Sulfated Diglycolamides

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ABSTRACT

Pure sulfated diglycolamides were prepared by the sulfation of products from the alkali-catalyzed reaction of diglycolamide with fatty methyl esters. Products containing 70% of methyl-substituted diglycolamides were obtained by the addition of 1 mole of propylene oxide to a mole of hydroxyethylamide under alkaline catalysis. Sulfated monooxypropylated hydroxyethyl-stearamide $C_{17}H_{35}CONHC_2H_4OCH_2CH(CH_3)OSO_3Na$, and sulfated diglycolstearamide, $C_{17}H_{35}CONH(C_2H_4O)_2\text{-}SO\ Na$, have good solubility, lime soap dispersing power and detergency.

INTRODUCTION

Sulfated alkanolamides have been shown to have excellent detergent and lime soap dispersing properties (1), but susceptibility to hydrolysis of the sulfate ester of 2-hydroxyalkylamides is assisted by participation of the neighboring amide group, and considerably more stable compounds are obtained when the amide and sulfate groups are separated by more than two atoms (1,2). Sulfated diglycolamides have been proposed as particularly stable products suitable for use in liquid shampoo preparations (3).

Two methods were considered for the preparation of diglycolamides: (a) the direct reaction of diglycolamine with fatty acids or esters to give pure diglycolamides, or (b) the oxyalkylation of amides or alkanolamides to give mixtures in which a selected addition product has been caused to predominate by selection of reaction conditions. Using the reaction with propylene oxide, which has been shown to give a predominance of monoaddition (4), products with 70% of methyl-substituted diglycolamides were obtained. Fractional crystallization gave a 35% yield of purified monooxypropylated hydroxyethylstearamide.

Although the literature mentions the desirable properties of sulfated diglycolamides (3), the preparation and properties of pure diglycolamides has not been described,

and no mention has been made of pure alkyl-substituted products which may be made by oxypropylation. This paper is a study of the preparation and properties of sulfated diglycolamides and sulfated methyl-substituted diglycolamides to relate the effect of structure to chemical and physical properties.

EXPERIMENTAL PROCEDURES

Materials

Pelargonic, lauric, palmitic and stearic acids were purified by standard distillation and crystallization procedures. Oleic acid was purchased from Applied Science Laboratories, Inc. All of the fatty acids were found to have a purity in excess of 99% by gas chromatography of the methyl esters.

Diglycolamine, $HOC_2H_4OC_2H_4NH_2$, and ethanolamine were redistilled to a purity greater than 99.5%.

Ethylene oxide and propylene oxide were the best available grade of laboratory reagents.

Amidation

The reactions of the methyl esters with ethanolamine and diglycolamine were carried out as described in a previous publication (1). The methyl ester was heated with 10% excess of amine in the presence of a small amount of freshly cut sodium. Heating at 115-125 C was continued until by-product methanol ceased to be evolved, which took about 40 min. After crystallization from ethanol or petroleum ether purified products were obtained in the yields shown in Table I. Elemental analyses checked theoretical values within 0.4% for C, 0.3% for H, and 0.2% for N, with an overall average deviation of less than 0.2%.

Oxyalkylation

Oxypropylation of hydroxyethylamides was carried out like the oxypropylation of fatty alcohols (4). The reaction with hydroxyethylstearamide is cited as an example.

Propylene oxide, 7.6 g (9.5 ml) was added dropwise to 33 g (0.098 moles) of hydroxyethylstearamide containing 0.6 g KOH while the temperature was maintained at 160-165 C. The reactants were stirred under an efficient reflux system to prevent loss of the low boiling propylene oxide. A weight increase of 6.1 g showed that 0.105 mole

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TABLE I

Yield and Melting Point of Alkanolamides Prepared by Aminolysis of Methyl Esters

	Ethanolamides[a], i = 1			Diglycolamides, i = 2		
	Solvent 1 Crystallization	Yield[b], %	Melting point, C	2 Crystallizations	Yield[b], %	Melting point, C
$C_8H_{17}CONH(C_2H_4O)_iH$	1 Ethanol: 6 petr. ether	75	69.8-70.8	1 Ethanol: 9 petr. ether	55	47.0-48.3
$C_{11}H_{23}CONH(C_2H_4O)_iH$	1 Ethanol 10 petr. ether	90	87.2-89.2	Ethanol	64	64.0-65.2
$C_{15}H_{31}CONH(C_2H_4O)_iH$	Ethanol	91	98.7-99.5	95% Ethanol	61	82.0-83.1
$C_{17}H_{35}CONH(C_2H_4O)_iH$	Ethanol	95	102.2-103.0	95% Ethanol	83	87.2-88.5
$C_{17}H_{33}CONH(C_2H_4O)_iH$	Petr. ether	78	62.0-63.6	Petr. ether	77	38.0-39.2

[a]Ethanolamides have been prepared previously (1,7).
[b]Yield of purified material.

TABLE II

Hydrolysis of Sulfated Alkanolamides in 1 Hr[a]

	In 0.05 N NaOH at 80 C, %	In 0.05 N HCl at 100 C, %
$C_{15}H_{31}CONHC_2H_4OSO_3Na^b$	30	40
$C_{15}H_{31}CONH(CH_2)_3O_5O_3Na^b$	9	16
$C_{17}H_{35}CONHC_2H_4[OCH_2CH(CH_3)]_nOSO_3Na^c$	5	30
$C_{17}H_{35}CONH(C_2H_4O)_2SO_3Na^d$	0.5	8

[a]Starting concentration of sulfated alkanolamide was 0.05 N.

[b]Compounds previously prepared (1) and included here for comparison.

[c]Not a pure compound but a product for which the average number of oxypropyl groups, n = 1.

[d]Systematic name: N-2(2 hydroxyethoxy)ethyloctadecanamide H sulfate, Na salt.

of propylene oxide had reacted.

The first derivative (monoadduct) from the reaction of propylene oxide and hydroxyethylstearamide was separated and purified as follows. The reaction mixture was taken up in 700 ml of boiling (60 C) petroleum ether and insoluble matter containing a mixture of product and starting material was removed. The monooxypropylated product, 13.9 g (37%), melting at 68.5-70.5 C was crystallized from the petroleum ether solution at 25 C and used for preparation of the sulfated product of Table III. A similar preparation was crystallized to constant melting point (11 times) to give a product melting at 75.7-76.9 C with an analysis in agreement with the theoretical for $C_{23}H_{47}NO_3$, a single GLC peak, and the same IR spectra as the above.

The product from the reaction of ethanolamine with methyl ester can also be used directly without purification, making use of the same alkaline catalyst.

The mixture of products from hydroxyethylpalmitamide and hydroxyethylstearamide were sulfated without separation and their properties are shown in Tables II and III along with those of pure amide sulfates.

GLC Analysis

A dual column F & M model 810 chromatograph with an Infotronics Integrator was used for GLC analysis. The column was 2 ft long and 1/8 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 C/min, with injection port at 200 C and detector at 320 C.

Because of the difficulties in chromatographing higher molecular weight amides, complete composition studies were confined to the oxyalkylated pelargonamides.

Examples of the data obtained in the oxyalkylation of hydroxyethylpelargonamide are shown on Table IV.

Sulfation

Procedures for sulfation and purification of the sulfated product have been described (1). A 10% excess of chlorosulfonic acid was added dropwise with stirring to a cold 15% solution of the alkanolamide in chloroform. Ten minutes after HCl evolution had stopped, cold ethanol was added and the mixture neutralized with 18 N NaOH. Recrystallization of the crude sulfation products, yields 50-90%, from 95% ethanol gave the purified products in yields of 45-75%. Elemental analyses checked theoretical values within 0.3% for C, 0.3% for H, 0.2% for N, 0.2% for S and 0.2% for Na with an overall average deviation of less than 0.2%.

Double Bond Analysis

The Wijs method for unsaturation was found to be unreliable for sulfated oleamides. Double bond retained in the sulfation process was determined by hydrogen number and confirmed by analysis for the elements. Sulfated hydroxyethyloleamide had a hydrogen number of 460 indicating 93% double bond retention and C, H, N, Na and S analyses were all within 0.3% of theory. Sulfated diglycolamide had a hydrogen number of 556 indicating 85% double bond retention; calculations based on elemental analysis showed 81% to 89% double bond retention.

Product Evaluation

Methods for the evaluation of surface active properties have been described in a previous publication (4). The

TABLE III

Surface Active Properties of Sulfated Amides

	Krafft point, 1% °C	Critical micelle concentration mmoles/liter	Surface tension 0.1% dynes/cm	Lime soap dispersing power, %	Foam height,[a] mm	Detergency[a] ΔR^b
$C_{11}H_{23}CONH(C_2H_4O)_2SO_3Na$	< 0	12.2	56.1	5[c]	135	15
$C_{15}H_{31}CONH(C_2H_4O)_2SO_3Na$	30	0.62	40.4	4	215	25
$C_{15}H_{31}CONHC_2H_4[OCH_2CH(CH_3)]_{n=1}OSO_3Na$	35[d]	---[d]	36.4	5	180	20
$C_{17}H_{33}CONH(C_2H_4O)_2SO_3Na$	< 0	0.27	40.8	4	210	26
$C_{17}H_{35}CONH(C_2H_4O)_2SO_3Na$	31	0.18	41.2	4	180	27
$C_{17}H_{35}CONHC_2H_4OCH_2CH(CH_3)OSO_3Na$	30	0.16	39.0	4	175	27
$C_{17}H_{35}CONHC_2H_4[OCH_2CH(CH_3)]_{n=1}OSO_3Na$	37[d]	---[d]	40.1	6	110	20
$C_{17}H_{33}CONHC_2H_4OSO_3Na$	< 0	0.16	38.6	5	220	31
$C_{17}H_{35}CONHC_2H_4OSO_3Na$	53	0.16	---[e]	5	195	32
$C_{18}H_{37}OCH_2CH(CH_3)OSO_3Na$	43	0.11	---[e]	8	100	31
$C_{15}H_{31}CON(CH_3)CH_2CH_2SO_3Na$	32	0.75	---	7	220	27

[a]Foam height and detergency were measured on 0.25% solutions (0.05% sulfated alkanolamide + 0.2% builder containing 10% $Na_4P_2O_7$, 55% $Na_5P_3O_{10}$, 1% CMC, 10% Na_2SiO_3 and 24% sodium sulfate) in hard water of 300 ppm at 60 C.

[b]ΔR = Increase in reflectance after washing standard soiled cloth (Testafabrics printed cotton GDC 26).

[c]For example a value of 5% means that 5 mg of the agent is sufficient to prevent the deposition of calcium oleate from 100 mg of sodium oleate in an excess of hard water.

[d]Not sharp because composition is a mixture.

[e]Insufficient solubility for measurement.

Krafft point is the temperature at which a 1% solution becomes clear on gradual heating, the critical micelle concentration was determined by dye titration, Borghetty and Bergman's method was used for lime soap dispersing power and the Ross-Miles test for foam height. Detergency was measured in the Terg-O-Tometer. Foam height and detergency were run at 60 C on built solutions, 0.05% active and 0.20% with respect to a conventional builder formulation.

Conditions for measurement of hydrolytic stability were those used in previous studies (1). Acid hydrolysis was measured by the increase in acidity obtained when a 0.05 N amide sulfate was heated in 0.05 N HCl at 80 C. Alkaline hydrolysis was measured by the disappearance of free alkali when 0.05 N amide sulfate was heated in 0.05 N NaOH at 100 C.

RESULTS AND DISCUSSION

Melting points are considered because of their potential relationship to solubility as measured by the Krafft point. Table I lists the melting points for ethanolamides and diglycolamides of pelargonic, lauric, palmitic, stearic and oleic acids. Diglycolamides generally melted about 20 C below the corresponding ethanolamides. A melting point of 77 C was found for the pure monooxypropylated hydroxyethylstearamide, 11 C below that of the corresponding diglycolstearamide without the methyl side chain.

Oxypropylation has been used rather than oxyethylation when high yields of first derivative are desired (1). Table IV compares the analyses obtained by GLC with that calculated by the equations of Weibull and Nycander (5) for the oxyethylation and oxypropylation of hydroxyethylpelargonamide. Agreement between theory and found values showed that products are distributed in accordance with theory and that the values for the distribution constant, C, are valid. Agreement with theory was better for the oxypropylation process. The value for C indicated that oxypropylated hydroxyethylpelargonamide was only 0.125 times as reactive as hydroxyethylpelargonamide, permitting yields of first derivative to go as high as 70% with the addition of 1 mole of propylene oxide. The oxyethylation process with a distribution constant of 0.71 gave less than 50% of first derivative.

Although complete chromatograms were not obtained for the product from the oxypropylation of hydroxyethylpalmitamide, the parent compound and first two derivatives were found in the same ratio as for the oxypropylation of hydroxyethylpelargonamide. The analyses for the products from pelargonamide were therefore considered to be typical of reactions of propylene oxide with hydroxyethylpalmitamide and hydroxyethylstearamide.

The sulfation of saturated alkanolamides was carried out like the sulfation of fatty alcohols. Unlike the sulfation of oleyl alcohol, however, hydroxyethyloleamide was sulfated with little effect (less than 10%) on the double bond and diglycololeamide was sulfated with at least 80% retention of unsaturation. This protective action of the amide may be related to the complexes of nitrogen and oxygen compounds used for this purpose in the sulfation of oleyl alcohol (6). Spada and Gavioli (7) have reported the sulfation of hydroxyethyloleamide.

Table II compares the amount of hydrolysis which takes place with sulfated alkanolamides and diglycolamides when heated for 1 hr in 0.05 N NaOH at 80 C and in 0.05 N HCl at 100 C. The measured value is the sum of hydrolysis of both ester and amide. Diglycolstearamide sulfate was the most stable compound in either acid or alkaline systems. The unseparated mixture of compounds from the oxypropylation of hydroxyethylstearamide was less stable than

TABLE IV

Distribution of Products in the Oxyalkylation of Hydroxyethylpelargonamide

| | Oxypropylation | | Oxyethylation | |
	Found[a]	Calculated[b]	Found[a]	Calculated[b]
μc	0.915		1.261	
n_0/n_{00}[d]	0.191		0.232	
n_1/n_{00}[d]	0.710	0.711	0.419	0.421
n_2/n_{00}	0.092	0.091	0.243	0.235
n_3/n_{00}	0.007	0.007	0.078	0.084
n_4/n_{00}			0.019	0.022
n_5/n_{00}			0.010	0.013
C[e]		0.125		0.713

[a]By GLC analysis, converted to mole fraction.

[b]Calculated by Weibull-Nycander Equation 3:

$$n_i/n_{00} = c^{i-1}/(c-1)^i \left\{ n_0/n_{00} - (n_0/n_{00})^c \sum_{j=0}^{i-1} \frac{1}{j!} [(c-1)\ln n_{00}/n_0]^j \right\}$$

In the equation, n_0/n_{00} is the experimentally determined value.

c_μ is moles of epoxide per mole of starting ethanolamide.

[d]n_0/n_{00}, moles of starting material remaining per mole of original starting material; n_1/n_{00} is moles of first derivative per mole of original starting material; etc.

[e]Distribution constant, C, is the ratio of reactivity of oxyalkylated product to reactivity of hydroxyethylamide.

the pure diglycolamide but more stable to alkali than sulfated 3-hydroxypropylpalmitamide.

Solubility as shown by Krafft point and surface active properties of the sulfation products are summarized in Table III. All of the sulfated diglycolamides were considerable more soluble than the corresponding sulfated ethanolamides. Sulfated monooxypropylated hydroxyethylstearamide has a Krafft point only 1 C lower than sulfated diglycolstearamide, even though the melting point of the unsulfated alcohol is 11 C lower. The mixtures of products had slightly higher indefinite Krafft points because small amounts of less soluble products were present. All of the sulfated diglycolamides had good calcium stability and were effective lime soap dispersing agents.

Sulfated diglycolamides from palmitic, stearic and oleic acid were good detergents but slightly less effective than the corresponding sulfated ethanolamides. Sulfated monooxypropylated hydroxyethylstearamide and sulfated diglycolstearamide had the same detergency.

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