Soap-based Detergent Formulations: XIX. Amphoteric Alkylsuccinamide Derivatives as Lime Soap Dispersants

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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 amines containing 8 to 18 carbon atoms, with N,N-dimethyl-1,3-propanediamine or N,N-dimethyl-ethylene-diamine neat. The amphoteric products were isolated as bygrosopic crystals 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 

\[ \text{R}^+\text{N}(\text{CH}_2)_x\text{CH}_2\text{CH}_2\text{SO}_3^- \]

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 amphoteric compounds (5) containing an amido group have good water solubility with marked decreases occurring when \( y = 2 \) or 4.

In this program we studied a homologous series of amphoteric succinamides 

\[ \text{RNHCONH}[(\text{CH}_2)_x\text{N(CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-] \]

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 \( \beta \)-carboxymethoxypropionyl chloride in anhydrous diethyl ether to give excellent yields of methyl N-alkylsuccinamates (1). The succinamate intermediate (I) 

\[
\text{CICOCH}_2\text{CH}_2\text{CO}_2\text{CH}_3 + \text{RNH}_2 \xrightarrow{\text{pyridine}} \text{RNHCOCH}_2\text{CH}_2\text{CO}_2\text{CH}_3
\]

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

\[ \text{RNHCOCH}_2\text{CH}_2\text{CONH(CH}_2)_x\text{N(CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^- \]

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

\[
(I) + \text{CH}_2\text{CH}_2\text{SO}_3^- \rightarrow \text{RNHCOCH}_2\text{CH}_2\text{CONH(CH}_2)_x\text{N(CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^- \quad (III)
\]

In view of the carcinogenic hazards of propanesultone, an alternate route to the amphoteric 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 sulfopropylated amphoteric.

EXPERIMENTAL PROCEDURES

Materials

The primary aliphatic amines (Eastman Organic Chemicals, Rochester, NY) were purified by distillation; their purity (99.8%) 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, CO₂-free atmosphere. Propanesultone was fractionally distilled to give a center cut, b.p. 103-104 °C/0.9 mm, nD20 1.4515. β-carboxymethoxypropionyl 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-carboxymethoxypropionyl 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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The following procedure typifies the sulfopropylation reaction. To a 250 ml flask equipped with a mechanical stirrer, condenser, and drying tube was added N-tetradece


dimethylaminopropyl) succinamide, 14.0 g (83% yield). The remaining amphoteric were similarly prepared in yields ranging from 70-87%. Purity of these compounds RNHCO(CH2)2CONH(CH2)xN(CH3)2(CH2)3SO3 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: C8H17, 3, 98; C10H21, 3, 93; C12H25, 3, 99; C14H29, 3, 99; C16H33, 3, 99; C18H37, 3, 96; C16H33, 2, 95; C12H25, 2, 95; C16H33, 2, 96.

Hydrolysis Studies

The alkaline hydrolysis of RNHCOCH2CH2CONH(CH2)xN(CH3)2(CH2)3SO3 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 amphoteric 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 (I) 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)