Fatty Amidoamine Derivatives: N,N-Dimethyl-N-(3-alkylamidopropyl)amines and Their Salts[1]

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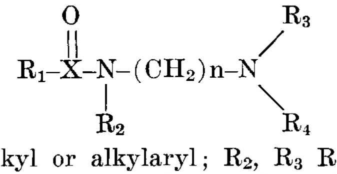
Abstract

A group of cationic surfactants based on N-alkylamidopropyl - N,N - dimethylamines, $R–CONHCH_2CH_2CH_2N(CH_3)_2$, was studied. Caprylamidopropyl, capramidopropyl, lauramidopropyl, stearamidopropyl and oleamidopropyl dimethylamines were prepared, purified and characterized. NMR, IR, and pK_b data are reported. The acetate and methylchloride quaternary salts of these amines were also prepared and evaluated as bactericides gelling agents, and foaming surfactants. Surface tensions, interfacial tensions, critical micelle concentrations and Ross-Miles foam heights were determined. N-(3-dimethylaminopropyl)stearamide formed well structured gels in white mineral oil and deodorized kerosene. Further, these amidoamines and their salts showed excellent antistatic properties and were substantive to hair and skin.

Introduction

CATIONIC SURFACTANTS with an amide functionality are interesting compounds that exhibit unusual surface active properties compared to their alkyl cationic counterparts. In a broad scope these compounds may be represented as follows:



$$R_1–\overset{\overset{O}{\|}}{X}–\underset{\underset{R_2}{|}}{N}–(CH_2)n–N\begin{matrix}\diagup R_3\\ \diagdown R_4\end{matrix}$$

where R_1 = alkyl or alkylaryl; R_2, R_3 R_4 = H or alkyl; n = 1 to 6 and X = C, S = O, or P(O)OH.

This paper will deal with one group of these general types of compounds, namely the N,N-dimethyl-N-(3-alkylamidopropyl)amines, their acetate salts and their methylchloride quaternary salts.

These amidoamines have been known for some time (1,2) but their surfactant properties have not been studied extensively, especially in relation to cosmetic applications. In our study, key physical properties of several amidoamines were compared with those of corresponding carbon chain length dimethylalkylamines.

Amidoamines can be named as substituted amides or as substituted amines. The substituted amide nomenclature is more descriptive for the simple amidoamines but the substituted amine nomenclature enables easier handling of the amine derivatives. Using decanoic (capric) acid as an example: N-(3-dimethylaminopropyl)decanamide or N-(3-dimethylaminopropyl)capramide and N,N-dimethyl-N-(3-decanamidopropyl)amine or N,N-dimethyl-N-(3-capramidopropyl)amine. Although other names appear in the literature they are generally more cumbersome and less descriptive.

Synthesis and Characterization

Materials

Reagent grade (Eastman or Fisher, or both) caprylic, capric, lauric, stearic and oleic acids were used without further purification. Dimethylaminopropylamine (Jefferson) was dried and distilled (purity 99+% as determined by gas chromatography). The dimethylalkylamines were used as received (Baird and Armour), after titrations and gas chromatography established purities. All other chemicals were reagent grade and were used as received.

Synthesis of N,N-Dimethyl-N-(3-alkylamidopropyl)amines

The aminolysis of fatty acid chlorides and fatty methyl esters did not result in easily purified products. The following technique yielded 98% to 99% pure amidoamines.

Solutions of 1.4 moles dimethylaminopropylamine and 1.0 mole fatty acid in 200 ml toluene were refluxed for 3 hr. Water was removed by azeotropic distillation over a 29 hr period using a Barrett trap. About 21 g of water was generally removed. Toluene and unreacted dimethylaminopropylamine was removed in a flash evaporator (65–70 C/15 mm Hg) and finally by drying in a vacuum oven to constant weight. Solid amidoamines were recrystallized from hexane. The products were characterized by primary-tertiary amine titrations, (3), free fatty acid titrations, (4), nitrogen analyses, infrared, ultraviolet and NMR spectra.

The amidoamines have a great affinity for water (probably as amide hydrates) but this technique resulted in complete water removal. Interestingly enough, amidoamines could not be produced in refluxing (azeotroping) benzene. Apparently temperatures above 80 C are needed for this reaction. An excess of dimethylaminopropylamine was needed to react with the last traces of fatty acid. Table I shows

TABLE I

Characterization of Amidoamines and Alkyldimethylamines

Source	R	MW	% N (theory)	% N (found)	Neut. Eq.	mp C
$R–CONH(CH_2)_3N(CH_3)_2$	C_7H_{15}	228.4	12.2	12.0	216	[a]
	C_9H_{19}	156.4	10.9	10.7	248	[a,b]
	$C_{11}H_{23}$	284.5	9.8	9.6	266	28.5–30.0[c,d]
	$C_{17}H_{35}$	368.6	7.6	7.6	367	58.5–59.5[e]
	$C_{17}H_{32}$	366.6	7.6	7.6	337	[a]
$R–N(CH_3)_2$						
Baird	$C_{10}H_{21}$	185.4			177	[f]
Baird	$C_{12}H_{35}$	214.0			210	[f]
Baird	$C_{18}H_{37}$	297.6			276	[f]
Armour	$C_{18}H_{35}$	295.5			272	ca. 25

[a] Amber liquid at 20 C.
[b] Bp 175–8 C/2 mm (11).
[c] Rosette Needles.
[d] Bp 195–204 C/1 mm (11).
[e] Plates.
[f] Light Yellow Liquids.

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[1] Presented at the AOCS Meeting, Chicago, October 1967.

the characterization of these products along with the dimethylalkylamines.

Preparation of Amine Acetate Salts

Tertiary amine acetate salts were prepared by dissolving .25 mole of amine in 10.0 to 20.0 g reagent grade isopropyl alcohol. Acetic acid (.25 mole as a 7.45 N solution) was slowly added. The acetate salts were generally 60.0% salt, 28.0% water and 12.0% isopropyl alcohol (all percents by weight). Some of the higher molecular weight salts were not soluble in this system so that additional isopropyl alcohol was needed. The solutions were light amber to colorless with pH values of 6.0 to 6.3 (as 1% aqueous solutions). The addition of a stoichiometric amount of acetic acid was used in preference to a titration technique since no inflection was observed when these amines were titrated with acetic acid.

Preparation of Methylchloride Quaternary Salts

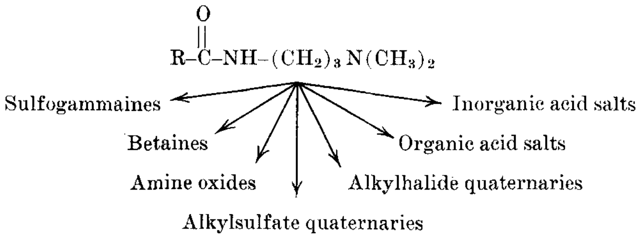
The methylchloride quaternary salts were prepared by bubbling methylchloride through a refluxing isopropanol-water solution of .25 mole of tertiary amine and 0.2 g $NaHCO_3$. The addition periods were 6 to 8 hr, after which excess $NaHCO_3$ was filtered off.

These quaternaries were 25% to 60% solids depending on the amine used. Yields were near quantitative based on per cent tertiary amine and per cent quaternary salt analyses (3).

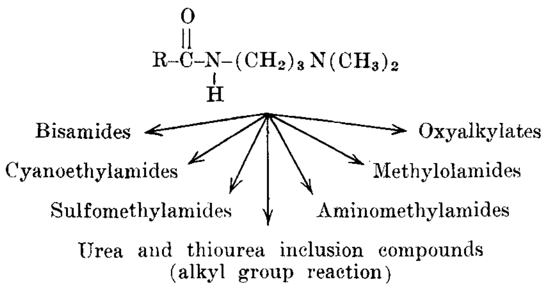
Physical and Chemical Properties of Amidoamines and Their Acetate Salts

Reactivity

The amidoamines have two main functional sites for reactions: the tertiary amine group and the amide hydrogen. The tertiary amine reactions are well known.



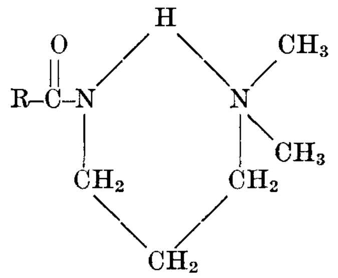
The reactions at the amide hydrogen have not been as exhaustively studied:



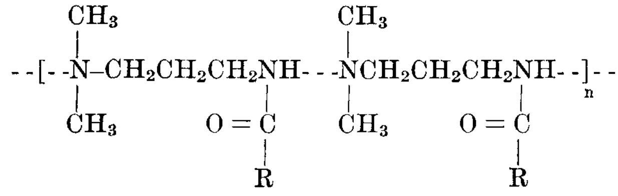
The amide hydrogen is moderately reactive; it undergoes deuterium exchange reactions and may be directly titrated in perchloric-acetic acid systems.

Structure

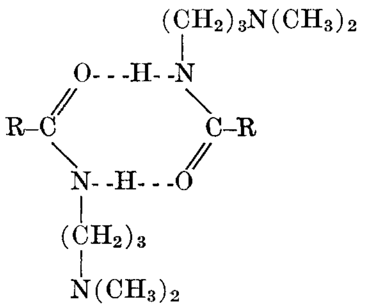
The amidoamines are unusual in that they may exist in a number of intra or intermolecularly bonded forms or both. Molecular models show that the following form is possible:



Other possibilities include:

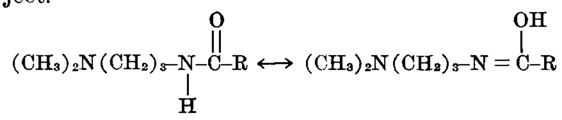


$$--[--\underset{CH_3}{\overset{CH_3}{N}}-CH_2CH_2CH_2\underset{\underset{R}{O=C}}{NH}---\underset{CH_3}{\overset{CH_3}{N}}CH_2CH_2CH_2\underset{\underset{R}{O=C}}{NH}--]--_n$$



In addition to this "self" hydrogen bonding amidoamines can bond with many polar substrates. They appear to have an affinity for water which probably hydrates with the amide functionality. Structured gel formation is also attributed to amide hydrogen bonding.

The purported enolization is still an unsettled subject.



$$(CH_3)_2N(CH_2)_3-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-R \longleftrightarrow (CH_3)_2N(CH_2)_3-N=\overset{OH}{\overset{|}{C}}-R$$

Base Properties

Amidoamines are moderately strong bases. Their pk_b values are between 5 and 6 as determined titrimetrically. Figure 1 shows a typical titration curve. Weak acid titrations show no inflection under similar conditions. Strong or weak acid neutralizations are fairly exothermic.

Infrared Spectra

Infrared spectra show the following adsorptions for amidoamines: amide H stretch at 3300 cm^{-1}, bonded *trans*; amide I carbonyl band 1650 cm^{-1}; amide II 1550 cm^{-1}. These values are in good agreement with Link (6) who noted that the amide II absorption shifts from 1575 cm^{-1} to 1550 cm^{-1} as fatty amides are monosubstituted. Figure 2 shows a spectrum of N-3(dimethylaminopropyl)stearamide.

NMR Spectra

The NMR spectra of N,N-dimethyl-N-(3-lauramidopropyl)amine were run on a Varian A-60 spectrometer. The following peaks (δ) were observed relative to TMS external: terminal CH_3 – .9 ppm; insulated

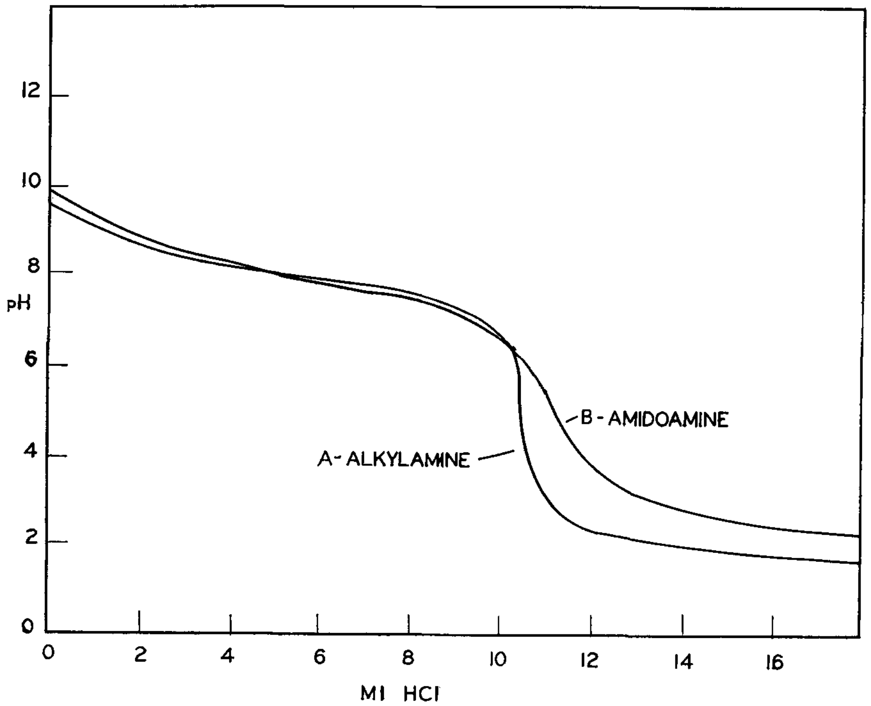


FIG. 1. Titration curve, ml 0.1 N HCl vs. pH; A, N,N-dimethyl-N-stearylamine; B, N,N-dimethyl-N-(3-lauramidopropyl)amine.

CH_2 – 1.2 ppm; $(CH_3)_2N$ – 2.1 ppm; amide H – 7.5 ppm. The dimethylalkylamines showed similar peaks with the absence of the amide H peak. Samples were run neat and in carbon tetrachloride. The absorption values for the diluted samples were similar to those found by Hopkins (7) in his work with lipids.

Hydrolytic Stability

N,N-Dimethyl-N-(3-lauramidopropyl)amine was subjected to hydrolysis in refluxing dioxane-water (91 C). Aliquots were withdrawn periodically and titrated with .1 N HCl. Figure 3 shows the titration curves after 2 hr and after 150 hr. The hydrolysis after 150 hr was 12.5%. Acid hydrolysis is expected to be more rapid.

Surface Tensions and Critical Micelle Concentrations

Surface tensions at various concentrations were determined for the amidoamine acetate salts using a du Nouy tensiometer (8). All surface ages were 15 sec. Figure 4 shows a typical concentration (wt %) surface tension (dynes/cm) plot for N,N-dimethyl-N-(3-decanamidopropyl)ammonium acetate. Figure 5 shows a log concentration (wt %) surface tension plot for N,N-dimethyl-N-(3-oleamidopropyl)ammo-

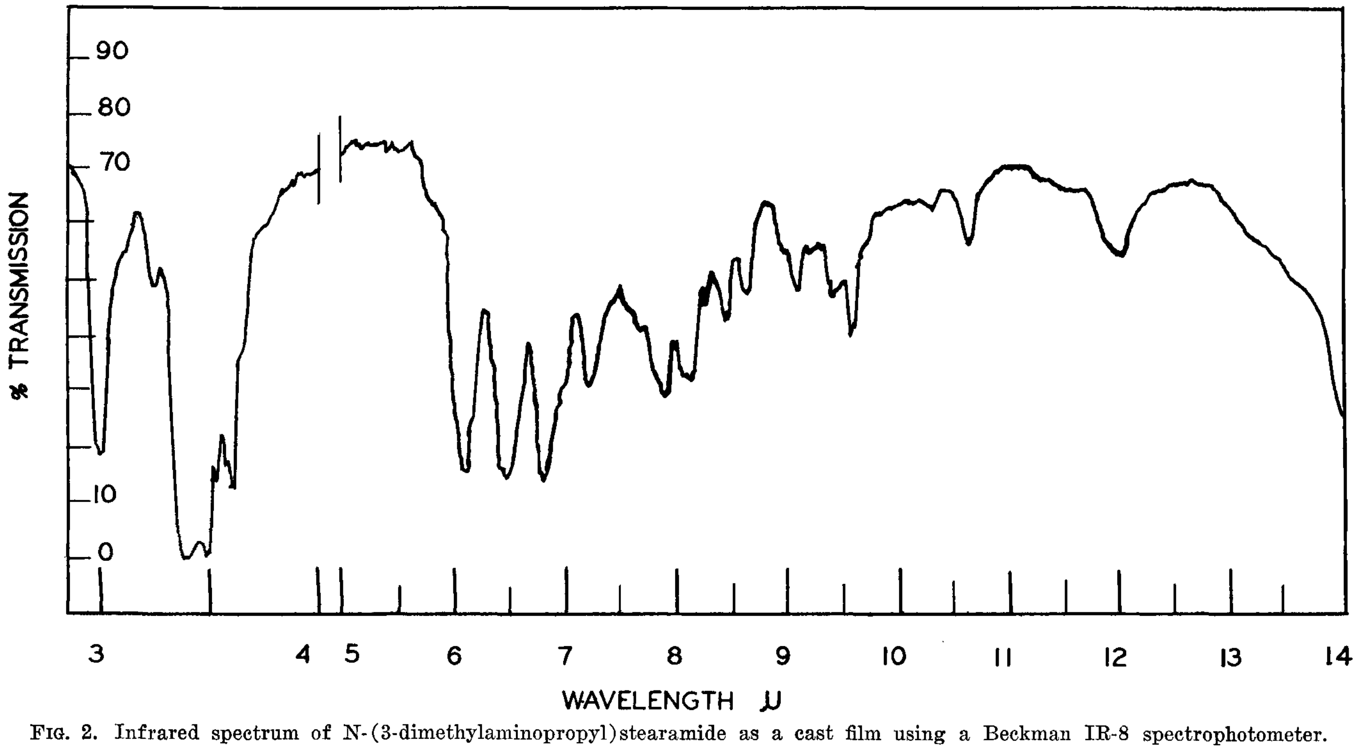


FIG. 2. Infrared spectrum of N-(3-dimethylaminopropyl)stearamide as a cast film using a Beckman IR-8 spectrophotometer.

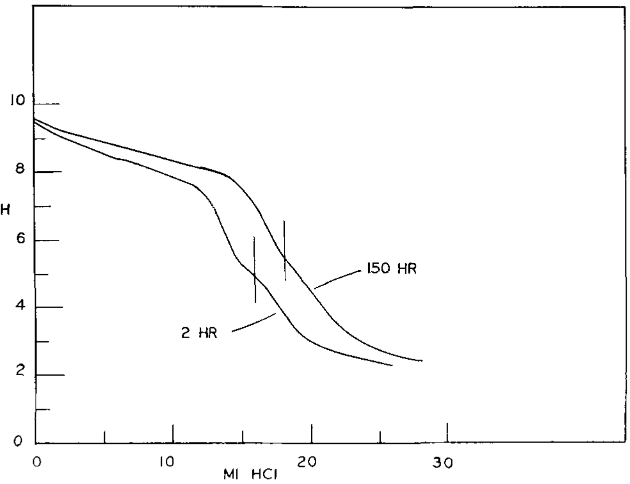


FIG. 3. Hydrolytic stability tests, titration curves after 2 hr and after 150 hr. N-(3-dimethylaminopropyl)lauramide refluxed in aqueous dioxane at 91 C.

nium acetate and N,N-dimethyl-N-(3-stearamidopropyl)ammonium acetate. The CMC values are quite low (.035 M) but this is understandable considering that the extended equivalent carbon chain length would be similar to $C_{22}N$–. Table II summarizes these data.

When comparing the amidoamines to their dimethylalkylamine counterparts it should be borne in mind that the amidopropyl group has an extended carbon chain length of about 6 A so that N,N-dimethyl-N-(3-caprylamidopropyl)amine and N,N-dimethyl-N-laurylamine are roughly equivalent (c.a. 18 A). It appears that the lower molecular weight amidoamines are better wetting agents at CMC concentrations than are the higher molecular weight species. The higher molecular weight species do, however, have much lower CMC values.

Klevins (9) indicates that any surfactant having the same equivalent extended hydrocarbon chain length should have a very similar CMC.

This was not found for several of the amidoamines and may be attributable to the many types of hydrogen bonds that these compounds are capable of forming.

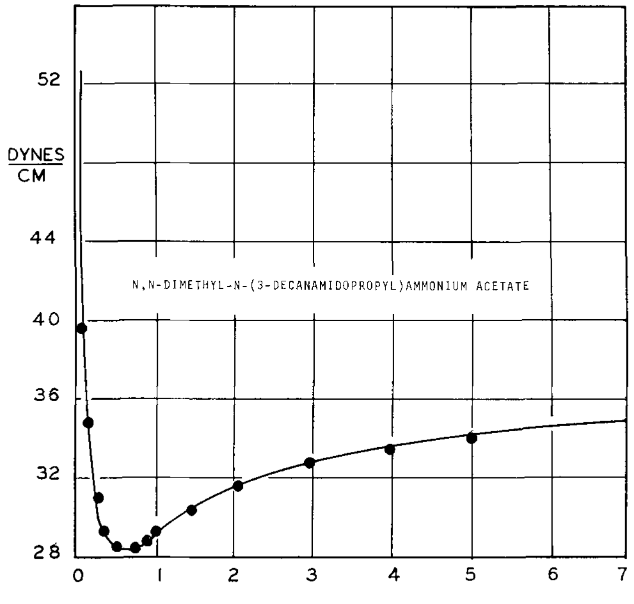


FIG. 4. Concentration vs. surface tension curve for N,N-dimethyl-N-(3-decanamidopropyl)ammonium acetate.

Only N,N-dimethyl-N-(3-lauramidopropyl)amine fit the following relationship:

$$\log CMC = A - BN \qquad (9)$$

Where N = number of carbon atoms in the chain, B = constant (log 2), A = constant, dependent on a particular series and temperature. A was found to be about 1.4.

When the number of carbon atoms in the hydrophobic portion of the amidoamine acetate salt was plotted against the surface tensions at .1% (wt) and .5% (wt) concentrations, minima were observed for N,N-dimethyl-N-(3-lauramidopropyl)ammonium acetate. This indicates that this acetate salt has the

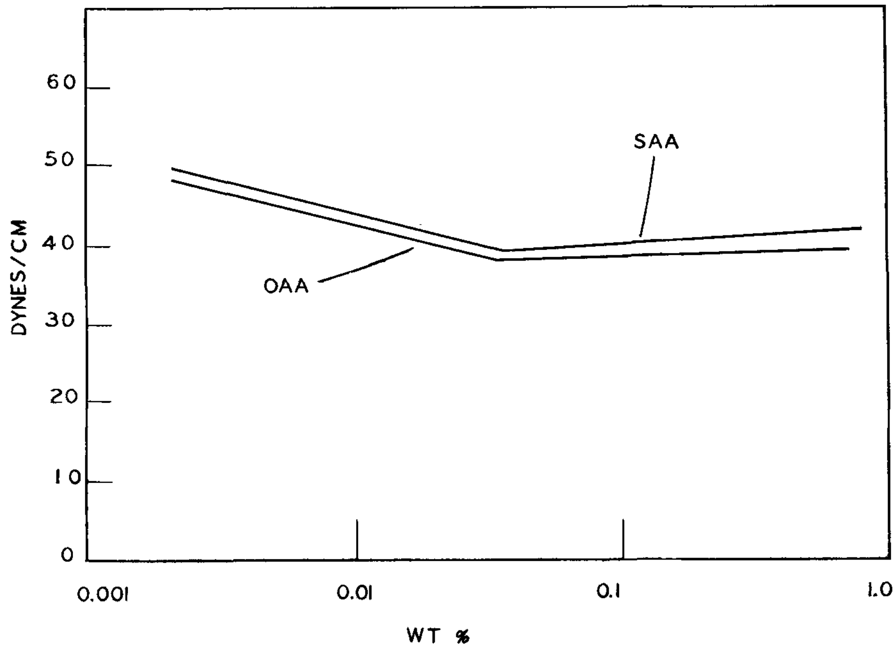


FIG. 5. Concentration of surfactant vs. surface tension SAA, N,N-dimethyl-N-(3-stearamidopropyl)ammonium acetate OAA, N,N-dimethyl-N-(3-oleamidopropyl)ammonium acetate.

TABLE II

Surface Tensions and Critical Micelle Concentrations of Tertiary Amine Acetate Salts[a]

Compound	MW	Surface Tension (25 C) .01 (wt %)	Surface Tension (25 C) at CMC	CMC % (wt)
$\mathrm{R{-}\overset{O}{\overset{\|}{C}}NH(CH_2)_3\overset{+}{N}(CH_3)_2H\overset{-}{O}\overset{O}{\overset{\|}{C}}CH_3}$				
$CH_3(CH_2)_6$	288.4	67.0	27.5	......
$CH_3(CH_2)_8$	316.4	68.0	28.4	0.6
$CH_3(CH_2)_{10}$	344.5	28.1	25.5	0.2
$CH_3(CH_2)_{17}$	428.6	44.1	39.9	0.03
$CH_3(CH_2)_7CH = CH(CH_2)_7$	426.6	43.3	37.7	0.03
$\mathrm{R{-}\overset{+}{N}(CH_3)_2H\overset{-}{O}{-}\overset{O}{\overset{\|}{C}}CH_3}$				
$CH_3(CH_2)_9$	236.4	68.0	28.2	.6
$CH_3(CH_2)_{11}$	274.0	59.4	27.2	.4
$CH_3(CH_2)_{17}$	357.6	33.0	28.4	.02
$CH_3(CH_2)_7CH = CH(CH_2)_8$	355.6	39.0	33.0	.1

[a] du Nouy tensiometer (8).

best wetting properties of the five amidoamine acetate salts tested at these two concentration levels.

Interfacial Tension

Table III shows the interfacial tension for two amidoamines and two fatty amines at .001, .01 and .1, and 1.0% (wt) concentrations. Mineral oil (Nujol) was used as the hydrocarbon. The surface age was 15 sec and the temperature was 25 C. N-(3-Dimethylaminopropyl)octanamide and N,N-dimethyl-N-dodecylamine have approximately the same extended chain length of about 18 A, yet at the four concentration levels this amidoamine shows a much lower interfacial tension. In general both amidoamines showed lower surface tensions than either of the dimethylalkylamines.

Applications of Amidoamines in Cosmetic Chemistry

Ross-Miles Foam Test

Amidoamine acetates show unusually good foaming properties. In the acetate series (Table IV) all of the amidoamine salts outperformed the two representative dimethyalkylammonium acetate salts except for the caprylamidoamine. Since these tests were conducted at an average pH of 6.1 several cosmetic formulations suggest themselves. Actually the amidoamine acetates show excellent foaming properties from pH values of 5.5 to 9.0. The trimethylalkylammonium chloride quaternaries showed much better foam properties, but were still inferior to the amidoamine counterparts (Table V).

Compatibilities With Other Surfactants

The amidoamine salts in general are compatible with anionic and nonionic surfactants. Both clear and pearlescent formulations can be prepared. Mixtures of various amidoamines have definite hydrotroping or cosolvency properties but are surface active in addition. Both amidoamines and their acetate salts are good emulsifiers for light oils.

TABLE III

Interfacial Tension[a] *dynes/cm* (White oil/Water, 25 C)

Compound	Concentration (wt %) 1.0	0.1	0.01	0.001
$CH_3(CH_2)_9N(CH_3)_2$	33.3	35.3	41.2	45.0
$CH_3(CH_2)_{11}N(CH_3)_2$	32.7	40.8	44.6	45.6
$CH_3(CH_2)_6CONH(CH_2)_3N(CH_3)_2$	5.6	24.6	30.9	40.6
$CH_3(CH_2)_{10}CONH(CH_2)_3N(CH_3)_2$	8.4	12.9	21.5	42.7

[a] du Nouy tensiometer (8).

TABLE IV

Ross-Miles Foam Test 25 C 0.1% (wt) Surfactant[a]

Surfactant	Foam height (cm) Initially	Foam height (cm) After 5 min
Amines		
$CH_3(CH_2)_7CH = CH(CH_2)_7CONH(CH_2)_3N(CH_3)_2$	.6	0.6
Amidoamine acetate salts[b]		
$\mathrm{R{-}CONH(CH_2)_3N^+(CH_3)_2H\,\overline{O}OCCH_3}$		
R		
$CH_3(CH_2)_6$	1.3	0.3
$CH_3(CH_2)_8$	4.4	2.5
$CH_3(CH_2)_{10}$	12.7	12.1
$CH_3(CH_2)_{16}$	10.8	10.8
$CH_3(CH_2)_7CH = CH(CH_2)_7$	15.9	15.9
Amine acetates		
$\mathrm{R{-}N^+(CH_3)_2H\,\overline{O}OCCH_3}$		
R		
$CH_3(CH_2)_{11}$	1.9	1.9
$CH_3(CH_2)_{17}$	1.3	0.0

[a] The surfactant was mixed with distilled water.
[b] The average acetate salt pH was 6.1.

Antistatic Properties

Amidoamines and their salts are excellent antistatic agents. Their ability to hold water coupled with their high polarity enables them to dissipate static charges even at relatively low humidities. Coating polyethylene slabs with .1 to .5% (wt) solutions, drying and then subjecting these slabs to the smoke box test showed excellent results.

Hair and Skin Substantivity

The amidoamines by their structural nature provide multiple sites for adsorption onto keratin protein coils. The available negatively charged groups of hair and skin are able to bond with the cationic portion of an amidoamine salt. Also the carbonyl group and the amide hydrogen are available for additional or more complete bonding. The amidoamines themselves are similar to hair and skin proteins in that they contain amine and amide functional sites. We have done a limited amount of research in this area but initial results show that amidoamine salts do have a definite place in hair care formulations.

Thickeners

The amidoamines have unusual thickening properties. N-(3-dimethylaminopropyl)stearamide can convert mineral oil to a stable thixotropic gel that has the consistency of vaseline when it is mixed with mineral oil in 5/95 ratios by weight. This property suggests many hair and skin preparations. Various other types of structured viscosities are possible in aqueous as well as nonaqueous systems.

Bacteriostatic Properties

The amidoamines, their acetate salts and their methylchloride quaternary salts have bacteriostatic activity as shown in Table VI. The methylchloride quaternary of N-(3-dimethylaminopropyl)lauramide is particularly active against β-hemolytic strep. An

TABLE V

Ross-Miles Foam Test 25 C 0.1% (wt) Surfactant

Surfactant	Foam height (cm) Initially	Foam height (cm) After 5 min
Quaternaries		
$[CH_3(CH_2)_{10}CONH(CH_2)_3N^+(CH_3)_3]Cl^-$	14.0	13.3
$[CH_3(CH_2)_{16}CONH(CH_2)_3N^+(CH_3)_3]Cl^-$	15.9	15.2
$[CH_3(CH_2)_{11}N^+(CH_3)_3]Cl^-$	1.3	1.3
$[CH_3(CH_2)_{17}N^+(CH_3)_3]Cl^-$	13.3	13.3
Anionics		
$CH_3(CH_2)_{11}OSO_3Na$	15.0	13.5

TABLE VI

Serial Dilution Tests

Sample	β-Hemolytic strep.	*E. coli.*	*Staph aureus*	*B. subtilus*	*C. albicans*
Q-A-12[a]	1:500,000	1:12,500	1:50,000	1:200,000	1:26,000
Q-B-12[b]	1:2,000,000	1:3,200	1:12,500	1:12,000	1:3,200
Q-A-18[c]	1:2,000,000	under 1:200	1:1,000,000	1:1,000,000	1:50,000
Q-B-18[d]	1:1,000,000	under 1:200	1:50,000	1:200,000	1:50,000
A-12[e]	1:100,000	under 1:200	1:12,000	1:25,000	1:25,000
S-12[f]	1:25,000	under 1:200	1:12,000	1:25,000	1:6,400

[a] Dodecyltrimethylammonium chloride (65% actives).
[b] N,N,N-trimethyl-N-(3-lauramidopropyl)ammonium chloride (25% actives).
[c] Octadecyltrimethylammonium chloride (67% actives).
[d] N,N,N-trimethyl-N-(3-stearamidopropyl)ammonium chloride (65% actives).
[e] N-(3-dimethylaminopropyl)lauramide (100% actives).
[f] N,N-dimethyl-N-(3-lauramidopropyl)ammonium acetate (60% actives).

excellent comparative review of fatty amine bacteriostatic activities has recently been published (10).

ACKNOWLEDGMENTS

C. Micklesen determined the surface and interfacial tensions for this series of compounds. W. Ludwig ran the foam tests.

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