Surface-Active Properties of Novel Cationic Surfactants with Two Alkyl Chains and Two Ammonio Groups

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ABSTRACT: A series of *bis*-quaternary ammonium salts was easily prepared by the reaction of a long-chain *tert*-alkylamine with epichlorohydrin, and their surface-active properties were measured. The prepared amphipathic compounds had good water solubility and showed characteristic surface-active properties, particularly, extremely excellent foaming ability and foam stability for some specific compounds, such as the compound with a dodecyl and a tetradecyl group as the lipophilic chains. Their critical micelle concentration, which decreased with increased alkyl chainlength, is two orders of magnitude lower compared with the conventional *mono*-quaternary ammonium salts. In comparison with surface-active properties of *bis*-quaternary ammonium salts, prepared from various organic dichlorides, there are little differences based on the kind of connecting group in the surface-active properties except for foaming.

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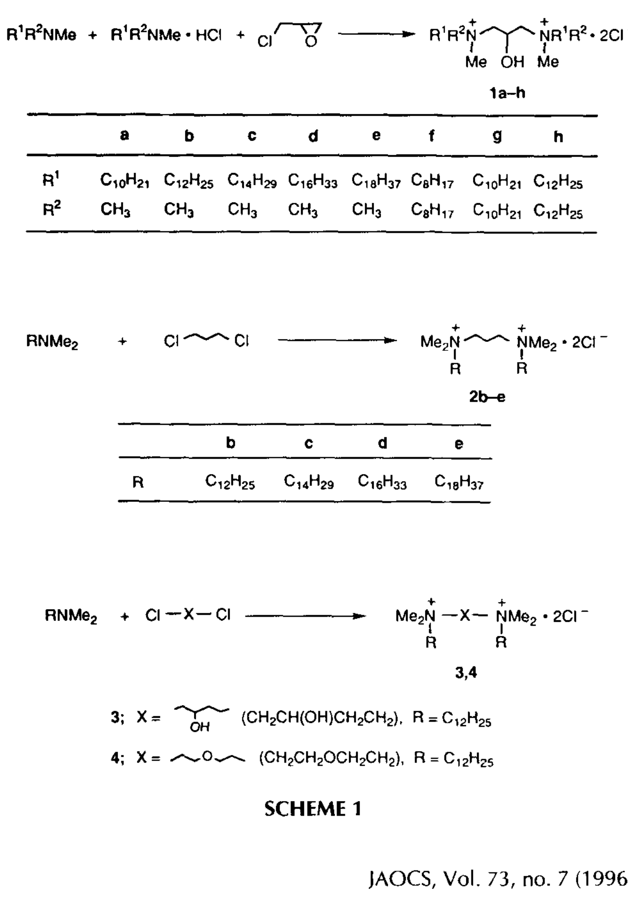
KEY WORDS: Amphipathic compound, *bis*-quaternary alkylammonium salt, foaming property, surface-active properties.

For the purpose of synthesizing a new type of cationic surfactant, we have reported the reaction of an alkyldimethylamine with epichlorohydrin to afford a *bis*-quaternary ammonium salt (1). Amphipathic compounds with two alkyl chains and two hydrophilic groups in a molecule show unusual physicochemical properties in comparison with conventional surfactants that have one alkyl chain and one hydrophilic group. For example, some gemini surfactants with two or three alkyl chains and two anionic groups (carboxylate, phosphate, sulfate, and sulfonate head groups) (2–4) are characteristic in lowering surface tension of aqueous solutions and in forming micelles at quite low concentrations. Some *bis*-quaternary ammonium compounds with two alkyl chains and two ammonio groups also show excellent surface-active properties as anionic types (5), good antimicrobial activity (6), and good extractive abilities as phase transfer catalysts (7).

In this work, a series of *bis*-quaternary ammonium salts was prepared from a long-chain alkyldimethylamine and dialkylmethylamine with epichlorohydrin. The surface-active properties were measured with changing alkyl chainlength. To compare the effect of the connecting moiety on the surface activity, the surface-active properties of *bis*-quaternary ammonium salts that were obtained from various organic dichlorides were also measured.

EXPERIMENTAL PROCEDURES

Materials. The reagents used were all purchased from commercial sources except for didodecylmethylamine. *bis*-Alkyldimethylammonium salts from epichlorohydrin, 1,4-dichloro-2-butanol, and *bis*-2-chloroethyl ether were prepared according to the method mentioned in a previous paper (1). *bis*-Dialkylmethylammonium salts from epichlorohydrin and *bis*-alkyldimethylammonium salts from 1,3-dichloropropane were prepared as shown in Scheme 1.



	a	b	c	d	e	f	g	h
R^1	$C_{10}H_{21}$	$C_{12}H_{25}$	$C_{14}H_{29}$	$C_{16}H_{33}$	$C_{18}H_{37}$	C_8H_{17}	$C_{10}H_{21}$	$C_{12}H_{25}$
R^2	CH_3	CH_3	CH_3	CH_3	CH_3	C_8H_{17}	$C_{10}H_{21}$	$C_{12}H_{25}$

	b	c	d	e
R	$C_{12}H_{25}$	$C_{14}H_{29}$	$C_{16}H_{33}$	$C_{18}H_{37}$

3; X = $(CH_2CH(OH)CH_2CH_2)$, R = $C_{12}H_{25}$

4; X = $(CH_2CH_2OCH_2CH_2)$, R = $C_{12}H_{25}$

SCHEME 1

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Structures of the studied compounds are also given in Scheme 1.

The structures of the prepared compounds were confirmed from spectral data and elemental analysis [mass: JMS-DX303; JEOL, Ltd., Tokyo, Japan; ^{1}H nuclear magnetic resonance (NMR): AM600, 600 MHz; Bruker, Fallanden, Switzerland].

Preparation of didodecylmethylamine. A mixture of dodecylamine (22.24 g, 0.12 mol), dodecyl bromide (14.96 g, 0.06 mol), sodium carbonate (31.80 g, 0.30 mol), and ethanol (70 mL) was heated to reflux until the bromide had been consumed, which took five hours. The reaction was followed by thin-layer chromatography [silica gel plate eluted with a mixture of ethyl acetate/acetone/aqueous ammonia (29%)/water (6:7:1:1, by vol)]. After removal of the solvent by evaporation, the organic compounds were extracted with dichloromethane. The extract was washed with distilled water for deionization. Removal of the solvent gave the crude product of didodecylamine, mixed with dodecylamine, as a pale yellow solid (34.82 g). Methylation to didodecylmethylamine was performed with this crude material as follows: Formic acid (43.64 g, 0.95 mol) was added slowly to the mixture of the crude product (34.82 g) and methanol (120 mL) under cooling with ice water. After the addition of formaldehyde (53.36 g of 37 wt% solution, 0.66 mol), the mixture was heated to reflux for 12 h. After low-boiling compounds were evaporated at 50°C, sodium hydroxide solution (25 wt%) was added to the mixture until the solution became weakly alkaline (pH 9). The solution was then heated to reflux for 3 h. The extracts of the mixture with ethyl ether were condensed to give the crude product (24.85 g). Didodecylmethylamine was purified by fractional distillation under reduced pressure (153–157°C/0.1 mmHg, 8.71 g, 41% yield). ^{1}H NMR ($CDCl_3$): 0.89 (*t*, 6H), 1.20–1.40 (*m*, 36H), 1.72–1.90 (*br*, 4H), 2.75 (*s*, 3H), 2.82–3.11 (*br*, 4H); mass [CI(positive): *m/e*, relative intensity]: 368 [$(M + 1)^+$, 100], 212 [11]; anal. found: C, 81.61; H, 14.59; N, 3.91%. Calcd. for $C_{25}H_{53}N$: C, 81.66; H, 14.53; N, 3.81%.

Preparation of bis-*dialkylmethylammonium salts from epichlorohydrin.* A typical procedure for the preparation of *bis*-didodecylmethylammonium salt (**1h**) is as follows: Epichlorohydrin (0.56 g, 6.0 mmol) was added to a mixture of didodecylmethylamine (11.02 g, 30.0 mmol), its hydrochloride (2.42 g, 6.0 mmol), and 1-propanol (10 mL). The mixture was heated to reflux for 24 h, and the yield of product was determined by ^{1}H NMR by using the unreacted excess amine as an internal standard (81% NMR yield). The purification was done by silica gel column chromatography with chloroform/methanol (1:1, vol/vol) eluent. A waxy product was obtained (2.70 g, 51% yield). ^{1}H NMR ($CDCl_3$): 0.88 (*t*, 12H), 1.20–1.48 (*m*, 72H), 1.51–1.99 (*m*, 8H), 3.30–3.53 (*m*, 8H), 3.41 (*s*, 6H), 3.55–3.68 (*m*, 2H), 4.45 (*d*, 2H), 5.11–5.22 (*br*, 1H); fast atom bombardment–mass spectrometry (FAB–MS) (*m/e*, relative intensity): 827 [$(M–Cl)^+$, 2], 424 [100], 212 [35], 100 [28], 58 [30], 43 [22].

Preparation of bis-*alkyldimethylammonium salts from 1,3-dichloropropane.* A typical procedure for the preparation of *bis*-dodecyldimethylammonium salt (**2b**) is as follows: A mixture of dodecyldimethylamine (12.80 g, 60.0 mmol), 1,3-dichloropropane (1.13 g, 10.0 mmol), and 1-propanol (30 mL) was heated to reflux for 24 h. The amount of product was determined by ^{1}H NMR by using the unreacted excess amine as an internal standard (76% NMR yield). After the solvent was evaporated under reduced pressure to give a waxy material, the *bis*-ammonium salt was isolated by washing the waxy material with hexane and then purifying by recrystallization from acetone. A white powder was obtained (3.76 g, 70% yield). ^{1}H NMR ($CDCl_3$): 0.88 (*t*, 6H), 1.21–1.43 (*m*, 36H), 1.66–1.82 (*br*, 4H), 2.80–2.91 (*br*, 2H), 3.33 (*s*, 12H), 3.41–3.49 (*br*, 4H), 3.92–4.01 (*br*, 4H); FAB–MS (*m/e*, relative intensity): 503 [$(M–Cl)^+$, 13], 290 [13], 254 [100], 212 [13], 84 [26], 58 [57].

Methods. The Krafft point was measured by the naked eye with 1 wt% aqueous solution of the *bis*-quaternary ammonium salt. The surface tension of the *bis*-quaternary ammonium salt aqueous solution was measured with a Wilhelmy tensiometer (Surface Tensometer ST-1, glass plate; Shimadzu Corporation, Kyoto, Japan) at 20°C. The critical micelle concentration (CMC) and γ_{CMC} (surface tension at CMC) values were determined from the break point of each surface tension vs. concentration (log scale) plot. The pC_{20} (adsorption efficiency) values were determined from the negative logarithm of the concentration of *bis*-quaternary ammonium salt required to produce a 20 mN/m reduction in the surface tension of water (8). The foaming properties were measured by the semi-micro TK method with a 0.1 wt% aqueous solution (9).

RESULTS AND DISCUSSION

The synthetic results of *bis*-quaternary ammonium salts are summarized in Table 1 with the elemental analyses. Characterization of the *bis*-quaternary ammonium salts from 1,4-dichloro-2-butanol (**3**) and *bis*-2-chloroethyl ether (**4**) was shown in a previous paper (1).

The *bis*-alkyldimethylammonium salts from epichlorohydrin (**1a–e**) were all obtained with ease and almost quantitatively under mild conditions (Table 1). For dialkylmethylamine, the reactivity is expected to decrease because of the increased steric hindrance due to the additional alkyl chain. However, the *bis*-dialkylmethylammonium salts from epichlorohydrin (**1f–h**), which have four alkyl chains and two ammonio groups, were still obtained in good yields (Table 1). The *bis*-quaternary ammonium salts (**2b–e**) from 1,3-dichloropropane were obtained in good yields, but a higher temperature (refluxing in 1-propanol) and longer time (24 h) were needed for the preparation than for those from epichlorohydrin (see the Experimental Procedures section) (Table 1). With respect to the reaction of alkyldimethylamine with epichlorohydrin, the ease of reaction, based on the reactive epoxide and the assistance by the hydroxyl group, was discussed in a previous paper (1).

Compounds **2b–e** melted at high temperatures to decompose in comparison with **1a–e**, which have a hydroxyl group

TABLE 1
Characterization of *bis*-Quaternary Ammonium Salts

Compound	Yield[a] (%)	m.p. (°C)	Anal. found (calcd.), %[b]
1a	>95	82–83	H, 12.02 (12.07) C, 62.27 (62.64) N, 5.30 (5.41) Cl, 13.94 (13.70)
1b	>95	86–87	H, 12.34 (12.29) C, 64.16 (64.28) N, 4.84 (4.84) Cl, 12.08 (12.24)
1c	>95	88–89	H, 12.75 (12.46) C, 65.95 (65.80) N, 4.36 (4.38) Cl, 11.10 (11.10)
1d	>95	91–92	H, 12.54 (12.67) C, 70.08 (70.12) N, 4.20 (4.19) Cl, 10.85 (10.61)
1e	>95	95–96	H, 12.50 (12.75) C, 68.79 (68.76) N, 3.70 (3.73) Cl, 9.41 (9.44)
1f	86	Waxy	H, 12.17 (12.56) C, 67.73 (67.54) N, 4.26 (4.26) Cl, 10.90 (10.78)
1g	82	Waxy	H, 12.72 (12.83) C, 70.48 (70.18) N, 3.66 (3.64) Cl, 9.39 (9.21)
1h	81	Waxy	H, 12.92 (13.02) C, 71.92 (72.14) N, 3.17 (3.18) Cl, 8.33 (8.04)
2b	76	192–194[c]	H, 12.62 (12.65) C, 66.45 (66.75) N, 4.89 (5.02) Cl, 12.58 (12.71)
2c	61	190–192[c]	H, 12.91 (12.74) C, 65.69 (65.59) N, 4.32 (4.37) Cl, 11.16 (11.06)
2d	67	189–191[c]	H, 12.77 (12.91) C, 69.10 (68.99) N, 4.06 (4.13) Cl, 10.59 (10.44)
2e	63	185–187[c]	H, 12.85 (13.02) C, 69.93 (70.25) N, 3.77 (3.81) Cl, 10.28 (9.65)

[a] Calculated from ^1H nuclear magnetic resonance.

[b] Calculated values are based on the assumption that the compound contains bonding water.

[c] Decomposed.

in the connecting group between nitrogen atoms, which is different from compounds **2b–e**.

The surface-active properties of *bis*-quaternary ammonium salts from epichlorohydrin and 1,3-dichloropropane at 20°C are summarized in Table 2, except for **1f–h**, along with reported data for conventional quaternary ammonium salts.

The properties of compounds **1f–h** could not be investigated because they are insoluble in water even at higher temperatures (up to 80°C), although they are dispersible to a stable turbid state. Concerning their low solubility, the following two reasons may be stated: (i) the presence of four long alkyl chains, which are responsible for the hydrophobicity of compounds **1f–h** and which are too large for them to dissolve in water, even for the short octyl chains (**1f**) and (ii) the hydrophobic group is much bulkier than the hydrophilic group, making it difficult for compounds **1f–h** to form water-soluble aggregates, such as micelles.

All other compounds are soluble in water, and their Krafft points are below 0°C, except for those with a stearyl group (**1e** and **2e**). However, **1e** and **2e** clearly dissolved in water at 40°C at 1 wt% concentration, and the resulting solutions remained clear, even on chilling to 0°C. However, precipitation occurred after standing at room temperature for one day. Their surface-active properties were not measured.

For the *bis*-quaternary ammonium salts from epichlorohydrin, the CMC values of compounds **1a–d** are smaller by about one to two orders of magnitude than those of the conventional quaternary ammonium salts. As recognized in anionic gemini surfactants, due to the presence of the two alkyl chains, it is likely that the *bis*-quaternary ammonium salts exhibit larger intermolecular hydrophobic interactions that make it easier for them to form aggregates in water than the *mono*-quaternary ammonium salts (5).

Among compounds **1a–d**, compounds **1a** and **1b** with decyl and dodecyl chains show the maximum ability to lower surface tension. Their γ_{CMC} values increased slightly with increased alkyl chainlength in their homologous series.

The pC_{20} of *bis*-quaternary ammonium salt **1b** is higher by about one order of magnitude than that of the *mono*-quaternary ammonium salt with the same alkyl chainlength (dodecyl group). The value of pC_{20} is a useful parameter to measure the efficiency of adsorption of the surfactant on an air–water interface (8), and the result shown in Table 2 indicates that the *bis*-quaternary ammonium salt adsorbs more efficiently at the interface than the *mono*-quaternary ammonium salt.

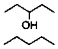
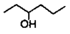
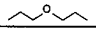
The foaming ability and foam stability of the *bis*-quaternary ammonium salts from epichlorohydrin are interesting. The foaming ability of the compound with decyl groups (**1a**) is low at 0.1 wt%, which is below the CMC. At 1 wt%, above the CMC of **1a**, the foam volume is large, like that of **1b** and **1c**, but foam stability is low. The foaming ability of conventional dodecyltrimethylammonium chloride is almost zero (Table 2), whereas that of the *bis*-quaternary ammonium salt with the same dodecyl chains (**1b**) is extremely high, and even higher than that of sodium dodecylsulfate (240 mL at 0 min under the same conditions). The foam stability is also high. The maximum foaming ability and foam stability were observed at the lipophile size of dodecyl and tetradecyl length and dramatically decreased above these alkyl chainlengths.

TABLE 2
Surface-Active Properties of *bis*-Quaternary Ammonium Salts at 20°C[a]

Compound	R	Krafft point (°C)	CMC (M)	γ_{CMC} (mN/m)	pC_{20}	Foam (mL)[b] 0′	Foam (mL)[b] 30′
1a	$C_{10}H_{21}$	<0	3.2×10^{-3}	36.5	2.9	40	0
						(280	0)[c]
1b	$C_{12}H_{25}$	<0	7.8×10^{-4}	37.0	3.2	280	270
1c	$C_{14}H_{29}$	<0	1.4×10^{-4}	39.0	4.4	270	270
1d	$C_{16}H_{33}$	<0	1.9×10^{-5}	42.2	5.3	100	10
1e	$C_{18}H_{37}$	—[d]	—[d]	—[d]	—[d]	0	0
2b	$C_{12}H_{25}$	<0	9.8×10^{-4}	39.2	3.3	270	270
2c	$C_{14}H_{29}$	<0	1.1×10^{-4}	41.8	4.5	270	260
2d	$C_{16}H_{33}$	<0	1.5×10^{-5}	42.0	5.4	60	10
2e	$C_{18}H_{37}$	—[d]	—[d]	—[d]	—[d]	0	0
$C_{12}H_{25}\overset{+}{N}(CH_3)_3Cl^-$		<0[e]	1.2×10^{-2e}	39.0[e]	2.6[e]	20[e]	0[e]
$C_{14}H_{29}\overset{+}{N}(CH_3)_3Cl^-$		—[f]	4.5×10^{-3g}	—[f]	—[f]	—[f]	—[f]
$C_{16}H_{33}\overset{+}{N}(CH_3)_3Cl^-$		—[f]	1.3×10^{-3h}	—[f]	—[f]	—[f]	—[f]

[a] γ_{CMC}, Surface tension at critical micelle concentration (CMC); pC_{20}, adsorption efficiency.
[b] Evaluated by semi-micro TK method with a 0.1 wt% solution.
[c] At 1 wt% aqueous solution, above CMC of compound **1a**.
[d] Not evaluated.
[e] Reported values in Reference 5 (at 20°C).
[f] Not reported.
[g] Reported values in Reference 10 (at 25°C).
[h] Reported values in Reference 11 (at 30°C).

TABLE 3
Surface-Active Properties of *bis*-Dodecyldimethylammonium Salts at 20°C[a]

Compound	—X—	Krafft point (°C)	CMC (M)	γ_{CMC} (mN/m)	pC_{20}	Foam (mL) 0′	Foam (mL) 30′
1b		<0	7.8×10^{-4}	37.0	3.2	280	270
2b		<0	9.8×10^{-4}	39.2	3.3	270	270
3		<0	6.5×10^{-4}	40.9	3.5	230	0
4		<0	5.0×10^{-4}	39.2	3.6	250	0

[a] See Table 2 for abbreviations.

In general, the lower the CMC, the more efficient foamer the surfactant is, and it is reported that the efficiency of a surfactant as a foamer increases with increased alkyl chainlength (12). The reason for the decreased foaming ability of compounds **1d–e** may be due to the lack of elasticity (i.e., rigidity) of a monolayer film made with *bis*-quaternary ammonium salts.

For the *bis*-quaternary ammonium salts from 1,3-dichloropropane (**2b–e** in Table 2), the surface-active properties, including foaming properties, are almost the same as those from epichlorohydrin (**1a–e**). It may be concluded that the hydroxyl group in the connecting group has a large effect on the melting point of the crystalline state but little effect on the γ_{CMC}, CMC, pC_{20}, and foaming properties.

The surface-active properties of the *bis*-quaternary ammonium salts from epichlorohydrin, 1,3-dichloropropane, 1,4-dichloro-2-butanol, and *bis*-2-chloroethyl ether are summarized in Table 3 to compare the effect of connecting groups on the properties.

The differences in γ_{CMC}, CMC, and pC_{20} among compounds **1b, 2b, 3,** and **4** are small and in the same order of magnitude. The decrease in foaming ability of **3** and **4** compared with **1b** and **2b** is small, but their foam stability decreased dramatically, and foam volumes became almost zero after 3 min (for compound **3**, 130 mL at 1 min, 0 mL at 3 min; for compound **4**, 120 mL at 1 min, 0 mL at 3 min). This indicates that foam stability is strongly affected by the nature of the connecting group in contrast to foaming ability.

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