Tallow Alkanolamides: Preparation and Effect on Surfactant Solutions[1]

J.K. WEIL, N. PARRIS, W.R. NOBLE, F.D. SMITH and A.J. STIRTON,[2]
Eastern Regional Research Laboratory,[3] Philadelphia, Pennsylvania 19118

Abstract

Oxyalkylation of N-(2-hydroxyethyl)amides and N,N-bis-(2-hydroxyethyl)amides gave products which were valuable as detergent additives and detergent intermediates. Oxyalkylation of simple amides was difficult to carry out, and the product contained large quantities of unreacted amide which had an adverse effect on surfactant properties. Amides with short oxyalkyl chains and long fatty chains were not soluble by themselves but were solubilized by aqueous detergent solutions and had characteristic "Krafft Points." This temperature, at which the mixed solution became clear, was independent of detergent used, amide to detergent ratio up to 1.4, total concentration, and water hardness. Krafft point of poorly soluble detergents such as sodium octadecyl sulfate and disodium α-sulfostearate was lowered by mixing with alkanolamides. N,N-Bis-(hydroxyethyl)-hexadecanamide and the oxyalkylated products of N,N-bis-(hydroxyethyl) hexadecanamide and N,N-bis-(hydroxyethyl)octadecanamide increased the viscosity of solutions of linear alkylbenzene sulfonate and sodium dodecyl sulfate in the same was as the N,N-bis-(hydroxyethyl)amide prepared from coconut oil. Foam stabilizing properties ere observed for some of oxyethylated amides. One per cent N,N-bis-(2-hydroxyethyl)oleamide and 2-(2-hydroxyethoxy)-ethyloleamide formed petrolatum-water emulsions which were stable for more than a month.

Introduction

Coconut-based dialkanolamides are important ingredients of formulated detergents and cosmetics. They contribute foam stability in the presence of soil and are helpful in the control of viscosity of aqueous detergent solutions (1). It has been stated that the presence of up to 50% unsulfated alkanolamide improves the detergency of sulfated 2-hydroxyethyl lauramide (2).

A number of alkanolamides were prepared for sulfation in previous studies (3,4). This paper describes the properties of these amides and some of their oxyalkylated products and explores their use as detergent additives. For convenience the following common names will be used: ethanolamides [(N-(2-hydroxyethyl)amides], isopropanolamides [(N-(2-hydroxypropylamides)], n-propanolamides [(N-(3-hydroxypropyl)amides], diglycolamides [2-(2-hydroxyethoxy)amides], diethanolamides [N,N-bis-(2-hydroxyethyl)amides] and methyl ethanolamides [N-methyl-N-(2-hydroxyethyl)amides]. Compounds available for this study were the above named amides derived from pelargonic, lauric, palmitic, stearic and oleic acids and a number of oxyethylated and oxypropylated ethanolamides and diethanolamides.

Preparative methods which have been considered for oxyalkylated amides are: (A) the reaction of fatty acids or esters with alkanolamine, followed by oxyalkylation if desired, or (B) the direct oxyalkylation of unsubstituted amides (5). Previous work from this laboratory (3,4) has followed the former route to high purity products. Since products from the oxyalkylation of simple amides have not been adequately described a portion of this paper has been devoted to preparation by method B to compare its products with those from method A.

Experimental Procedures

Materials

Pelargonic, lauric, palmitic and stearic acids were converted to methyl esters and the latter purified by fractional distillation at reduced pressure. Methyl oleate was purchased from Applied Science Laboratories. Vapor phase chromatography showed all esters to be more than 99% pure.

Alkanolamines were the best available laboratory grade, redistilled at 10 mm pressure through a 1 ft column packed with stainless steel protruded packing. Ethylene oxide and propylene oxide were the best available laboratory grades.

Amidations

The preparation of alkanolamides and diglycolamides has been described in earlier publications (3,4). Diethanolamides were prepared similarly, except that it was necessary to limit reaction time to 30 min to minimize isomerization to ester amine. Diethanolamides were purified by two crystallizations from petroleum ethers. Table 1 lists the melting points of the purified alkanolamides.

Oxyalkylations

Ethanolamides were reacted with ethylene oxide and propylene oxide by standard alkali-catalyzed oxyalkylation procedures. Reaction conditions and composition of the products have been described elsewhere (4).

Diethanolamide oxyalkylations were carried out at 60 C, catalyzed by triethylamine as recommended by Carnes (6). This procedure prevents the isomerization to ester which takes place when diethanolamides are oxyalkylated at higher temperatures in the presence of stronger alkaline catalysts. The method is illustrated by the following example in which two moles of propylene oxide are added per mole of diethanolstearamide.

Propylene oxide was added dropwise to a mixture of 24.3 g (0.0654 moles) of diethanolstearamide and 4.9 ml (3.8 g) of triethylamine while stirring under reflux (70 C). At the end of 4 hr, the weight had increased to 8.1 g (0.139 moles of propylene oxide

---

[1] Presented at the AOCS Meeting, Houston, May, 1971.

[2] Deceased.

[3] E. Market. Nutr. Res. Div., ARS, USDA.

TABLE I

Melting Point[a] of Alkanolamides, C

Amide	Fatty acid				
	Pelargonic	Lauric	Palmitic	Stearic	Oleic
Hydroxyethyl[b]	69.8–70.8	87.2–89.2	98.7–99.5	102.2–103.0	62.0–63.6
2-Hydroxypropyl[b]	....	68.2–69.8	79.2–80.1	85.0– 86.0	....
3-Hydroxypropyl[b]	56.0–57.4	75.8–76.8	91.0–92.2	95.6– 96.8	....
N-Methyl, N-Hydroxyethyl[b]	<0	19.5[d]	45.2–46.6	59.6– 60.7	<0
Diethanol	<0	49.8–51.0	67.1–68.5	71.6– 73.5	[e]
Diglycol[c]	47.0–48.3	64.0–65.2	82.0–83.1	87.2– 88.5	38.0–39.2

[a] All melting points corrected.
[b] Previously reported (3).
[c] Previously reported (4).
[d] Freezing point.
[e] Not crystalline.

added). The crude product was taken up in 200 ml of 95% ethanol and extracted with three 75 ml portions of petroleum ether (63–70 C). Solvent was removed from the alcoholic solution of the product, and then it was dissolved in 150 ml of diethyl ether and washed three times with 30 ml portions of water. Solvent was removed at room temperature under reduced pressure, using a final pressure of 0.2 mm. Yield was 16.0 g (49.5% of theory).

Oxyethylations were carried out similarly after charging ethylene oxide to a closed reaction vessel.

Gas Liquid Chromatography Analysis

A dual column F & M model 810 chromatograph with an Infotronics Integrator was used for gas liquid chromatography (GLC) analysis. The column was 2 ft long and 1/8 in. in diameter, packed with 10% J X R silicone on Gas-Chrom Q. The oven was programmed from 100 to 300 C at a rate of 8°/min, with injection port at 200 C and detector at 320 C. Table II shows typical GLC analyses for the oxypropylation of pelargonamide and hydroxyethylpelargonamide.

Solubility

"Krafft Point" of mixtures were measured to determine ease of amide solubilization. Solutions containing 0.8% sodium methyl α-sulfopalmitate and 0.2% amide were heated slowly until clear after having been recently clouded by cooling. These clarification points are recorded on Table III.

Emulsion Stability

Ability to form emulsions was measured in an Atlab Emulsion Test Apparatus. A half gram of amide was dissolved in 25 ml of organic phase (petrolatum, carbon tetrachloride or benzene) and shaken with 25 ml of water in a 2 oz wide mouth bottle for 3 min. The emulsion was poured into the viewer, and the time was recorded for a 10% separation of either phase or a total of both phases.

TABLE II

Composition of Products
From Oxyalkylation of Pelargonamides

	Mole Fraction of Products[a]	
	Pelargonamide + propylene oxide	Hydroxyethylpelargonamide + propylene oxide
θ, moles epoxide per mole amide	1.11	0.92
Amide, $C_8H_{17}CONH_2$	0.373	....
Alkanolamide, $C_8H_{17}CONHCH_2CH(R)OH$[b]	0.317	0.191
Diglycolamide, $C_8H_{17}CONHCH_2CH(R)\text{-}OCH_2CH(CH_3)OH$	0.204	0.710
Third derivative, $C_8H_{17}CONHCH_2CH(R)\text{-}[OCH_2CH(CH_3)]_2OH$	0.083	0.092
Fourth derivative, $C_8H_{17}CONHCH_2CH(R)\text{-}[OCH_2CH(CH_3)]_3OH$	0.027	0.007
Fifth derivative, $C_8H_{17}CONHCH_2CH(R)\text{-}[OCH_2CH(CH_3)]_4OH$	0.006	0.000

[a] Determined by GLC and converted to mole fraction.
[b] R is CH_3 for first column; R is H for second column.

Viscosity

Amide and linear alkylbenzene sulfonate (LAS) or sodium dodecyl sulfate were combined in varying proportions to give a total concentration of 15% aqueous solution, and viscosity was measured with Cannon-Manning semimicro viscosimeter tubes. Figure 1 shows the variation of viscosity with composition for selected examples of alkanolamides mixed with LAS. Figure 2 shows a similar relation for mixtures of amides with commercial sodium lauryl sulfate.

Foam Stabilization

The effect of amide additives on foam stability was measured by the miniature dishwashing test of Anstett and Schuck (7). The method scales down test conditions so that a 1½ in. watch glass with 0.36 g of hydrogenated vegetable oil is equivalent to three dinner plates, and a 1 in. watchglass containing 0.12 g is equivalent to one plate. The dishwashing solution was 0.12 g of sodium dodecyl sulfate and 0.024 g of additive dissolved in 400 ml of local tap water (100 ppm hardness) at 114 F. Pure sodium dodecyl sulfate was used as the active ingredient, because it had poor stability by itself (two plates) and responded well to additives. Foam stabilizing power of amides by this test are listed on Table IV.

Results and Discussion

Exploratory experiments were carried out on the direct oxyethylation and oxypropylation of simple amides. Pelargonamide was used so that the products could be analyzed by vapor phase chromatography. Conventional oxyalkylations carried out at 120–140 C in the presence of less than 1% base failed, because the catalyst was quickly used up in hydrolyzing the amide. A study of reaction conditions indicated that best yields and purities were obtained at high catalyst ratios and at lower temperature in a closed reaction

TABLE III

Krafft Points[a] of Detergent Mixtures
0.2% Alkanolamide + 0.8% Sodium Methyl α-Sulfopalmitate, C

Amide	Pelargonic	Lauric	Palmitic	Stearic	Oleic
Ethanolamide	24	30	61	67	28
3-Propanolamide	27	41	65	62	....
2-Propanolamide	26	26	53	59	....
Diethanolamide	....	25	26	33	27
Diglycolamide	27	25	44	52	29
N-Methylethanolamide	26	23	28	36	27

[a] Temperature at which the mixture becomes clear on gradual heating.

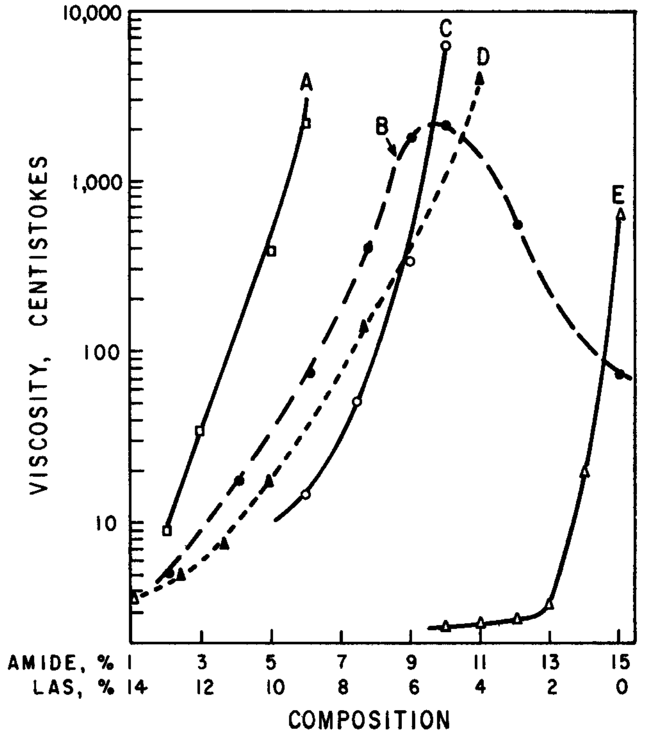

FIG. 1. Log viscosity vs. composition for mixtures of amides with linear alkylbenzene sulfonate. Total concentration 15%. (A) Diethanolpalmitamide; (B) diethanollauramide; (C) diethanolpalmitamide plus 2.2 moles ethylene oxide; (D) diethanolpalmitamide plus 2.06 moles propylene oxide; (E) diethanolpalmitamide plus 4.45 moles ethylene oxide.

system. Table II shows a typical analysis of a product from the reaction of 1.11 moles of propylene oxide with one mole of pelargonamide in the presence of 10% sodium methoxide by weight at 60–75 C. Composition of a product from the addition of 0.92 moles of propylene oxide to a mole of hydroxyethylpelargonamide is included for comparison. The high content of nonoxyalkylated amide made the former product unsatisfactory for use as a detergent additive. The oxyalkylation of hydroxyethylamides, however, led to products which were of interest as detergent additives or for sulfation.

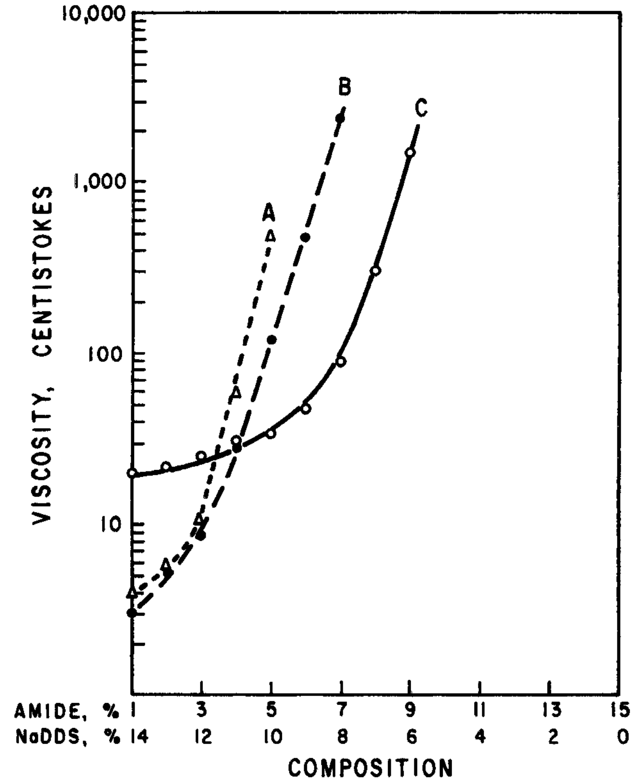

FIG. 2. Log viscosity vs. composition for mixtures of amide with sodium dodecyl sulfate. Total concentration 15%. (A) Diethanolpalmitamide; (B) diethanollauramide; (C) diethanolpalmitamide plus 2.2 moles of ethylene oxide.

TABLE IV

Foam Stabilization of Sodium Dodecyl Sulfate Solution[a]

Amide	Plates Washed[b]				
	Pelargonic	Lauric	Palmitic	Oleic	Stearic
2-Hydroxypropyl amide	0	10	9	..	4
N-methyl,N-2-hydroxyethylamide	7	19	25	..	19
Diglycolamide	6	22	24	8	13
Hydroxyethylamide plus 1 mole propylene oxide	..	....	4	..	....
Diethanolamide	4	11[c]	4	8	....
Diethanolamide plus 2 moles ethylene oxide	..	....	7	..	10
Diethanolamide plus 1.5 moles propylene oxide	..	....	0	..	....

[a] Sodium dodecyl sulfate alone shows foam dissipation after two plates in this test.
[b] Foam stability measured by miniature dishwashing test (7).
[c] Commercial product.

Although most of the long chain alkanolamides were insoluble in water, they were solubilized by water soluble detergents such as LAS, sodium methyl α-sulfopalmitate, or sulfated dioxypropylated hexadecanol. Each alkanolamide had a critical solution temperature, similar to a Krafft Point, which was independent of the surfactant used, the ratio of surfactant to amide up to 1:4, and the total concentration and presence of hard water ions. The temperature at which the cloud reforms on cooling is not as reproducible as the clarification temperature.

Krafft Points for 0.2 g of amide and 0.8 g of sodium methyl α-sulfopalmitate dissolved in 100 ml of distilled water have been listed on Table III. These values serve as a means of characterizing the amide and as a guide to compatability with more soluble detergents. The data of Table III demonstrate the good solubility of diethanolamides and methyl ethanolamides in detergent mixtures.

Table V shows use of alkanolamides to increase the solubility of sodium octadecyl sulfate, which has a Krafft point of 56 C. For this series of experiments concentrations are standardized at 0.20% alkanolamide and 0.80% sodium octadecyl sulfate, but similar results were obtained at lower total concentration. All of the amides lowered the Krafft point of sodium octadecyl sulfate, but oxypropylated diethanolamides

TABLE V

Effect of Alkanolamides on Krafft Point, °C
0.80% Sodium Octadecyl Sulfate[a] + 0.20% Alkanolamide

Amide	Fatty acid				
	Pelargonic	Lauric	Palmitic	Stearic	Oleic
Hydroxyethylamide	50	45	50	....	....
2-Hydroxypropyl-amide	49	52	48	....	....
N-Methyl,N-hydroxyethyl amide	47	50	49	....	52
Diethanol amide	46	51	....	54	54
Diglycol amide	51	49	50	....	58
Oxypropylated hydroxyethylamide	50	....	50	....	....
Oxypropylated diethanolamide	46	....	48	46	....
Oxyethylated diethanolamide	....	....	49[b]	50[b]	....

[a] Pure sodium octadecyl sulfate has a Krafft Point of 56 C.
[b] Krafft Point was not sharp. Amount of oxyethylation is 2.2 and 3.4, respectively.

were the most effective. These amides also lowered the Krafft point for solutions of disodium α-sulfostearate, another surfactant with limited solubility.

Several of the alkanolamides were effective emulsifiers at the 1% level. Diethanololeamide and diglycololeamide formed emulsions with petrolatum and water which were stable for more than a month. Diethanolpelargonamide produced a carbon tetrachloride-water emulsion that was stable for about 24 hr, and the emulsion formed by diglycol pelargonamide in the same system was stable for more than 8 hr. All of the 2- and 3-hydroxypropylamides, regardless of fatty acid chain length, were not effective emulsifiers for any of these systems. Attempts to explain differences in emulsifying power by relating to HLB or polarity index (8) were unsuccessful.

Figure 1 shows the change of viscosity with composition for 15% aqueous solutions containing mixtures of amide and LAS. The product from the addition of two moles of ethylene oxide or propylene oxide to diethanolpalmitamide had about the same effect on viscosity as diethanollauramide in the range 20–60% amide. The curve shown for diethanollauramide prepared in the laboratory is in good agreement with the results reported for the commercial material derived from coconut oil (9).

Figure 2 shows similar effects on mixtures of sodium dodecyl sulfate with some of these amides.

Our experience with the miniature dishwashing test of Anstett and Schuck (7) gave sharp end points at 28 to 35 plates for established commercial liquid products. Commercial sodium lauryl sulfate, ether alcohol sulfate and LAS alone gave values of 25, 30 and 25 plates respectively, and addition of amide to those systems resulted in little or no change. LAS compositions had the further disadvantage of giving foam disappearance end points over a greater number of plates. Pure sodium dodecyl sulfate was found to be the best material for this test, because it had poor foam stability by itself (two plates) and was sensitive to foam stabilizing action. Sawyer and Fowkes (10) state that primary alcohol sulfates, as a class, are the most susceptible to foam stabilization.

Table IV shows that N-methyl,N-hydroxyethylamides and diglycolamides have the best stabilizing action with sodium dodecyl sulfate. Addition of oxyethyl groups often increased foam stabilization, but oxypropylation reduced it. The pelargonic acid chain was too short for this purpose. Table IV along with viscosity and other properties suggests that oxyethylated amides of stearic and particularly palmitic acid may be considered as a potentially beneficial additive to detergent formulations.

REFERENCES

1. Kritchevsky, T.H., Soap Chem. Spec. 34(11): 48–50 (1958).
2. Dutton, K.R., and W.B. Reinisch, Mfg. Chem. 28(3): 124–127 (1957).
3. Weil, J.K., N. Parris and A.J. Stirton, JAOCS 47: 91–93 (1970).
4. Weil, J.K., N. Parris and A.J. Stirton, Ibid. 48: 35–37 (1971).
5. Jungermann, E., and D. Taber, "Nonionic Surfactants," Edited by M.J. Schick, Marcel Dekker, Inc., New York, 1967, p. 208–246.
6. Carnes, J.J., U.S. Patent 2,520,381 (1950).
7. Anstett, R.M., and E.J. Schuck, JAOCS 43: 576–580 (1966).
8. Metcalfe, L.D., Presented at the AOCS Meeting, New Orleans, 1970, Paper No. 62.
9. Sanders, H.L., O.E. Libman and Y.G. Kardish. Chem. Spec. Mfr. Assoc. Proc. 1955 Dec.: 176–180.
10. Sawyer, W.M., and F.M. Fowkes, J. Phys. Chem. 62: 159–166 (1958).

[Received March 15, 1971]