Surfactants & Detergents Technical

♣ Synthesis and Surface Properties of N-Long Chain Alkyl Dihydroxy Monoazacrown Ethers

Isao Ikeda, Yoshihide Ozawa, Yohji Nakatsuji and **Mitsuo Okahara***
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka, Japan 565

A series of N-alkyl dihydroxy monoazacrown ethers (*1*) was synthesized, and their surface properties were investigated compared to those of N-alkyl monoazacrown ethers (*2*) and open chain oxyethylenated long chain alkylamines (*3*). The complexation ability of *1* toward alkali metal cations, a distinguished characteristic of crown compounds, was deduced to work even in the aqeuous solution from the values of ΔT_{CP}, although it is weaker than typical monoazacrown ethers (*2*). The presence of two hydroxyl groups contributes to the large increase in hydrophilicity of monoazacrown ring and to the large surface excess of the surfactant molecule (*1*). A small occupation area to the solution surface is noted as a characteristic feature of the title coumpound (*1*).

Because crown compounds have characteristic and useful properties based on their selective complexing ability toward specific cations, a wide range of application has been proposed. A crown ring, the cyclic oligooxyethylene group, works as a hydrophilic group and shows surface active property when a suitable lipophilic moiety, such as an alkyl or acyl group of proper chain length, is bound. This kind of surfactant has attracted much attention (1–4) because of the selective complexing ability toward cations, together with the surface activity in aqueous solution.

In contrast to the open chain polyoxyethylene group, the hydrophilic group of usual nonionics, the hydrophilicity of the crown ring is rather low (2,4,5), since it contains only a limited number of oxyethylene units and no hydroxyl group, and its structure is considered to be hydrated rather weakly. To improve the hydrophilicity, various crown ether derivatives have been developed (2–4). We have also synthesized several kinds of surface active crown compounds (6–8) and studied their surface activity (5,9). Displacement of one donor oxygen atom with a nitrogen atom to make N-alkyl monoazacrown ether resulted in the enhancement in hydrophilicity (9). Also, alkyl lariat ethers (11) or N-alkyl lariat ethers (12) that contained oxyethylene units between the alkyl group and the crown ring possess the increased hydrophilicity and the unaffected or increased cation-complexing ability (11). Moreover, it was clarified that the hydrophilicity augmented selectively when the surface active crown compound complexed with a cation, depending on the kind of cation added (13,14).

The authors have reported a facile method to prepare dihydroxy monoazacrown ethers (1) (15) by the reaction of primary amine with oligo(ethylene glycol)diglycidyl ethers (16). Recently we also studied the preparation and surface properties of alkoxy hydroxy crown ethers, which

were prepared from long chain alcohol and oligo(ethylene glycol) diglycidyl ethers (17,18).

The contribution of two hydroxyl groups to hydrophilicity and effect of the distorted structure of the crown ring toward complexing ability should be an interesting and important thesis to investigate concerning this new type of hydrophilic group.

In this report, long chain alkyl derivatives of 1 were synthesized, and their surface active properties were evaluated. The effect of the structure of the hydrophilic group on the surface property was discussed compared with those of the corresponding N-alkyl monoazacrown ethers (2) and the open chain analogues, oxyethylenated long chain alkylamine (3).

(1)   (2)   (3)
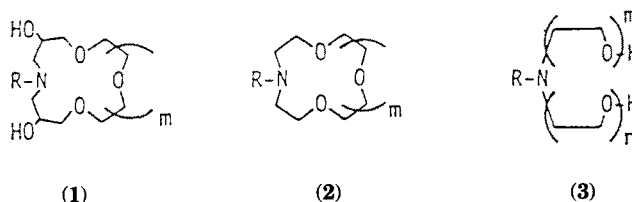
Scheme 1

EXPERIMENTAL PROCEDURES

Materials. Oligo(ethylene glycol) and epichlorohydrin of chemical grade reagent and alkylamines of guaranteed grade reagent were used without further purification. Oligo(ethylene glycol) diglycidyl ethers were prepared from oligo(ethylene glycol) and epichlorohydrin according to the method reported previously (16).

Long chain N-alkyl dihydroxy azacrown ethers. The preparation of **1a** (m = 1, $R = C_{10}H_{21}$) is described as a typical procedure (15). Di(ethylene glycol) diglycidyl ether (16) (6.6 g, 0.03 mol) and decylamine (4.7 g, 0.03 mol) were dissolved in 150 ml of methanol and stirred at 50 C for 10 hr. At this time, the consumption of di(ethylene glycol) diglycidyl ether was confirmed by gas liquid chromatography (Silicone SE 30, 5% on Celite 545, 2m, 100–250 C). After methanol was removed by distillation, the reaction mixture was fractionated with a Kugelrohr distillation apparatus to yield **1a** as a pale yellow viscous liquid, 5.1 g yield 45%, bp 145 C/0.03 torr (Kugelrohr). IR 3430, 2940, 2870, 1475, 1355, 1300, 1260, 1140 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 3H), 1.1-1.6 (m, 16H), 2.4-2.8 (m, 6H), 2.8-3.1 (br, 2H), 3.5-3.9 (m, 14H); MS (70 eV) m/e (rel. int.) 375 (M$^+$, 6), 248 (100), 184 (18), 174 (32), 170 (31), 100 (87), 43 (19), 42 (18). Anal. calcd for $C_{20}H_{41}NO_5$: C, 63.97; H, 11.00; N, 3.73. Found: C, 63.52; H, 11.20; N, 3.80.

A series of compounds **1b–1f**, was prepared by the same procedure; their boiling points, yields and analytical data are as follows:

1b (m = 2, $R = C_{10}H_{21}$): yield 43%, bp 155 C/0.03 torr (Kugelrohor). IR 3430, 2950, 2880, 1480, 1365, 1310, 1270, 1150 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.86 (t, 3H), 1.1-1.6 (m,

16H), 2.3-2.9 (m, 6H), 2.9-3.4 (br, 2H), 3.4-4.0 (m, 18H); MS (70 eV) m/e (rel. int.) 419 (m$^+$, 4), 292 (100), 218 (57), 184 (19), 170 (32), 144 (34), 58 (17), 43 (19). Anal. calcd for $C_{22}H_{45}NO_6$: C, 62.97; H, 10.81; N, 3.34. Found: C, 62.61; H, 10.93; N,3.38.

1c (m = 3, R = $C_{10}H_{21}$): yield 43%, bp 160 C/0.01 torr (Kugelrohr). IR 3420, 2940, 2870, 1475, 1360, 1300, 1255, 1130 cm^{-1}; ^1H NMR (CDCl$_3$) δ 0.87 (t, 3H), 1.1-1.6 (m, 16H), 2.4-2.8 (m, 8H), 3.5-4.0 (m, 22H); MS (70 eV) m/e (rel. int.) 463 (M$^+$, 4), 336 (100), 262 (66), 188 (22), 184 (23), 170 (30), 100 (31), 44 (24). Anal. calcd for $C_{24}H_{49}NO_7$: C, 62.17; H, 10.65; N, 3.02. Found: C, 61.89; H, 10.87; N, 3.02.

1d (m = 1, R = $C_{12}H_{25}$): yield 40%, bp 150 C/0.03 torr (Kugelrohr). IR 3410, 2920, 2850, 1460, 1340, 1290, 1245, 1125 cm^{-1}; ^1H NMR (CDCl$_3$) δ 0.87 (t, 3H), 1.1-1.6 (m, 20H), 2.3-2.9 (m, 8H), 3.4-4.0 (m, 14H); MS (70 eV) m/e (rel. int.) 403 (M$^+$, 5), 248 (100), 212 (15), 198 (24), 174 (26), 100 (71), 58 (18), 44 (16). Anal. calcd for $C_{22}H_{45}NO_5$: C, 65.47; H, 11.24; N, 3.47. Found: C, 65.47; H, 11.45; N, 3.54.

1e (m = 2, R = $C_{12}H_{25}$): yield 44%, bp 165 C/0.03 torr (Kugelrohr). IR 3440, 2930, 2860, 1475, 1350, 1300, 1255, 1130 cm^{-1}; ^1H NMR (CDCl$_3$) δ 0.87 (t, 3H), 1.1-1.6 (m, 20H), 2.4-2.9 (m, 6H), 2.9-3.2 (br, 2H), 3.3-4.0 (m, 18H); MS (70 eV) m/e (rel. int.) 447 (M$^+$, 4), 292 (100), 218 (47), 198 (26), 144 (27), 59 (24), 43 (22). Anal. calcd for $C_{24}H_{49}NO_6$: C, 64.39; H, 11.03; N, 3.13. Found: C, 64.19; H, 11.17; N, 3.22.

1f (m = 3, R = $C_{12}H_{25}$): yield 38%, bp 175 C/0.01 torr (Kugelrohr). IR 3400, 2900, 2830, 1455, 1340, 1280, 1240, 1105 cm^{-1}; ^1H NMR (CDCl$_3$) δ 0.88 (t, 3H), 1.0-1.6 (m, 20H), 2.3-2.9 (m, 6H), 3.1-4.0 (m, 24H); MS (70 eV) m/e (rel. int.) 491 (M$^+$, 3), 336 (100), 262 (58), 212 (19), 198 (22), 188 (19), 100 (19), 58 (25). Anal. calcd for $C_{26}H_{53}NO_7$: C, 63.51; H, 10.86; N, 2.85. Found: C, 63.73; H, 10.98; N, 2.80.

Surface activity. With respect to the aqueous solution of surface active compounds, surface tension was measured at 20 C with a Wilhelmy surface tensiometer (Shimadzu ST-1). From the surface tension concentration plots, critical micelle concentration (cmc, break point), surface tension lowering ability (γ_{cmc}, surface tension at cmc) and occupation area of molecule at surface (A nm^2, from surface excess calculated with Gibbs' equation) were decided.

Cloud point T_{CP}. Concerning the 1% aqueous solution of surface active compounds, the temperature at which turbidity occurred was measured within an accuracy of ±0.5 C by the naked eye with a thermometer dipped in the solution and was taken to be cloud point. After adding 1.0 molar weight of alkali halide to the solution (1.0 m), the cloud point was measured again, and the difference of these two temperatures is represented as ΔT_{CP}.

Foaming properties. Using 0.1% aqueous solution of surface active compounds, foaming properties were evaluated by the semimicro TK method (20).

RESULTS AND DISCUSSION

Interfacial properties. Surface tension (γ)–concentration (c) plots concerning N-alkyl dihydroxy azacrown ethers (1) are shown in Figure 1, together with those of **2i** and **3r**. The cmc, γ_{cmc} and A of these compounds are summarized in Table 1.
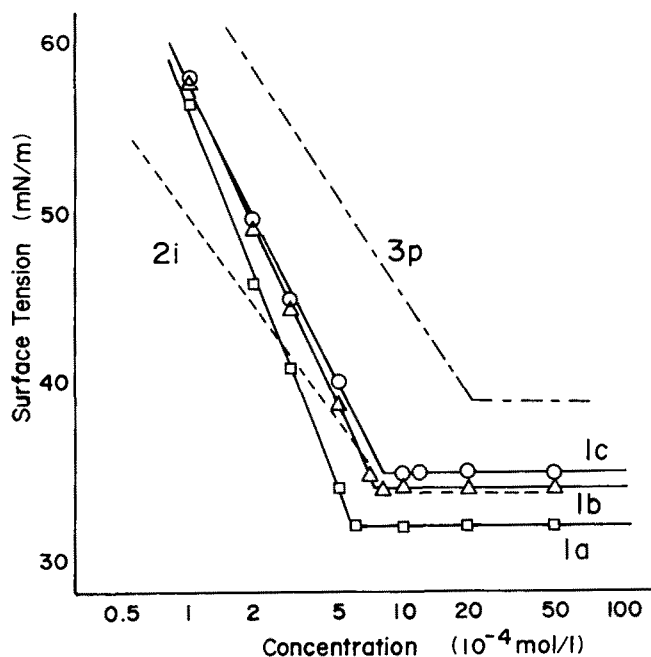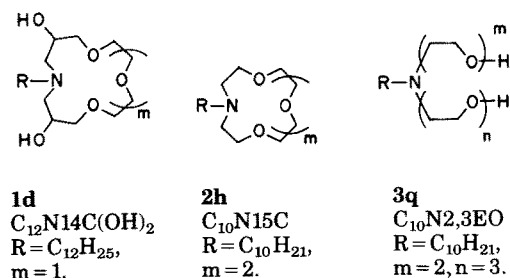

FIG. 1. Surface tension-concentration plots.

TABLE 1

Interfacial Properties of Surfactants

Compound	Abbreviation[b]	Interfacial properties[a]		
		cmc x 10^4 (mol/1)	τcmc (mN/m)	A x 10^2 (nm^2)
1a	$C_{10}N14C(OH)_2$	5.7	31.9	29
1b	$C_{10}N17C(OH)_2$	7.3	34.0	34
1c	$C_{10}N20C(OH)_2$	7.8	34.8	38
1d	$C_{12}N14C(OH)_2$	1.8	31.5	24
1e	$C_{12}N17C(OH)_2$	2.0	32.0	28
1f	$C_{12}N20C(OH)_2$	2.8	35.3	29
2h	$C_{10}N15C^{9)}$	4.5	34.0	46
2i	$C_{10}N18C^{9)}$	8.0	34.0	53
3q	$C_{10}N2,3EO^{19)}$	14.5	36.2	46
3r	$C_{10}N3,3EO^{19)}$	21.0	38.8	48

[a]Values at 20 C.

[b]For example:

1d
$C_{12}N14C(OH)_2$
R = $C_{12}H_{25}$,
m = 1.

2h
$C_{10}N15C$
R = $C_{10}H_{21}$,
m = 2.

3q
$C_{10}N2,3EO$
R = $C_{10}H_{21}$,
m = 2, n = 3.

With respect to cmc, the shorter the alkyl chain and the higher the number of oxyethylene units, the higher the cmc values. This is the usual tendency and can be seen in the case of nonionic surfactant of polyoxyethylene type. The cmc values of **1** are lower than those of oper

TABLE 2

Salt Effects on Cloud Point (T_{CP}) of Surfactants[a]

Compound	Abbreviation[b]	T_{CP} (C)	ΔT_{CP} (C)				
			LiCl	NaCl	KCl	RbCl	CsCl
1a	$C_{10}N14C(OH)_2$	42.0	−7.5	−12.0	−12.0	−12.0	−11.5
1b	$C_{10}N17C(OH)_2$	50.0	−4.5	−9.5	−9.0	−9.0	−8.5
1c	$C_{10}N20C(OH)_2$	60.0	−5.0	−7.5	−6.5	−8.0	−8.5
1d	$C_{12}N14C(OH)_2$	34.0	—	—	—	—	—
1e	$C_{12}N17C(OH)_2$	44.0	—	—	—	—	—
1f	$C_{12}N20C(OH)_2$	56.5	−6.5	−9.5	−7.5	−9.5	−9.5
2g	$C_8N18C^{(9,13)}$	33.5	−2.0	+8.0	+27.0	+13.0	+3.0
2h	$C_{10}N15C^{(9)}$	17.5	—	—	—	—	—
2i	$C_{10}N18C^{(9)}$	30.0	—	—	—	—	—
2j	$C_{10}N21C^{(9)}$	42.5	—	—	—	—	—
2k	$C_{12}N15C^{(9)}$	13.0	—	—	—	—	—
2m	$C_{12}N18C^{(9)}$	27.0	—	—	—	—	—
2n	$C_{12}N21C^{(9)}$	41.0	—	—	—	—	—
3p	$C_8N1,4EO^{(9,13)}$	77.0	−9.5	−17.5	−18.0	−18.0	−18.0
3s	$C_{12}N3,3EO^{(9)}$	78.0	—	—	—	—	—

[a]Concentrations of surfactants are 1.0% and of salts are 1.0 M.
[b]See Table 1.

chain compounds (3) and are close to those of monoaza-crown ethers (2), probably representing the dependence of the hydrophilicity on a cyclic structure of hydrophilic group.

It is the same tendency for usual surface active crown compounds—the occupation area at surface (A) enlarged as the size of hydrophilic crown ring increased.

The characteristic features in the case of dihydroxy azacrown ethers (1) are that a shorter alkyl chain analogue has a larger A value and values of A are generally smaller compared with the usual surface active crown ethers (2). The intermolecular interaction due to two hydroxyl groups on the crown ring probably located near the aqueous surface may contribute to the unusual phenomenon.

Cloud point (T_{CP}). Cloud points are summarized in

Table 2. It can be concluded that the hydrophilicity of crown ethers of 1 is much improved compared with N-alkyl monoazacrown ethers (2), since the cloud points of 1 are higher than those of 2, although lower than the corresponding open chain compounds (3). It is difficult to evaluate quantitatively the effect of hydroxyl group on the hydrophilicity of 1 by comparing the cloud points (T_{CP}) of 1 and 2 because these surfactants have different ring structures. However, the comparison seems to give important information on the general trend of hydrophilicity of 1. For example, T_{CP} of $C_{12}N17C(OH)_2$ (1e) is 31.0 C higher than that of monoazacrown ether $C_{12}N15C$ (2K), which has the same alkyl group and the same number of ether oxygen atoms. The ring structures of 1e and 2k are 17-crown-5 and 15-crown-5, respectively. The 17-crown-5 ether without a hydroxyl group is naturally

TABLE 3

Foaming Property of Surfactants

Compound	Abbreviation[b]	Foaming property[a] (mm)				
		0 min.	0.5 min.	1 min.	3 min.	5 min.
1a	$C_{10}N14C(OH)_2$	105	30	30	10	5
1b	$C_{10}N17C(OH)_2$	35	2	0	-	-
1c	$C_{10}N20C(OH)_2$	55	10	5	0	-
1d	$C_{12}N14C(OH)_2$	245	225	165	40	25
1e	$C_{12}N17C(OH)_2$	180	90	35	20	10
1f	$C_{12}N20C(OH)_2$	175	110	50	20	15
2i	$C_{10}N18C^{14)}$	55	4	4	0	-
2m	$C_{12}N18C^{14)}$	165	130	50	8	8
3q	$C_{10}N2,3EO^{c,19)}$	45	8	4	0	-
3t	$C_{12}N2,3EO^{c,19)}$	180	90	45	20	15

[a]By semimicro TK method, 0.1% aqueous solution, 25 C unless otherwise stated..
[b]See Table 1.
[c]Measured at 20 C.

expected to be less hydrophilic than the 15-crown-5 ether since the former has two more ring carbons. In spite of this opposite factor, 1e is more hydrophilic than 2k. This fact strongly demonstrates the contribution of hydroxyl group to the hydrophilicity of 1e. On the other hand, T_{CP} of 1e is 34.0 C lower than that of open chain compound $C_{12}N3,3EO$ (3s), which has the same two hydroxyl groups and the same number of nitrogen, oxygen and carbon atoms.

The positive role of the hydroxyl group and the negative effect of the cyclic structure of the hydrophilic group affecting its hydrophilicity may have been deduced from these cloud points.

The effects of alkali chloride added to the solution of compound 1 on the cloud point are summarized as the difference of temperature (ΔT_{CP}) in Table 2. Enhancement of cloud point, which was marked in the cases of compound 2 and alkyl crown ethers (13,14), was not noted. However, the values of decreases (ΔT_{CP}) are small compared with open chain compounds (3), especially the decrease in the combination of 20-membered ring analogues [1, $C_nN2OC(OH)_2$] and potassium chloride; they are the smallest with significant differences in this experiment, except for the cases with lithium chloride. The lithium cation may represent a different effect concerning the clouding phenomenon, since this cation has very low affinity to crown rings in water, based on its strongly hydrating character, and shows the low salting-out effect (13). On the contrary, in the case of open chain compounds, the values of decreases are large and almost equal regardless of the kind of cation. In the case of 14-crown-4 (1a), which can be considered to have the poorest complexing ability toward alkali cations among 1, the values of decreases (ΔT_{CP}) are intermediate between those of 17-crown-5 (1b) and 20-crown-6 (1c,f) and those of 3p. These facts suggest that dihydroxy monoazacrown ethers (1) may show a considerable degree of complexation between their crown ring and alkali cations even in an aqueous solution, although it is weak compared with 2 and alkyl crown ethers. The weakness of complexing ability toward the alkali cation and the low selectivity may depend on the asymmetrical ring structure of 1.

Foaming property. Foaming properties of 1 are shown in Table 3, together with some of 2 and 3. In the range of the present experiment, dodecyl derivatives exhibited larger foaming abilities than decyl derivatives, as similarly observed in 2 and 3. 14-Membered crowns 1a and 1d showed larger foaming abilities than the corresponding 17- and 20-membered derivatives, which had almost the same abilities with each other.

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