Soap-Based Detergent Formulations: IV. The Synthesis and Surface Active Properties of Sulfopropyl Esters of N-Substituted Iminodiacetic Acids[1]

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ABSTRACT

A series of di(potassium 3-sulfopropyl) N-alkyl and N-acyliminodiacetates were prepared by reacting 1,3-propanesultone with the corresponding dipotassium N-alkyl and N-acyliminodiacetates, respectively. The washing ability of these products was examined alone and in combination with soap. Whereas the surfactant properties of the precursor iminodiacetates were poor, the addition of two sulfopropyl groups resulted in products with excellent lime soap dispersing power, calcium ion stability and water solubility.

INTRODUCTION

Efficient lime soap dispersing agents are of considerable interest because of their potential application in detergent compositions using soap. Early work in this laboratory showed that exceptionally good lime soap dispersing power was obtained with fatty acid derivatives containing a sulfate or sulfonate, or both, as the two hydrophilic groups (1). It was of interest to determine whether carboxylate groups would be similarly effective. After finding that the precursor iminodiacetates had deficient surface active properties, we prepared the corresponding di(3-sulfopropyl) esters to determine if good surface active properties, especially lime soap dispersing power, could be regained. The overall synthetic approach is summarized in Figure 1.

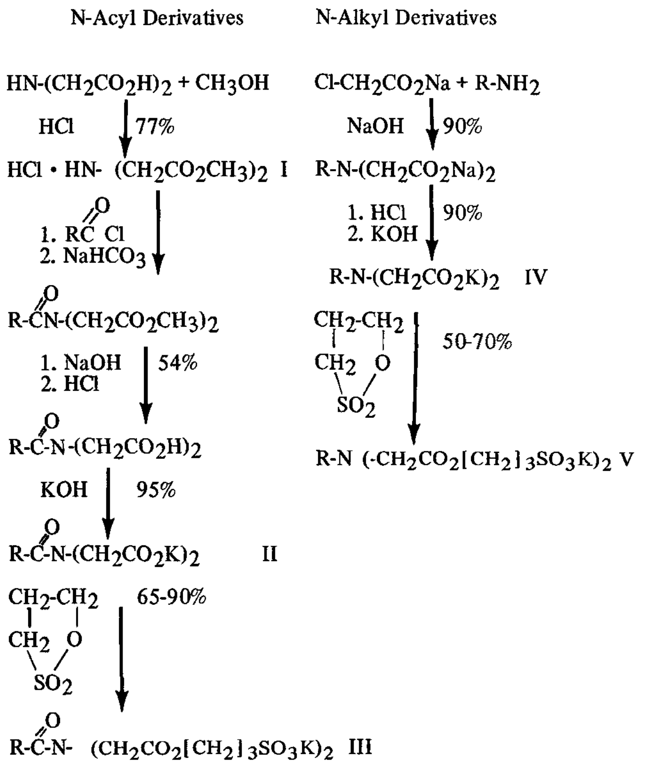

FIG. 1. Reaction scheme.

Various fatty acid derivatives react with propanesultone to give 3-sulfopropyl compounds (2,3) with surface active properties (4) comparable to sodium alkyl sulfates. The reaction proceeds smoothly in good yields (2). N-Alkyliminodiacetates have found use as foam stabilizers (5); however the low water solubility of the C_{16} and C_{18} derivatives precludes their general use in this application. N-Acyliminodiacetates have been used in rust inhibitor compositions (6). The present study was made to prepare propanesultone addition products of N-alkyl and N-acyliminodiacetates and to compare their surface active properties with those of the corresponding disodium iminodiacetates.

EXPERIMENTAL PROCEDURES

Materials

The fatty acid chlorides were prepared from purified acids (gas liquid chromatography of methyl esters indicated purity better than 99%) with thionyl chloride. The acid chlorides were used directly after evaporation of the excess thionyl chloride. The fatty amines were purified by distillation at reduced pressure through a 2 ft column of protruded packing under a nitrogen atmosphere. Gas chromatography of the center cuts showed the amines were better than 98% pure. Disodium iminodiacetate monohydrate and *p*-dioxane were Eastman practical grade, while the chloroacetic acid was "white label" grade. 1,3-Propanesultone was obtained from Shell Chemical Co. and fractionally distilled, bp 103-104 C at 0.9 mm, n^{40}_{D} 1.4515. N-methyl-2-pyrrolidone was a commercial grade solvent, bp 79-80 C/10 mm from Matheson Coleman and Bell.

Methods

Dimethyl iminodiacetate hydrochloride (I): This synthesis is based on the procedure by Koelsch and Robinson (7). To a 2 liter flask equipped with a condenser and stirrer was added 700 ml reagent methanol, 148 g (4.05 moles) anhydrous hydrogen chloride and 80 ml water. After the solution was cooled, 195.1 g (1 mole) disodium iminodiacetate monhydrate was added in 10 min. The mixture was refluxed for 6 hr and then cooled to 25 C. The precipitated sodium chloride, 86% of theory, was removed by filtration. The filtrate was evaporated to 500 ml, cooled to -30 C and filtered to give 136.2 g of product. Concentration of this filtrate to 200 ml yielded an additional 16.8 g of product. The dimethyl iminodiacetate hydrochloride (77% yield) was used in the acylation reactions without further purification.

Dipotassium N-acyliminodiacetate (II): To a liter reaction flask equipped with a stirrer, thermometer and graduated dropping funnel was added 150 ml water and 53 g (0.63 mole) sodium bicarbonate. After the mixture was cooled to 0-5 C, a solution of 55 g (0.30 mole) of dimethyliminodiacetate hydrochloride in 150 ml water was added in 15 min, while the temperature was maintained below 5 C. After the frothing subsided, 68.4 g (0.25 mole) palmitoyl chloride was added over a 1 hr period. The reaction mixture was stirred for 4 hr at 0-5 C and then overnight at 25 C. The mixture was filtered, and the solid

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TABLE I

$R\text{-}N(CH_2CO_2[CH_2]_3K)_2$

Elemental Analysis of Propanesultone Addition Products with N-Alkyl and N-Acyliminodiacetates

Substituent, R	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %		Potassium, %	
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found
1) $C_{12}H_{25}$-	42.49	42.56	6.64	6.45	2.25	2.16	10.31	10.51	12.57	12.60
2) $C_{14}H_{29}$-	44.34	44.48	6.98	7.10	2.15	2.08	9.86	9.74	12.02	11.97
3) $C_{16}H_{33}$-	46.04	46.12	7.28	7.47	2.06	1.99	9.46	9.58	11.53	11.40
4) $C_{18}H_{37}$-	47.61	47.80	7.57	7.72	1.98	1.86	9.28	9.82	11.07	10.88
5) $C_{15}H_{31}\overset{O}{\overset{\|}{C}}$-	45.13	44.96	6.85	7.10	2.02	2.17	9.27	9.20	11.30	11.89
6) $C_{17}H_{35}\overset{O}{\overset{\|}{C}}$-	46.75	46.76	7.14	7.40	1.95	1.78	8.92	9.30	10.85	10.38

was vacuum dried at 45 C to give 97 g of crude dimethyl N-palmitoyliminodiacetate. The solid was dissolved in 700 ml 95% ethanol at 45 C. The solution was filtered by gravity to give 7.5 g of insoluble solid. The filtrate was cooled to 20 C and treated with 97 ml 5N sodium hydroxide (.49 mole) in 180 ml 95% ethanol. After 30 min at room temperature, the solvent was removed on a rotary evaporator at 25 C. The partially dried solid was dispersed in 1100 ml water and filtered by gravity to give 22.0 g of byproduct sodium palmitate. The clear filtrate was acidified with 6N hydrochloric acid to pH 2 or less. The gel-like mixture was extracted eight times with 150 ml portions of ether. The extracts were combined, filtered by gravity, decolorized with carbon black and dried over anhydrous sodium sulfate. The solid obtained after evaporating the ether solvent was dried at 45 C/ .2 mm to yield 50 g (54% yield) of N-palmitoyliminodiacetic acid (N.E. found 388, theory 371.4). The acid was dissolved in 250 ml 95% ethanol and neutralized with 17.5 g (0.27 mole) potassium hydroxide in 50 ml water. The solution was evaporated to dryness at 45 C/ .3 mm to give 56.9 g (51% yield) dipotassium N-palmitoyliminodiacetate. The same procedure was used to prepare the analogous N-stearoyl derivative.

Di (potassium 3-sulfopropyl) N-acyliminodiacetate (III): To a flask equipped as described in the preceding paragraph was added 6.2 g (.014 mole) dipotassium N-palmitoyliminodiacetate, 3.38 g (.28 mole) propane-sultone and 40 ml 1:1 N-methyl 2-pyrrolidone: *p*-dioxane. The mixture was heated for 2 hr at 90 C. After most of the solvent was evaporated at 60 C/ .1 mm, the residue was washed with 95 ml reagent acetone and air-dried to yield 8.70 g (90% yield) of di(potassium 3-sulfopropyl)N-palmitoyliminodiacetate. The stearoyl derivative was prepared in the same way with a reaction time of 12 hr. One recrystallization of the product from methanol gave a 66% yield. The elemental analysis are shown in Table I.

Dipotassium N-alkyliminodiacetate (IV): N-Hexadecyliminodiacetate and the other members of the homologus series were prepared according to the method by Stein et al. (8) with minor modifications. Chloroacetic acid 75.6 g (0.8 mole) was dissolved in 340 ml 12% aqueous ethanol and neutralized to a phenolphthalein end point with 10N sodium hydroxide. The solution was transferred to a liter flask equipped with a condenser, stirrer and graduated dropping funnel. Hexadecylamine 48.3 g (0.20 mole) was added, and the solution was heated to reflux. Forty milliliters of 10N sodium hydroxide was added over a 30-40 min period to maintain the mixture at a phenolphthalein end point. At this point an additional 40 ml of 10N sodium hydroxide was added, and the mixture was refluxed overnight (ca. 20 hr). During the reflux period, 150 ml absolute ethanol was added to the mixture to minimize frothing. The mixture was cooled to 25 C, diluted with 150 ml absolute ethanol and filtered by suction. The solid was recrystallized twice from 50% aqueous ethanol to yield 75 g (ca. 90% yield) disodium N-hexadecyliminodiacetate. The elemental analyses of all disodium N-alkyliminodiacetates were within experimental error. The sodium salt was dissolved in 750 ml water and acidified with 90 ml 6N hydrochloric acid. The free acid was washed with water till free of chloride ion. The partially dried acid was dispersed in 375 ml 95% ethanol and neutralized with 24.2 g (.37 mole) potassium hydroxide in 150 ml water. The solution was evaporated at 80 C/ .1 mm to give dipotassium N-hexadecyliminodiacetate weighing 63 g (77% yield).

Di(potassium 3-sulfopropyl) N-alkylinimodiacetate (V): A suitable reaction flask was equipped with a stirring bar, reflux condenser and a calcium chloride drying tube. To the flask was added 16.8 g (.039 mole) dipotassium N-hexadecyliminodiacetate, 75 ml N-methyl-2-pyrrolidone and 14.1 g (.116 mole) propanesultone. The mixture was heated to 95 C for 5.5 hr. After most of the solvent was removed at 70 C/ .1 mm, the semisolid residue was washed with 250 ml acetone. The product was recrystallized twice from a minimum quantity of 20% aqueous methanol and vacuum-dried at 70 C/ .1 mm to constant weight (17.5 g, 67% yield). The elemental analysis of the product and other members of the series prepared by the same method are shown in Table I.

TABLE II

$R\text{-}N(CH_2CO_2Na)_2$

Surface Active Properties of Disodium N-Alkyl and N-Acyliminodiacetates

Substituent, R	Krafft Point, C	Lime Soap Dispersing Power, %	Ca^{++} Stability, ppm $CaCO_3$
1) $C_{12}H_{25}$	<1	>100	190
2) $C_{14}H_{29}$-	36.5	>100	300
3) $C_{16}H_{33}$-	56	>100	435
4) $C_{18}H_{37}$-	67	>100	410
5) $C_{15}H_{31}\overset{O}{\overset{\|}{C}}$-	<1	>100	75
6) $C_{17}H_{35}\overset{O}{\overset{\|}{C}}$-	<1	>100	185

TABLE III

$R\text{-}N(CH_2CO_2[CH_2]_3SO_3K)_2$

Surface Active Properties of Propanesultone Addition Products

Substituent, R	Lime soap dispersing power, %	Ca^{++} Stability, ppm $CaCO_3$	Critical micelle concentration, moles/liter x 10^{-4}	Krafft point,C	Foam height[a]	
					Distilled water	300 ppm $caCO_3$
1) $C_{12}H_{25}$-	8	>1800	Could not be measured	<1	105/15	140/15
2) $C_{14}H_{29}$-	4	>1800	30.27	<1	145/125	170/15
3) $C_{16}H_{33}$-	4	>1800	9.70	<1	165/150	160/50
4) $C_{18}H_{37}$-	7	>1800	2.78	<1	150/140	135/35
5) $C_{15}H_{31}\overset{O}{\overset{\|}{C}}$-	5	>1800	4.39	<1	185/175	175/25
6) $C_{17}H_{35}\overset{O}{\overset{\|}{C}}$-	5	>1800	2.18	<1	170/160	155/145

[a] Foam height was measured with 0.25% solutions at 60 C. Results are given as initial values over values obtained after 5 min.

Surface active properties: Lime soap dispersing power was determined according to the method of Borghetty and Bergman (9). It refers to the minimum number of grams of lime soap dispersing agent required to keep 100 g of sodium oleate from forming a precipitate in hard water. The differences in lime soap dispersing power shown in Table III are all significant and reproducible. A lime soap dispersing power value below 10 is considered good. A typical LAS gives a value of 40 which is considered poor. Krafft point, calcium ion stability (10) and critical micelle concentration (11) were measured by previously described methods. Foam height was measured by the Ross-Miles Test (12). Surface active properties for the disodium N-alkyl- and N-acyliminodiacetates are shown in Table II, while analogous results for the propanesultone addition products are given in Table III. Detergencies were obtained with the aid of a Terg-O-Tometer. All washings were run for 20 min at 120 F in 1 liter water of 300 ppm hardness with an agitation speed of 110 cpm. Five circular swatches (4 in. diameter) of EMPA 101 cotton, U.S. Testing Cotton and Test Fabric cotton-polyester with permanent press finish were washed together in each beaker. Formulation A consisted of .05% compound, while formulation B contained 0.20% compound. Formulation C was a mixture of 0.05% compound plus 0.15% sodium tallowate, while formulation D contained 0.04% compound plus 0.13% sodium tallowate plus .03% sodium silicate (Na_2O/SiO_2 1:2.4). 1% CMC, based on total solids, was added to all formulations tested. Detergency was measured in terms of increased reflectance ΔR of the washed cloth over the soiled cloth. Results are shown in Table IV.

RESULTS AND DISCUSSION

N-Alkyliminodiacetates were generally prepared using variations of the procedure given here. These compounds were readily purified as the disodium salts (monohydrate) in yields of 90%. Conversion to the dipotassium salts was advantageous, because the greater solubility of the potassium salts in organic solvents facilitated reaction with propanesultone.

The N-acyliminodiacetates were prepared in ca. 55% yield by reacting an acyl halide with dimethyl iminodiacetate at low temperature. Application of the Schotten-Bauman reaction conditions to disodium iminodiacetate, and an acyl halide gave poor yields of product. The use of aqueous DMSO, stronger bases or higher reaction temperatures again gave poor yields of product and excessive hydrolysis of the acyl halide. Saponification of dimethyl N-acyliminodiacetates with excess sodium hydroxide above 45 C resulted in hydrolysis of the amide linkage. The methyl ester appeared stable to hydrochloric acid in 95% ethanol. However heating the free N-acyliminodiacetic acid in the presence of hydrochloric acid hydrolyzed the amide linkage. The propanesultone addition to both the N-alkyl and N-acyl derivatives proceeded in high yields of crude product. Purification by one or two recrystallizations resulted in a substantial decrease in yield.

The disodium N-alkyliminodiacetate (Table II) showed low solubility, no lime soap dispersing power and poor calcium ion stability. The corresponding N-acyl derivatives (C_{16} and C_{18}) showed considerably improved water solubility and the same poor lime soap dispersing power

TABLE IV

$R\text{-}N(CH_2CO_2[CH_2]_3SO_3K)_2$

Detergency[a] of Propanesultone Addition Products

Formulation	A			B			C			D		
Test cloth	TF	EMPA 101	UST	TF	EMPA 101	UST	TF	EMPA 101	UST	TF	EMPA 101	UST
Substituent, R	Reflectance change, ΔR											
1) $C_{12}H_{25}$-	-0.1	5.8	-0.1	6.9	9.9	1.4	-5.8	8.1	-1.1	-7.6	7.3	-3.3
2) $C_{14}H_{29}$-	8.4	11.8	2.8	9.7	11.4	2.3	5.0	18.7	2.0	1.2	13.6	-0.6
3) $C_{16}H_{33}$-	10.5	13.1	3.6	11.7	15.6	2.9	9.8	29.6	4.4	9.3	26.9	2.4
4) $C_{18}H_{37}$-	9.9	13.6	3.1	12.0	13.8	3.1	11.7	28.2	3.6	11.1	28.9	2.8
5) $C_{15}H_{31}\overset{O}{\overset{\|}{C}}$-	12.4	16.0	3.5	13.5	17.2	2.7	5.5	14.9	2.1	2.3	13.7	0.3
6) $C_{17}H_{35}\overset{O}{\overset{\|}{C}}$-	11.9	13.6	2.9	13.7	13.2	3.3	10.9	31.1	4.0	10.8	27.3	3.0
7) Control[b]	11.3	10.1	2.3	22.5	32.1	6.6	22.5	32.1	6.6	22.5	32.1	6.6

[a] Formulation A: 0.05% compound; B: 0.20% compound; C: 0.05% compound + .15% sodium tallowate; D: 0.04% compound + .13% sodium tallowate + .03% sodium silicate 1:2.4. All detergency values obtained with 1 liter hard water 300 ppm containing 1% CMC based on total solids present.

[b] The control is a commercial household detergent tested at concentrations indicated.

and calcium ion stability. At .05% concentration in hard water (300 ppm), both types of compounds showed very poor detergency values not reported here.

The dramatic effect of incorporating two sulfonate groups into the molecule by converting the above compounds to the corresponding 3-sulfopropyl esters is clearly shown by the surface active properties summarized in Table III. All of the derivatives are highly water soluble in terms of Krafft points below 1 C. Calcium ion stability is greater than 1800 ppm $CaCO_3$ for all products, and lime soap dispersing power is excellent for all the samples evaluated. Foam stability in distilled water is fairly good, but poor in 300 ppm hard water. The critical micelle concentrations are of the expected order of magnitude similar to those reported for other dianionic surfactant types (1,13), and they decrease with increasing molecular weight.

The detergency behavior of both the intermediate N-substituted iminodiacetates and their 3-sulfopropyl derivatives was studied. The former compounds showed very poor detergency even in combination with soap and builder. However good detergency values (Table IV) were obtained with the sulfopropyl derivatives. All samples contained sodium carboxymethylcellulose as given in the table. A detergent concentration of 0.2% was adopted as a convenient screening level in previously reported hard water detergency studies (14). Formulation of 75% of the test compound in Formulation B with tallow soap results in formulation C. A 0.2% solution of formulation C thus contains 0.05% of the test compound. In order to ascertain possible detergency effects due to tallow soap, formulation A containing only the test compound at an 0.05% level and CMC was evaluated. Finally the replacement of 15% of the solids in formulation C by a mild silicate builder resulted in formulation D necessary to establish the effect of a builder.

A commercial household detergent was used as a control in the detergency evaluations, since the objective of this study was to arrive at a soap based detergent formulation that might perform as well as or better than the control. As the results of Table IV show, this objective is not attained with the lime soap dispersing agents of this study, unlike those of a previous study (14). All of the test compounds, except the C_{12} derivative, perform as well as the control at an 0.05% level (formulation A). At an 0.2% level (formulation B) of the test compounds, the detergency values (ΔR) are only slightly higher than those of the lower level (formulation A), whereas the control ΔR values increase substantially. The detergency of soap containing Formulation C increase substantially on EMPA cotton over that of Formulation B or A. Since at 300 ppm water hardness there is more than a stoichiometric amount of calcium and magnesium ions present to react with all of the sodium soap, the observed increase in detergency of formulation C over that of A and B indicates that the soap contributed substantially to the detergency of this formulation. Tallow soap alone at a level of 0.2% and 300 ppm water hardness exhibits essentially no detergency because of extensive curd formation. As a result the data were not reported. The introduction of sodium silicate builder (formulation D) does not give further increases in detergency. The control detergent was superior to all formulations of this study.

We may conclude therefore that the salts of N-alkyl and N-acyliminodiacetic acid are inadequate lime soap dispersing agents or detergent compounds. On the other hand, the salts of di(3-sulfopropyl) N-substituted iminodiacetates are excellent lime soap dispersing agents with good detergent properties alone or in combination with soap. As expected, the C_{12} homologs in this study showed poor detergency and lime soap dispersing power.

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