Hydration to the Poly(oxyethylene) Derivative Complexes of Alkali Metal Ions and Barium Ion in 1,2-Dichloroethane

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A series of poly(oxyethylene) derivatives (POE compound) complexes of alkali metal and barium ions were extracted into 1,2-dichloroethane (1,2-DCE) by forming ion-pairs with picrate ion. Water molecules were coextracted into 1,2-DCE with the ion-pairs. The mean number of water molecules bound to the POE compound, $X_{\mathrm{H_2O,S}}$, and its complex, $X_{\mathrm{H_2O,comp}}$, in water saturated with 1,2-DCE was determined by means of aquametry. The $X_{\mathrm{H_2O,S}}$ value increases with the increase in the number of the oxyethylene units (EO unit) of the POE compound. The $X_{\mathrm{H_2O,comp}}$ value decreases in the order $\mathrm{Li^+ > Na^+ > K^+ \approx Rb^+ \approx Cs^+}$ in any POE compound systems, and increases with the number of EO units of the POE compounds for a given metal ion. These results are interpreted by the hypothesis that the water molecules bound to the complex are those hydrated to the central metal ion, and the hydrated metal ion is surrounded by the EO chain with a helical conformation in the complex. The large number of water molecules are coordinating to the lithium ion complexes and bring about a serious distortion in the helical structure of the complexes. Because of the ion-pair formation with two picrate ions, the $X_{\mathrm{H_2O,comp}}$ values of barium ion complexes are smaller than those of potassium ion complexes.

The noncyclic poly(oxyethylene) derivatives (POE compound) are known to form cationic complexes with alkali and alkaline earth metal ions similarly to crown ethers. The complexes are extracted into organic solvents by forming ion-pairs with lipophilic anions.[1—4] In previous papers,[5—7] we studied the ion-pair extraction of a series of POE compound complexes of alkali and alkaline earth metal ions with picrate ion into 1,2-dichloroethane (1,2-DCE). The extraction equilibria, ion-pair dissociation and structures of the extracted ion-pairs were reported.

The water in nonaqueous solution sometimes exerts quite a large effect on the equilibria of solutes.[8—11] The POE compound involves a hydrophilic part, the oxyethylene chain (EO chain), and the coordination of this EO chain to the metal ion is not so strong. Consequently, in the case of a solvent extraction system, in which the nonaqueous phase is saturated with water, we anticipate that the water affects the equilibria and the structure of the POE compound complex of the metal ion. Nevertheless, insufficient attention has been paid to the contribution of water to the complex formation in nonaqueous solution. Iwachido et al.[12] investigated the coextraction of water into nitrobenzene with alkali and alkaline earth metal salts of hexanitrodiphenylamine in the absence and the presence of crown ether. They suggested that the coextraction of water is caused by the hydration of the metal ion, and the number of water molecule hydrating to the metal ion decreases by the complexation with the crown ether.

In the present study, the coextraction of water into 1,2-DCE with a series of POE compound complexes of alkali metal ions and barium ion has been investigated. The effect of water on the structure of the ion-pair of the complex with picrate ion is discussed.

Experimental

Reagents. α-Dodecyl-ω-hydroxypoly(oxyethylene)s (DEOn: $n=4$, 6 and 8, where n refers to the number of the oxythylene units: EO unit) were purchased from Nikko Chemicals. α-Alkylphenyl-ω-hydroxypoly(oxyethylene)s (Triton X-100 and Triton X-405) and 18-crown-6 were purchased from Wako Pure Chemicals. Triton X-100 and Triton X-405 are polydisperse POE compounds. The average number of EO units, n_{av}, of Triton X-100 and Triton X-405 were determined to be 9.6 and 42.8, respectively, by a vapor pressure osmometry. Picric acid (Wako Pure Chemicals) was recrystallized twice from distilled water. 1,2-Dichloroethane (1,2-DCE, Wako Pure Chemicals) was washed three times with distilled water. Alkali metal picrates and barium picrate were prepared from their hydroxide and picric acid. These metal picrates were recrystallized twice from distilled water, while lithium picrate was recrystallized from ethanol.

Measurements. Pure 1,2-DCE or the POE compound solution ($0—8\times10^{-2}$ M: $\mathrm{M=mol\,dm^{-3}}$) was shaken with an equal volume of water in a centrifuge tube (50 ml) in a thermostated water bath for 30 min at 25.0±0.1°C. After centrifugation, the aqueous phase was removed. Then the water concentration of 1,2-DCE phase was determined by means of the coulometric Karl–Fischer titration (Kyoto Electronics MKC-210). The distribution coefficients of Triton X-100 and Triton X-405 were determined by spectrophotometric measurements of both phases. The distribution coefficients of DEOn and 18-crown-6 were determined by weighing both phases after evaporation of solvents.

A portion of a 1,2-DCE solution (20 ml) of POE compounds (the concentration of POE compound: $C_{\mathrm{S}}=2\times10^{-2}—3\times10^{-2}$ M) and an equivolume of an aqueous solution containing alkali metal picrate or barium picrate (the concentration of picrate ion: $C_{\mathrm{Pic}}=3\times10^{-2}—0.1$ M) were placed in a centrifuge tube (50 ml). In order to prevent the extraction of picric acid, the pH of the aqueous solution was adjusted to 8—10 by using alkali metal hydroxide or barium hydroxide. After being shaken in a thermostated water bath for 30 min at 25.0±0.1°C, the solution was centrifuged. The concentrations of water, $C_{\mathrm{H_2O,org}}$, and picrate ion, $C_{\mathrm{Pic,org}}$, in 1,2-DCE solution were determined by means of the Karl–Fischer method and spectrophotometry,[5] respectively.

The amount of metal picrates extracted with DEO4 is not enough for the quantitative analysis of the water coextracted with the ion-pair.

Results and Discussion

Hydration of Free POE Compounds. The values of the distribution coefficient of studied POE compounds, except for 18-crown-6, were determined to be larger than 10^3. Thus, the equilibrium concentration of these POE compounds in the 1,2-DCE solution, $[\mathrm{S}]_{\mathrm{org}}$, can be approximated by the initial concentration, C_{S}. The value of the distribution coefficient of 18-crown-6 was determined to be 1.05. The equilibrium concentration of 18-crown-6 in the 1,2-DCE solution was calculated by using the distribution coefficient.

The concentration of water in pure 1,2-DCE equilibrated with aqueous phase was determined to be 0.131 M. The water concentration in the 1,2-DCE increases with the increase in the concentration of the POE compounds. The increments of water concentration in the 1,2-DCE solutions, $\Delta C_{\mathrm{H_2O,org}}$, are plotted in Fig. 1 as a function of the concentration of POE compounds in 1,2-DCE, $[\mathrm{S}]_{\mathrm{org}}$. From the slope of the plot in Fig. 1, we obtained the mean number of water molecules bound to one molecule of each POE compound in water saturated with 1,2-DCE, $X_{\mathrm{H_2O,S}}$. The values of $X_{\mathrm{H_2O,S}}$ are listed in Table 1.

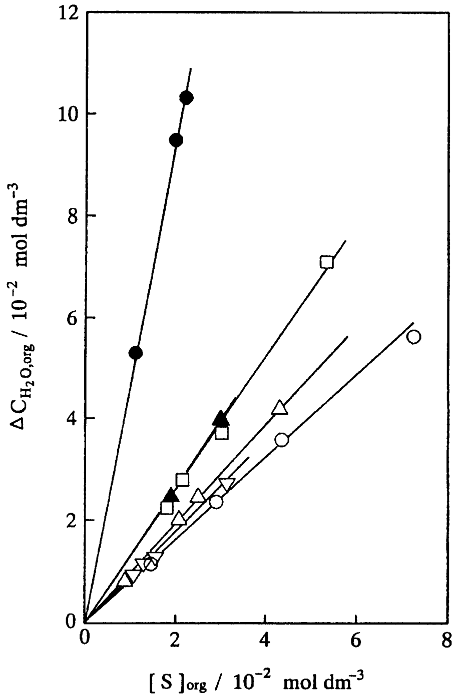

Fig. 1. Plots of the coextracted water concentration, $\Delta C_{\mathrm{H_2O,org}}$, with POE compounds as a function of the concentration of POE compounds in 1,2-DCE. Symbols: ●; Triton X-405, ▲; Triton X-100, □; α-Dodecyl-ω-hydroxyocta(oxyethylene)s (DEO8), △; α-Dodecyl-ω-hydroxyhexa(oxyethylene)s (DEO6), ○; α-Dodecyl-ω-hydroxytetra(oxyethylene)s (DEO4), ▽; 18-crown-6.

The values of $X_{\mathrm{H_2O,S}}$ show a fractional number in all POE compounds, which indicates that the POE compounds involve several hydrated and nonhydrated species in equilibrium. We examined the coextraction of water with 1-dodecanol ($\mathrm{C_{12}H_{25}OH}$, i.e., the number of EO units, n, is zero) into 1,2-DCE at 25.0 °C, and confirmed the very low coextraction of water with 1-dodecanol ($X_{\mathrm{H_2O,ROH}}=0.08$). Consequently, the water molecules which were coextracted with the POE compound are those which substantially interacted with the hydrophilic part of the POE compound, i.e. the EO chain. As seen from Table 1, the values of $X_{\mathrm{H_2O,S}}$ increase with the increase in the EO units. The mean number of water molecules bound to one EO unit of DEOn is almost the same among DEOn. ($(X_{\mathrm{H_2O,S}}-X_{\mathrm{H_2O,ROH}})/n=0.16$—$0.18$) This supports the hypothesis of interaction of water molecules with the EO chain.

Baldwin et al.[13] investigated conformations of EO chain by molecular mechanics calculations. According to their results, there is little difference in the conformational energy of the EO chain between the helical conformation and the zigzag one in a solvent with a medium dielectric constant (ca. 10). In the present system, since the solvating ability of 1,2-DCE is quite low, the hydrating water molecule may interact with ether oxygens and is inlaid in the cavity of the helical EO chain.

Hydration of Metal Complexes of POE Compound. The alkali metal ion ($\mathrm{M^+}$) and the barium ion ($\mathrm{M^{2+}}$) form a 1 : 1 cationic complex with POE compounds (S), SM^{n+}, and are present as an ion-pair with picrate ion ($\mathrm{Pic^-}$), $\mathrm{SM}^{n+}\cdot(\mathrm{Pic}^-)_n$ in 1,2-DCE.[5—7] The dissociation of this ion-pair, $\mathrm{SM}^{n+}\cdot(\mathrm{Pic}^-)_n$, is negligible under the present experimental conditions. Thus, the extraction of metal picrate with the POE compound is expressed by taking into consideration the contribution of the water molecules as follows:

$$\mathrm{M}^{n+} + n\mathrm{Pic}^- + \mathrm{S_{org}} + m\mathrm{H_2O} \overset{K_{\mathrm{ex}}}{\rightleftharpoons} \mathrm{SM}^{n+}(\mathrm{H_2O})_m\cdot\mathrm{Pic}^-_{n,\mathrm{org}}, \qquad (1)$$

where the subscript "org" refers to the organic phase.

Metal picrates are not extracted into 1,2-DCE in the absence of POE compounds, and the change in the ionic strength in the aqueous solution has no effect on the concentration of water in 1,2-DCE under the conditions of the present study. Thus, the amount of water bound to the POE–M^{n+} complex was evaluated by subtracting the water content of the uncomplexed free POE compound and the pure solvent from the total water content of the 1,2-DCE solution. By dividing the wa-

Table 1. The Mean Number of the Water Molecules Attached to the POE Compound, $X_{\mathrm{H_2O,S}}$, and the POE–M^{n+} Complex, $X_{\mathrm{H_2O,comp}}$ in 1,2-DCE[a)]

M^{n+}	Triton X-405	Triton X-100	DEO8	DEO6	DEO4	18-Crown-6
free	4.54	1.33	1.32	1.03	0.81	0.87
Li^+	7.72	3.35	3.72	2.41		1.98
Na^+	5.43	1.43	1.43	0.93		0.98
K^+	4.42	0.97	0.77	0.60		0.37
Rb^+	4.48	1.07	0.86	0.70		0.40
Cs^+	3.97	0.98	0.91	0.70		0.52
Ba^2+	4.95	0.64	0.59	0.27		0.20

a) Estimated errors are ±0.1 except for Li^+ complex system (±0.4). DEO8: α-Dodecyl-ω-hydroxyocta(oxyethylene)s, DEO6: α-Dodecyl-ω-hydroxyhexa(oxyethylene)s, DEO4: α-Dodecyl-ω-hydroxytetra(oxyethylene)s.

ter concentration attributed to the POE–M^{n+} complex with the concentration of the POE–M^{n+} complex, we obtained the mean number of water molecules bound to one complex molecule in water saturated with 1,2-DCE, $X_{\mathrm{H_2O,comp}}$. The $X_{\mathrm{H_2O,comp}}$ values are summarized in Table 1 and are plotted in Fig. 2 as a function of ionic radius of alkali metal.

The value of $X_{\mathrm{H_2O,comp}}$ decreases in the order $Li^+ > Na^+ > K^+ \approx Rb^+ \approx Cs^+$ in any POE compound system. This order is roughly the same as that of the decreasing hydration energy of alkali metal ions. $X_{\mathrm{H_2O,comp}}$ of the lithium ion complex is larger than that of free POE compound, $X_{\mathrm{H_2O,S}}$, in any POE compound system. $X_{\mathrm{H_2O,comp}}$ of the complexes of large size ions, K^+, Rb^+, and Cs^+, are practically the same among the metal ions, and smaller than $X_{\mathrm{H_2O,S}}$. These results indicate the water molecules bound to the complex are those hydrated to the central metal ion. The water molecule hydrating to the metal ion may also interact with the ether oxygen of surrounding EO chain by forming a hydrogen bond.

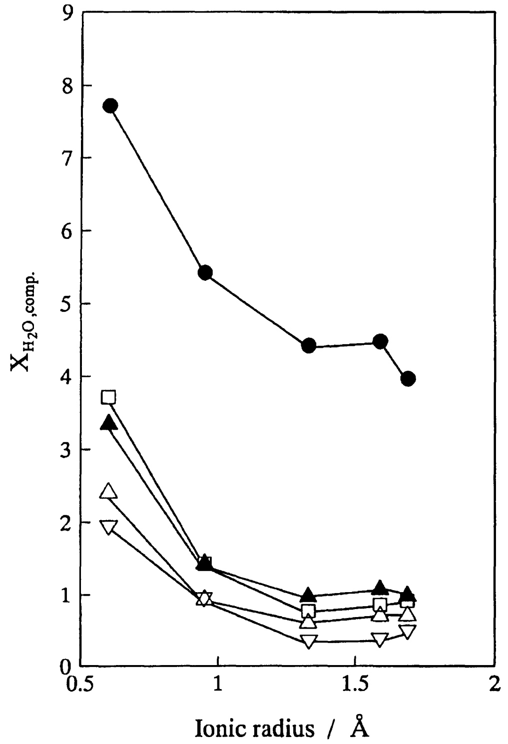

Fig. 2. Plots of the mean number of water molecules attached to the POE compounds complexes of alkali metal ions, $X_{\mathrm{H_2O,comp}}$, as a function of the ionic radius of alkali metals. Symbols: see Fig. 1.

The values of $X_{\mathrm{H_2O,comp}}$ increase with the increase in the number of EO units of the POE compounds for a given metal ion. The difference of those values between the different POE compound systems decreases with increasing size of the metal ion. For example, the increment of $X_{\mathrm{H_2O,comp}}$ from the DEO6 complexes to the DEO8 complexes are 1.39, 0.50, and about 0.2 for Li^+, Na^+, and large size ions (K^+, Rb^+, Cs^+), respectively. The $X_{\mathrm{H_2O,comp}}$ values of 18-crown-6 complexes are smaller than those of the corresponding DEO6 complexes, in which the number of EO units is the same as that of 18-crown-6.

The dominant species of the K^+, Rb^+, and Cs^+ complexes of DEO6, DEO8, and Triton X-100 are monohydrated complexes. Because of the flexible structure of the EO chain of the noncyclic POE compounds, it can surround the hydrated metal ion. In the K^+ and Rb^+ complexes of 18-crown-6, the 18-crown-6 molecule is surrounding the metal ion in an almost planar structure.[14,15)] In this rigid structure, the ether oxygen may not interact very much with the hydrating water molecule. Thus the values of $X_{\mathrm{H_2O,comp}}$ of K^+ and Rb^+ complexes of 18-crown-6 are smaller than those of the corresponding DEO6 complexes.

On the other hand, in the case of the Li^+ complexes, the $X_{\mathrm{H_2O,comp}}$ values are quite large. That is, the Li^+ complexes of DEO8 and Triton X-100 are predominantly hydrated by three or four water molecules. According to the results of conductometric measurements,[16)] the limiting ionic equivalent conductivity, $\lambda^\circ(SM^+)$, of the lithium ion complexes of DEO6 and DEO8 in water saturated 1,2-DCE is considerably smaller than that of other alkali metal ion complexes, i.e., the Stokes radius of SLi^+ is much larger than that of other metal ions. This large value of ionic radius of the lithium ion complexes can not be interpreted by the increase in the molar volume of the complex cation caused by the coordination of water molecules. Thus, these results suggest that the EO chain of POE compounds surrounds loosely the bulky hydrated lithium ion and that the structure of the lithium ion complexes may be considerably distorted from the normal helical structure of other alkali metal ion complexes. The values of $X_{\mathrm{H_2O,comp}}$ of 18-crown-6 complexes of $\mathrm{Li^+}$ and $\mathrm{Na^+}$ are also relatively large and comparable to those of DEO6 complexes. In these complexes, the distorted structure of crown ether was reported.[17,18] This distortion may result in a configuration of EO chain favorable for the interaction with the hydrated metal ion.

Although the hydration energy of barium ion is much higher than that of potassium ion and their ionic radii are almost the same, the $X_{\mathrm{H_2O,comp}}$ value of barium ion complex is smaller than that of potassium ion complex, except for Triton X-405 complexes. In the case of barium ion systems, the barium ion complex of POE compounds forms a contact ion-pair with two molecules of the picrate ion. Thus, the hydrated water may be squeezed out by the approach of two picrate ions.

The $X_{\mathrm{H_2O,comp}}$ values of Triton X-100 roughly agree with the values predicted from the average number of EO units ($n_{\mathrm{av}}=9.6$) in spite of it's being a polydisperse compound. On the other hand, the values of $X_{\mathrm{H_2O,S}}$ and $X_{\mathrm{H_2O,comp}}$ of Triton X-405 are much larger than those of Triton X-100. The differences of the $X_{\mathrm{H_2O,comp}}$ values between Triton X-405 complexes and Triton X-100 complexes are roughly equal among the alkali metal ions. This suggests that, since the Triton X-405 complex also contains one alkali metal ion, the residual part of the long chain of EO units ($n_{\mathrm{av}}=42.8$) is not subject to any coordination to the metal ion. Thus, the increment of the $X_{\mathrm{H_2O,comp}}$ from Triton X-100 to Triton X-405 systems is mainly attributed to water molecules bound to the EO chain of Triton X-405, which are not participating to the coordination to a metal ion. Relatively large differences of $X_{\mathrm{H_2O,comp}}$ of $\mathrm{Li^+}$ and $\mathrm{Na^+}$ ($X_{\mathrm{H_2O,comp}}$ (Triton X-405) $-$ $X_{\mathrm{H_2O,comp}}$ (Triton X-100) $=4.4(\mathrm{Li^+})$ and $4.0(\mathrm{Na^+})$) suggest the higher hydration number of a metal ion in Triton X-405. In the barium complex of Triton X-405, the effect of the counter picrate ion may not be so serious because of its very long EO chain. Thus, the $X_{\mathrm{H_2O,comp}}$ value of the barium complex is larger than that of the potassium complex, as expected from the hydration energy of the barium ion being higher than that of the potassium ion.

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