# Soap-Based Detergent Formulations: XXII. Sulfobetaine Derivatives of *N*-Alkylglutaramides and Adipamides

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## ABSTRACT AND SUMMARY

The acid chlorides of methyl hydrogen glutarate and methyl hydrogen adipate were allowed to react with various primary fatty amines. The resulting amido esters were converted into the corresponding amino diamides by sodium catalyzed reaction with N,N-dimethylaminoalkylamines. The desired sulfobetaines were obtained by reaction of the resulting N-alkyl-N′-(1,1-dimethylaminoalkyl) glutaramides and adipamides with 1,3-propanesultone. The compouds possess the same excellent lime soap dispersing ability, water solubility, calcium ion stability, and detergency properties as the analogous succinamide derivatives previous reported. This indicates that the spacing between the two amido groups or that between the quaternary nitrogen atom and the nearest amido group does not affect surface active properties.

## INTRODUCTION

Previous studies of quaternary type amphoteric surfactants (sulfobetaines) of the general structure $R\overset{+}{N}(CH_3)_2CH_2CH_2CH_2SO_3^-$ have shown that these compounds possess excellent lime soap dispersing characteristics superior to those of anionic surfactant types (1-3). In formulations with soap or with soap and sodium silicate, they exhibit excellent detergency. Since they are readily compatible with all classes of surface active agents and are stable to acid and alkaline hydrolysis (4,5), they are potentially very useful surfactants. However, most simple sulfobetaines have limited water solubility, which could be a deterrent to their usefulness. This problem is fortuitously remedied in soap formulations because soap solubilizes sulfobetaines. It was observed that the introduction of an amido group into a sulfopropylated amphoteric molecule improved water solubility (2,5). Introduction of a second amido group into the sulfobetaine molecule to give, for example, the succinamide derivatives

$$RNHCOCH_2CH_2CONHCH_2CH_2CH_2\overset{+}{N}(CH_3)_2CH_2CH_2CH_2SO_3^-$$

further enhances water solubility. Recent work (5) on sulfoquaternary ammonium lime soap dispersants showed that water solubility increases as spacing between the anionic and cationic sites is increased from two to three carbon atoms. It was therefore of interest to determine if the spacing between the amido groups or the spacing between the cationic site and the nearest amido group would affect solubility and surface activity. Accordingly, a series of sulfopropylated amphoteric derivatives of glutaramide and adipamide of the general structure

$$RNHCO(CH_2)_xCONH(CH_2)_y\overset{+}{N}(CH_3)_2CH_2CH_2CH_2SO_3^-$$

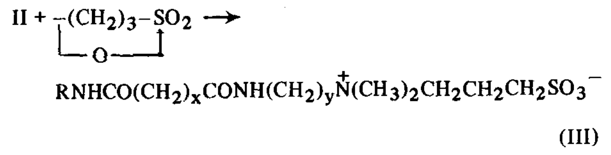
(where R is $C_{10}H_{21}$, $C_{12}H_{25}$, or $C_{16}H_{33}$ and x or y = 2, 3, or 4) was synthesized and evaluated for surface active properties.

The following reaction sequence indicates the method of synthesis:

$$\text{(A)}\quad ClCO(CH_2)_xCO_2CH_3 + RNH_2 \xrightarrow{\text{Pyridine}} RNHCO(CH_2)_xCO_2CH_3 \qquad \text{(I)}$$

$$\text{(B)}\quad \text{I} + H_2N(CH_2)_yN(CH_3)_2 \xrightarrow{\text{Na}} RNHCO(CH_2)_xCONH(CH_2)_yN(CH_3)_2 \qquad \text{(II)}$$

(C)



$$\text{II} + \underset{\llcorner\,\text{O}\,\lrcorner}{-(CH_2)_3-SO_2} \longrightarrow RNHCO(CH_2)_xCONH(CH_2)_y\overset{+}{N}(CH_3)_2CH_2CH_2CH_2SO_3^- \qquad \text{(III)}$$

## EXPERIMENTAL PROCEDURES

### Materials

Dodecylamine and hexadecylamine (Eastman Organic Chemicals, Rochester, NY) were fractionally distilled at reduced pressure through a 24 in. spinning band column. Purity of >98% was obtained as determined by gas liquid chromatography (GLC). Decylamine (99%) (Aldrich Chemical Co., Milwaukee, WI) was used as received, N,N-dimethyl-1,2-ethanediamine, b.p. 107 C (Aldrich Chemical Co.) and N,N-dimethyl-1,3-propanediamine, b.p. 132-133 C (Jefferson Chemical Co., Austin, TX) were fractionally distilled. N,N-dimethyl-1,4-butanediamine (K&K Laboratories, Plainview, NY) was used as purchased. Glutaric anhydride, thionyl chloride, and methyl hydrogen adipate were Eastman practical or white label grade. Propanesultone[1], b.p. 103-104 C/0.9 mm, $n_D^{40}$ 1.4515, was purified by fractional distillation.

### Synthesis of ω-Carbomethoxyalkanoyl Chloride

A greatly simplified version of the organic syntheses procedure (6) was applied to the preparation of acid chlorides of methyl hydrogen glutarate and methyl hydrogen adipate. The glutarate half ester was obtained after heating glutaric anhydride (2 moles) and methanol (2.4 moles) for 2-2-1/2 hr on the steambath. Distillation of the reaction mixture through a 2 ft spinning band column gave 58% yield of the half ester, b.p. 107-108 C/1.1 mm, $n_D^{22}$ 1.4390. Methyl hydrogen adipate was similarly purified, b.p. 99-100 C/0.1 mm, $n_D^{27}$ 1.4390. The corresponding acid chlorides were obtained by stirring the half esters with a 25% excess of thionyl chloride at 35-45 C for 2-3 hr, and then letting the solution stand overnight. Simple vacuum distillation gave quantitative yields of product. γ-Carbomethoxybutyroyl chloride, b.p. 70-71 C at 2.4 mm, $n_D^{25}$ 1.4446, and δ-carbomethoxyvaleroyl chloride, b.p. 75 C/1.0 mm, $n_D^{28}$ 1.4445.

### Synthesis of Methyl N-Dodecylglutaramate (I)

To a liter flask equipped with a mechanical stirrer, reflux condenser and graduated dropping funnel was added 37.1 g (0.2 mole) dodecylamine, 19.8 g (0.25 mole) pyridine, and 350 ml anhydrous ether. γ-Carbomethoxybutyroyl chloride

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[1] Propanesultone is a known carcinogen in animals, so contact with this reagent should be avoided.

32.9 g (0.2 mole) in 100 ml ether was added at a rate to maintain gentle reflux (25-30 min) while stirring the mixture. The suspension was refluxed for about 1 hr and filtered rapidly by suction. The hygroscopic pyridine hydrochloride was washed twice with 200 ml portions of boiling ether. The filtrates were combined, and the solvent was evaporated to give 59 g of solid. The product was crystallized twice from 300 ml portions of hexane and then from 200 ml of 80/20 hexane-acetone to yield 53 g (85%) of crystalline solid. All reactions between fatty amides and half ester acid chlorides were carried out in a similar manner, and all yields were of the order of 70-85%. The saponification equivalents of all of these intermediates were within 1% of theory. The melting points of the homologous methyl N-alkylglutaramates are as follows: N-decyl 54-55 C, N-dodecyl 65-66 C, N-hexadecyl 78.5-79.5 C; and these of the analogous adipamates: N-decyl 57.5-58.5 C, N-dodecyl 68-69 C, and N-hexadecyl 81.5-82 C.

TABLE I

Melting Points of Diamides
$RNHCO(CH_2)_xCONH(CH_2)_yN(CH_3)_2$

| R | x | y | m.p. °C |
|---|---|---|---|
| $C_{10}H_{21}$ | 3 | 2 | 94.5-95.5 |
| $C_{10}H_{21}$ | 3 | 3 | 90-91 |
| $C_{10}H_{21}$ | 4 | 2 | 121-122 |
| $C_{10}H_{21}$ | 4 | 3 | 117-118 |
| $C_{12}H_{25}$ | 3 | 2 | 97-98 |
| $C_{12}H_{25}$ | 3 | 3 | 90-91 |
| $C_{12}H_{25}$ | 4 | 2 | 118-118.5 |
| $C_{16}H_{33}$ | 3 | 2 | 105-106 |
| $C_{16}H_{33}$ | 3 | 3 | 99-100 |
| $C_{16}H_{33}$ | 4 | 2 | 124-125 |
| $C_{16}H_{33}$ | 4 | 3 | 121-122 |
| $C_{16}H_{33}$ | 4 | 4 | 121-122 |

TABLE II

Detergency of Sulfobetaines $RNHCO(CH_2)_xCONH(CH_2)_y\overset{+}{N}(CH_3)_2(CH_2)_3SO_3^-$

| Structure of test Compound | | | Detergency[a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 0.05% Surfactant | | | 0.2% Surfactant | | | 0.2% Binary mixture[b] | | | 0.2% Ternary mixture[c] | | |
| R | x | y | TF | EMPA | UST | TF | EMPA | UST | TF | EMPA | UST | TF | EMPA | UST |
| $C_{10}H_{21}$ | 3 | 2 | 20 | 11 | 5 | 29 | 26 | 11 | 37 | 25 | 9 | 27 | 26 | 4 |
| $C_{10}H_{21}$ | 3 | 3 | 20 | 11 | 4 | 27 | 26 | 10 | 33 | 23 | 6 | 24 | 25 | 4 |
| $C_{10}H_{21}$ | 4 | 2 | 25 | 13 | 6 | 29 | 27 | 11 | 36 | 25 | 9 | 26 | 26 | 5 |
| $C_{10}H_{21}$ | 4 | 3 | 22 | 12 | 5 | 28 | 26 | 10 | 36 | 25 | 7 | 24 | 23 | 5 |
| $C_{12}H_{25}$ | 3 | 2 | 30 | 24 | 12 | 32 | 27 | 13 | 37 | 25 | 11 | 34 | 30 | 11 |
| $C_{12}H_{25}$ | 3 | 3 | 30 | 23 | 12 | 31 | 28 | 12 | 37 | 27 | 11 | 32 | 30 | 12 |
| $C_{12}H_{25}$ | 4 | 2 | 29 | 23 | 11 | 31 | 26 | 12 | 37 | 26 | 11 | 32 | 30 | 11 |
| $C_{12}H_{25}$ | 4 | 3 | 29 | 23 | 11 | 30 | 27 | 12 | 34 | 26 | 12 | 35 | 29 | 11 |
| $C_{16}H_{33}$ | 3 | 2 | 27 | 16 | 12 | 28 | 22 | 13 | 35 | 19 | 13 | 33 | 27 | 11 |
| $C_{16}H_{33}$ | 3 | 3 | 30 | 17 | 12 | 32 | 24 | 12 | 37 | 19 | 13 | 36 | 29 | 10 |
| $C_{16}H_{33}$ | 4 | 2 | 28 | 19 | 13 | 28 | 22 | 12 | 35 | 19 | 14 | 32 | 30 | 11 |
| $C_{16}H_{33}$ | 4 | 3 | 31 | 18 | 13 | 31 | 21 | 13 | 36 | 21 | 14 | 33 | 27 | 12 |
| $C_{16}H_{33}$ | 4 | 4 | 26 | 19 | 12 | 31 | 19 | 12 | 35 | 23 | 12 | 30 | 31 | 12 |
| Control @0.2%[d] | | | | | | 37 | 30 | 9 | 37 | 30 | 9 | 37 | 30 | 9 |

[a] Detergency was measured as increased in reflectance (ΔR) after washing EMPA 101 Cotton (EMPA) (distributed by Testfabrics Inc., Middlesex, NJ), U.S. Testing Cotton (UST) (Hoboken, NJ), and Testfabrics cotton-polyester blend with a permanent press finish (TF) in the Tergotometer for 20 min at 120 F and 300 ppm water hardness.

[b] 75% tallow soap + 25% test surfactant.

[c] 65% tallow soap + 20% test surfactant + 15% sodium silicate ($SiO_2$:$Na_2O$ = 1.6:1).

[d] Commercial detergent: containing 50% phosphate builder.

### Synthesis of Aminodiamides $RNHCO(CH_2)_xCONH(CH_2)_yN(CH_3)_2$ (II)

These intermeidates were prepared by the previously described method (4) for succinamides except that the sodium metal catalyst was added in small portions during the entire reaction time. The yields were about 55%. Occasionally, induction periods of as long as 7 hr were observed. Average reaction time was ∿3 hr at 125 C, but a few compounds were prepared at 140-150 C. The melting points of these intermediates are given in Table I. All natural equivalents of these intermediates were within 1% of theory.

### Synthesis of N-dodecyl-N′{3-[3-Sulfopropyldimethyl) ammonio] propyl}adipamide (III)

The aminodiamides of this study were reacted with propanesultone by a modified verison of the procedure described for the succinamide derivatives (4) as is illustrated by the following procedure.

To a 250 ml flask equipped with a bar magnet and a reflux condenser was added 15 g (0.038 mole) N-dodecyl-N′-(3,3-dimethylaminopropyl) adipamide and 125 ml of 1,2-dichloroethane. Ten to fifteen ml of solvent was distilled to remove water azeotropically, then 4.6 g (0.038 mole) 1,3-propanesultone was added. The mixture was stirred at reflux 2-3 hr, diluted with 150 ml acetone, and cooled. The suspension of microcrystalline product was filtered and then extracted with boiling acetone (300 ml portions) till water-insoluble material was no longer removed. A crystalline solid 15.1 g (77% yield) was obtained after vacuum drying at 60-70 C.

All amphoterics of this study were prepared in this manner and obtained in 70-80% yields generally as microcrystalline solids exhibiting perceptibly less hydroscopicity than with the analogous succinamide derivatives (4). All compounds were purified by repeated acetone extractions to remove water insoluble materials. Elemental analyses indicate that all compounds were at least 95% pure.

### Surface Active Properties

Krafft point is the temperature at which a 1% suspension of compound becomes a clear solution. The Krafft points of all compounds, except two $C_{16}$ derivatives, were below 1 C and are not shown in the tables. Lime soap dispersant requirement (LSDR) and calcium ion stability of 0.5% solutions were measured by previously described methods (7,8). Detergency evaluations shown in Table II are expressed as an increase in reflectance $\Delta R$ after washing. The control is a commercial detergent containing 50% phosphate builder. The wash tests were carried out in Tergotometer operated at 120 F in hard water (300 ppm calculated as $CaCO_3$) as described previously (4). Four washing systems were used containing (a) 0.05% test compound, (b) 0.2% test compound, (c) a binary mixture at 0.2% containing 25% test compound and 75% sodium tallowate, and (d) a ternary mixture at 0.2% containing 20% compound, 65% sodium tallowate, and 15% sodium silicate ($SiO_2$:$Na_2O$, 1.6:1).

## RESULTS AND DISCUSSION

The synthetic route is fairly straightforward. Purification of the crude products from the Schotten-Baumann reaction may be tedious as described previously (4), and the final sulfobetaines may have to be washed repeatedly in order to attain high purity.

The surface active properties of this series of compounds are entirely comparable to those of the analogous succinamide derivatives (4). The lime soap dispersant requirement (LSDR) of the compounds all lie between 2 and 3. An LSDR below 2 has never been observed and a value of 2 probably represents the lowest attainable. Like the analogous succinamides, the compounds of this study are very water soluble. Like all of the water-soluble sulfobetaines (3) examined, the compounds of this study have a calcium ion stability of greater than 1800. The detergency behavior of this series of compounds relative to the control detergent is very similar to that of the succinamides (4). Variation of x and y had no effect on detergency. Optimum detergency is attained with the dodecyl derivatives of the glutaramides and adipamides. The succinamides also showed the highest detergency when the alkyl side chain had 12 to 14 carbon atoms. The detergency of ternary mixtures of soap, sulfobetaine, and sodium silicate is excellent and essentially equal to that of the control.

It is concluded that the spacing between the two amido groups or that between the cationic site and the nearest amido group have no significant influence on surface activity.

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