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Soap-Based Detergent Formulations: XXV. Synthesis and Surface Active Properties of Higher Molecular Weight Betaine Lime Soap Dispersants

JOAN M. KAMINSKI[1,2] and **WARNER M. LINFIELD,**
Eastern Regional Research Center [3], Philadelphia, Pennsylvania 19118

ABSTRACT

A series of surface active betaines have been prepared via the quaternization of a tertiary amine with a haloacid or with a halonitrile and subsequent hydrolysis. The betaines possessed a hydrophobic (C_{12}-C_{16}) alkyl side chain, and the anionic and cationic sites were separated by one, two, or three methylene groups or a benzyl group. The betaines were more water soluble and were poorer lime soap dispersants than analogous sulfobetaines. Detergency of most soap-based detergent formulations containing the betaine lime soap dispersants was good and generally close to that of a commercial control detergent containing 50% sodium tripolyphosphate in screening tests conducted in water of 300 ppm hardness.

INTRODUCTION

Sulfur-containing amphoteric lime soap dispersing agents (LSDA) having the general structure $Z\overset{+}{N}(CH_3)_2(CH_2)_nA^-$, where Z is a higher molecular weight alkyl group or an acylamido group of the structure $RCONHCH_2CH_2CH_2$, n is an integer from 2 to 4, and A is a sulfo or sulfato group, have been shown to possess excellent lime soap-dispersing properties (1–3). In fact, the so-called sulfobetaines of the structure $R\overset{+}{N}(CH_3)_2CH_2CH_2CH_2SO_3^-$ were found to be the most effective lime soap dispersants of this series of studies, and, after being blended with tallow soap and a silicate builder, the resulting detergent formulations possessed excellent detergency properties often surpassing in laboratory screening tests those of high sodium tripolyphosphate-containing commercial control detergents.

The solution properties of surface active betaines, of the structure $R\overset{+}{N}(CH_3)_2CH_2COO^-$, have been investigated by Herrmann (4), however, their suitability as lime soap dispersants in soap-based detergent formulations has not been studied. Therefore, we undertook this study to establish a relationship between chemical structure and detergency and lime soap dispersing properties of surface active betaines.

One of the parameters investigated was the effect of the spacing between the anionic and cationic sites of the molecule in analogy to investigations carried out on the sulfobetaines (2,5). Simple betaines or amidobetaines such as:

$$R\overset{+}{N}(CH_3)_2CH_2COO^- \text{ and}$$

$$RCONHCH_2CH_2CH_2\overset{+}{N}(CH_3)_2CH_2COO^-$$

are commercially available, and the former has been reported to be a fair lime soap dispersant (5).

Betaines are synthesized by one of two pathways depending on the length of the carbon bridge. Betaines possessing a one or two carbon atom bridge between the anionic and cationic sites are facilely prepared by reaction of a tertiary amine with the appropriate monohalogenated acetic or propionic acid in an alkaline medium (6,7). Three carbon atom-bridged or benzyl-bridged betaines, on the other hand, are produced via the reaction of tertiary amines with 4-chlorobutyronitrile or with α-bromo-o-tolunitrile (4) and subsequent acid hydrolysis (8).

EXPERIMENTAL

Materials

Lauric and palmitic acids were obtained from Ashland Chemical Co. (Columbus, OH) and were distilled and recrystallized, respectively to 99% purity by gas liquid chromatography (GLC). Armak Chemical Division, Akzona, Incorporation (Chicago, IL), supplied N,N-dimethyldodecylamine (Armeen DM 12D) and N,N-dimethyl-hexadecylamine (Armeen DM 16D), which were 97–99% pure by GLC. N,N-Dimethyl-1,3-propanediamine ("dimethylaminopropylamine") was obtained through the courtesy of Jefferson Chemical Co., Inc. (Houston, TX). Ortho- and paratolunitrile, p-toluic acid, and benzoyl peroxide were obtained from Eastman Chemical Company (Rochester, NY). N-Bromosuccinimide, 4-chlorobutyronitrile, chloroacetic acid, 4-chlorobutyroyl chloride (distilled wherever specified), 3-chloropropionyl chloride, and chloroacetyl chloride were products of Aldrich Chemical Co. (Milwaukee, WI). 3-Chloropropionic acid, also obtained from Aldrich, was declorized with carbon black and recrystallized from hexane/ether before use. Bio-Gel P-2 was obtained from Bio-Rad Laboratories (Richmond, CA).

Carbon tetrachloride and 1,2-dichloroethane were purified and dried according to literature methods. Other solvents were used without further purification.

Synthesis of α-Bromo-o-Tolunitrile

In analogy to previously published α-bromination procedures (9,10), o-tolunitrile (40.7 g; 0.347 mole) was brominated with N-bromosuccinimide (61.8 g; 0.347 mole) with the aid of benzoyl peroxide (6 g). Each reactant was rinsed into the flask with dry carbon tetrachloride, and a

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[1] Fats and Proteins Research Foundation fellow stationed at Eastern Regional Research Center.

[2] Current address: Mobil Research and Development Corporation, Paulsboro, NJ 08066.

[3] Federal Research, Science and Education Administration, U.S. Department of Agriculture.

total of one liter carbon tetrachloride was added. The reaction mixture was refluxed for 6 hr and allowed to cool to room temperature. The resulting white precipitate was filtered off and discarded. The yellow-orange filtrate (nitrile) was stripped of solvent and pumped in vacuo for 6 hr at 45 C. The crude product (76.6 g) was vacuum-distilled at 111 C, 1.5 mm, and subsequently recrystallized from 95% ethanol at −30 C, yielding 29.6 g (43.5% yield) pure product (m.p. 70.8–71.8 C; literature m.p. 71.5–72.5 C) (11).

Synthesis of α-Bromo-o-Toluic Acid (9,10)

p-Toluic acid was brominated by the above procedure, except that after the reaction had subsided, the filtrate was stripped of solvent, and the resulting white solid was stirred in 300 ml of chloroform. The insoluble white precipitate (67%) which was free of succinimide by infrared spectroscopy was filtered off and used without further purification.

Synthesis of Amides

The fatty amides of N,N-dimethylaminopropylamine were prepared from their corresponding fatty acids as previously described (5).

Synthesis of One-carbon-, Two-carbon-, and p-Benzyl-Bridged Betaines

Equimolar amounts of chlorinated acid, tertiary amine, and sodium hydroxide were heated in refluxing isopropanol to bring about quaternization according to the procedure of Linfield et al. (6); however, specific purification procedures were developed for each betaine.

The dodecyl and hexadecyl one-carbon-bridged betaines (#1 and 5, Table I) were recrystallized twice from acetone at 0 C and room temperature, respectively. For the two-carbon-bridged betaines, ether was added to the crude reaction product (200 cc/23 g), and the resulting white precipitate was filtered and recrystallized from ethyl acetate at −30 C. The fourth and fifth crops of crystals were homogeneous and salt-free, while preceding crops contained decreasing amounts of salt and were more amorphous. The ether filtrate (60 ml) was shaken with 200 ml of water. The water layer contained 4.5 g of off-white solid material which could not be recrystallized from ethyl acetate. The ether layer contained primarily amine (6.9 g).

The crude p-benzyl-bridged betaines were boiled in acetone, and the precipitate (74% yield) was found to contain the desired product and an almost stoichiometric amount of inorganic salt as determined by ash and elemental analyses. The dodecyl derivative (#4) was used without further purification. The hexadecyl derivative (#8) was dissolved in a minimum amount of warm water, allowed to precipitate, filtered and washed at least six times with water. The resulting water-insoluble compound contained only a trace of ash. Its elemental analysis was in good agreement with theory, and the product was used without further purification. The crude lauramido betaine (#14) reaction product was dissolved in boiling acetone and filtered. The filtrate was stripped of solvent and vacuum-dried. The clear gelatinous residue was dissolved in a minimum amount of water and purified in 2 ml portions on a Bio-Gel P-2 (200/400 mesh) column (30 × 5.5 cm). No ash was present in the chromatographed product. The palmitamido betaine was recrystallized from acetone/ethanol at −30 C and used in subsequent evaluation tests.

Quaternization of α-Bromo-o-Tolunitrile

In analogy to a previously reported procedure (5), the appropriate amine (0.024 mole) and 4.7 mg (0.024 mole) of α-bromo-o-tolunitrile were dissolved in 100 ml of isopropanol. The reaction mixture was refluxed overnight, after which the isopropanol was stripped off and traces of solvent were removed in vacuo at 50–55 C. The crude product was recrystallized from 125 ml ethyl acetate at 0 C in yields of 76 to 93 %.

Quaternization of 4-Chlorobutyronitrile

In analogy to the preceding procedure, the appropriate amine was quaternized with 4-chlorobutyronitrile. The crude quaternary ammonium compounds were recrystallized from ethyl acetate at room temperature (32% yield).

Hydrolysis of Nitriles to Carboxylic Acids

A modification of the procedure by Fuson and Rabjohn (8) was utilized to hydrolyze all nitriles. The nitrile (0.0365 mole) was mixed with a dilute sulfuric acid solution (7.5 ml acid in 9 ml water), and the solution was allowed to reflux gently for 6 hr. The solution was cooled in an ice bath and maintained below 40 C while 20% sodium hydroxide was added gradually to adjust the pH to 9 or 10. The following purification procedures were employed.

Hydrolysate of o-Cyanobenzyl Derivatives

The aqueous solution of the crude hydrolysate was concentrated to a volume of 25 ml, and the solid matter formed was filtered off and discarded. The pH of the filtrate was adjusted to 11, water was stripped off, and the residue was vacuum-dried for 7 hr at 60 C. The product was dissolved in absolute ethanol at room temperature; the solution was filtered and solvent was stripped off. The orange-colored oily residue was vacuum-dried at 60 C for 7 hr and recrystallized twice from acetone. The resulting white crystalline product gave the expected IR spectrum and had no ash.

Hydrolysate of Cyanopropyl Derivatives

The aqueous solution was concentrated to 20 ml, and the insoluble inorganic salts were filtered off and discarded. Upon standing, the aqueous filtrate formed more insoluble matter, which was filtered off and discarded. The filtrate was adjusted to pH 8.2, evaporated, vacuum-dried at 55 C, and the residue was dissolved in ethanol. The ethanol solution was filtered, and the filtrate was stripped and dried in vacuo at 55 C. The n-hexadecyl derivative (#7) was recrystallized from 350 ml acetone at −30 C. The first crop was discarded because of high ash content and the second crop, which still contained 2.25% ash, was utilized for lime soap dispersant requirements (LSDR) and detergency evaluations. The dodecyl derivative (#3) could not be recrystallized, and the crude betaine contained 4.56% ash. It was used in subsequent tests without further purification.

Lime soap dispersant requirements. LSDR were obtained by the Borghetty-Bergman procedure (12). Test solutions of the betaines were adjusted as needed to make allowance for salt impurities. The data are shown in the table.

Krafft points. Solubility of 1% solutions of the betaines was determined by a standard method (13), and the data recorded in the table.

Detergency evaluations. Screening tests were run in a Tergotometer for 20 min at 120 F with 2 g of test detergent dissolved in 1 liter of 300 ppm hardness water. Five swatches each of EMPA 101 cotton (EMPA), EMPA 104 cotton polyester, and Testfabrics cotton-polyester blend with permanent press finish (TF) were washed together in each beaker. Ternary formulations consisting of 65% tallow soap, 20% betaine and 15% glassy sodium silicate ($Na_2O:SiO_2 = 1:1.6$) were prepared with each betaine, and allowance was made, as needed, for the salt impurities of some of the betaine samples. Detergency of 0.2% solutions of the formulations was determined by difference in light reflectance before and after washing. Detergency of the

TABLE I

Surface Active Properties of Betaines and Selected Sulfobetaines

No.	Compound	Krafft point C[a]	LSDR[b]	Detergency % of control[f]		
				TF[c]	EMPA 101[d]	EMPA 104[f]
1	$C_{12}H_{25}\overset{+}{N}(CH_3)_2CH_2CO_2^-$	<4	20	97	103	97
2	$C_{12}H_{25}\overset{+}{N}(CH_3)_2C_2H_4CO_2^-$	<4	17	62	90	83
3	$C_{12}H_{25}\overset{+}{N}(CH_3)_2C_3H_6CO_2^-$	<4	11	85	103	94
4	$C_{12}H_{25}\overset{+}{N}(CH_3)_2\text{-}p\text{-}CH_2C_6H_4CO_2^-$	<4	9	85	100	97
5	$C_{16}H_{33}\overset{+}{N}(CH_3)_2CH_2CO_2^-$	18	14	74	84	75
6	$C_{16}H_{33}\overset{+}{N}(CH_3)_2C_2H_4CO_2^-$	<4	16	82	87	83
7	$C_{16}H_{33}\overset{+}{N}(CH_3)_2C_3H_6CO_2^-$	<4	7	97	103	103
8	$C_{16}H_{33}\overset{+}{N}(CH_3)_2\text{-}p\text{-}CH_2C_6H_4CO_2^-$	55	8	91	100	92
9	$C_{16}H_{33}\overset{+}{N}(CH_3)_2C_2H_4SO_3^-$[g]	>90	6[g]	18	58	47
10	$C_{16}H_{33}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$[g]	27	4[g]	97	97	100
11	$C_{16}H_{33}\overset{+}{N}(CH_3)_2\text{-}p\text{-}CH_2C_6H_4SO_3^-$[h]	>90	4[h]	97	68	47
12	$C_{12}H_{25}\overset{+}{N}(CH_3)_2\text{-}o\text{-}CH_2C_6H_4CO_2^-$	<4	>20	56	55	31
13	$C_{16}H_{33}\overset{+}{N}(CH_3)_2\text{-}o\text{-}CH_2C_6H_4CO_2^-$	—	—	9	42	22
14	$C_{11}H_{23}CONHC_3H_6\overset{+}{N}(CH_3)_2CH_2CO_2^-$	<4	7	103	100	86
15	$C_{15}H_{31}CONHC_3H_6\overset{+}{N}(CH_3)_2CH_2CO_2^-$	16	6	79	84	72

[a] Reference 13.

[b] Number of grams of surfactant required to prevent precipitation at 100 g of sodium oleate in 333 ppm hard water.

[c] TF Testfabrics Inc., Middlesex, NJ, soiled cotton-polyester blend cloth with permanent press finish.

[d] EMPA 101, EMPA, St. Gallen, Switzerland, soiled cotton cloth.

[e] EMPA 104, EMPA, St. Gallen, Switzerland, soiled cotton-polyester cloth.

[f] % Detergency of 0.2% solution of tertiary formualtion of soap, betaine, and silicate with respect to detergency of 0.2% of control detergent, all at 300 ppm water hardness and 120 F.

[g] From Reference 2.

[h] From Reference 5.

formulations is expressed in the table below as the percentage of the detergency of a 0.2% solution of a control detergent, a leading commercial product containing anionic surfactants and 50% sodium tripolyphosphate.

RESULTS AND DISCUSSION

Synthesis

Two straightforward methods were employed to synthesize the betaines.

A. From haloacids: Betaines were synthesized from haloacids according to the method of Daimler and Platz (7). Two-carbon-bridged betaines have been synthesized by Gresham et al. (14) from β-propiolactone; however, due to the carcinogenicity of this reagent, the haloacid synthesis was preferred for the two-carbon-bridged betaines. The major problem with this synthesis is removal of inorganic salt, which is a side-product of the reaction. Although salt impurities do not appear to interfere with surface activity, salt-free betaines were utilized for testing wherever possible so that the properties of the pure betaines could be determined. Fractional crystallization proved to be the most useful technique for desalting the betaines. In addition, Bio Gel P-2 removed traces of inorganic salts from the lauramido derivative, $C_{11}H_{23}CONHC_3H_6\overset{+}{N}(CH_3)_2CH_2CO_2^-$.

B. From halonitriles: The three-carbon- and o-benzyl-bridged betaines cannot be prepared from the haloacids, since in basic medium the starting materials, α-bromo-o-toluic acid and 3-chlorobutanoic acid, cyclize to form phthalide and γ-butyrolactone, respectively. Therefore, three-carbon- and o-benzyl-bridged betaines were prepared by quaternizing the appropriate tertiary amine with 4-chlorobutyronitrile or α-bromo-o-tolunitrile, respectively (5). The resulting quaternary compounds were hydrolyzed in a strong sulfuric acid solution to yield betaines (8). This step proceeded quantitatively, but the same desalting problems were encountered as mentioned above. While most preparations of this study were purified so that they ultimately gave no ash, compounds 3, 4, and 7 included in the table still contained 1.75%, 4.04%, and 0.89% wt ash, respectively.

Attempts to bring about reaction between tertiary fatty amines and haloacid chlorides were unsuccessful, and dehydrohalogenation instead of quaternization was observed even at temperatures as low as −78 C.

Surface Active Properties

In general the betaines (e.g., compounds 6, 7, and 8) are more water-soluble, i.e., possess lower Krafft points than analogous sulfobetaines (compounds 9, 10, and 11), which should give the former an inherent advantage over the latter in soap-based formulations. On the other hand, the range of LSDR values from 6 to 20 for betaines is higher than that for sulfobetaines or sulfatobetaines (2 to 6) which indicates that a more acidic anionic group, such as sulfo or sulfato, gives rise to greater lime soap dispersing ability than does a COO^- group. It has been observed with anionic and sulfobetaine type lime soap dispersants that lime soap dispersing ability is enhanced by introduction of an amido group into the molecule (15). The introduction of an amido group into a sulfobetaine or an anionic dispersant usually results also in a lowering of the Krafft point. Since the betaines generally possess low Krafft points to begin with, this enhancement of solubility could not be observed with the betaines; however, the lowering of the LSDR of betaines 14 and 13, which contain the amido group, is obvious.

Another factor affecting LSDR and Krafft point is the length of the bridge between anionic and cationic sites. In general, a C_3H_6 bridge between the sites gives rise to a lower LSDR than a CH_2 or C_2H_4 bridge. The same phenomenon occurs also with the sulfobetaines. Introduction of a $CH_2C_6H_4$ bridge does not produce a substantial improvement over a C_3H_6 bridge. Whereas the size of the bridge has a pronounced effect on the Krafft points of sulfobetaines and sulfatobetaines (2), the analogous effect on betaines was not apparent because of their inehrent greater water solubility.

Water solubility at the washing temperature and a low LSDR, as has been pointed out previously (15), are prerequisites for detergency but do not affect detergency directly (15). The o-$CH_2C_6H_4$-bridged betaines give poor detergency, and the short methylene bridge also had a slightly adverse effect on detergency. Otherwise, the effects of the size of the bridging gorup or the length of the hydrophobic alkyl chain on detergency appear to be negligible. In fact, detergency of the soap-silicate-betaine formulations is exceptionally good and surpassing that of the control in a few instances (#1, 3, 4, 7, 8, and 14). This is somewhat surprising in view of the fact that the betaines possess substantially poorer lime soap dispersing ability than most of those anionic dispersants or sulfobetaines previously reported in this series of publications. This gives further evidence (15) that LSDR and detergency are not directly related physical properties.

Of all the various types of lime soap dispersants studied by us, the betaines are among the few now produced commercially, albeit as chemical specialties, and thus this study may have considerable practical significance in view of the generally favorable detergency properties cited above.

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