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An Evaluation of the Effective HLB of Surface-active Crown Compounds

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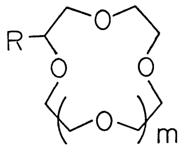
The hydrophilicity of surface-active crown compounds and their change upon the addition of electrolytes were investigated by measuring the phase-inversion temperature (PIT), the phenol index, and the cloud point. Sodium chloride and potassium chloride were observed to raise the hydrophilicity of 15-crowns and 18-crowns respectively, in contrast with their lowering effect on the hydrophilicity of usual poly(oxyethylene)-type nonionics. The effective HLBs of dodecyl crown ethers, estimated from both the PIT and the phenol index, were compared with those of poly(oxyethylene) dodecyl ethers, and the hydrophilicity of the crown rings were discussed in conjunction with that of the poly(oxyethylene) chain.

Although some studies of surface-active crown compounds have recently been made,[1–4] and a little fragmental information on the hydrophilicity of the crown ring have been given,[2–4] the function of this new type of hydrophilic group has not yet been fully clarified.

We have previously prepared long-chain alkyl crown ethers (**1**) and long-chain *N*-alkyl monoaza crown ethers (**2**),[5,6] which are the most typical surface-active crown compounds, and their surface-active properties[7,8] and the selective increase in the cloud points of their aqueous solutions upon the addition of electrolytes[9] have been reported.

In this paper, the effective HLBs of crown compounds and their changes upon the addition of electrolytes are evaluated by measuring the phase-inversion temperature (PIT), reported by Shinoda,[10–12] and the phenol index, proposed by Marszall;[13–16] they are also compared with those estimated from the cloud points in order to get information about the hydrophilicity of a crown ring.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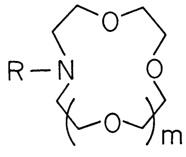
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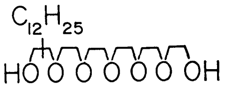
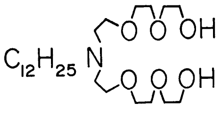
R = C_8H_{17}, $C_{12}H_{25}$ m = 2, 3





Experimental

Materials. Surface-active crown compounds (octyl-15-crown-5 (C_8O15C), octyl-18-crown-6 (C_8O18C), dodecyl-18-crown-6 (C_{12}O18C), *N*-octylmonoaza-18-crown-6 (C_8N18C), and *N*-dodecylmonoaza-18-crown-6 (C_{12}N18C)) were synthesized according to the reported method of intramolecular cyclization from the corresponding open-chain compounds (dodecyl-substituted hexaethylene glycol (C_{12}O18H), *N*,*N*-bis(8-hydroxy-3,6-dioxaoctyl)dodecylamine (C_{12}N18H)),[5,6] and their purity was ascertained by means of GLC. The monodispersed poly(oxyethylene) dodecyl ethers ($C_{12}H_{25}O$-$(EO)_nH$, $n=4,5,6,7,8$) were supplied by the Nikko Chemical Co. The KCl, NaCl, and dodecane ($n_D^{25}=1.4195$) were commercial guaranteed-grade reagents.

Phenol Index. Because of the low hydrophilicity of crown compounds, the method reported by Marszall[13] was modified and a dilute phenol solution was used. Thus, a 0.5% aqueous phenol solution was added, drop by drop, to a 5-ml portion of a 0.025 M (mol dm^{-3}) aqueous solution of surface-active compounds at a constant temperature (5, 10, 15, 25 °C). The end point was determined as the aqueous solution became distinctly turbid. The number of milliliters of the phenol solution used to reach the end point of titration is given as its phenol index. Crown ethers, C_8O15C and C_{12}O18C, which have low cloud points were measured at 5, 10, and 15 °C, while other crown compounds were all titrated at 25 °C.

Phase-inversion Temperature (PIT).[11] A 4 wt%/system amount of surface-active crown compounds (C_{12}O18C, C_{12}N18C) or the corresponding open-chain compounds (C_{12}O18H, C_{12}N18H) were added to a dodecane/water mixture (1:1 by volume) to make an emulsion. The emulsion was heated under stirring while the temperature was being raised. The inversion of O/W into W/O on heating (about 1 °C/2 min) or of W/O into O/W on cooling was visually observed. The differences between these two inversion temperatures were within about 3 °C. Also, the temperature at which the electric conductivity of the emulsion dropped abruptly on heating was measured. The temperatures obtained by these two methods showed almost the same value; the average values were marked as PIT.

Results and Discussion

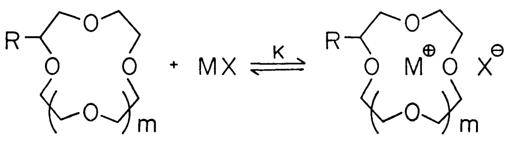
As for the hydrophilicity of the crown ring, Kuwamura[2,3] reported, from his study of the cloud point, that the acetal-type crown ring obtained from hexaethylene glycol and aldehyde is almost equivalent to 4 oxyethylene units in poly(oxyethylene) monoalkyl ether, and that the crown ring made of hexaethylene glycol and a triazine subunit exhibits almost the same performance as monoaza-18-crown-6 and 1,10-diaza-18-crown-6. Moroi[4] concluded, from a comparison of the CMCs, that a diaza-18-crown-6 ring is equivalent to 20 oxyethylene units in a polyoxyethylene-type nonionic surfactant with an identical alkyl-chain length.

As the properties of surfactants are considered to be changed under the application conditions, the concept of effective HLB has been proposed[13,15,16] in order to compare the hydrophilicity of surfactants under different conditions. The HLB of the usual nonionics with the poly(oxyethylene) group as hydrophile can be estimated by Griffin's equation[17) or other similar equations.[18) However, because of the lack of a hydroxyl group in the hydrophilic group, and because of the specific cyclic structure, the HLB values of crown compounds are considered to be different from those of the usual poly(oxyethylene) nonionics; they can not be estimated by the equations mentioned above.

The interaction of phenol with polyethylene glycols or nonionic surfactants in water has recently been studied in detail.[19–24) Though the phenol added to an aqueous solution of a nonionic surfactant increases the water-structuring, a major portion of it complexes with the poly(oxyethylene) chain[19) and is included in the micelle.[22) The phenol-micelle binding increases the micelle aggregation number and lowers the cloud point.[23,24) After a certain amount of a phenol solution is added, the solution of nonionics becomes turbid. Therefore, the nonionics having a higher hydration ability requires a greater volume of a phenol solution to induce turbidity.[13–16,19–21) Marszall utilized the correlation between the required amount of phenol and the hydrophilicity of a nonionics to estimate the effective HLB of the nonionics in the presence of additives.[13–16) Thus, it is reasonable to expect that the hydration ability of crown compounds and its change upon the addition of an electrolyte can be evaluated from an investigation of the interaction of the crown compound with phenol.

The phenol-index values of alkyl crown ether and *N*-alkyl monoaza crown ether were measured; the results are shown in Table 1. It was found that the phenol-index values of crown compounds increased with an increase in ring size and with a decrease in alkyl-chain length, and decreased with an increase in the temperature.

The phenomenon that the addition of alkali metal salts to an aqueous solution of nonionics reduces the phenol index has been reported[15,21) and interpreted to indicate that the presence of an electrolyte increases the micellar binding with phenol, probably as a result of lowering the solubility of phenol and surfactant and increasing the aggregation number of surfactant.[21) This means that the effective HLB of a nonionics decreases as a result of the salting-out effect of electrolytes. The phenol indices of crown compounds, however, increased upon the addition of KCl or NaCl to the aqueous solutions. Thus, the phenol index of crown compounds which have the hydrophilic group of the 18-crown ring (C_8O18C, C_8N18C) was significantly increased (by 14.80 and 4.18) with KCl, but by only 1.27 and 0.70 with NaCl. Conversely, the phenol index of C_8O15C, which has the 15-crown ring as the hydrophilic group, increased slightly (by 0.10) with KCl, but remarkably (by 0.86) with NaCl. The finding that the effective HLB of a crown compound in water selectively increased depending on the kind of salt and the ring size of the crown compound can be explained by the formation of the cationic complexes of crown compound shown in Eq. 1, and hence the increase in the hydration of surface-active species. These phenomena are in line with the tendency for salts selectively to increase the cloud point of an aqueous solution of crown compounds.[9)



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Marszall reported that the nonionics with a given lipophilic group showing the same phenol-index value have the same effective HLB, and that the effective HLB of a nonionics in the presence of additives can be obtained from the plot of the phenol index versus HLB.[13–16)

In order to evaluate the effective HLB of crown compounds in the absence or presence of salt, the phenol-index values of $C_{12}H_{25}O(EO)_nH$ (n=4,5,6,7,8) at 5, 10, 15, and 25 °C versus their Griffin HLB values were plotted (Fig. 1). The effective HLBs of crown compounds were estimated from the phenol index using these plots; it was thus found that the effective HLB of *N*-dodecyl monoaza crown ether ($C_{12}N18C$) is 0.6 higher than that of dodecyl crown ether ($C_{12}O18C$). Under the conditions shown in Table 1, the extent of the effective HLB increase (1.8, 0.7) of 18-crowns ($C_{12}O18C$, $C_{12}N18C$) by KCl was larger than that by NaCl (0.3, 0.2). These salts increased the effective HLB of alkyl crown ether ($C_{12}O18C$)

TABLE 1. THE PHENOL INDICES OF ALKYL-SUBSTITUTED CROWN AND MONOAZA CROWN ETHERS IN THE ABSENCE AND PRESENCE OF K(Na)Cl[a)

Crown ether	t/°C	—	KCl	NaCl
C_8O15C	10	0.42	0.52	1.28
C_8O18C	25	1.28	16.08	2.55
C_8N18C	25	4.52	8.70	5.22
$C_{12}O18C$	25	—	16.22(12.3)[b)	0.48(10.6)[b)
	15	0.60(–)	31.60(12.1)[b)	1.95(10.7)[b)
	5	2.44(10.4)[b)	60.80(—)	4.26(10.7)[b)
$C_{12}N18C$	25	0.82(10.9)[b)	5.00(11.7)[b)	1.82(11.2)[b)
	15	3.10(11.0)[b)	7.78(11.5)[b)	3.90(11.1)[b)

a) The concentrations of KCl and NaCl are 0.5 M, while those of crown compounds are 0.025 M. b) The data in the parentheses are effective HLBs evaluated from phenol index using the plots shown in Fig. 1.

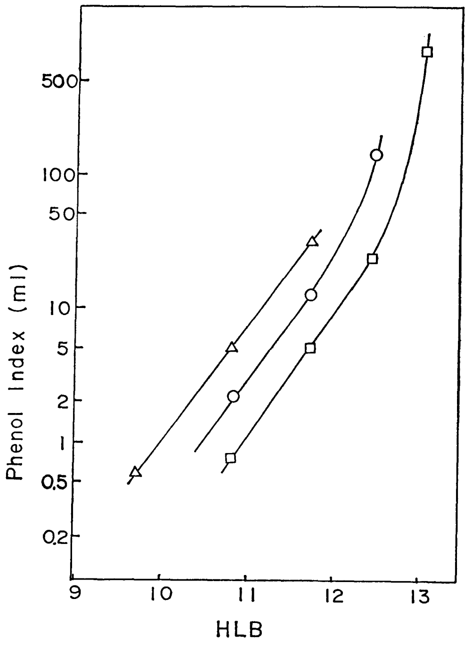

Fig. 1. The relationship between the phenol index and the HLB calculated by Griffin's method for $C_{12}H_{25}O$-$(EO)_nH$ (n=4,5,6,7,8) at 5 °C (—△—), 15 °C (—○—), and 25 °C (—□—).

more than that of *N*-alkyl monoaza crown ether (C_{12}N18C), much as with the tendency of the alkali-salt effect on the cloud point of these two kinds of crown compounds.

The O/W-type emulsion produced by using a proper nonionic surfactant as an emulsifier becomes unstable on heating and is inverted into a W/O-type emulsion. The temperature at which phase inversion occurs is called the PIT. The higher the HLB of the emusifier is, the higher PIT the emulsion exhibits. The PITs of C_{12}O18C and C_{12}N18C acting as the emulsifier for the dodecane/water system were 12 °C and 25 °C respectively, but those of the corresponding open-chain compounds, C_{12}O18H and C_{12}N18H, were 82 °C and 83 °C respectively (Table 2). By adding KCl to the emulsion under the conditions described in Table 2, the PITs of two crown compounds, C_{12}O18C and C_{12}N18C, increased by 27 °C, and 13 °C. Those of open-chain compounds, C_{12}O18H and C_{12}N18H, decreased by 8 °C and 7 °C respectively in the same way as the PIT was observed to decrease in usual poly(oxyethylene) nonionics.[12] The fact that the PIT of the emulsion prepared by the use of a crown-compound emulsifier increased upon the addition of salts can also be explained by postulating that the salt enables alkyl crown ethers (**1**) or monoaza crown ethers (**2**) to form cationic complexes and to enhance their hydrophilicity, as has been described in the case of the phenol index.

The HLB of an emulsifier can be estimated from the PIT of the emulsion.[10,12] Using the plot of the PIT of 1:1 dodecane/water system emulsified with poly(oxyethylene) dodecyl ether[25] versus its Griffin HLB value, the effective HLB values of crown compounds were estimated from the PIT obtained under the same conditions; *i.e.*, the effective HLB values of C_{12}O18C and C_{12}N18C are 9.2 and 9.8, while those of C_{12}O18H and C_{12}N18H are 12.8 and 12.9 repectively. Upon the addition of KCl, the effective HLB values of C_{12}O18C and C_{12}N18C increased by 1.4 and 0.7 respectively, but those of the corresponding open-chain compounds, C_{12}O18H and C_{12}N18H, decreased to almost the same extent, 0.4 and 0.5 respectively. Furthermore, KCl raised the effective HLB of C_{12}O18C more than that of C_{12}N18C. This fact can be explained by the same reason that KCl raised the phenol index and cloud point of 18-crown ethers more than those of monoaza 18-crown ethers. Because of the restriction of emulsion stability, the amount of KCl added is limited to a triple mole of surfactant for PIT measurements. For the phenol-titration method, however, the concentration of KCl is 0.5 M, which corresponds to twenty times the molar amount of the surfactant. Therefore, in the presence of KCl, the extent of the increase in the effective HLB obtained by the phenol-titration method may be larger than that obtained by the PIT method.

TABLE 2. THE PITs AND EFFECTIVE HLBs OF CROWN COMPOUNDS AND THE CORRESPONDING OPEN-CHAIN COMPOUNDS[a)]

Compound	PIT(°C)		Effective HLB	
	—	KCl	—	KCl
C_{12}O18C	12	39	9.2	10.6
C_{12}O18H	82	75	12.8	12.4
C_{12}N18C	25	38	9.8	10.5
C_{12}N18H	83	75	12.9	12.4

a) The mole ratio of KCl to the surfactant is 3:1, and the concentration of surfactants is 4 wt%/system.

Furthermore, it is well known that HLB also has a linear relationship with the cloud point below 100 °C.[13,26] The plot of the cloud point versus HLB for oligoethylene glycol dodecyl ether[18] was used to estimate the hydrophilicity of the crown ring, and it was found that the HLB values of C_{12}O18C and C_{12}N18C were 10.3 and 10.6 respectively, resembling the values obtained by the phenol-titration method, which is essentially similar to the cloud point method. Also, the fact that the effective HLB values of C_{12}O18C and C_{12}N18C obtained by the phenol-titration method were 0.9 and 1.2 larger than those obtained by the PIT method, is attributed to the deviation caused by different evaluating methods.

From the evaluations described above, the hydrophilicity of 18-crown-6 and monoaza-18-crown-6 rings with a dodecyl group can be concluded to be approximately equivalent to that of 4.0 and 4.5 units of oxyethylene chains respectively.

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