Thermal Rearrangement of Sulfated Tallow Alkanolamides

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ABSTRACT

A study of reaction variables in the sulfation of tallow alkanolamides revealed that a molecular rearrangement to aminoester occurs as a result of prolonged heating in the unneutralized state. Heating sulfated isopropanolamide for 4 hr at 60 C resulted in a 60% loss of active ingredient. The sulfated diglycolamide heated at 60 C for 12 hr suffered a loss of 22% active ingredient. A 50:50 mixture of these sulfated alkanolamides heated for 12 hr at 40 C incurred no loss of active ingredient content, whereas at 60 C a 40% loss of active ingredient was observed. Thus, careful temperature control and rapid neutralization after sulfation are required to obtain sulfated alkanolamides with a high percentage of active ingredient.

INTRODUCTION

Sulfated alkanolamides are a class of highly efficient surfactants whose synthesis, via the Schotten-Baumann reaction, was first reported by Guenther et al. (1). A more commercially feasible procedure, the direct sulfation of alkanolamides, was subsequently described by Orelup (2). Weil et al. (3) described surface active properties, such as critical micelle concentration, calcium ion stability, foaming ability, lime soap dispersing power and detergency of pure sulfated alkanolamides. These authors also noted the sulfated alkanolamides hydrolyzed in alkaline as well as acid media. Lilienfeld (4) found that the pH of soap stabilized the sulfate ester bond and prevented hydrolysis. Noble et al. (5) showed the feasibility of compounding soap with sulfated alkanolamides and sodium silicate builder to obtain a detergent which, in laboratory screening tests, equaled the washing performance of a commercial control detergent that contained ca. 50% sodium tripolyphosphate.

The sulfated alkanolamide used for this soap-based detergent was the product of the cosulfation of equal parts of the diglycolamide and isopropanolamide of tallow fatty acid and 10% n-butanol (6-8); the sulfation was carried out in the absence of solvent at 40-45 C. A 95-100% conversion of the alkanolamide to the sulfate was achieved in the laboratory under these conditions. Problems resulted, however, when the synthetic procedure was scaled up.

Since in production scale batch equipment, heat transfer was generally poor and agitation somewhat inadequate, a longer sulfation time and temperatures of 50 C or above were frequently required. The product formed under such conditions before neutralization showed a reduced active ingredient content. The neutralized product displayed much poorer surface active properties than expected from just a reduction in active ingredient content. These findings suggest a molecular rearrangement had occurred other than hydrolysis, since the active ingredient was lost in the acidic state when no water was present. The literature shows several related studies that also suggest rearrangements of alkanolamides.

Desnuelle et al. (9) revealed that aliphatic N-(2-hydroxyethyl) amides were readily converted into the corresponding aminoesters $RCOOCH_2CH_2NH_2$ at 135 C in the presence of dry HCl. After standing at room temperature, the aminoesters were reconverted into the alkanolamides. Trowbridge and coworkers (10) reported that, under acidic conditions, the lauric acid diethanolamide rearranged to the unstable aminoester and reconverted to the alkanolamide. Smith et al. (11) observed a similar conversion of α-sulfo fatty alkanolamides to the aminoester and reversion to the alkanolamide after standing. Makino and coworkers (12) investigated the sulfation of various fatty acid alkanolamides and found the reaction products contained several types of byproducts such as aminoesters, amidoester ($RCONHCH_2$-CH_2OOCR) and other unidentified substances. The amount of byproduct was dependent on the structure of the initial alkanolamide. After standing at 60-80 C, the acid sulfated alkanolamide was transformed into aminoester and amidoester. Makino concluded that aminoester was formed in the sulfation process concurrently from both the alkanolamide and its sulfation product by rearrangement during synthesis of these compounds. The presence of aminoester and amidoester in the sulfated alkanolamide resulted in a detergency loss. Since the neutralized sulfated alkanolamides were relatively stable, it was theorized that rearrangement occurred only in the unneutralized state.

Our objective was to study the effects of time and temperature on the sulfation reaction and to determine the chemical nature of the products formed.

EXPERIMENTAL PROCEDURES

Materials

Methyl esters of tallow fatty acids (TE1618) were supplied by Procter and Gamble Chemical Division, Cincinnati, OH. 1-Amino-2-propanol (isopropanolamine) and chlorosulfonic acid were purchased from Aldrich Chemical Co., Milwaukee, WI. 2-(2-Aminoethoxy)ethanol (diglycolamine) was obtained from MCB Manufacturing Chemists, Inc., Cincinnati, OH. Hyamine 1622 is a product of the Rohm and Haas Co., Philadelphia, PA. Dichlorofluorescein was supplied by Eastman Kodak Co., Rochester, NY.

Synthesis

Preparation of tallow alkanolamides. Mixed tallow alkanolamides, tallow monoisopropanolamide and tallow diglycolamide were prepared from fatty acid methyl esters and isopropanolamine and/or diglycolamine, according to the method described in a previous publication (7). Mixed tallow alkanolamide is a 50:50 mixture of tallow monoisopropanolamide and tallow diglycolamide.

Preparation of sulfated tallow isopropanolamide (STIA). Tallow isopropanolamide, 113.1 g (0.34 mol), was melted at 55 C, and n-butanol, 11.5 g (0.16 mol), was added. The mixture was cooled slightly to 50 C, and chlorosulfonic acid, 70.9 g (0.61 mol), was added by drops over a 90 min period. Rapid chlorosulfonic acid addition caused severe foaming, resulting from the generation of excessive amounts of hydrogen chloride gas. Upon completion of the addition, agitation was continued for ½ hr while hydrogen chloride vapors were withdrawn under a slight vacuum. A 1 g sample of STIA was removed, neutralized rapidly to pH 8-9 and analyzed for the percentage of active ingredient by the Cahn test (13). An active ingredient content of 69.7%, which corresponded to 97% sulfation, was obtained. The unneutralized product STIA was then held at 60 ± 1 C for 12 hr, and small samples were withdrawn at periodic

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intervals to determine the sulfated alkanolamide content by cationic titration (13). The titration data are plotted in Figure 1. At the conclusion of the 12-hr aging period, STIA, 128 g (0.31 mol), was neutralized to pH 9-10 by pouring it slowly into an aqueous solution of sodium hydroxide, 19.0 g (0.48 mol), and sodium carbonate, 11.3 g (0.11 mol), in 50 ml distilled water, and dried to constant weight in a vacuum oven at 50 C.

Preparation of sulfated tallow diglycolamide (STDA). The sulfation of the diglycolamide was carried out by cosulfation with 10% n-butanol as described above for STIA. The finished acid sulfate was held at 60 ± 1 C, and samples were taken periodically during a 12-hr aging period, after which the batch was neutralized and dried to constant weight as described earlier for STIA. The titration results during aging are shown in Figure 1.

Preparation of sulfated tallow alkanolamide mixture (STAM). STAM was prepared by cosulfation with 10% butanol as described earlier for STIA and held at 40 ± 1 C for a 12-hr aging and sampling period as described above. Similarly, batches of STAM were aged for 12 hr at 50 ± 1 C and 60 ± 1 C, respectively. The neutralized batches of STAM were then dried to constant weight and analyzed as described below. The sulfated alkanolamide data collected during the aging period are shown in Figure 1.

Ether Extraction. The dried samples of STIA, STDA and STAM were extracted in the following manner. A 30 to 40 g sample of neutralized, sulfated amide was extracted for 16 hr with diethyl ether in a Soxhlet apparatus. The ether extract was evaporated to dryness and weighed to determine the percentage of ether-extractable components. The results are recorded in Table I. The aminoester content was determined by two methods. First, the saponification equivalent, by a modified AOCS procedure (14), was calculated using a smaller sample weight than specified by the AOCS method. This test method gave the ester content of the ether extract. In addition, a direct titration with standard acid, according to AOCS Test Methods N-3-62 and N-4-62, gave the aminoester content in terms of free amine. Since we found essentially no differences between the aminoester content data obtained by these two methods, only the saponification data are recorded in Table I.

The alkanolamide content was calculated by differences between the total ether extractable material and the aminoester content. Infrared (IR) spectra of the ether extracted material showed the presence of large amounts of amide as well as some ester.

The residue in the Soxhlet thimble was then extracted with absolute ethanol for 16 hr. The alcohol extract was evaporated and dried to constant weight. The alcohol-insoluble residue was also dried to constant weight. The data are recorded in Table I. The sulfated alkanolamide content of the alcohol extract residue was determined by cationic titration (13), using a standard solution of Hyamine 1622 as titrant and dichlorofluorescein as indicator. The sodium butyl sulfate content of the alcohol extract was calculated by difference (Table I).

The alcohol insolubles were analyzed for inorganic content (essentially Na_2SO_4) by the sulfated ash ignition method (15). The small amount of sulfated alkanolamides present in the alcohol insoluble fraction was determined by cationic titration as described above.

Cationic titrations for the determination of sulfated alkanolamides were also carried out on the freshly sulfated unaged samples which were neutralized and dried to constant weight. Similarly the whole aged neutralized and dried samples were analyzed for sulfated alkanolamide content before extraction. All analytical data are given in Table I.

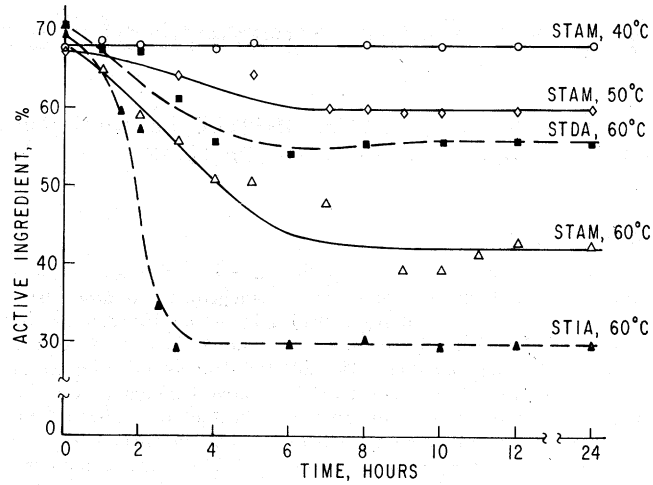

FIG. 1. Effect of temperature and time on the decomposition of unneutralized sulfated tallow alkanolamides.

RESULTS AND DISCUSSION

To facilitate agitation, 10% n-butanol was added to the tallow alkanolamides, prior to sulfation (6-8). Although aging studies at 40, 50 and 60 C were planned for all three alkanolamides, both STIA and STDA were too viscous to be stirred at 40 and 50 C; hence these two were aged at 60 C only. The sulfated mixed amide STAM was fluid at 40 C and could be aged at all three temperatures.

The decomposition or rearrangement course was followed by determining the active ingredient (sulfated alkanolamide content) of the reaction mixture at regular time intervals. The results of this phase of the study are shown graphically in Figure 1.

Wherever loss of active ingredient occurs, the decomposition stops after a period of time (4 hr for STIA and 6 hr for STDA). This suggests that, after a given time interval, equilibrium has been attained. Obviously STIA is much less stable than STDA, STIA having lost almost 2/3 of its original activity at 60 C, whereas STDA, lost only ca. 15%. The 60 C curve for STAM, as expected, runs about halfway between those for STIA and STDA. A comparison of the three STAM curves show the extent of decomposition is governed entirely by temperature. STAM is completely stable at 40 C, loses ca. 1/6 of its activity at 50 C and ca. 1/2 at 60 C. From a practical point of view, these findings indicate the temperature of the sulfation reaction mixture should not exceed 40 C. Since the decomposition rate appears to be somewhat slower during the first hour of aging at 50 or 60 C, the sulfation mixture could be held at temperatures as high as 60 C for as long as an hour without serious loss of active ingredient and consequent lower surface activity.

In order to characterize the decomposing with age at higher temperatures, the reaction mixtures were analyzed after the 12-hr aging period. The neutralized dried samples were first extracted with diethyl ether to remove unsulfated materials such as amides and aminoesters, then with ethanol to remove sulfated components, leaving a residue of essentially inorganic compounds. The results are shown in Table I.

During heat aging, desulfation somehow takes place so that, after neutralization, the samples with the lowest sulfated alkanolamide content have the highest content of unsulfated aminoester or unsulfated alkanolamide and the highest inorganic salt content (mostly Na_2SO_4). The first indication of presence of ester as well as substantial amounts of unsulfated alkanolamide in the soluble fractions was found in the IR spectra. The aminoester

TABLE I

Composition of Thermally Rearranged Sulfated Alkanolamides

Component	STIA[a], 60 C		STDA[b], 60 C		STAM[c], 40 C		STAM[c], 50 C		STAM[c], 60 C	
	% Component in		% Component in		% Component in		% Component in		% Component in	
	Extract	Total sample	Extract	Total sample	Extract	Total sample	Extract	Total sample	Extract	Total sample
Total ether solubles		24.5		12.8		3.2		15.4		20.3
Aminoester by saponification	13.7	3.4	14.5	1.8	17.8	0.5	22.0	3.8	17.3	3.3
Alkanolamide by difference	86.3	21.1	85.5	11.0	82.2	2.6	78.0	11.6	82.7	17.0
Total alcohol solubles		45.8		65.6		90.0		72.6		56.1
Sodium sulfated alkanolamide by titration	58.3	26.7	74.1	48.6	76.6	69.0	73.4	53.8	68.7	39.0
Sodium butyl sulfate by difference	41.7	19.1	25.9	17.0	23.4	21.0	26.6	18.8	31.3	17.1
Alcohol insolubles		26.5		20.7		6.6		11.7		21.6
Inorganics by sulfated ash	92.5	25.3	92.8	19.0	93.2	6.1	92.1	11.0	93.4	20.4
Sulfated alkanolamide	7.5	1.2	7.2	1.7	6.8	0.5	7.9	0.7	6.6	1.2
Extraction loss		3.2		0.9		0.3		0.3		2.0
Sulfated alkanolamides,[d]										
Initial		69.7		70.8		67.7		67.6		67.9
After 12 hr heating		29.4		55.0		67.6		59.8		42.0
Loss		40.3		15.8		0.1		7.8		25.9

[a]STIA = sulfated tallow isopropanolamide.
[b]STDA = sulfated tallow diglycolamide.
[c]STAM = sulfated tallow alkanolamide mixture.
[d]Sulfated alkanolamides, % determined by Cahn Test.

content was determined by saponification number as well as by titration of the amine content. The results obtained by these two methods were in close agreement; therefore, only the data calculated from saponification are recorded in Table I. This close agreement also indicated no amidoester $RCONHCH_2CH(CH_3)OOCR$ was formed. Part of the aminoester $RCOOCH(CH_3)CH_2NH_2$ rearranges back to the amide $RCONHCH_2CH(CH_3)OH$ upon neutralization, as has been found in earlier publications (9-11). Thus, the aminoester content found is probably much smaller than that originally present before neutralization. The ester content of the ether soluble fraction varies only between 13.7 and 22.0%. Some of the variability results from the limits of the analytical methodology. The amide content was not measured directly but was calculated by difference.

The alcohol soluble fraction represents the sum of sulfated butanol and sulfated alkanolamide. The sulfated alkanolamide determined directly by cationic titration, whereas the sulfated butanol was calculated by difference. All efforts to separate these two components from each other with acetone or chlorinated solvents failed. Since butyl sulfate is thermally and hydrolytically stable, the butyl sulfate content of all samples should be reasonably constant, and, indeed, varied only between 17 and 21% (Table I).

The alcohol insoluble fraction is essentially all inorganic except for 6.5 to 8% of sulfated alkanolamide, which appears to be entrapped in the salt.

The data for active ingredient content of the freshly sulfated samples and of the whole aged and neutralized samples before extraction and the difference between these two values are shown on the botton of Table I. These sets of data readily indicate that sulfation at 40 C is safe and results in no loss of active ingredient. The relatively high stability of the sulfated diglycolamide discussed above parallels the hydrolytic stability data established by Weil et al. (3). Since the sulfations were carried out such that water was excluded from the reaction mixture, the desulfation and subsequent rearrangement to aminoester is apparently complex but follows the above mentioned rearrangement of amide to ester under acidic conditions and reversion to amide under neutral or alkaline conditions.

While the mechanism of the sulfated alkanolamides decomposition is still unknown, the practical significance of these findings is evident. The sulfation temperature ideally should not exceed 40 C. The addition of n-butanol to the alkanolamide permits a reduction of viscosity of the sulfation mixture and hence better heat transfer. If, for some reason, the sulfation temperature needs to be raised to 50-60 C., the unneutralized material should not be maintained at such a temperature longer than 1 hr to avoid a severe loss of active ingredient. The product that results from sulfation at 40 C will possess high detergency and excellent lime soap dispersing properties.

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