series of compounds are somewhat poorer than those for simpler N-alkyl sulfobetaines which have values in the range of 2-4 (1).

The detergency behavior of this series of surfactants shows in general that the cyclic compounds I-A, I-B, and I-C, particularly the palmitic and oleic acid derivatives, are superior to the uncyclized ones and under the test conditions wash about as well as the control containing 50% sodium tripolyphosphate. In formulations with soap (C) and with soap and silicate builder (D) none of the uncyclized compounds comes close to the effectiveness of the control. The I-B imidazoline derivative, in spite of its good performance, is unsuitable because of its poor hydrolytic stability. A few compounds such as I-A (palmitic acid derived) or I-B show potentiation of detergency on some test cloths upon addition of soap and subsequent addition of silicate. This type of synergism has been observed previously for various anionic and amphoteric lime soap dispersants (1,4). On the whole, the surface-active properties of the lime soap dispersnats of this study are disappointing and and inferior to those of simpler sulfobetaines (1). The incorporation of an imidazoline ring into the amphoteric lime soap dispersant molecule does not particularly enhance surface-active properties.

ACKNOWLEDGMENTS

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