ORIGINAL

Synthesis and Properties of α , ω -Bisamidobetaine-type Amphoteric Surfactants from Long-chain Dibasic Acids

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α , ω -Type amphoteric surfactants containing bisbetaine groups were synthesized by reactions of alkanedioic acids with *N*, *N*-dimethyl-1,3-propanediamine, followed by quaternization of the resulting bisaminoamides with sodium chloroacetate. The latter process was carried out in water or a mixture of isopropyl alcohol and water using sodium hydrogencarbonate or sodium hydroxide as the catalyst.

The properties of the α , ω -bisamidobetaine in aqueous solution were studied. α , ω -Bisamido-betaines derived from hexadecanedioic and icosanedioic acid showed good catalytic activity for the halide displacement reaction and a excellent ability to bring about lime soap dispersion.

1 Introduction

Interest in amphoteric surfactants of betaine-type has increased since they combine a positive as well as a negative charge in one molecule and have unique properties such as compatibility with any type of surfactants, high stability in hard water and very low eye and skin irritation¹⁾.

α , ω -Type surfactants possessing two functional groups in both sides of the molecule have been known to show the large molecular area because of bulkiness of molecule and disturbance of dense adsorption²⁾. Most of the works deal with anionic and nonionic surfactants; α , ω -alkanedicarboxylates^{3),4)}, α , ω -bis(3-sulfopropoxycarbonyl) alkanes⁵⁾, α , ω -alkane disulfates⁶⁾, α , ω -bis(*p*-sulfophenoxy) alkanes⁷⁾, and α , ω -alkane bis[poly(oxyethylene)] ethers⁸⁾.

Recently, the synthesis of α , ω -type amphoteric surfactants from α , ω -dihalododecane have been reported⁹⁾.

More recently, we also have reported a new type of bis[2-(trimethylammonio)ethyl] α , ω -alkanedioate diiodides⁹⁾ and α , ω -bisamido-betaines¹⁰⁾.

This paper describes the synthesis of α , ω -bisamidobetaines from α , ω -dicarboxylic acids,

which have become commercially available, and the properties of resulting α , ω -bisamido-betaines. We have expected that the introduction of the bulky α , ω -difunctional groups and amido groups into the molecule would result in an enhancement of the lime soap dispersing ability.

2 Experimental

2.1 Materials

Dodecanedioic acid was the commercial reagent (Tokyo Kasei Co., extra pure grade). Hexadecanedioic and icosanedioic acids were obtained from Okamura Oil Mill Ltd., Their purities determined by gas chromatography of their methyl esters exceeded 98%. *N*, *N*-Dimethyl-1,3-propanediamine and sodium chloroacetate were obtained from Tokyo Kasei Kogyo Co. and Wako Pure Chemical Co., respectively. 3-(Decanoylamino)propyldimethylammonioacetate (C 10 monoamidobetaine) was synthesized from the reaction of decanoic acid and *N*, *N*-dimethyl-1,3-propanediamine, followed by quaternization of the resulting aminoamide. Commercial *N*-dodecylbetaine (AM-301, commercial C 12 monobetaine) and 3-(dodecanoylamino) propyldimethylammonioacetate (AM 3130, commercial C 12 monoamidobetaine) were supplied by NIKKO Chemical

Co. Ltd. and were used after drying *in vacuo*.

Tetraethylammonium bromide (TEAB) and tetrabutylammonium bromide (TBAB) were commercial reagents (Tokyo Kasei Kogyo Co.) and were used without further purification.

2.2 Synthesis of *N,N'*-Bis [3-(dimethylamino) propyl] dodecanediamide (C 12 Bisaminoamide)

A mixture of *N,N*-dimethyl-1,3-propanediamine (0.72 mol, 73.6 g), dodecanedioic acid (0.30 mol, 69.0 g) and xylene (70 mL) was charged into a four necked 300 mL flask equipped with stirrer, a thermometer and a Dean-Stark water separator. The solution was heated while stirring at the reflux temperature (140~146°C). Theoretical amounts (10.8 g) of water were removed azeotropically for about 5 h. The product was crystallized twice from benzene to yield 109.0 g (96%) of crystalline solid. The following melting point and analytical data were observed for this derivative.

mp : 112.3~112.8°C

Analysis: C 66.18%, H 11.66%, N 13.90%

Calcd. for $C_{22}H_{46}N_4O_2$: C 66.29%, H 11.63%, N 14.05% IR(KBr): 3320, 2920, 2850, 2760, 1645, 1550, 1485, 1420, 1385, 1340, 1240, 1190, 1040, 840, 720 cm^{-1} .

NMR(in $CDCl_3$, δ ppm): 1.28 (12 H, s, CH_3), 1.5~1.9 (8 H, m, N-C- CH_2 and CO-C- CH_2), 2.05~2.2 (4 H, m, CH_2 CO), 2.23 (12 H, s, N- CH_3), 2.38 (4 H, t, $J=7.0$ Hz, N- CH_2), 3.2~3.5 (4 H, m, CO-N- CH_2), 6.8~7.0 (2 H, m, NH).

2.3 Synthesis of *N,N'*-Bis[3-(dimethylamino)propyl]hexadecanediamide (C 16 Bisaminoamide)

A mixture of *N,N*-dimethyl-1,3-propanediamine (0.40 mol, 40.9 g), hexadecanedioic acid (0.16 mol, 47.7 g) and xylene (100 mL) was refluxed (138°C) for 7.5 h. The product was crystallized from acetone to yield 63.3 g (87%) of C 16 bisaminoamide. The following melting point and analytical data were observed for this derivative.

mp : 117~117.5°C

Analysis: C 69.04%, H 11.83%, N 11.97%

Calcd. for $C_{26}H_{54}N_4O_2$: C 68.67%, H 11.97%, N 12.32%

IR(KBr): 3300, 2900, 2840, 2800, 2750, 1638,

1530, 1470, 1418, 1380, 1295, 1250, 710 cm^{-1} .

NMR(in $CDCl_3$, δ ppm): 1.22 (20H, s, CH_3), 1.45~1.80 (8 H, m, CH_2 -C-CO and N-C- CH_2), 2.05~2.16 (4 H, m, CH_2 CO), 2.23 (12 H, s, N- CH_3), 2.38 (4 H, t, $J=6.7$ Hz, N- CH_2), 3.2~3.4 (4 H, m, CO-N- CH_2), 6.8~6.9 (2H, m, NH).

2.4 Synthesis of *N,N'*-Bis [3-(dimethylamino) propyl] icosanediamide (C 20 Bisaminoamide)

A mixture of *N,N*-dimethyl-1,3-propanediamine (0.36 mol, 36.7 g), icosanedioic acid (0.15 mol, 51.4 g) and xylene (50 mL) was refluxed (135~150°C) for 16 h. The product was crystallized from acetone to yield 71.2 g (93%) of C 20 bisaminoamide. The following melting point and analytical data were observed for this derivative.

mp : 120~120.5°C.

Analysis: C 70.34%, H 12.40%, N 10.40%.

Calcd. for $C_{30}H_{62}N_4O_2$: C 70.54%, H 12.23%, N 10.97%.

IR(KBr): 3280, 2880, 2830, 2740, 1630, 1520, 1450, 1410, 1375, 1255, 1230, 1200, 1175, 1035 cm^{-1} .

NMR(in $CDCl_3$, δ ppm): 1.24 (28 H, s, CH_3), 1.5~1.8 (8 H, m, CH_2 -C-CO and N-C- CH_2), 2.07~2.2 (4 H, m, CO-N- CH_2), 6.8~7.0 (2 H, m, NH).

2.5 Quaternization of Bisaminoamide

To a 100 mL flask equipped with a bar magnet and a condenser were added C 12 bisaminoamide (20 mmol, 7.9 g), sodium chloroacetate (50 mmol, 5.8 g), sodium hydrogen carbonate (4 mmol, 0.3 g) or sodium hydroxide (4 mmol, 0.2 g) and 9 mL of water or the mixture of isopropyl alcohol and water. The mixture was refluxed (83~86°C) for 6 h, after which the solvent was stripped off. The filtrate was concentrated and purified on silica-gel (Wakogel C 200) column (30×500 mm) using the mixed solvents of methyl alcohol/ethyl alcohol/isopropyl alcohol/28% ammonia (3/3/3/0.6~3). The resulting white crystalline product was analyzed by the usual technique and had no ash. The reaction mixtures of other bisaminoamides were treated in the same procedure and the products were isolated.

2.6 Surface Tension Measurements

The purified α , ω -bisamidobetaines were

dissolved in quartz-distilled water. All surface tension measurements were made by Du Nouy tensiometer.

2.7 Catalytic Activity for the Halide Displacement Reaction

A 10 mL flask was charged with α, ω -bisamidobetaine (0.25 mmol, 5 mol% based on 1-bromooctane), 1-bromooctane (5 mmol, 1 g), sodium iodide (6.7 mmol, 1 g) and 5 mL of water. This mixture was stirred by means of a magnetic stirrer, and the flask immersed in an oil bath maintained at 100°C for 7 h. The product was determined by gas liquid chromatography (silicone OV-1 1.5% on Shimalite W, 2 m $\times$ 3 mm) using an internal standard of 6-undecanone.

2.8 Lime Soap Dispersing Ability

Lime soap dispersant requirement (LSDR) was obtained by the Borghetty-Bergman procedure¹¹⁾. The values represent the grams of compound required to prevent precipitation of 100 g of sodium oleate in hard water of 333 ppm (Ca/Mg=3/2).

3 Results and Discussion

3.1 Synthesis of α, ω -Bisamidobetaines

The reaction of bisaminoamide (**1 a~c**) with sodium chloroacetate in the presence of sodium hydrogencarbonate in refluxing a mixture of isopropyl alcohol and water gave α, ω -alkanedioylbis[(3-aminopropyl)dimethylammonioacetate] (**2 a~c**) in the yield of 64~79%.

Thin-layer chromatography using the mixed developing solvent (3/3/2 vol/vol) of methanol,

Table-1 Analytical data of the products.

Product	Elemental analysis (%)			NMR (in D ₂ O) δ (ppm)	IR (cm ⁻¹)
	Obs. (Calcd.)	C	H	N	
2 a ^{*1}	54.99 (54.91)	9.85 (9.92)	9.67 (9.85)	1.3~1.5(16 H, m, CH ₂), 2.1~2.4(8 H, m, COCH ₂ and N-C-CH ₂), 3.23 (12 H, s, N ⁺ -CH ₃), 3.3~3.8(8 H, m, N ⁺ -CH ₂ and N-CH ₂), 3.87(4 H, s, N ⁺ -CH ₂ -COO ⁻)	3280 1635 1550
2 b ^{*2}	61.14 (61.19)	10.02 (10.27)	9.39 (9.52)	1.28(20 H, s, CH ₂), 1.5~1.7(4 H, m, CO-C-CH ₂), 1.9~2.3 (8 H, m, COCH ₂ and N-C-CH ₂), 3.22(12 H, s, N ⁺ -CH ₃), 3.3~3.7(8 H, m, N ⁺ -CH ₂ and N-CH ₂), 3.83(4 H, s, N ⁺ -CH ₂ -COO ⁻)	3300 1630 1600 1535
2 c ^{*2}	63.29 (63.32)	10.73 (10.63)	8.57 (8.69)	1.28(28 H, s, CH ₂), 1.6~2.8(12 H, m, COCH ₂ CH ₂ and N-C-CH ₂), 3.33(12 H, s, N ⁺ -CH ₃), 3.4~3.7(8 H, m, N ⁺ -CH ₂ and N-CH ₂), 3.83(4 H, s, N ⁺ -CH ₂ -COO ⁻)	3300 1630 1535
3 a ^{*1}	56.37 (56.44)	10.73 (10.66)	10.51 (10.97)	1.2~1.5(16 H, m, CH ₂), 1.5~2.3(10 H, m, COCH ₂ , CON-C-CH ₂ and N-CH ₂), 2.5(6 H, s, N-CH ₃), 3.23(6 H, s, N ⁺ -CH ₃), 3.1~3.6(6 H, m, N ⁺ -CH ₂ and CON-CH ₂), 3.78(2 H, s, N-CH ₂ -COO ⁻)	3250 1640 1550
3 b ^{*2}	63.42 (63.36)	10.76 (11.02)	10.45 (10.56)	1.26(20 H, s, CH ₂), 1.5~2.04(8 H, m, CO-C-CH ₂ and CON-C-CH ₂), 2.19 (4 H, t, <i>J</i> =6.7 Hz, COCH ₂), 2.54 (6 H, s, N-CH ₃), 2.74(2 H, t, <i>J</i> =5.1 Hz, N-CH ₂), 3.18(6 H, s, N ⁺ -CH ₃), 3.1~3.6(6 H, m, N ⁺ -CH ₂ and CON-CH ₂), 3.78(2 H, s, N ⁺ -CH ₂ -COO ⁻)	3300 1630 1540
3 c ^{*2}	65.71 (65.49)	11.31 (11.34)	9.60 (9.55)	1.26(32 H, s, CH ₂), 1.6~2.5(10 H, m, COCH ₂ and CON-C-CH ₂ , N-CH ₂), 2.56(6 H, s, N-CH ₃), 3.1~3.6(6 H, m, CON-CH ₂ and N ⁺ -CH ₂), 3.2(6 H, s, N ⁺ -CH ₃), 3.80(2 H, s, N ⁺ -CH ₂ -COO ⁻)	3300 1635 1540

*1 The values in parentheses are calculated for the hydrate containing 3 mol of water.

*2 The values in parentheses are calculated for the hydrate containing 1 mol of water.

NMR measurements were carried out under the following conditions: 60 MHz; conc., 25~30 mg/0.4 mL; pulse width, 60; pulse interval, 5 s; number of scan; 25; reference, DSS.

ethanol, isopropyl alcohol and 28% ammonia aqueous solution applied to the detection of products.

The component which has the R_f value of 0.16 was isolated on silica gel column using the similar developing solvents as TLC and this structure was confirmed as C12 bisamidobetaine (**2a**) by elementary analysis, IR and NMR spectral data. The structure of the component having the R_f value of 0.40 was confirmed as C12 monoamidobetaine (**3a**) by analysis of the isolated one. Similarly, other monoamidobetaines and bisamidobetaines obtained from the reactions of C16 or C20 bisaminoamides and sodium chloroacetate were isolated and these structures were confirmed. Analytical data of C16 bisamidobetaine (**2b**), C16 monoamidobetaine (**3b**), C20 bisamidobetaine (**2c**) and C20 monoamidobetaine (**3c**)

as well as C12 derivatives are shown in **Table-1**.

The reactions of bisaminoamides with sodium chloroacetate were studied under various conditions. As shown in **Table-2**, in the case of sodium hydrogencarbonate catalyst the reaction in water or mixed solvent of isopropyl alcohol and water gave bisamidobetaine in good yield. In the case of sodium hydroxide catalyst, the reaction in isopropyl alcohol gave bisamidobetaine in good yield while that in water gave low yield and the recovery of bisaminoamide was diminished. This may be due to the hydrolysis of sodium chloroacetate and bisaminoamide and Hofman degradation of bisamidobetaine by sodium hydroxide.

3.2 Surface Tension of Aqueous Solution of α - ω -Bisamidobetaine

Plots of surface tension (γ) vs. logarithm of concentration for α , ω -bisamidobetaines are given in **Fig.-1**. There is no sharp discontinuity in the curve for C12 bisamidobetaine. The sharp discontinuities for C16 and C20 bisamidobetaines appeared in their curves. Critical micelle concentrations (cmc) and areas/molecule at the liquid/air interface were determined from the surface tension vs. log (concentration) plots. The values obtained for

Table-2 Reactions of bisaminoamides with sodium chloroacetate.

Bisaminoamide (mmol)	Sodium chloroacetate (mmol)	Catalyst (mmol)	Solvent (mL)	Recovered bisaminoamide (%)	Yield of monobetaine (%)	Yield of bisbetaine (%)
C12 (20)	50	NaHCO ₃ (4)	H ₂ O (9)	3	17	75
C12 (25)	25	NaHCO ₃ (4)	H ₂ O (9)	35	21	35
C12 (20)	50	NaHCO ₃ (4)	H ₂ O/IPA (2/7)	2	15	77
C12 (20)	50	NaOH (4)	IPA (30)	4	14	67
C12 (20)	50	NaOH (4)	H ₂ O (9)	3	20	47
C16 (10)	25	NaHCO ₃ (2)	H ₂ O/IPA (12/28)	3	16	69
C16 (12)	30	NaHCO ₃ (2)	H ₂ O/IPA (7/23)	6	17	64
C20 (4.4)	11	NaOH (11)	IPA (10)	—	8	76
C20 (8.5)	30	NaHCO ₃ (2)	H ₂ O/IPA (12/28)	—	14	68

Fig.-1 Plots of surface tension *vs.* logarithm of concentration for α , ω -bisamidobetaine.

Table-3 Surface active properties of α , ω -bisamidobetaines.

Bisamido betaine	cmc (M)	γ_{cmc} (mN/m)	Surface excess $\times 10^{10}$ (mol/cm ²)	Area/molecule ($\text{\AA}^2$)
C16	3.5×10^{-3}	45.8	3.1	54
C20	2.0×10^{-4}	49.3	0.87	192

cmc and areas/molecule are listed in **Table-3**. The molecular area of C16 bisamidobetaine is comparatively large and that of C20 bisamidobetaine is very large in contrast with 33 $\text{\AA}^2$ for sodium dodecyl sulfate¹²⁾. This fact may rise from the loosely packed micelle of C20 bisamidobetaine because of the presence of the two polar groups having the large sectional area in the molecule.

3.3 Catalytic Activity for the Halide Displacement Reaction

Halide displacement is one of the most important reaction for the synthesis of alkyl iodides and fluorides. Catalytic activity of α , ω -bisamidobetaines for this reaction was studied. As shown in **Table-4**, the catalytic activity of α , ω -bisamidobetaine was increased with increasing chain length. The activity of C20 bisamidobetaine was superior to that of tetraethylammonium bromide (TEAB), although it was slightly lower than that of tetrabutylammonium bromide (TBAB), C10 monoamidobetaine and commercial monoamidobetaine.

3.4 Lime Soap Dispersing Ability

The lime soap dispersant requirements (LSDR) of α , ω -bisamidobetaines are shown in **Table-5**. LSDR of C20 bisamidobetaine

Table-4 Halide displacement reactions in the presence of bisamidobetaines.
 $C_8H_{17}Br + MI \rightarrow C_8H_{17}I + MBr$

Reagent	Catalyst	$C_8H_{17}I$ (%)
NaI	C12-Bisamidobetaine (2a)	4
NaI	C16-Bisamidobetaine (2b)	48
NaI	C20-Bisamidobetaine (2c)	82
KI	C16-Bisamidobetaine (2b)	61
KI	C20-Bisamidobetaine (2c)	79
NaI	TEAB*	5
NaI	TBAB**	95
NaI	C10-Monoamidobetaine***	92
NaI	Commercial C12 monobetaine	93
NaI	Commercial C12 monoamidobetaine	92

* Tetraethylammonium bromide

** Tetrabutylammonium bromide

*** $C_9H_{19}CONHC_3H_6N^+(CH_3)_2CH_2COO^-$

Table-5 Lime soap dispersing power of α , ω -bisamidobetaines.

Amidobetaine	LSDR*
C12-Bisamidobetaine (2a)	200<
C16-Bisamidobetaine (2b)	8.5
C20-Bisamidobetaine (2c)	2.5
C10-Monoamidobetaine**	35
Commercial C12 monobetaine	20
Commercial C12 monoamidobetaine	7

* Minimum number of surfactant required to prevent precipitation of 100 g sodium oleate in hard water (300 ppm)

** $C_9H_{19}CONHC_3H_6N^+(CH_3)_2CH_2COO^-$

is 2.5, which is one of the most excellent values among those available from the literature, and is much better than that of C10 monoamidobetaine having the same hydrophilicity. This may be explained by the large molecular area of C20 bisamidobetaine. LSDR of C16 bisamidobetaine was comparable to that of sodium α -sulfomethyltallowate¹³⁾, which is known as a readily available lime soap dispersing agent.

4 Conclusion

New type of α , ω -amphoteric surfactants containing bisamidobetaine groups in both sides of the molecule were synthesized from long-chain dibasic acids in good yield. In

comparison of α, ω -bisamidobetaines with monoamidobetaines containing same proportions of the hydrophilic group, the catalytic activity for the halide displacement reaction of both types of amidobetaines was comparable. The lime soap dispersing ability of the former was superior to that of the latter. The excellent lime soap dispersing ability of α, ω -bisamidobetaines may be attributed to bulkiness of the two polar amphoteric groups.

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長鎖二塩基酸からの α, ω -ビスアミドベタイン型両性界面活性剤の合成と性質

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2 個のベタイン基をもつ α, ω -型両性界面活性剤が、アルカン二酸と *N, N*-ジメチル-1,3-プロパンジアミンとの反応とそれに続くクロロ酢酸ナトリウムでの第四級化反応によって合成された。第四級化反応は、炭酸水素ナトリウムあるいは水酸化ナトリウムを触媒として用い水中あるいはイソプロピルアルコールと水の混合溶媒中で行った。

α, ω -ビスアミドベタイン水溶液の性質について検討した。ヘキサデカン二酸及びイコサン二酸から合成した α, ω -ビスアミドベタインは、ハライド置換反応に対して良好な触媒活性を示し、また優れたカルシウムセッケン分散能を示した。