Amphoteric Surfactants from Mixed N-Alkylethylenediamine[1]

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ABSTRACT

The preparation of amphoteric surfactants by the condensation of mixed N-alkylethylenediamines and unsaturated acid derivatives, particularly acrylic acid esters, was studied. The reaction proceeded readily near 100 C either neat or with solvents. Saponification of the ester products yielded salts which were water-soluble. The mono- and disodium salts of mixed N-alkyl ($C_{11.5\ av}$) ethylenediamine dipropionic and diisobutyric acid (crotonic acid derived) as 1% active in water were completely soluble at all pH levels. The solutions demonstrated no perceptible isoelectric range on addition of 1-10% concentrations of sodium chloride. Data on surface tension, solubility, calcium tolerance, foam, viscosity, color, and density are presented.

INTRODUCTION

Amphoterics are a class of surfactant compounds with properties which are important in a wide variety of applications. Those products which are commercially available can be classified into three major chemical groups: N-alkyl amino acids and salts, the betaine (and sulfobetaine) types, and the imidazoline derivatives. Estimates indicate that there is a potential market for nonirritating amphoterics alone of 10 million lb/year (1). Major industrial uses are in cosmetics, textiles, and in cleaning products; a limited market exists in metal processing, pigment dispersion, and polymerization emulsification applications. Since amphoterics are higher cost surfactants, they are not utilized in as extensive quantities as other surfactants, but they may be blended readily with the less expensive surfactants to give many useful commercial formulations.

A basic intermediate in the preparation of most amphoterics is fatty amines. The price of tallow has doubled in the past year to $.14/lb and the increases have been reflected in the higher prices of its derivatives. A study of new specialties and surfactants, based upon new synthetic raw materials, is extremely important at this time. The current investigation is concerned primarily with the synthesis of novel derivatives based upon the reaction of a mixed N-alkyl substituted ethylenediamine (2) with unsaturated acids and their esters. The N-alkyl substituted ethylenediamines also are readily converted to imidazoline derivatives; however, the surfactant properties of the imidazolines are more applicable to oil systems, rather than aqueous systems, and will be reported elsewhere. The properties of alkoxylates prepared from the N-alkylethylenediamines also have been reported (3).

The mono- and di-N-alkylamino acids and salts, which are commercially available, are manufactured by the reaction of aliphatic fatty amines and acrylic, methacrylic, or crotonic esters as illustrated by the following reactions:

$$RNH_2 + CH_2{=}CHCO_2CH_3 \rightarrow RNHCH_2CH_2CO_2CH_3 \xrightarrow{NaOH} RNHCH_2CH_2CO_2Na$$

$$RNH_2 + 2CH_2{=}CHCO_2CH_3 \rightarrow RN(CH_2CH_2CO_2CH_3)_2 \xrightarrow{2NaOH} RN(CH_2CH_2CO_2Na)_2$$

The esters are saponified to form salts, and the salts may be partially or fully neutralized to acids. Alternatively the direct reaction of the amines with acrylic acid is feasible in some cases. Various procedures are described in the patent literature (4,5).

The reaction of dodecyl amine and methyl acrylate, followed by hydrolysis of the reaction products to obtain N-dodecyl-β-amino-propionic acid, has been studied by Isbell and others (6-9). A gamma-aminobutyric derivative obtained from the reaction of crotonic acid similarly is described. A series of amino acids was obtained by the reaction of amines and ammonia with epoxidized fatty acids (10). Amphoteric derivatives of β-alanine were prepared by the reaction of both primary and secondary amines and propiolactone as reported by Gresham, et al., (11). Piperidine and piperazine amphoterics also have been described (12,13).

Since amphoterics have partial anionic and cationic character, they can be made compatible under specific conditions with both anionic and cationic surfactants. Many of them demonstrate exceptional foaming, detergency, and lime dispersing properties combined with antistatic properties, textile softening, and hair conditioning effects. The relationship between chemical structure and surface activity was investigated by Linfield, et al., (14). β-alkylaminopropionic acids produce an excellent shampoo base when blended with lauryl alcohol sulfate (15).

Although the preparation of sym-ethylenediamine dipropionic acid has been reported (16), there is little information available on the preparation and physical properties of amphoterics derived from mixed N-alkyl-substituted ethylenediamine. It was decided to study a potentially available mixture of this type, a $C_{11.5\ av}$ paraffin-substituted ethylenediamine, and its reaction products with unsaturated acids and derivatives. For comparison purposes, similar preparations utilizing commercial mixed N-alkylpropylenediamine and a laboratory prepared N-n-dodecylethylenediamine also were investigated.

EXPERIMENTAL PROCEDURES

Materials

The mixed N-alkylethylenediamines were prepared from secondary chlorinated straight chain paraffin hydrocarbons and ethylenediamine. Typical properties of the mixture have been published (3). Results obtained from gas chromatographic analysis indicated that the distribution of the ethylenediamino moiety along the paraffin chain was 40-50% 1-substituted, 20-30% 2-substituted, and 20-40% 3- and internally substituted.

N-n-dodecylethylenediamine was prepared in 70% yield from n-dodecyl chloride and ethylenediamine. Its structure was confirmed by conversion with urea to 1-dodecyl-2-imidazolidinone, MP 67-69 C, and additionally to the dipicrate (17).

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TABLE I

Preparation and Analysis of Amphoteric Compounds

Acid or ester	Amine	Mole ratio acid amine	Product	Equivalent wt.	
				Calculated	Found
Acrylic	mixed N-alkylethylenediamine	1/1	mixed N-alkylethylenediamine propionic acid	144	154
Acrylic	mixed N-alkylethylenediamine	2/1	mixed N-alkylethylenediamine dipropionic acid	180	187.5
Maleic	mixed N-alkylethylenediamine	1/1	mixed N-alkylethylenediamine succinic acid	166	169
Methacrylic	mixed N-alkylethylenediamine	1/1	mixed N-alkylethylenediamine α-methyl propionic acid	151	145
Methacrylic	mixed N-alkylethylenediamine	2/1	mixed N-alkylethylenediamine di-α-methyl propionic acid	190	196
Crotonic	mixed N-alkylethylenediamine	1/1	mixed N-alkylethylenediamine isobutyric acid	151	147.3
Crotonic	mixed N-alkylethylenediamine	2/1	mixed N-alkylethylenediamine diisobutyric acid	190	191.4
Acrylic	C_{11}-C_{12}β-amino-propylenediamine	1/1	alkylpropylenediamine propionic acid	153	158
Maleic	N-n-dodecylethylenediamine	1/1	N-dodecylethylenediamine succinic acid	172	177
Maleic	N-oleylpropylenediamine	1/1	N-oleylpropylenediamine succinic acid	220	216
Crotonic	N-cocopropylenediamine	1/1	N-cocopropylenediamine isobutyric acid	163	157

The alkylpropylenediamine derivatives were obtained from the Akzona Corp., Chicago, Ill. and N-alkylamino acids and salts from General Mills, Minneapolis, Minn. The acrylic monomers were supplied by Rohm and Haas, Philadelphia, Pa. and n-dodecyl chloride by Humphrey Chemical Co., North Haven, Conn.

Procedure

The mixed N-alkylethylenediamines, as well as commercial alkyldiamines, condense readily at 100 C with unsaturated acids, such as acrylic, methacrylic, crotonic, and maleic acids in n-propanol or methyl cellosolve. Syntheses utilizing increasing acid to amine stoichiometry were difficult, however, because of large increases in viscosity during the reaction. Products which could not be prepared by a direct acid condensation were made by reacting the amine with the methyl ester of the acid followed by saponification.

In the following procedure the mixtures and intermediates were fluid during the entire course of the reaction. Mixed N-alkylethylenediamine (1100g, 5M) was stirred in a five liter flask equipped with a nitrogen inlet tube, an addition funnel, and a condenser. Methyl acrylate (860g, 10M) was added in a slow stream from an addition funnel for 50 min, maintaining a maximum temperature of 55 C with a cooling bath. After the addition, the mixture was heated to 70-75 C for 1 1/2 hr and then distilled at 88 C/10 mm to remove excess acrylate. The total wt of the residue was 1888g which corresponded to a condensate containing 1.83 moles of ester/mole mixed N-alkylethylenediamines.

A portion (1150g, 3 moles) of the above ester was stirred and blanketed with nitrogen, and 320 ml (4M) of 50% (wt/vol) sodium hydroxide was added together with 400 ml water. After ca. 15 min, an exotherm was noted, the temperature rose to 63 C, and the mixture was heated at ca. 60 C for an additional 2 hr. An additional quantity of 500 ml water was added, and the mixture was neutralized to pH 6.9 with 3 moles of glacial acetic acid. Methanol and minor quantities of insoluble oils were removed by heating the mixture and collecting 1500 ml of distillate, while simultaneously adding 1500 ml water. The resulting amber solution contained 51-52% actives.

Analyses and Test Procedures

Analytical procedures for total amine values were based upon American Oil Chemists' Society Tf la 64 and American Society of Testing Materials (ASTM) D2073-56, with necessary modifications. The total amine values were determined by titration with perchloric acid in glacial acetic acid.

Surfactant properties were determined by the procedures described below. Surface tension was determined by ASTM D-1331-56; pH was determined by ASTM D-1172-56. Foaming was determined by agitating 200 ml of 0.05% actives in a Waring Blendor for 2 min and noting liquid-foam levels at 0 and 5 min intervals after agitation. Calcium tolerance was determined by a modified Hart Method (18) in which 100 ml of 1% actives in water is titrated with 1% $CaCl_2$ solution at pH 10.0. The appearance of turbidity is taken as the end point and is defined as tolerance in ppm $CaCO_3$. Stability to acid and alkali was determined by the method of J.C. Harris (19) in which 100 cc of 1% actives is refluxed for 15 min in 10% sulfuric acid and 25% sodium hydroxide, noting any changes in appearance as degrees of instability. Stability to hydrolysis was determined by noting whether there was a significant change in surface tension of 1% actives solution in water when the solution was maintained at 70 C for 2 weeks. Solubility studies were made with 100 ml of 1% active amphoteric solution contained in a 250 ml beaker equipped with magnetic stirrer. Acidity and alkalinity were varied by additions of 5N HCl and 5N NaOH, and the changes were followed potentiometrically. Clarity and turbidity were noted throughout the pH 2-11 range.

Incremental additions of NaCl were made to the same solutions, pH of each was varied throughout the same pH range, and again clarity and turbidity were noted.

Amphoterics Derived from Condensation Reactions

The products obtained from the condensation of mixed N-alkylethylenediamines and unsaturated acids or esters are summarized in Table I. Compounds prepared from the commercial propylenediamine derivatives and N-n-dodecylethylenediamine also are shown. The products were analyzed to be certain that there was no free residual amine and for equivalent weight, and each is noted in the table. The compounds formed clear solutions in water at the 25-50% active level and were adjusted to pH 7.0 before testing.

Compounds were made at the 1:1 or 2:1 mole ratio of

TABLE II

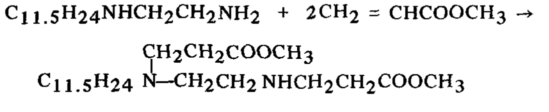
Amphoterics–Effects of pH on Foam, Solubility, Surface Tension, and Isoelectric Point

	0.1% S.T.[a]			Foam test mm liquid - mm foam		
Compound	dynes/cm	pH	Solubility[b]	0 min.	5 min	Isoelectric Pt., pH
Mixed N-alkylethylenediamine propionic acid	32.0	10.1	s	0-84	35-45	
	30.5	9.1	d	0-70	34-28	
	33.8	7.4	d	0-60	37-19	
	---	7.0	d	0-50	40-0	7.0
	---	6.4	d	0-65	35-27	
	---	4.5	s	0-78	34-35	
Mixed N-alkylethylenediamine dipropionic acid	36.7	10.9	s	0-92	34-52	
	33.8	5.9	s	0-75	35-30	
	29.3	4.6	d	0-70 Broke	40-0	4.0
	---	4.0	d	0-70 Broke	40-0	
	31.3	3.6	d	0-75 Broke	40-0	
	---	3.0	s	0-90	33-31	
Mixed N-alkylethylenediamine succinic acid	41.4	10.5	s	0-110	33-50	
	52.5	3.9	i	40-0	40-0	4.0
	45.2	2.6	d	0-83	38-5	
Mixed N-alkylethylenediamine α-methyl propionic acid	---	10.3	s	0-77	36-37	
	---	9.6	d	0-58	36-15	
	---	7.2	d	0-65	40-0	7.0
	---	6.5	d	0-70	38-3	
	---	3.8	d	0-67	38-4	
Mixed N-alkylethylenediamine di(α-methyl propionic acid)	32.1	10.4	s	0-83	35-40	
	---	9.1	d	0-62	36-22	
	30.5	6.6	d	0-63	38-15	None evident
	33.5	5.0	d	0-73	34-35	
Mixed N-alkylethylenediamine isobutyric acid	31.4	10.2	s	0-90	32-55	
	---	9.2	s	0-75	34-36	
	---	8.0	d	0-60	37-35	None evident
	30.6	6.2	d	0-77	37-33	
	37.6	5.0	s	0-75	36-28	
Mixed N-alkylethylenediamine diisobutyric acid	---	10.4	s	0-80	33-50	
	---	9.1	s	0-75	35-35	None evident
	---	5.2	s	0-78	37-23	
	---	3.2	s	0-75	37-8	
C_{11}-C_{12}-β-aminopropylenediamine propionic acid	31.0	10.4	d	0-73	36-36	
	33.0	8.7	d	36-5	39-0	8.0
	---	7.5	d	35-8	38-0	
	---	6.5	d	0-60	35-19	
	---	3.3	s	0-87	33-45	
N-dodecylethylenediamine succinic acid	27.5	10.0	d	0-83	36-44	None evident
	32.5	6.5	d	0-90	35-45	
	---	2.7	d	0-95	37-33	
N-oleylpropylenediamine succinic acid	40.0	10.7	s	0-100	34-65	
	43.0	7.9	i	40-2	40-1	8.0
	52.0	2.2	i	0-63	36-14	
N-cocopropylenediamine isobutyric acid	---	10.8	s	0-66	35-28	
	28.5	10.4	d	0-57	37-19	
	---	9.7	d	0-53	40-0	9.5
	---	9.0	d	0-53	37-16	
	29.5	6.1	s	0-92	34-53	
	29.8	3.0	s	0-100	33-67	

[a] ST = surface tension.

[b] S = soluble, d = dispersible, and i = insoluble.

acid to amine. Even though there are three potential reactive sites on the N-alkylethylenediamine, it was not possible to prepare a 3 mole ratio acrylate condensate. The 2 mole acrylic ester condensate is shown in the equation, the structure of which is based on our analytical work.



$$C_{11.5}H_{24}NHCH_2CH_2NH_2 + 2CH_2 = CHCOOCH_3 \rightarrow$$

$$C_{11.5}H_{24}\overset{\displaystyle CH_2CH_2COOCH_3}{\underset{|}{N}}{-}CH_2CH_2NHCH_2CH_2COOCH_3$$

Surface Active Properties of Prepared Amphoterics

By their nature, amphoterics are capable of forming "zwitterions" at the isoelectric point. This is possible because the molecule contains both a cationic and an anionic group. In the N-alkylamino acid amphoterics, the cationic group is a substituted ammonium group, while the anionic group is the carboxylate. In acidic solution cationic properties predominate, and in alkaline solution the anionic properties predominate. In the isoelectric range there is a decrease in surfactant proroperties and hence the isoelectric range generally can be determined by differences in foaming, surface tension, or solubility. Because of the dual functionality of amphoterics in both acidic and alkaline media, a number of properties can be conferred by the same molecule, unlike the properties of either the cationic or anionic surfactant. These include unusually good solubility and compatibility with electrolytes. Thus, solubility can be used as a basis for comparison between products, as well as an indicator of utility for the compound itself. Solubility

TABLE III

Amphoterics—Solubility and Isoelectric Range Data

Compound	Solubility at 1% active			Isoelectric range, pH
	% NaCl	Clarity[a]	pH	
Mixed N-alkylethylenediamine propionic acid	0	CR	1.7-11.6	None evident
	1	CR	1.7-11.6	None evident
	5	CR	1.9-11.4	None evident
Mixed N-alkylethylenediamine dipropionic acid	0	CR	1.8-11.0	None evident
	5	CR	2.0-11.0	None evident
	10	CR	3.6-11.0	None evident
	10	CY	2.3-3.4	2.3-3.4
Mixed N-alkylethylenediamine α-methyl propionic acid	0	CY	2.7-10.5	2.7-10.5
Mixed N-alkylethylenediamine di α-methyl propionic acid	0	CY	2.0-9.5	2.0-9.5
	1	CY	2.5-9.5	
Mixed N-alkylethylenediamine isobutyric acid	0	CR	2.0-11.0	None evident
	1	CR	2.2-11.2	None evident
	5	CR	2.4-11.4	None evident
C_{11}-C_{12}β-amino-propylenediamine propionic acid	0	CR	2.0-7.2	
	0	CY	7.3-10.5	7.3-10.5
	0	CR	11.6-11.5	
	1	CY	10.6-11.5	

[a]CR = clear and CY = cloudy.

has, therefore, been relied upon in this compilation to characterize the products; this is shown in Table II.

Part of this characterization is the determination of the isoelectric range in which foam and solubility play an important role. Foam generally can be relied upon to identify the isoelectric range by a substantial and obvious decrease, but the tests are cumbersome and time consuming. Solubility cannot be used exclusively for determination, because insolubility over an extended pH range may be due to contaminant or incomplete reaction, rather than the isoelectric range which is usually ca. 2 pH units.

Table III identifies the isoelectric range, as determined by solubility studies on a number of representative laboratory preparations. Mono- and dipropionic acid derivatives of mixed N-alkylethylenediamines showed a narrow isoelectric range. An isobutyl derivative prepared from crotonic acid demonstrated no perceptible isoelectric point from the solubility data but isomeric mono- and di-α-methyl propionic compounds showed insolubility over an extended pH range.

Since the sample of mixed N-alkylethylenediamine dipropionic acid had the narrowest isoelectric range and excellent solubilization characteristics, it was compared more fully with some of the commercially available amphoterics. The commercial amphoterics had active contents ranging from 30-50% and pH values at the 1% level ranged from 6.7-8.7. Surface tension measurements at 0.1% dilution were made on both the laboratory preparations and commercial amphoterics. All of them gave values in the 28-34 dynes/cm range for both acid and basic media.

TABLE IV

Comparison of Commercial Amphoterics to N-Alkylethylenediamine Dipropionic Acid

Compound	Solubility at 1% active			Calcium Tolerance ppm $CaC0_3$
	% NaCl	Clarity[a]	pH	
Mixed N-alkylethylenediamine dipropionic acid	0	CR	2.0-11.0	4500
	5	CR	2.0-11.0	
	10	CR	3.5-11.0	
	10	CY	2.3-3.4	
C_{11}-C_{12}β-amino-propylenediamine dipropionic acid	0	CY	2.0-8.5	1800
	0	CR	8.6-11.0	
	1	CY	2.7-8.5	
	1	CR	8.6-11.0	
N-coco-β-amino-propionic acid (General Mills)	0	CY	2.8-4.6	650
	0	CR	4.7-11.0	
	1	CY	2.6-4.8	
	1	CR	4.9-11.0	
Disodium N-lauryl-β-iminodipropionate (General Mills)	0	CY	2.4-4.5	1000
	1	CY	2.3-4.1	
	1	CR	4.2-10.5	
Coco amino sulfonate (Northern Petrochem)	0	CR	2.0-11.0	4500
	10	CR	2.0-11.0	
N-coco-β-amino butyric acid (Akzona Corp.)	0	CR	2.0-7.2	100
	0	CY	7.3-10.9	
	5	CY	2.0-11.1	
Disodium salt of chloroacetylated hydroxyethyl imidazoline (Miranol)	0	T	2.0-3.5	450
	0	CR	3.5-11.0	
	5	T	1.9-3.2	
	5	CR	3.3-11.0	

[a]CR = clear, CY = cloudy, and T = translucent.

Solubilization characteristics in water and in sodium chloride were then compared; the information is presented in Table IV. Also, calcium tolerances in ppm of calcium carbonate were determined and are noted in Table IV. The N-alkylethylenediamine dipropionic acid prepared compares favorably with the commercial materials and should, thus, make a good candidate for further evaluation in practical applications.

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