The Solvent Extraction and Dissociation of the Ion Pair of Alkali Metal Complex of Monodisperse Poly(oxyethylene) Derivatives with Picrate Ion

Yoichi Kikuchi, Yasuhiko Nojima, Hiroyuki Kita,
Toshio Suzuki, and Kiyoshi Sawada*
Laboratory of Analytical Chemistry, Faculty of Science, Niigata University, Niigata 950-21

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The ion pair extraction of the alkali metal ion complex of poly(oxyethylene) monododecyl ethers (DEO*n*: n=4, 6, and 8, where n refers to the number of the oxyethylene unit) with picrate ion into 1,2-dichloroethane (1,2-DCE) has been studied by means of a vapor pressure osmometry and a solvent extraction. The extraction equilibria have been interpreted by taking into consideration the ion pair dissociation in 1,2-DCE. Thermodynamic constants of the extraction and the dissociation of the ion pairs have been evaluated from a quantitative analysis of the extraction data. The extractability of the alkali metal ion increases in the order $\mathrm{Li^+}<\mathrm{Na^+}<\mathrm{Cs^+}<\mathrm{K^+}$, irrespective of the number of oxyethylene (EO) unit of DEO*n*. This order was interpreted by the formation constant of the DEO*n*–alkali metal ion complex in the aqueous phase. The formation constants of the DEO*n*–alkali metal ion complex both in the aqueous phase and in 1,2-DCE increase with the increase in the number of EO unit. The interionic distance between the cationic complex and picrate ion of the ion pair was estimated from the dissociation constant in 1,2-DCE.

The cationic complexes of the noncyclic poly(oxyethylene) derivatives (POE compounds) with alkali and alkaline earth metal ions are extracted into organic solvents by forming ion pairs with lipophilic anions. These extraction systems have been mainly investigated from a viewpoint of the analytical application[1—9] and only a few systematic investigations have been reported on a mechanism of the ion pair extraction.[10—12]

In the previous paper,[12] we reported the ion pair extraction of poly(oxyethylene) alkylphenylether (Triton X-100) complexes of alkali metals with picrate ion into 1,2-dichloroethane. An analysis of a vapor pressure osmometry revealed a partial dissociation of the extracted ion pair in 1,2-dichloroethane. Thus, the extraction equilibria have been interpreted by taking into consideration the ion pair dissociation. From a quantitative analysis of the extraction data, we obtained the following conclusions: (1) The composition of the extracted ion pair is 1 : 1 : 1 with respect to Triton X-100 : alkali metal ion : picrate ion. (2) The effect of an ion size of the alkali metal ion on the selectivity of the Triton X-100 system for alkali metals is less important compared with that of crown compounds.[13—16] (3) The interionic distance between the cationic complex and picrate ion of the ion pairs are the almost same, irrespective of the kind of alkali metal ion. Triton X-100 is a polydisperse compound whose average number of oxyethylene units is 9.6. For the close discussion of this extraction system, consequently, it is required to study the extraction with monodisperse poly(oxyethylene) derivatives.

In the present paper, we have studied an extraction of alkali metal picrates into 1,2-dichloroethane with monodisperse poly(oxyethylene) monododecyl ethers, where the number of oxyethylene units (EO unit) are 4, 6, and 8. The effects of the number of EO unit on the extractability of alkali metal ions and on the dissociation of the extracted ion pairs are discussed.

Experimental

Reagents. Poly(oxyethylene) monododecyl ethers (Nikkol BL-*n*SY, DEO*n*: n=4, 6, and 8, where n refers to the number of the oxyethylene unit) were purchased from Nikko Chemicals, and were used without further purification. 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. Potassium picrate synthesized from potassium hydroxide and picric acid was recrystallized twice from distilled water. Other chemicals used were of reagent grade.

Vapor Pressure Measurement. The vapor pressure measurements of the 1,2-DCE solutions of DEO*n* (2.5×10^{-3}—1.5×10^{-2} M: M≡mol dm^{-3}) were performed with Corona model 117 osmometer. 1,2-DCE solutions (30 ml) of DEO8 (2.5×10^{-3}—1.5×10^{-2} M) were shaken with potassium picrate crystals in centrifuge tubes for 30 min at 25±0.1 °C. After separation of crystals, the vapor pressure of the solutions were measured. A portion of the solutions (5 ml) was transferred to the other centrifuge tubes and allowed to evaporate. After the residue was dissolved in 10^{-3} M sodium hydroxide, the picrate concentration of the solutions was determined by spectrophotometry (ε=14400 at 356 nm, Hitachi U-3400). No distribution of picrate ion to 1,2-DCE in the absence of DEO8 was measured spectrophotometrically.

Extraction Procedure. Alkali metal picrates were extracted with DEO*n* by the method described elsewhere.[12] A portion of an aqueous solution (20 ml) containing picric acid and alkali metal chloride, whose pH was adjusted to 8—10 by alkali metal hydroxide, was shaken with an equal volume of a 1,2-DCE solution containing DEO*n* in a centrifuge tube (50 ml) in a thermostated water bath for 30 min at 25±0.1 °C. After centrifugation, the concentrations of picrate in both phases were determined by means of spectrophotometry.

The following three types of experiments were performed for potassium ion, and Exp. (a) and (c) for the other alkali metal ions.

Exp. (a) $C_{\mathrm{Pic,i}}=2\times10^{-5}-5\times10^{-4}$ M, $C_{\mathrm{M,i}}=10^{-1}$ M, $C_{\mathrm{S,i}}=10^{-2}$ M,

Exp. (b) $C_{\mathrm{Pic,i}}=10^{-4}$ M, $C_{\mathrm{M,i}}=10^{-3}-10^{-1}$ M, $C_{\mathrm{S,i}}=10^{-2}$ M,

Exp. (c) $C_{\mathrm{Pic,i}}=10^{-4}$ M, $C_{\mathrm{M,i}}=10^{-1}$ M, $C_{\mathrm{S,i}}=10^{-3}-5\times10^{-2}$ M,

where $C_{\mathrm{Pic,i}}$ and $C_{\mathrm{M,i}}$ refer to the initial concentrations of picrate and alkali metal ion in the aqueous solution, and $C_{\mathrm{S,i}}$ refers to the initial concentration of DEO*n* in the organic solution.

Results and Discussion

Vapor Pressure Osmometry. Vapor pressure measurements of 1,2-DCE solutions of DEO*n* revealed that a mean molecular weight of DED*n* in 1,2-DCE is constant irrespective of a concentration of DEO*n* ($2.5\times10^{-3}-1.5\times10^{-2}$ M). The mean molecular weight agreed with a value calculated from a molecular formula. Thus, it was confirmed that DEO*n* exists as a monomeric form in 1,2-DCE under these experimental conditions, i.e., it forms neither aggregate nor micelle.

The results of the vapor pressure measurements of the 1,2-DCE solution of DEO8 containing potassium picrate are shown in Fig. 1, where *i* refers to the van't Hoff's factor with respect to potassium picrate and a contribution of free DEO8 is eliminated.[12] As can be seen from Fig. 1, the values of *i* are larger than unity, and this fact suggests the dissociation of the ion pair similar to the Triton X-100 system.[12] If we assume the composition of the ion pair of the DEO8-alkali metal complex with the picrate ion is 1 : 1 : 1 with respect to DEO8 : alkali metal ion : picrate ion, the dissociation of the ion pair is written by

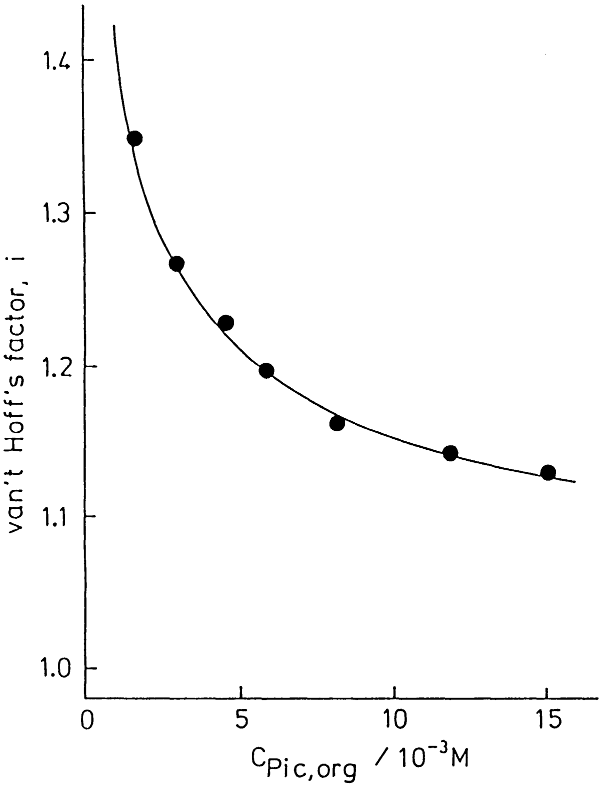


Fig. 1. Van't Hoff's facter, *i*, of the 1,2-DCE solution containing the ion pair of DEO8–K$^+$ complex with picrate ion as a function of the total concentration of picrate. The solid line is a calculated curve. See text.

$$\mathrm{SM^+\cdot Pic^-_{org}} \rightleftarrows \mathrm{SM^+_{org}+Pic^-_{org}} \tag{1}$$

where subscript "org" refers to the organic phase, and S, M$^+$, and Pic$^-$ refer to DEO8, alkali metal ion and picrate ion, respectively. The dissociation constant of the ion pair is defined by

$$K_{\mathrm{dis}}=\frac{[\mathrm{SM^+}]_{\mathrm{org}}[\mathrm{Pic^-}]_{\mathrm{org}}}{[\mathrm{SM^+\cdot Pic^-}]_{\mathrm{org}}}. \tag{2}$$

From Eq. 1, *i* is given by Eq. 3.

$$i=\frac{[\mathrm{SM^+\cdot Pic^-}]_{\mathrm{org}}+[\mathrm{SM^+}]_{\mathrm{org}}+[\mathrm{Pic^-}]_{\mathrm{org}}}{C_{\mathrm{Pic,org}}}, \tag{3}$$

where $C_{\mathrm{Pic,org}}$ refers to a total concentration of picrate in the organic phase. Substitution of Eq. 2 into Eq. 3 leads to Eq. 4.

$$i=1+\frac{-K_{\mathrm{dis}}+(K_{\mathrm{dis}}^2+4K_{\mathrm{dis}}C_{\mathrm{Pic,org}})^{1/2}}{2C_{\mathrm{Pic,org}}}. \tag{4}$$

The solid line in Fig. 1 is the best fit curve calculated by using Eq. 4. The good fitting of the experimental data with the calculated curve confirms the dissociation of the ion pair shown by Eq. 1. Although the data were not analysed by a rigorous treatment such as correction of activity, the dissociation constant of the ion pair of DEO8–K$^+$ complex ion with picrate ion was estimated as roughly $K_{\mathrm{dis}}=10^{-3.6}$.

Solvent Extraction Study. If we assume the composition of the complex of the alkali metal ion with DEO*n* as 1 : 1, an extraction of alkali metal picrate with DEO*n* is expressed by Eq. 5.

$$\mathrm{M^+ + Pic^- + S_{org}} \overset{K_{\mathrm{ex}}}{\rightleftarrows} \mathrm{SM^+\cdot Pic^-_{org}} \overset{K_{\mathrm{dis}}}{\rightleftarrows} \mathrm{SM^+_{org}+Pic^-_{org}}, \tag{5}$$

where S refers to DEO*n*. The thermodynamic constants of extracion, K°_{ex}, and dissociation, K°_{dis}, of the ion pair are defined as

$$K^{\circ}_{\mathrm{ex}}=\frac{[\mathrm{SM^+\cdot Pic^-}]_{\mathrm{org}}}{[\mathrm{M^+}][\mathrm{Pic^-}][\mathrm{S}]_{\mathrm{org}}f_{\pm}^2}, \tag{6}$$

$$K^{\circ}_{\mathrm{dis}}=\frac{[\mathrm{SM^+}]_{\mathrm{org}}[\mathrm{Pic^-}]_{\mathrm{org}}f_{\pm,\mathrm{org}}^2}{[\mathrm{SM^+\cdot Pic^-}]_{\mathrm{org}}}, \tag{7}$$

where $f_{\pm}$ refers to a mean activity coefficient of M$^+$ and Pic$^-$ in the aqueous phase. $f_{\pm,\mathrm{org}}$ refers to that of $\mathrm{SM^+_{org}}$ and $\mathrm{Pic^-_{org}}$ in the 1,2-DCE phase. $f_{\pm}$ and $f_{\pm,\mathrm{org}}$ were evaluated by using an extended Debye–Hückel equation. The concentrations of ionic species in 1,2-DCE ($\mathrm{SM^+_{org}}$ and $\mathrm{Pic^-_{org}}$) are low under the experimental conditions used. Nevertheless, it is necessary to correct the activity coefficients of the ionic species because of the low dielectric constant of the 1,2-DCE (ε=10.36 at 25 °C).

The distribution ratio of picrate, D, is defined by

$$\mathrm{D} = C_{\mathrm{Pic,org}}/C_{\mathrm{Pic,aq}} = \frac{[\mathrm{SM^+\cdot Pic^-}]_{\mathrm{org}} + [\mathrm{Pic^-}]_{\mathrm{org}}}{[\mathrm{Pic^-}]}. \tag{8}$$

From Eqs. 6—8, we obtain Eq. 9.

$$\log D = \log K^{\circ}_{\mathrm{ex}} + \log[\mathrm{M^+}] + \log[\mathrm{S}]_{\mathrm{org}} + 2\log f_{\pm} + \log F, \tag{9}$$

where the function F is given by

$$F = \frac{2}{-1 + (1 + 4C_{\mathrm{Pic,org}}f_{\pm,\mathrm{org}}{}^2K^{\circ}{}_{\mathrm{dis}}{}^{-1})^{1/2}}. \tag{10}$$

The initial concentrations of alkali metal ion, $C_{\mathrm{M,i}}$, and DEOn, $C_{\mathrm{S,i}}$, are much higher than that of picrate under the conditions of Exp. (a) and the distribution constant of DEOn is larger than 10^3. Therefore, the free concentrations of alkali metal ion in the aqueous phase, $[\mathrm{M^+}]$, and DEOn in the organic phase, $[\mathrm{S}]_{\mathrm{org}}$, can be approximated by $C_{\mathrm{M,i}}$ and $C_{\mathrm{S,i}}$, respectively, and can be taken as constant. The change of $\log D$, consequently, depends only on $\log F$ term under the conditions of Exp. (a). Thus, Eq. 9 can be normalized to a function given by

$$Y = \log\left(1 + \frac{2}{-1 + (1 + 4x)^{1/2}}\right),\quad X = \log x, \tag{11}$$

where x corresponds to $C_{\mathrm{Pic,org}}f_{\pm,\mathrm{org}}{}^2K^{\circ}{}_{\mathrm{dis}}{}^{-1}$.

The plots of $\log D$ vs. $\log C_{\mathrm{Pic,org}}$ under the conditions of Exp. (a) are shown in Fig. 2(a). The values of K°_{ex} and K°_{dis} can be obtained by means of a curve fitting of the plots in Fig. 2(a) with the normalized curve, Eq. 11. The mean activity coefficient in 1,2-DCE, $f_{\pm,\mathrm{org}}$, depends on concentrations of the dissociated ions, i.e. on the value of K°_{dis}. As a first approximation, the value of K°_{dis} was evaluated by the curve fitting by using proper value of $f_{\pm,\mathrm{org}}$. Then concentrations of the dissociated ions were calculated from K°_{dis}, and the value of $f_{\pm,\mathrm{org}}$ was evaluated by using an extended Debye—Hückel equation. The curve fitting was repeated by using the value of $f_{\pm,\mathrm{org}}$ newly obtained. Three iterations of the successive approximation were enough to give the converged values of K°_{dis} and $f_{\pm,\mathrm{org}}$. The best fit curves obtained finally are depicted in Fig. 2(a) by solid lines.

By using the values of K°_{ex} and K°_{dis} thus obtained, we analyzed the experimental results of Exp. (b) and Exp. (c). The plots of $\log D - \log F - 2\log f_{\pm}$ vs. $\log[\mathrm{M^+}]$ for Exp. (b) are shown in Fig. 2(b). These plots show straight lines with a slope of unity as predicted from Eq. 9. This fact confirms that the number of alkali metal ion in the ion pair is one. The plots of $\log D - \log F$ vs. $\log[\mathrm{S}]_{\mathrm{org}}$ for Exp. (c) are shown in Fig. 2(c). The plots for the DEO6 and DEO8 systems agree well with straight lines with a slope of unity. This fact confirms that the number of the DEO6 or DEO8 molecule in the ion pair is one. On the other hand, the slopes of the plots for the DEO4 system, irrespective of the kind of alkali metal ion, are higher than unity, and increase with increasing the concentration of DEO4.

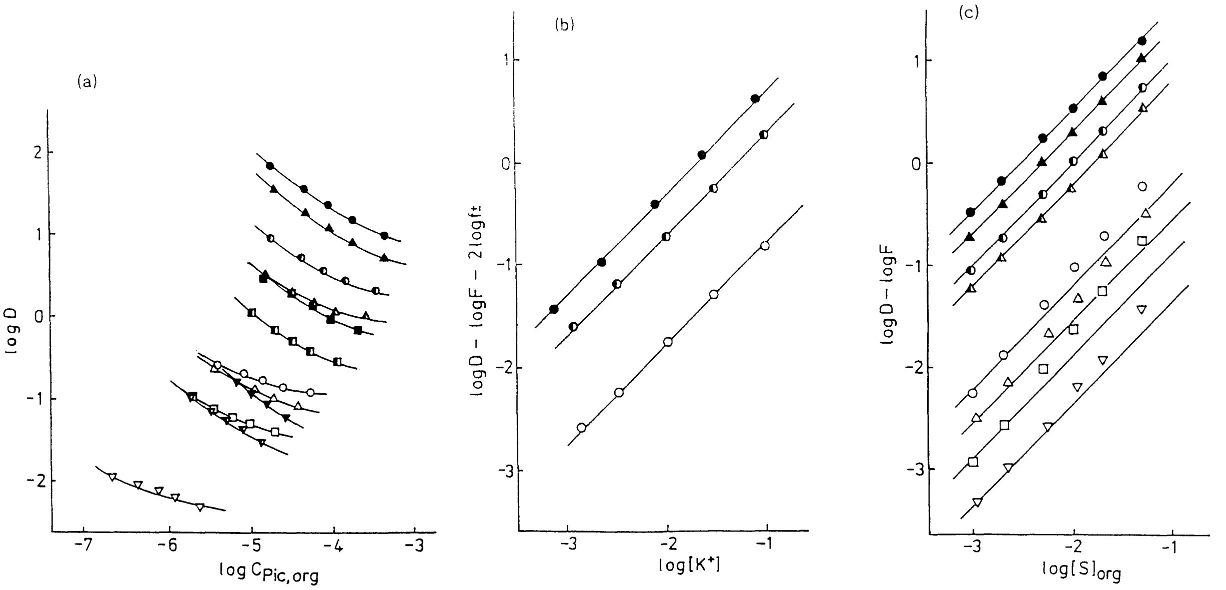


Fig. 2. The ion pair extraction of the DEOn-alkali metal ion complex with picrate ion into 1,2-DCE. (a): Plots of log D vs. log $C_{\mathrm{Pic,org}}$ for Exp. (a). Solid lines are the normalized curves. See text. (b): Plots of log $D-$log $F-2$ log$f_{\pm}$ vs. log $[\mathrm{K^+}]$ for Exp. (b). Solid lines are straght lines with a slope of unity. (c): Plots of log $D-$ log F vs. log $[\mathrm{S}]_{\mathrm{org}}$ for Exp. (c). Solid lines are straght lines with a slope of unity. Symbols: ▽; Li$^+$, □; Na$^+$, ○; K$^+$, △; Cs$^+$. Open symbols; DEO4, half-filled symbols; DEO6, filled symbols; DEO8.

These facts suggest that the DEO4-M^+ system partially forms a complex coordinating two DEO4 molecules at the higher DEO4 concentration. Thus, the results depicted in Figs. 2(a)—(c) confirmed that the extracted ion pair consists of 1 : 1 DEO*n*-M^+ complex and one picrate ion, i.e., $S:M^+:Pic^-=1:1:1$ (Eq. 5). In the case of DEO4 system, 2 : 1 : 1 ion pair of the complex with picrate ion is additionally formed.

The thermodynamic constants of the extraction, K°_{ex}, and the dissociation, K°_{dis}, thus obtained are summarized in Table 1. The value of $\log K^\circ_{dis}$ of DEO8-K^+–

Table 1. The Logarithmic Extraction Constant and Dissociation Constant, and the Interionic Distance of the Ion Pair, *a*

M^+	*n*	$\log K^\circ_{ex}$	$\log K^\circ_{dis}$	*a*/Å
Li^+	4	0.75	−6.41	2.6
	6	1.25	−4.85	3.9
	8	1.26	−4.08	4.6
Na^+	4	1.58	−5.86	2.7
	6	2.29	−4.18	4.5
	8	2.66	−3.92	4.8
K^+	4	2.11	−5.64	2.9
	6	3.22	−4.00	4.7
	8	3.81	−3.64	5.4
Cs^+	4	1.83	−5.23	3.5
	6	3.01	−4.33	4.4
	8	3.48	−3.56	5.7

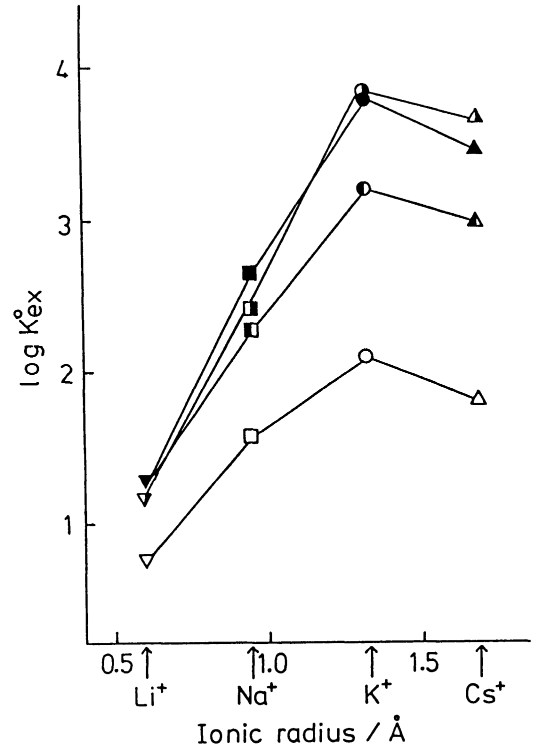
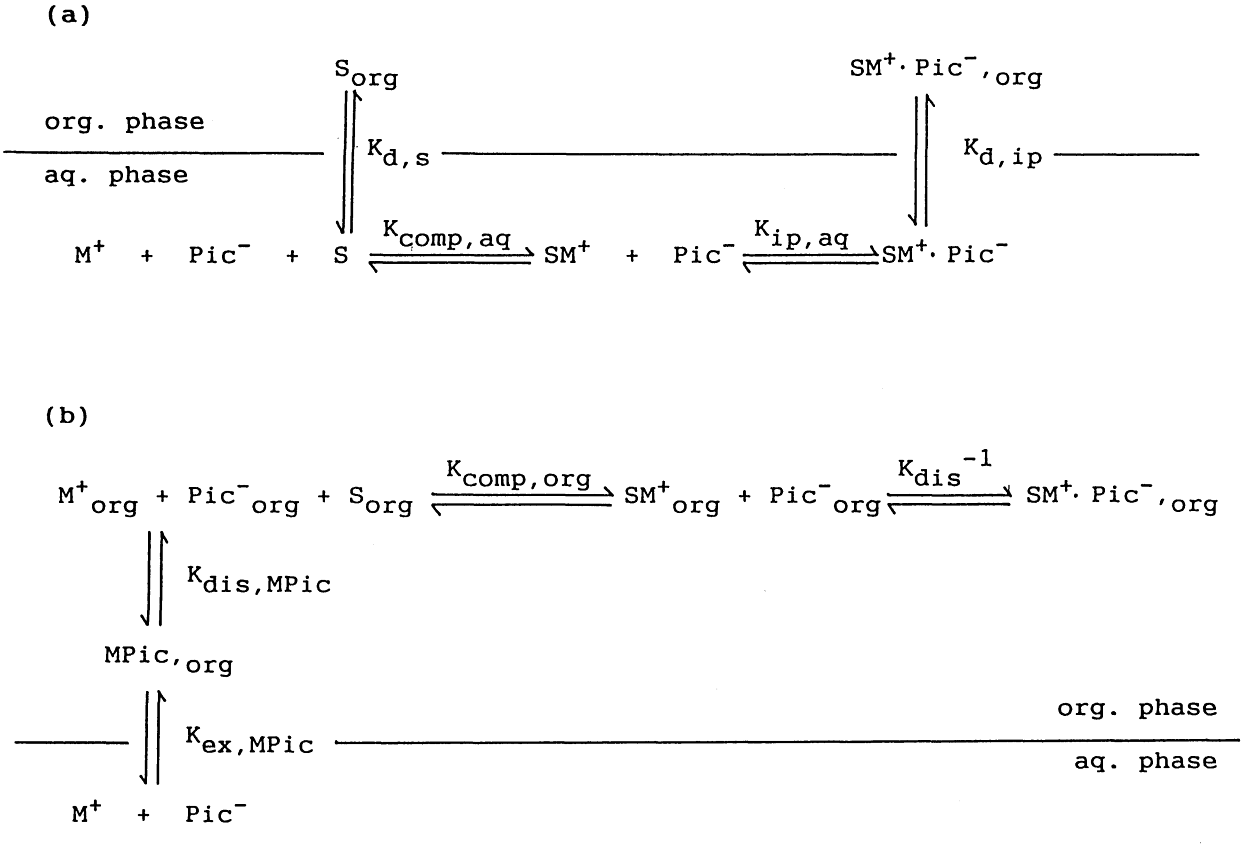


Fig. 3. Plots of the logarithmic extraction constant as a function of the ionic radius of the alkali metals. The right-half-filled symbols refer to the Triton X-100 system (Ref. 12). The other symbols: see Fig. 2.



Scheme 1.

Pic^- listed in Table 1 agrees with that estimated by osmometry ($\log K_{dis}=-3.6$).

In the case of the DEO4 system, we evaluated the values of K°_{ex} and K°_{dis} by taking into consideration the formation of the ion pair of 2:1 complex, $S_2M^+\cdot Pic^-$. Since the precision of the data is not so high, individual constants of the formation of $S_2M^+\cdot Pic^-$ and its ion pair dissociation were not obtained, although the product of these constants was estimated.

Extraction Constant. The values of $\log K^\circ_{ex}$ of the ion pair are plotted as a function of a ionic radius of alkali metal ion in Fig. 3. As can be seen from Fig. 3, the extraction constant shows a maximum at the potassium ion, and the extractability decreases in the order $K^+>Cs^+>Na^+>Li^+$, irrespective of the number of EO unit. This order of the extractability of alkali metal ions with the noncyclic POE compounds agrees with that with the 18-crown-6.[13]

The extraction process of the ion pair can be explained by Scheme 1(a), i.e., the formation of the alkali metal complex with the POE compound in the aqueous phase ($K_{comp,aq}$), the ion pair formation of the $S-M^+$ complex with picrate ion ($K_{ip,aq}$), and the distribution of the ion pair into 1,2-DCE ($K_{d,ip}$). The distribution constant of the POE compound is given by $K_{d,s}$. Therefore, the extraction constant of the ion pair, K°_{ex}, is expressed by Eq. 12.

$$K^\circ_{ex}=K_{comp,aq}K_{ip,aq}K_{d,ip}K_{d,s}^{-1}. \qquad (12)$$

$K_{d,s}$ is common to a given POE compound. The value of $K_{d,ip}$ can be assumed to be the same irrespective of the kind of the alkali metal ion, because the molar volume of the ion pair scarcely changes by the central metal ion. Thus, the values of $K_{d,ip}$ and $K_{d,s}$ can be approximated to be the same between the different metal ions for a given POE compound. Moreover, as will be mentioned below, the interionic distance of any ion pair studied here is longer than 2 Å even in 1,2-DCE. Thus, as suggested by the Fuoss's equation,[17] the values of the ion pair formation constant in the aqueous phase, $K_{ip,aq}$, can be assumed to be constant for all ion pairs.

Consequently, the term of $K_{ip,aq}K_{d,ip}K_{d,s}^{-1}$ in Eq. 12 can be assumed to be constant, i.e., the difference of $\log K^\circ_{ex}$ shown in Fig. 3 corresponds to the difference of the complex formation of $S-M^+$ in the aqueous phase, $\Delta\log K_{comp,aq}$. Therefore, the order of the extractability of alkali metal ions is interpreted by the formation constant of the $S-M^+$ complex in the aqueous phase. Potassium ion has the largest $\log K_{comp,aq}$ among alkali metal ions irrespective of the number of EO unit.

On the other hand, we can compare the formation constant of the complex in 1,2-DCE by considering the extraction process shown by Scheme 1(b). In this process, since the constants of $K_{ex,MPic}$ ad $K_{dis,MPic}$ are common for a given metal ion. The difference of $\log K^\circ_{ex}$ between the POE compounds for a given metal ion corresponds to the difference of the values of $\log K_{comp,org}K^\circ_{dis}{}^{-1}$. Thus, the difference of the formation constant of the complex of the alkali metal with the POE compound in 1,2-DCE for the same alkali metal ion, $\Delta\log K_{comp,org}$, is given by $\Delta\log K^\circ_{ex}K^\circ_{dis}$. The values of $\Delta\log K_{comp,org}$ obtained by using the values of $\log K^\circ_{dis}$ listed in Table 1 are plotted in Fig. 4 as a function of the number of EO unit, where the value of DEO8-K^+-Pic^- is used as a reference ($\Delta\log K_{cop,org}$-(DEO8-K^+)=0). As can be seen from Fig. 4, the value of $\Delta\log K_{cop,org}$ increases with the increase in EO unit, irrespective of the kind of alkali metal ions, and its increment decreases with the increase in EO unit. Because of the considerable difference of $K_{ex,MPic}$ between the metal ions, we can not compare the values of $\Delta\log K_{comp,org}$ between alkali metal ions.

In the case of the crown ether system, it is well known that the extractability of alkali metal ion depends on a cavity size of the crown ether as well as the dehydration energy of alkali metal ion. The alkali metal ion having an ion size identical to the cavity size of crown ether shows the largest extraction constant, e.g. potassium ion for 18-crown-6 or sodium ion for 15-crown-5.[13] A similar structure has been proposed for the complex of noncyclic POE compounds, i.e., the central metal ion is surrounded by the EO chain with the helical conformation[18,19] as may be called "turban" complex.[12] Therefore, it is considered that the difference of the formation constant of these "turban" complex also depends on the

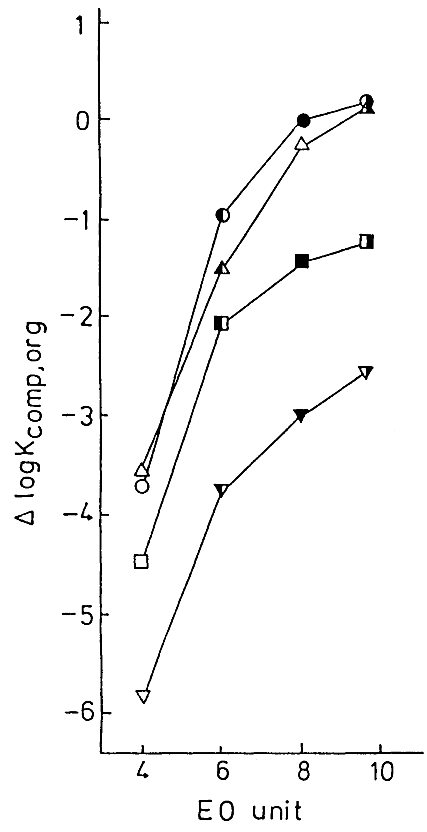


Fig. 4. Plots of the relative values of $\log K_{comp,org}$ as a function of the number of EO unit. Symbols: see Fig. 3.

cavity size of the POE compounds. As shown in Fig. 3, the order of the $\Delta\log K_{\mathrm{comp,aq}}$ values of alkali metal ions is independent of the number of EO unit. This fact may suggest that the cavity size of the noncyclic POE compounds is almost the same irrespective of the number of EO unit and is comparable to that of 18-crown-6.

The formation constant of the "turban" complex increases with the increase in EO unit both in the aqueous phase (Fig. 3) and in the 1,2-DCE phase (Fig. 4). This fact is interpreted by the increase in the number of the oxygen atom of the EO chain bonding to the alkali metal ion. The large difference between DEO4 and DEO6 suggests that the number of oxygen atom of DEO4 is not sufficient to form the stable complex. These results are consistent with the reports of Yanagida et al.[10] and Liu,[20] i.e., more than 7 EO units are required for enough interaction with K^+. The small difference of the values of $\Delta\log K_{\mathrm{comp,org}}$ between DEO8 and Triton X-100 (an average value of n is 9.6) may suggest that the EO units above 8th play no important role in the complexation.

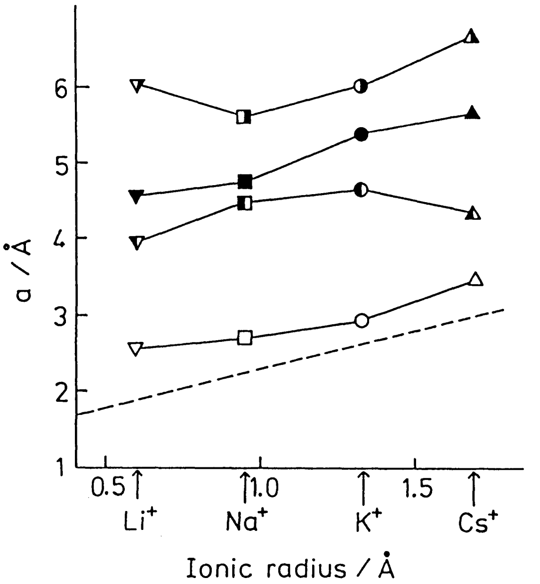
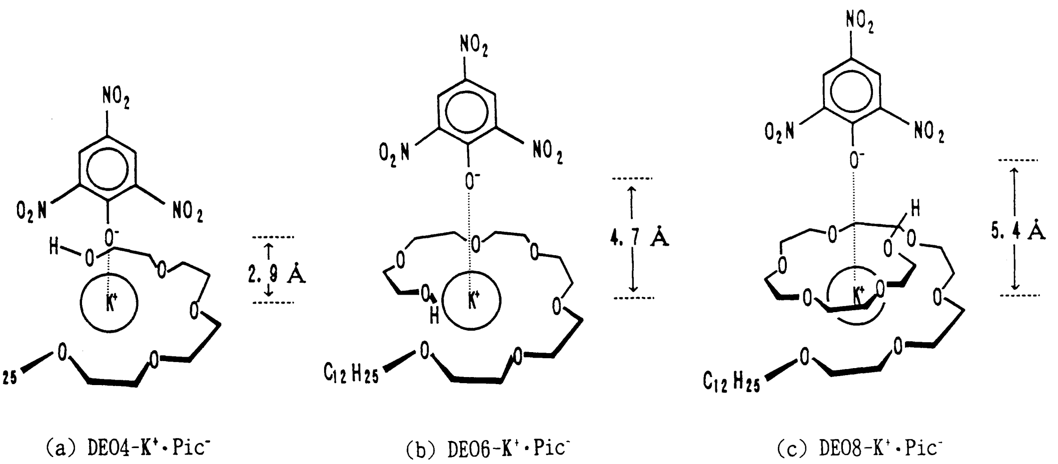


Fig. 5. Plots of the ionterionic distance of the ion pair, a, as a function of the ionic radius of the alkali metals. Symbols: see Fig. 3.

Interionic Distance of the Ion Pair in 1,2-DCE. By using the Bjerrum's equation,[21] a interionic distance, a, of the extracted ion pair was estimated from the dissociation constant of the ion pair in 1,2-DCE by the same manner as the previous paper.[12] These values thus calculated are listed in Table 1, and are plotted in Fig. 5 as a function of an ionic radius of alkali metal. As the charges of the cationic "turban" complex and picrate ion are assumed to be localized at the central metal ion of the complex and oxygen of picrate ion, respectively, the interionic distance, a, indicates roughly the distance between M^+ of the "turban" complex and O^- of picrate. The structure of the ion pairs considered from the a value is tentatively illustrated in Fig. 6, where the ion pairs of the potassium ion system are shown as an example.

The broken line drawn in Fig. 5 shows the interionic distnce of the contact ion pair between O^- of picrate and the central metal ion. As can be seen from Fig. 5, the values of a of the DEO4 system are close to the broken line. This fact suggests that the ion pairs of the DEO4 system is eventually regarded as a contact ion pair. Since the number of EO unit of DEO4 is not sufficient to wrap up the central metal ion, the DEO4 complex has a vacant space permitting the approach of O^- of picrate to the central metal ion (Fig. 6(a)). The fact that the DEO4 complex forms the complex coordinating two DEO4 molecules strongly supports this structure.

The interionic distance of the ion pair increases with increasing the number of EO unit. This finding is interpreted by the increase of a steric hindrance of the EO chain wrapping the central metal ion (Figs. 6(b),



(a) DEO4-K⁺·Pic⁻　(b) DEO6-K⁺·Pic⁻　(c) DEO8-K⁺·Pic⁻

Fig. 6. The model of the ion pairs of the DEOn-K^+ complexes with picrate ion. (a): DEO4 system, (b): DEO6 system, (c): DEO8 system.

(c)). In the case of the DEO6 system, the interionic distance of the ion pair of the DEO6–Cs^+ complex with picrate ion is shorter than that of the DEO6–K^+ complex. This fact may suggest that the number of EO unit of DEO6 is not sufficient to wrap up to the cesium ion as reported for 18-crown-6 complex.[13,16] In the case of the DEO8 system, the interionic distance of the ion pair slightly increases with increasing the ionic radius of the central metal. Since Triton X-100 is a polydisperse compound and the error of the a value increases with increasing the a value, it is difficult to discuss the a value in detail for the Triton X-100 systems.

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