# Soap-based Detergent Formulations: XIX. Amphoteric Alkylsuccinamide Derivatives as Lime Soap Dispersants[1]

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## ABSTRACT AND SUMMARY

A series of amphoteric surfactants was synthesized by reaction of 1,3-propanesultone with N-alkyl-N'-(ω,ω-dimethylaminoalkyl)succinamides. The intermediate succinamides were prepared by reacting methyl N-alkylsuccinamates, obtained from alkylamines containing 8 to 18 carbon atoms, with N,N-dimethyl-1,3-propylenediamine or N,N-dimethylethylenediamine neat. The amphoterics were isolated as hygroscopic crystalline solids having superior lime soap dispersing ability, water solubility, and calcium ion stability. Detergency studies at 0.2% concentration (300 ppm water hardness) indicated good washing ability when used alone and excellent performance in combination with soap or in soap-silicate formulations.

## INTRODUCTION

A wide variety of simple and complex fatty tertiary amines react with 1,3-propanesultone to form amphoteric compounds of the type $R^+N(CH_3)_2CH_2CH_2CH_2SO_3^-$ which have been found to be excellent lime soap dispersing agents (1,2). Sulfopropyl derivatives of tallowamines (3) or purified fatty amines (1) show excellent dispersing properties with the quaternary amphoteric derivatives from tertiary amines having detergency with soap and soap-silicate formulations equivalent to those of a commercial phosphate-built control. Simple amphoterics (1) as mentioned above or those derived from alkylbenzenes (4) like $R\text{-}\phi SO_2NH(CH_2)_3{}^+N(CH_3)_2CH_2CH_2CH_2SO_3^-$ exhibit superior surface active properties but have high Krafft points. Amphoteric compounds (5) containing an amido group $RCONH(CH_2)_3{}^+N(CH_3)_2(CH_2)_ySO_3^-$ where y = 3 show good water solubility with marked decreases occurring when y = 2 or 4.

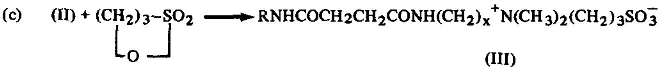
In this program we studied a homologous series of amphoteric succinamides $RNHCOCH_2CH_2CONH(CH_2)_x{}^+N(CH_3)_2CH_2CH_2CH_2SO_3^-$ wherein both R and x were varied. We anticipated that the introduction of two amido groups and the variation of x between 2 and 3 would lead to decided improvement in the lime soap dispersing properties and water solubility. Primary fatty amines react with β-carbomethoxypropionyl chloridein anhydrous diethyl ether to give excellent yields of methyl N-alkylsuccinamate (I). The succinamate intermediate (I)

$$\text{(a)}\quad ClCOCH_2CH_2CO_2CH_3 + RNH_2 \xrightarrow{\text{pyridine}} \underset{\text{(I)}}{RNHCOCH_2CH_2CO_2CH_3}$$

was treated neat with N,N-dimethyl-1,3-propanediamine or N,N-dimethylethylene-diamine in the presence of metallic sodium to form the aminosuccinamide (II).

$$\text{(b)}\quad \text{(I)} + H_2N(CH_2)_xN(CH_3)_2 \xrightarrow[x\,=\,2\text{ or }3]{Na} \underset{\text{(II)}}{RNHCOCH_2CH_2CONH(CH_2)_xN(CH_3)_2}$$

Treatment of (II) with 1,3-propanesultone in ethylene dichloride gave the amphoteric succinamide (III) as shown in equation (c).



$$\text{(c)}\quad \text{(II)} + \underbrace{(CH_2)_3\text{–}SO_2}_{O} \longrightarrow RNHCOCH_2CH_2CONH(CH_2)_x{}^+N(CH_3)_2(CH_2)_3SO_3^-$$

(III)

In view of the carcinogenic hazards of propanesultone, an alternate route to the amphoterics was desirable. A recent study (5) has shown the feasibility of preparing hexadecylammonium ethane sulfonic acid betaine. The method involves reaction between N,N-dimethylhexadecylamine and ethylene bromide to form the corresponding ammonium salt followed by treatment with sodium sulfite to give the sulfoethylated amphoteric.

## EXPERIMENTAL PROCEDURES

### Materials

The primary aliphatic amines (Eastman Organic Chemicals, Rochester, NY) were purified by distillation; their purity (>98%) was determined by gas liquid chromatography (GLC). Decylamine 99% (Aldrich Chemical Co., Milwaukee, WI) was used as such while N,N-dimethylethylene-diamine, b.p. 107 C, from the same company and N,N-dimethyl-1,3-propanediamine, b.p. 132-133 C, from Jefferson Chemical Co. (Austin, TX) were purified by distillation through a 24 in. spinning band column under a dry, $CO_2$-free atmosphere. Propanesultone was fractionally distilled to give a center cut, b.p. 103-104 C/0.9 mm, $n_D^{40}$ 1.4515. β-carbomethoxypropionyl chloride was prepared from methyl hydrogen succinate by a previously described method (7). (Propanesultone should be handled with care, since upon ingestion it has been found to be carcinogenic to test animals.)

### Methyl N-Hexadecylsuccinamate (I)

The following procedure is typical and generally gives moderately good yields of these compounds. To a liter flask equipped with a stirred, condenser, dropping funnel, and drying tube was added dry pyridine, 16.6 g (0.21 mole), hexadecylamine, 48.3 g (0.2 mole), and 400 ml of anhydrous ether. After the solids dissolved, the flask was immersed in a water bath at 20 C and β-carbomethoxypropionyl chloride 30.2 g (0.2 mole) in 100 ml of ether was added dropwise (15-20 min) with vigorous stirring. The mixture was refluxed 1 hr, diluted with 250 ml acetone, again brought to a boil and filtered by suction. The pyridine hydrochloride was dissolved in water to leave a residue of crude product which after drying was added to the ether filtrate. The ether solvent was evaporated on the steam bath and finally at reduced pressure to give 70 g (theory 71 g) of crude product. Repeated crystallizations from acetone gave 55 g (79%) of methyl N-hexadecylsuccinamate, m.p. 81.5-82.5 C; saponification equivalent: found 354, theory 356. Normal hexane was the crystallization solvent of choice for compounds derived from amines of chain length

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TABLE I

Surface Active Properties of Amphoterics
$RNHCO(CH_2)_2CONH(CH_2)_x{}^+N(CH_3)_2CH_2CH_2CH_2SO_3^-$

| R substituent | x | LSDR[a] | Krafft point °C | Calcium[b] ion stability | Surface tension dynes/cm |
|---|---|---|---|---|---|
| $C_8H_{17}$ | 3 | 19 | <1 | >1800 | 55.8 |
| $C_{10}H_{21}$ | 3 | 4.5 | " | " | 39.2 |
| $C_{12}H_{25}$ | 3 | 2 | " | " | 37.8 |
| $C_{14}H_{29}$ | 3 | 2 | " | " | 36.5 |
| $C_{16}H_{33}$ | 3 | 2.5 | " | " | 36.5 |
| $C_{18}H_{37}$ | 3 | 4[c] | >90 | - | - |
| $C_{10}H_{21}$ | 2 | 3 | <1 | >1800 | 37.6 |
| $C_{12}H_{25}$ | 2 | 2.5 | " | " | 37.8 |
| $C_{16}H_{33}$ | 2 | 4[c] | 95 | - | - |

[a] Lime soap dispersing requirement.
[b] Calcium ion stability as ppm $CaCO_3$.
[c] Measurements made on super cooled solutions.

less than $C_{14}$. The other methyl N-alkylsuccinamates were similarly prepared with minor variations in the mode of addition of reactants and the amount of solvent used. The saponification equivalents deviated by no more than three units from theory. The following melting points and percent yields were observed for these derivatives: N-octyl 45-46 C, 97; N-decyl 58.5-59.5, 62; N-dodecyl 68-69 C, 45; N-tetradecyl 75-76 C, 65; and N-octadecyl 86.5-87.5 C, 75. Saponification equivalents were determined by treating a sample with 0.2 N alcoholic potassium hydroxide at 100 C for 1 hr. The saponified sample and blank were titrated with 0.1 N hydrochloric acid to a phenolphthalein endpoint.

### N-Tetradecyl-N′-(3,3-dimethylaminopropyl)succinamide (II)

The following procedure is an example of the preparation of intermediate (II) as shown in equation (b) and is applicable to syntheses using N,N-dimethylethylenediamine. To a 250 ml round bottom flask containing a bar magnet was added methyl N-tetradecylsuccinamate 30 g (0.092 mole). The compound was dried at 120 C/0.1 mm for 30 min. After cooling the flask to about 110 C, N,N-dimethyl-1,3-propanediamine 9.9 g (0.097 mole) and sodium metal 0.2 g were added. The flask was now equipped with a Dean-Stark trap and a reflux condenser. The mixture was stirred 1.5 hr at 120-130 C. After this time, 3 ml of methanol (theory 3.7 ml) had collected and an IR spectrum of the mixture indicated little or no ester carbonyl absorption at 5.8 $\mu$. Upon cooling, the mixture solidified to a rust-colored wax weighing 37 g (theory 36.5 g). The crude product was crystallized twice from 200 ml portions of absolute ethanol to yield 24.5 g of tan amorphous solid. This material was repeatedly crystallized from acetone to eventually give N-tetradecyl-N′-(3,3-dimethylaminopropyl)succinamide 13.4 g (37% yield), equivalent weight: found 407, theory 398. For analogous derivatives of the formula $RNHCOCH_2CH_2CONH(CH_2)_x N(CH_3)_2$ the date are given as: R group, equivalent weight found/theory and % yeild: where x = 3, $C_8H_{17}$ 360/314 45; $C_{10}H_{21}$ 363/342 58; $C_{12}H_{25}$ 373/370 36; $C_{16}H_{33}$ 432/426 40; $C_{18}H_{37}$ 453/453 34; where x = 2, $C_{10}H_{21}$ 413/328 45; $C_{12}H_{25}$ 394/356 47; $C_{16}H_{33}$ 416/412 43. Equivalent weight was determined potentiometrically by titration in (1:1) isopropanol-ethylene glycol at 50-60 C using 0.1 N hydrochloric acid in the same solvent (8).

### N-Tetradecyl—N′-{3-[(3-sulfopropyldimethyl)ammonio] propyl} Succinamide (III)

The following procedure typifies the sulfopropylation reaction. To a 250 ml flask equipped with a mechanical stirrer, condenser, and drying tube was added N-tetradecyl-N′-(3,3-dimethylaminopropyl) succinamide, 13.0 g, (0.033 mole) which had been vacuum dried 1 hr at 60 C/0.1 mm and 70 ml of dry 1,2-dichloroethane. The mixture was heated to 60-65 C, and 1,3-propane-sultone, 4.25 g (0.035 mole) in 10 ml solvent was added to the flask. Within 10 min after addition at 65 C, a creamy suspension formed. The mixture was vigorously stirred at this temperature for 1.75 hr and then refluxed for 20 min. The mixture was cooled to 25 C, diluted with 100-200 ml acetone, and filtered. The microcrystalline solid was dispersed twice in 250 ml of boiling acetone and filtered hot. After vacuum drying at 60 C/0.1 mm, the product 15.6 g was found to be only partially soluble in water. The solid was heated with 100 ml of distilled water and the solution was filtered by gravity. Water was removed from the filtrate azeotropically with 1,2-dichloroethane. The anhydrous solution was evaporated at reduced pressure. The residual solid was dispersed in 300 ml acetone, filtered hot, and vacuum dried to give crystalline N-tetradecyl-N′-{3-[(3-sulfopropyldimethyl)ammonio] propyl} succinamide 14.0 g (83% yield). The remaining amphoterics were similarly prepared in yields ranging from 70-87%. Purity of these compounds $RNHCO(CH_2)_2CONH(CH_2)_x{}^+N(CH_3)_2(CH_2)_3SO_3^-$ determined from elemental analyses of C, H, N, and S are based on the maximum deviation from theory and are given as R group X, percent purity: $C_8H_{17}$, 3, 98; $C_{10}H_{21}$, 3, 93; $C_{12}H_{25}$, 3, 99; $C_{14}H_{29}$, 3, 99; $C_{16}H_{33}$, 3, 99; $C_{18}H_{37}$, 3, 96; $C_{10}H_{21}$, 2, 95; $C_{12}H_{25}$, 2, 95; $C_{16}H_{33}$, 2, 96.

### Hydrolysis Studies

The alkaline hydrolysis of $RNHCOCH_2CH_2CONH(CH_2)_x{}^+N(CH_3)_2CH_2CH_2CH_2SO_3^-$ where R is dodecyl and x = 2 was determined by heating 0.005 mole of amphoteric in 100 ml 0.05 N NaOH at 85 C. The extent of hydrolysis was measured by titrating 10 ml aliquots with 0.1 N hydrochloric acid at periodic intervals. Only qualitative results were obtained because of fading end points. After 1 hr, 10% of the compound was hydrolyzed. Attempted determination of a saponification equivalent for amphoterics where R is dodecyl and x = 2 or R is octyl and x = 3 using 1 mmol of amphoteric to 4 mmols of alcoholic potassium hydroxide at 100 C indicated about 25% hydrolysis in 1 hr. These qualitative results are somewhat higher than those for sodium 3-sulfopropylpalmitamide (1) at 60 C but still indicate good stability to hydrolysis.

### Surface Active Properties

The surface active properties of the amphoteric succinamides are given in Table I. Krafft point is the temperature at which a 1% suspension of compound becomes a clear solution. Lime soap dispersant requirement (LSDR)

TABLE II

Detergency of Amphoteric Succinamides $RNHCO(CH_2)_2CONH(CH_2)_x{}^+N(CH_3)_2(CH_2)_3SO_3^-$

| | | Detergency ΔR[a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.05% Compound | | | 0.20% Compound | | | 0.2% Binary[b] | | | 0.2% Ternary[c] | | |
| R substituent | x | TF | EMPA | UST | TF | EMPA | UST | TF | EMPA | UST | TF | EMPA | UST |
| $C_8H_{17}$ | 3 | -5 | 6 | 2 | -4 | 9 | 1 | -15 | 8 | 0 | -9 | 15 | -1 |
| $C_{10}H_{21}$ | 3 | 1 | 13 | 4 | 16 | 24 | 9 | -1 | 17 | 6 | 5 | 20 | 4 |
| $C_{12}H_{25}$ | 3 | 19 | 26 | 11 | 21 | 27 | 11 | 20 | 35 | 12 | 18 | 40 | 10 |
| $C_{14}H_{29}$ | 3 | 22 | 26 | 12 | 26 | 30 | 12 | 22 | 35 | 12 | 21 | 40 | 10 |
| $C_{16}H_{33}$ | 3 | 22 | 17 | 12 | 18 | 15 | 10 | 24 | 28 | 11 | 20 | 37 | 11 |
| $C_{18}H_{37}$ | 2 | 14 | 14 | 11 | 19 | 9 | 7 | 19 | 21 | 11 | 18 | 29 | 12 |
| $C_{10}H_{21}$ | 2 | 1 | 12 | 4 | 19 | 25 | 11 | 1 | 19 | 4 | 2 | 22 | 6 |
| $C_{12}H_{25}$ | 2 | 18 | 26 | 11 | 22 | 28 | 12 | 22 | 36 | 11 | 22 | 41 | 13 |
| $C_{16}H_{33}$ | 2 | 18 | 16 | 12 | 26 | 8 | 12 | 25 | 26 | 12 | 23 | 36 | 14 |
| Control[d] at 0.2% | | | | | 26 | 38 | 12 | | | | | | |

[a] Increase in reflectance after washing test fabric cotton polyester with a permanent press finish (TF), EMPA 101 cotton, and U.S. testing cotton (UST) in hard water 300 ppm hardness (calculated as $CaCO_3$) at 120 F.

[b] 25% compound + 75% sodium tallowate.

[c] 20% compound + 65% sodium tallowate + 14% sodium silicate 1.6:1.

[d] A leading commercial phosphate built detergent.

was determined by the Borghetty-Bergman method (9). The values represent the grams of compound required to prevent precipitation of 100 g of sodium oleate in 333 ppm hard water. The LSDRs of those compounds with Krafft points greater than 90 C were determined on supercooled solutions. Calcium ion stability of 0.5% solutions was measured in the usual manner (10). Surface tension values were obtained at 25 C on 0.1% solutions measured by the duNoüy method. Detergency values expressed as an increase in reflectance ΔR after washing are summarized in Table II. They were obtained with a Tergotometer operated at 120 F, 110 cpm for 20 min in one liter of water of 300 ppm hardness (calculated at $CaCO_3$). Five circular swatches (4 in. dia.) of EMPA-101 cotton, U.S. testing cotton (UST), and Test-fabrics cotton-polyester blend with a permanent press finish (TF) were washed in each beaker. Four washing formulations were used: (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% test compound, 65% sodium tallowate, and 15% sodium silicate ($SiO_2Na_2O$ 1.6:1). Each formulation contained 1% carboxymethylcellulose based on total solids. A commercial phosphate built detergent was used as a control.

## RESULTS AND DISCUSSION

An effort was made to maximize yields of methyl N-alkylsuccinamates (I) shown in equation (a). Essentially quantitative yields (95%) of (I) were obtained by reacting two moles of alkylamine with a mole of acid in anhydrous ether. This reaction gave only 80-85% yields of (I) when pyridine was used as a hydrogen chloride scavenger. Attempts to carry out either of these reactions with acetone solvent gave poorer yields and highly discolored reaction mixtures.

Intermediate succinamides (II) were prepared as shown in equation b. This synthesis was characterized by erratic reaction rates (0.25-3 hr) and induction periods neither of which was completely eliminated by maintaining anhydrous conditions. As is evident from the equivalent weights (Experimental Procedure) derivatives prepared from amines with alkyl chains less than $C_{14}$ were not readily purified even by repeated crystallizations from acetone. The equivalent weights are invariably higher than the theoretical values thereby suggesting the presence of neutral nontitratable components. Fortunately, most of the impurities because of their water insolubility could be removed from the amphoteric compounds.

In an attempt to develop a simpler synthetic route, we found that succinic anhydride reacted with a primary amine in ethylene dichloride giving essentially quantitative yields of N-alkylsuccinamic acid. Direct amidation of this derivative by Muzyczko's method (6) appeared to be an attractive alternate approach to intermediate (II). However preliminary evaluations revealed no advantage with regard to yield or purity of the product.

The amphoteric succinamides (III) were obtained as crystalline hygroscopic solids by reacting the appropriate intermediate (II) with propane-sultone in 1,2-dichloroethane. The surface active properties of these compounds given in Table I are listed in order of increasing chain length of the parent amine where x = 3 for 1,3-propanediamine and x = 2 for ethylene-diamine derived products. Both types of compounds showed excellent LSDR with values ranging from 2 to 4.5 for all samples except the octyl derivative. Maximum dispersing ability appears to occur with compounds derived from $C_{12}$ to $C_{14}$ amines. Water solubility is generally excellent as confirmed by the uniformly low Krafft points. When solubility changes occur, they are abrupt and gross as shown by the Krafft points (>90 C) for the $C_{16}$ and $C_{18}$ derivatives. Calcium ion stability was consistently greater than 1800 ppm (as calcium carbonate) except when low solubility precluded making a measurement. Likewise, both types of compounds are equally surface active as seen from the comparable surface tension values. A representative sampling of the compounds shown were evaluated by the Ross-Miles method for foam height and foam stability. In both distilled and hard water (300 ppm) these compounds showed minimal foam height and poor stability. Measurements of wetting times indicated the absence of wetting properties.

Detergency results for the amphoterics are shown in Table II. A comparison of the values found for decyl, dodecyl, and hexadecyl compounds where x = 2 with those where x = 3 shows the compounds to be equivalent in all formulations. At 0.05% the samples are comparable to the control only on UST fabric. At 0.2% they are comparable to the control on TF and UST fabric but still deficient on EMPA. At 0.2% in the binary and ternary systems the detergency of the test compounds from $C_{12}$ to $C_{16}$ are equal to the control on EMPA and UST fabric but are somewhat deficient on TF. Similar detergency patterns for these test fabrics have been observed with simpler amphoterics (1).

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