Cosulfation of Fatty Acid Alkanolamides and Lower Molecular Weight Alcohols[1]

R.G. BISTLINE, JR., W.R. NOBLE, F.D. SMITH, and **W.M. LINFIELD,**
Eastern Regional Research Center, ARS, USDA, Philadelphia, PA 19118

ABSTRACT AND SUMMARY

The process for the sulfation of tallow isopropanolamide or of a 50:50 mixture of tallow diglycolamide and isopropanolamide with chlorosulfonic acid was studied. The major obstacle to complete and uniform sulfation was the high viscosity of the sulfation mix. This could be overcome most advantageously by cosulfation with lower molecular weight alcohols, preferably isopropanol. The most fluid reaction mix and product were prepared from the mixed amides. No chlorinated solvent is required for such cosulfations.

INTRODUCTION

Soap compounded with various anionic lime soap dispersing agents (LSDA) has been found to wash fabric in hard and soft water as efficiently as commercial high phosphate detergents (1). Among the anionic LSDAs studied, the sulfated tallow alkanolamides appeared attractive from a performance as well as from an economic point of view.

Since monoethanolamine is the least expensive alkanolamine, a sulfated tallow monoethanolamide would appear to be the most likely candidate for a practical lime soap dispersant. However, the sulfated fatty monoethanolamindes were found to be less hydrolytically stable than the sulfated fatty monoisopropanolamides (2). On the other hand, sulfated fatty diglycolamides were found to be substantially more stable than either the above (3,4). A sulfated 50:50 mixture of the isopropanolamide and diglycolamide of tallow fatty acid appeared to be the most suitable lime soap dispersant of the sulfated alkanolamide class (5).

The sulfated fatty alkanolamides were first synthesized over forty years ago (6,7) and were found to be effective detergents. This type of surfactant has been produced intermittently on a commercial scale with the aid of a variety of sulfation techniques with varying degrees of success. According to Dutton and Reinisch (8), it is extremely difficult to control the sulfation procedure to insure that the product is free from undesirable by-products which impair efficiency. It is unusual for fatty alkanolamides to achieve maximum sulfation. There are several reasons for this: (a) The high viscosity of the molten alkanolamides prevents effective mixing with the sulfating agent which is usually chlorosulfonic acid; (b) the resulting unneutralized sulfated alkanolamides are even higher melting and much more viscous than the alkanolamides so that intimate contact with the sulfating agent is increasingly impeded; and (c) neutralization of such hot viscous material is difficult and slow, and a substantial amount of hydrolysis may occur during this step. The viscosity problems can be partially alleviated by sulfation at high temperatures (60-100 C), which leads to charring and side reactions (9). The use of large amounts of inert solvents such as dichloroethane, methylene chloride, carbon tetrachloride or 1,1,1-trichloroethane, eliminates the viscosity problem and the need for elevated temperatures. However, removal of solvents from such surfactant solutions by distillation is difficult and impractical on a commercial scale. Thus the solvent would have to remain in the product which would add to its cost, and removal of the solvent in the subsequent spray drying of the finished detergent slurry would cause a substantial safety and environmental hazard. Sulfation of a 50:50 mixture of isopropanolamide and diglycolamide of tallow fatty acid, as mentioned above, resulted in a product of improved hydrolytic stability (5). In addition, because of the lowered melting point of the mixed amide and lower viscosity of the sulfated product, some of the processing difficulties could be alleviated. However, some chlorinated solvent was still required to effect smooth sulfation.

Because of the attractive lime soap dispersing and detergency properties of the sulfated alkanolamides, the present process study was undertaken with the following three objectives: (a) Elimination of use of chlorinated solvent, (b) achievement of high sulfation yields, and (c) attainment of industrially feasible reaction conditions of low viscosity and moderate temperatures. These goals were reached most readily through cosulfation of the amides with low molecular weight alcohols as is shown below.

EXPERIMENTAL PROCEDURE

Materials

Methyl esters of tallow fatty acids (TE1618) were supplied by Procter and Gamble Chemical Division, Cincinnati, OH. 1-Amino-2-propanol (isopropanolamine) was purchased from Aldrich Chemical Co., Milwaukee, WI. 2(2-Aminoethoxy)-ethanol (diglycolamine) and chlorosulfonic acid were obtained from Matheson, Coleman and Bell, Norwood, OH.

Synthesis

Preparation of tallow alkanolamides: Methyl tallowate, 16.70 g (6.1 moles), and 1-amino-2-propanol, 490 g (6.2 moles), were heated at 145-155 C with stirring under nitrogen atmosphere for 18 hr or longer until an IR spectrum indicated a low amount of ester present, according to the calibration curve described below. Vacuum was then applied to remove methanol and unreacted 1-amino-2-propanol. Yield = 1,960 g (98% yield) containing 3% unreacted ester and 3% free amine. Tallow diglycolamide was prepared similarly from methyl tallowate and 2(2-aminoethoxy)-ethanol in 98% yield and contained 2% unreacted ester and 2% free amine. Mixed tallow alkanolamide, a 50:50 mixture of the tallow monoisopropanolamide and tallow diglycolamide prepared simultaneously, was obtained in 97.3% yield and contained 2% ester and 2% free amine. The alkanolamides are very hydroscopic and care must be taken to avoid moisture adsorption from the air.

Sulfations: The following serve as examples of the sulfation procedure used.

Neat sulfation: Tallow isopropanolamide, 100.2 g (0.305 mole), was sulfated with chlorosulfonic acid, 42.7 g (0.37 mole), at 55-60 C over a period of 80 min. The sulfated amide was quite viscous and was heated at 65 C so that it could be removed from the reaction flask. Hydrogen chloride vapors were removed by application of slight vacuum. Potassium hydroxide, 25 g (0.45 mole), dissolved in 20 ml distilled water and 20 g isopropanol, was required for neutralization to pH 9-9.5. This product was dark

---

[1] Presented at the AOCS Meeting, Chicago, September 1976.

TABLE I

Reaction Conditions and Analyses, Sulfated Tallow Alkanolamides

Number	Type of tallow amide	Cosulfation alcohol	%[a]	%[a] 1,1,1-Trichloroethane	Reaction Temperature C	Acid sulfated amide liquid at C	Active Ingredient Solid	% Sulfation
1	Isopropanolamide	---	---	---	60[b]	65	0.46	53
2		---	---	80	45[b]	60	0.41	53
3		Methanol	10	25	40	40	0.70	105
4		Etahnol	10	25	40	40	0.86	105
5		Isopropanol	10	25	45	40	0.83	95
6		Isobutanol	10	25	40	40	0.83	100
7		2-Ethylhexanol	10	25	45	50	0.89	102
8		Tergitol 15-S-12[c]	12	10	45[b]	65	0.42	52
9		Methanol	10	---	45	45	0.60	85
10		Methanol	15	---	40	30	0.59	93
11		Isopropanol	10	---	45	55	0.69	87
12		Isopropanol	15	---	40	40	0.51	80
13		Isopropanol	20	---	40	30	0.53	82
14		n-butanol	10	---	40	50	0.67	88
15		Isobutanol	20	---	40	30	0.57	86
16		2-butanol	10	---	45	55	0.51	77
17		2-butanol	20	---	40	30	0.49	75
18	Mixed alkanolamides	Isopropanol	10	25	45	35	0.66	94
19		Isopropanol	15	---	45	35	0.66	88
20		Isopropanol	20	---	40	20	0.61	91
21		n-butanol	10	---	40	25	0.80	99
22		n-butanol	15	---	40	23	0.60	86
23		Carbowax 200[d]	10	---	50[b]	60	0.43	60

[a] Basis weight of amide.

[b] Solidified at reaction temperature.

[c] Tergitol 15-S-12, Union Carbide Corp., Nonionic containing C_{11}-C_{15} alcohols plus 12 moles ethylene oxide.

[d] Carbowax 200, Union Carbide Corp., Polyethylene glycol average molecular weight 200.

TABLE II

Degree of Sulfation

Chlorosulfonic acid	
Alkanolamide + Isopropanol molar ratio	% Sulfation[a]
1.00:1	76
1.05:1	89
1.10:1	93
1.15:1	98
1.20:1	102

[a] Determined by Cahn Test Method (10).

colored. Yield: 203.1 g of a solution containing 36.2% active ingredient and corresponding to 53.2% sulfation.

Cosulfation procedure: The mixed tallow alkanolamide, 108.4 g (0.32 mole), was melted (about 50 C) and isopropanol, 20 g (0.33 mole), was added. The mixture was cooled to 40 C and chlorosulfonic acid, 92.1 g (0.78 mole), was added dropwise over a 75 min period. Rapid chlorosulfonic acid addition causes a severe foaming problem due to the generation of excessive amounts of hydrogen chloride gas. The reaction temperature was maintained at 40-45 C by means of a cold water bath. Upon completion of addition, agitation was continued at 30-40 C for a half hour while HCl vapors were removed under a slight vacuum. A small sample was removed, neutralized to pH 8-9, and analyzed for active ingredient content by cationic titration. An active ingredient content of 66.3% corresponds to 100% sulfation. A 95-100% sulfation was desirable. If the sulfation yield of the unneutralized sulfated alkanolamide was below 95%, more chlorosulfonic acid was added until 95% was attained.

The sulfated alkanolamide was neutralized continuously with potassium hydroxide with a potassium cabonate buffer system. Potassium carbonate, 14 g (0.1 mole), was dissolved in 15 ml distilled water, cooled at 20 C, and placed in a four neck, 1 liter round flask. Potassium hydroxide, 50 g (0.9 mole), was dissolved in 50 ml distilled water, cooled to 20 C, and placed in an addition funnel. The hydroxide solution was added to the carbonate solution as needed. The sulfated mixed tallow alkanolamide, which was quite fluid at room temperature, was poured in a thin stream into the alkaline solution, the temperature of which was maintained at 25-30 C. The potassium hydroxide solution was added in about ten increments at a point when the reaction mass began to effervesce. Isopropanol (80 g) was added in portions to the neutralization mixture in order to reduce viscosity. A total of 47.9 g of potassium hydroxide was required for neutralization to pH 9-10. Hydrogen peroxide, 5 g of a 30% solution, was added to bleach the product. Adequate provision must be made for foaming encountered in this step. The product was a soft paste which liquified at 30-35 C. Yield = 321 g containing 42.7% active ingredient corresponding to 91% of theory, solids content 70.2%. Other cosulfations were run similarly, and the reaction conditions and yields are shown in Table I.

Variation of chlorosulfonic acid/amide and Isopropanol Ratio

A series of cosulfation experiments of tallow isopropanolamide and isopropanol in the presence of 25% 1,1,1-trichloroethane was carried out in which the ratio of chlorosulfonic acid to alkanolamide plus isopropanol was changed and the degree of sulfation was determined (Table II).

Alcoholysis

The stability at 40-45 C of the unneutralized sulfated tallow isopropanolamide as a function of time was established in the following manner. Samples were withdrawn at 1 hr intervals from the sulfated reaction mixture and neutralized rapidly to pH 8-9. Each sample was then analyzed for active ingredient by cationic titration according to Cahn (10). The extent of transesterification of the acid sulfate with isopropanol was studied in the following manner. Isopropanol, 10 g (0.17 mole), was added to 0.16 mole of unneutralized sulfated tallow isopropanolamide and the active ingredient content after fixed time intervals was determined as indicated above. The results are shown in Figure 1.

Analyses

Free amine content of tallow alkanolamides was determined according to AOCS Test Method Nb 3-62.

Free ester content of alkanolamides was determined with the aid of a standard calibration curve from IR Spectra (ester absorption at 5.75μ and amide at 5.95μ) of known blends of amide and methyl tallowate. Purified stearic monoisopropanolamide, containing methyl tallowate at levels of 2.5, 5.0, 7.5, and 10%, respectively, was dissolved in chloroform, 2 g/100 ml total concentration, and the relative intensity of absorption was measured in a 0.5 mm cell in a Perkin-Elmer 257 Infrared Spectrophotometer. The ratio of absorption intensities $\frac{\text{ester } 5.75\mu}{\text{amide } 5.95\mu}$ plotted against the mole ratio $\frac{\text{ester}}{\text{amide}}$ formed a straight line. The calibration curve is given in Figure 2.

Percent active ingredient (a.i.) and degree of sulfation were determined by titration with 0.001 N solution of Hyamine 1622 (Rohm and Haas Co., Philadelphia, PA). Sulfated tallow alkanolamide, 0.5 g, was neutralized with sodium bicarbonate to pH 7, and the volume was made up to 1 liter with distilled water. A 10 ml aliquot, together with 10 ml chloroform, was placed in a 50 ml stoppered graduate cylinder and the indicator, 2,7-dichloro fluorescein (0.1% in 70% ethanol), 5 drops, was added. The end point was reached when the chloroform layer became slightly pink.

$$\%\,\text{a.i.} = \frac{10\text{ ml} \times \text{N} \times \text{Titer} \times \text{Molecular Weight (Sulfated Amide)}}{\text{Sample Weight}}$$

$$\%\text{ of sulfation} = \frac{\%\,\text{a.i.} \times 100}{\%\text{ theoretical a.i.}}$$

Physical and Surface Active Properties

The following two tests were carried out on each sample for "quality control" purposes.

Lime soap dispersant requirement (LSDR) was determined according to the method of Borghetty and Bergman (11).

Detergency measurements were carreid out in 300 ppm hard water in the Tergotometer at 120 F with three types of test soiled cloths, EMPA 101 cotton (EMPA, St. Gallen, Switzerland.), (EMPA), U.S. Testing Company Cotton (Hoboken, NJ) (UST), and Testfabrics (Middlesex, NJ) polyester-cotton blend with permanent press finish (TF). The tests were carried out as described in previous publications by Weil and co-workers (4,12). Solutions of 0.2% detergent in 300 ppm hard water were prepared of ternary mixtures containing 65% tallow soap, 20% lime soap dispersant, and 15% sodium silicate (Na_2O:SiO_2 = 1.:1.6). The detergency and LSDR data of all samples which were obtained in greater than 70% sulfation (see Table I) were identical within the limits of experimental error and are not shown.

RESULTS AND DISCUSSION

Since purification of the intermediate alkanolamides or of the finished sulfates is not feasible, it is extremely important that the reactions be run to completion as much as possible. The presence of unreacted fatty ester can depress detergency. Unreacted alkanolamine, residual methanol, glycerol, or moisture in the amide would require additional sulfating agents and give rise to inert nonsurface active by-products.

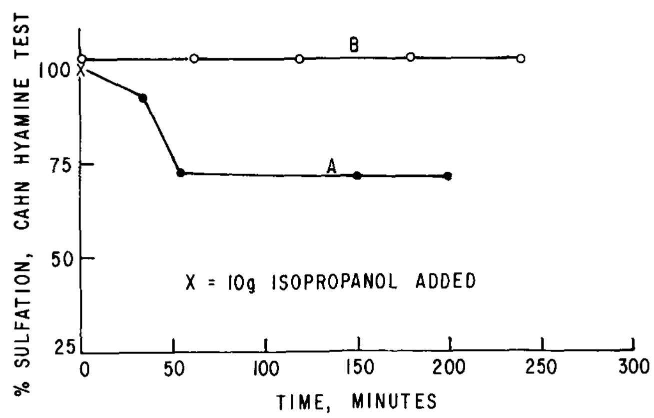

FIG. 1. Stability of sulfated tallow isopropanolamide at 40-45 C. Curve A – after addition of 0.17 mole of isopropanol; Curve B – no addition.

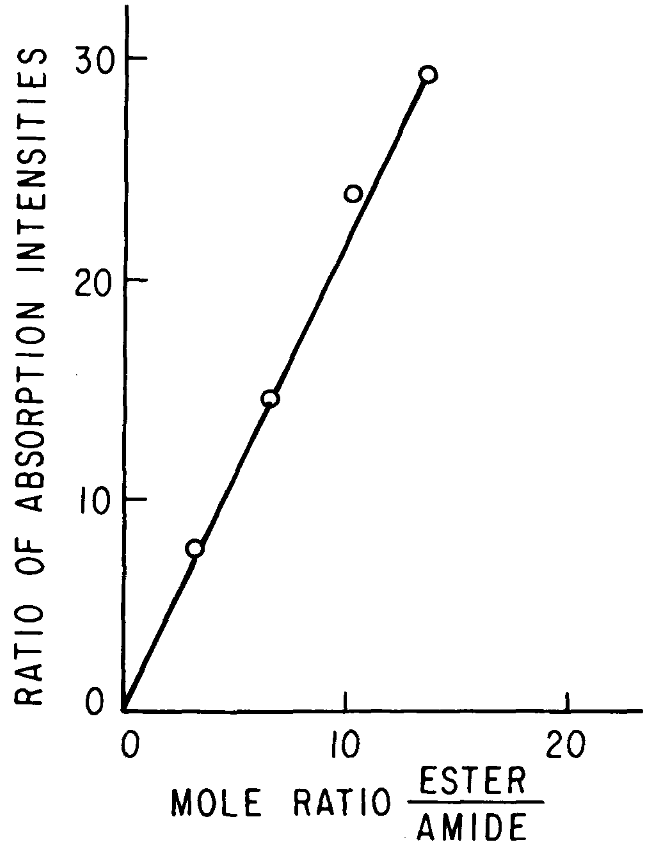

FIG. 2. Standard calibration curve, ratio of absorption intensities,

$$\frac{\text{ester } 5.75\mu}{\text{amide } 5.95\mu} \text{ vs. mole ratio } \frac{\text{ester}}{\text{amide}}.$$

The fatty alkanolamides were prepared either from tallow fatty acid or methyl tallowate by conventional technology. When fatty acid was used, a reaction period of 4-5 hr at 140-150 C was generally adequate to attain a 91% completion of the reaction. The course of the reaction was followed easily by free fatty acid titration. Since amidation of the acids leads to by-products as disclosed by Garrison et al. (13), the amidation of ester was the preferred route. Amidation of the methyl ester required usually 15-18 hr to reach a 98% completion of the reaction. Use of an alkaline catalyst did not offer any tangible advantage. Residual ester was determined by IR absorption spectroscopy with the aid of a calibration curve as shown in Figure 2. Preparation of the amides directly from tallow glyceride offers no advantage, since the glycerine formed in the reaction must be washed out thoroughly, which is a tedious procedure. A typical alkanolamide in this study contained up to 3% methyl ester or fatty acid and up to 3% unreacted amine.

Since the tallow derived hydrophobic portion of the surfactant molecule contains some unsaturation, attack by the sulfating agent upon the double bond can occur, although Weil et al. (3) found that the presence of the amide group gives some protection. We have observed that with a sufficient excess of chlorosulfonic acid, yields of sulfation above 100% [as determined by catonic titration (10)] can be obtained, which indicates the presence of more than one anionic functional group in the molecule. We have experimentally determined that 20% molar excess of chlorosulfonic acid results in a sulfation yield of 95-100% (Table II), and disulfation (or sulfonation) is kept to a minimum. Subsequent sulfations were carried out using this molar excess of chlorosulfonic acid.

In an effort to lower the viscosity of the unneutralized sulfation mixture, initially isopropanol was added to the unneutralized product. Unfortunately, as Figure 1, Curve A, shows, alcoholysis set in immediately so that the active anionic surfactant content of the product was reduced until an equilibrium was attained between the alkanolamide sulfate and isopropyl sulfate. This equilibrium at 75% was unexpected but was not explored further. The unneutralized sulfated amide was quite stable at 40-45 C, as indicated by Curve B.

The results of the various sulfations are summarized in Table I. Neat sulfation or sulfation in the presence of 80% chlorinated solvent were both unsatisfactory. Cosulfation of the isopropanolamide with 10% of a low molecular weight alcohol in a relatively small amount of chlorinated solvent brought about a drastic improvement in yield but the sulfated products still had to be maintained at 40 C or above to retain fluidity. Cosulfation with higher molecular weight alcohols such as 2-ethylhexanol or a nonionic surfactant (Tergitol 15-S-12) did not impart the degree of fluidity as was obtained with lower molecular weight alcohols.

Since the chlorinated solvent appeared to contribute very little to the fluidity of the cosulfated products, a series of cosultations without the solvent was carried out. This series of sulfations (9-16) indicated that by the use of 15-20% low molecular weight alcohol, the sulfated product attained about the same fluidity (in terms of temperature at which the product remains liquid) as could be achieved with the use of 10% alcohol and 25% chlorinated solvent. A further improvement in fluidity was accomplished by switching from the straight tallow isopropanolamide to the mixed amide in the cosulfation with isopropanol. A polyglycol, such as Carbowax 200 (No. 20), proved to be an unsatisfactory cosulfation alcohol for the mixed amide.

Because of poor sulfation yields, runs 1, 2, 8, and 23 gave poor detergency results. All the other sulfated batches gave good detergency data and there were no statistically significant differences between the runs, hence no detergency data are reported here.

In summary, we have found that the most manageable sulfation can be achieved by the cosulfation of the mixed tallow alkanolamides with 15-20% of a lower molecular weight alcohol. Because of their relatively low cost, only methanol and isopropanol need to be considered here, and isopropanol has a distinct advantage over methanol since it requires only about one-half the amount of chlorosulfonic acid for complete sulfation.

ACKNOWLEDGMENTS

The authors are indebted to Carl Pierce for experimental data and Annette Kravitz for detergency evaluation.

REFERENCES

1. Noble, W.R., R.G. Bistline, Jr., and W.M. Linfield, Soap Cosmet. Chem. Spec. 48(7):38 (1972).
2. Weil, J.K., N. Parris, and A.J. Stirton, JAOCS 47:91 (1970).
3. Weil, J.R., N. Parris, and A.J. Stirton, Ibid. 48:35 (1971).
4. Weil, J.K., and A.J. Stirton, "Sulfated Monoglycerides and Sulfated Alkanolamides"; "Anionic Surfactants," Edited by W.M. Linfield, Marcel Dekker, Inc., New York, NY 1976, pp. 219-232.
5. Bistline, Jr., R.G., W.R. Noble, and W.M. Linfield, JAOCS 50:294 (1973).
6. Guenther, F., F. Munz, and H. Haussmann, (I.G. Farbenindustrie), U.S. Patent 1,932,180 (1933).
7. Orelup, J.W., U.S. Patent 1,981,792 (1934).
8. Dutton, R., and W.B. Reinisch, Manuf. Chemist 28:124 (1957).
9. Henry, R.A., (The Proctor & Gamble Co.), U.S. Patent 2,551,125 (1951).
10. Cahn, F.J. (Emulsol Corp.), U.S. Patent 2,471,861 (1949).
11. Borghetty, H.C., and C.A. Bergman, JAOCS 27:88 (1950).
12. Weil, J.K., F.D. Smith, and W.M. Linfield, Ibid. 49:383 (1972).
13. Garrison, L.J., J.H. Paslean, and M.S. Edmundson, Deter. Age 5:(1):27, 98 (1968).

[Received May 5, 1977]