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Partition and Complex Formation of Alkali Metal Ions with Poly(oxyethylene) Derivatives in 4-Methyl-2-pentanone

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The partition equilibria of alkali metal picrates with or without a series of poly(oxyethylene) derivatives (POE compound, S) into 4-methyl-2-pentanone (MIBK) have been studied at 25.0 °C. The thermodynamic constants of the distribution and ion-pair formation in the water-saturated MIBK of ion pairs of alkali metal picrates ($\mathrm{M^+ \cdot Pic^-}$), $K^{\circ}_{\mathrm{dist,MP}}$ and $K^{\circ}_{\mathrm{ip,MP,o}}$, and the POE compounds-$\mathrm{M^+}$ complexes with $\mathrm{Pic^-}$ ($\mathrm{SM^+ \cdot Pic^-}$), $K^{\circ}_{\mathrm{dist,SMP}}$ and $K^{\circ}_{\mathrm{ip,SMP,o}}$, were determined. From these data, the partition coefficients of $\mathrm{M^+}$ and $\mathrm{Pic^-}$, $K^{\circ}_{\mathrm{d,M}} \cdot K^{\circ}_{\mathrm{d,P}}$, and the thermodynamic formation constants of the POE compounds-$\mathrm{M^+}$ complexes in MIBK, $K^{\circ}_{\mathrm{comp,o}}$, were evaluated. The interionic distances, a, of ion pairs were estimated from the ion-pair formation constants, $K^{\circ}_{\mathrm{ip,MP,o}}$ and $K^{\circ}_{\mathrm{ip,SMP,o}}$. These results were compared with those in an inert solvent, 1,2-dichloroethane (1,2-DCE). The complex formation constants, $K^{\circ}_{\mathrm{comp,o}}$, in MIBK are much smaller than those in 1,2-DCE, and their differences among alkali metal ions are small. The donating ability of the solvent has large effects on the stability of the complexes, whereas the polarity (dielectric constant) of the solvent is not very effective. A small metal ion, particularly lithium ion, is strongly hydrated in water-saturated MIBK. Hydration to the lithium ion brings about a serious structural change in the POE compound complex.

Many fundamental studies on the distribution of ion pairs from water to various organic solvents have been made.[1—12] The stability and structure of an ionic complex and its ion pair in inert or weakly solvating solvents are often greatly different from those in polar and/or solvating solvents. Nevertheless, the detailed equilibria and structures of complexes in the former solvents have not been fully elucidated because of a restriction of low solubility of electrolytes.

In previous work,[10—12] we studied the ion-pair formation of alkali metal ions ($\mathrm{M^+}$) and alkali metal ion complexes of POE compounds (S) with a picrate ion, $\mathrm{M^+ \cdot Pic^-}$ and $\mathrm{SM^+ \cdot Pic^-}$, and $\mathrm{SM^+}$ complex formation in 1,2-DCE. The solvent, 1,2-DCE, is typical of a non-coordinating and relatively low polar solvent. Thus, the solvent hardly participates in the equilibria and structures of complexes.

MIBK is one of the most popular solvents for ion-pair extraction, similar to 1,2-DCE. MIBK has a donor ability to some extent (the donor number (*DN*) of ketones is about 17)[13] in contrast to 1,2-DCE (*DN* = 0),[13] whereas the dielectric constant of MIBK ($\varepsilon = 13.1$) is comparable to that of 1,2-DCE ($\varepsilon = 10.3$). Thus, the MIBK system is suitable for investigating the solvent effect in a relatively low-dielectric-constant medium. In the present study, we studied the distribution and ion-pair formation of alkali metal ions and their complexes of POE compounds with the picrate ion, and complex formation in MIBK. The solvent effects upon the formation of the complexes and the ion pairs and the structures of these solutes are discussed based on a comparison with the 1,2-DCE system.

The water in organic solvents sometimes exerts a large effect on the equilibrium and structure of solutes.[2(b),3,10,11,14—18] The solubility of water in MIBK (0.87 mol dm^{-3}) is much larger than that in 1,2-DCE (0.13 mol dm^{-3}). The effects of water on the equilibrium and structure of the ion pairs are also discussed.

Experimental

Reagents. Poly(oxyethylene) monododecyl ethers (DEO*n*: $\mathrm{HO(C_2H_4O)}_n\mathrm{C_{12}H_{25}}$, n = 4, 6, and 8) were purchased from Nikko Chemicals. MIBK (Wako) was washed three times with distilled water. The dielectric constant of a water-saturated MIBK was determined to be 14.2 (anhydrous MIBK = 13.1). Alkali metal picrates were prepared from their hydroxide and picric acid (Wako), and were recrystallized twice from distilled water. Lithium picrate was recrystallized from MIBK. Other chemicals were of analytical reagent grade.

Distribution Procedure. In the case of a distribution of M·Pic without DEO*n*, a portion of an aqueous solution (20 ml) containing M·Pic (3×10^{-5}—2×10^{-3} mol dm^{-3}) and alkali metal chloride (0.1 mol dm^{-3} for $\mathrm{Li^+}$, 0.05 mol dm^{-3} for other alkali metal ions) was shaken with an equal volume of a water-saturated MIBK in a centrifuge tube (50 ml) at 25.0±0.1 °C. In the case of a distribution of M·Pic with DEO*n*, a portion of an aqueous solution (20 ml) containing M·Pic (3×10^{-5}—2×10^{-3} mol dm^{-3}) and alkali metal chloride (0.05 mol dm^{-3} for the DEO4 systems and $\mathrm{Li^+}$ systems, 0.01 mol dm^{-3} for the other systems) was shaken with an equal volume of a water saturated-MIBK solution containing DEO*n* (0.02 mol dm^{-3} for the DEO4 systems of $\mathrm{Li^+}$ and $\mathrm{Na^+}$, and 0.01 mol dm^{-3} for the other systems).

After centrifugation, the concentrations of picrate in both phases were determined by spectrophotometry (Hitachi U-3400).[9] In order to prevent the distribution of picric acid into the organic phase, these distribution experiments were carried out at pH 6—7.

Results

Distribution of Alkali Metal Picrate. Although the dielectric constant of MIBK is relatively low, the dissociation of the ion pair in MIBK is not negligible at the low concentration of the ion pair.[9—12] Thus, the distribution equilibria of alkali metal picrate are expressed by

$$\mathrm{M^+ + Pic^-} \xrightleftharpoons{K_{\mathrm{dist,MP}}} \mathrm{M^+{\cdot}Pic_o^-} \xrightleftharpoons{K^{-1}_{\mathrm{ip,MP,o}}} \mathrm{M_o^+ + Pic_o^-}, \qquad (1)$$

where the subscript "o" refers to the organic phase. The thermodynamic distribution constant, $K^{\circ}_{\mathrm{dist,MP}}$, is defined as

$$K^{\circ}_{\mathrm{dist,MP}} = \frac{[\mathrm{M^+{\cdot}Pic^-}]_\mathrm{o}}{[\mathrm{M^+}][\mathrm{Pic^-}]f_\pm^2}, \qquad (2)$$

where $f_\pm$ refers to the mean-activity coefficient of $\mathrm{M^+}$ and $\mathrm{Pic^-}$ in the aqueous phase. The thermodynamic ion-pair formation constant, $K^{\circ}_{\mathrm{ip,MP,o}}$, is defined as

$$K^{\circ}_{\mathrm{ip,MP,o}} = \frac{[\mathrm{M^+{\cdot}Pic^-}]_\mathrm{o}}{[\mathrm{M^+}]_\mathrm{o}[\mathrm{Pic^-}]_\mathrm{o}f_{\pm,\mathrm{o}}^2}, \qquad (3)$$

where $f_{\pm,\mathrm{o}}$ refers to the mean-activity coefficient of $\mathrm{M^+}$ and $\mathrm{Pic^-}$ in the organic phase.

The distribution ratio of picrate ion, D, is defined by

$$D \equiv \frac{c_{\mathrm{Pic,o}}}{c_{\mathrm{Pic}}} = \frac{[\mathrm{M^+{\cdot}Pic^-}]_\mathrm{o} + [\mathrm{Pic^-}]_\mathrm{o}}{[\mathrm{Pic^-}]}, \qquad (4)$$

where $c_{\mathrm{Pic,o}}$ and c_{Pic} refer to the total concentrations of picrate in the organic and aqueous phases, respectively. From Eqs. 2, 3, and 4, we obtain

$$\log D = \log K^{\circ}_{\mathrm{dist,MP}} + \log\,[\mathrm{M^+}] + 2\log f_\pm + \log F, \qquad (5)$$

where the function F is given by

$$F = 1 + \frac{2}{-1 + (1+4y)^{1/2}} \quad \text{and}$$
$$y = c_{\mathrm{Pic,o}} \cdot f_{\pm,\mathrm{o}}^2 \cdot K^{\circ}_{\mathrm{ip,MP,o}}. \qquad (6)$$

Since the total concentration of the alkali metal ion, c_M, is much higher than that of picrate under the experimental conditions, the free concentration of cation, $[\mathrm{M^+}]$, can be approximated as c_M and can be taken as a constant.

Plots of $\log D$ vs. $\log c_{\mathrm{Pic,o}}$ are shown in Fig. 1. The thermodynamic constants of the distribution, $K^{\circ}_{\mathrm{dist,MP}}$, and ion-pair formation, $K^{\circ}_{\mathrm{ip,MP,o}}$, of M·Pic were evaluated by a successive approximation with a non-linear regression.[10,11] In this calculation, $f_\pm$ and $f_{\pm,\mathrm{o}}$ were evaluated by using an extended Debye–Hückel equation.[11] The thus-obtained values of $K^{\circ}_{\mathrm{dist,MP}}$ and $K^{\circ}_{\mathrm{ip,MP,o}}$ are given in Table 1, and the calculated curves obtained from these constants are shown by the solid lines in Fig. 1. The fact that these curves reproduce the experimental results confirms the equilibria of Eq. 1.

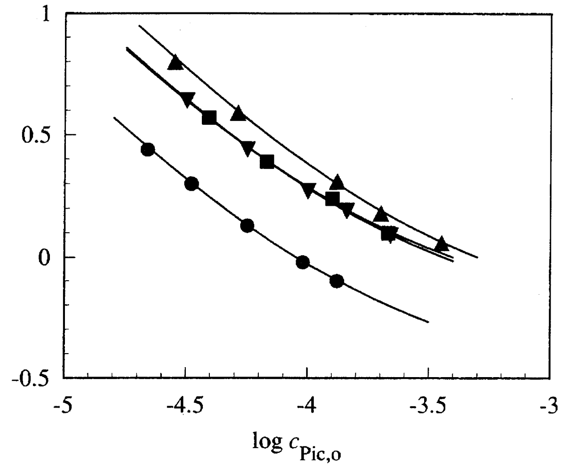


Fig. 1. The distribution of the ion pairs of alkali metal ions with picrate ion into MIBK. Plots of $\log D$ vs. $\log c_{\mathrm{Pic,o}}$. Symbols: ▲; $\mathrm{Li^+}$, ●; $\mathrm{Na^+}$, ■; $\mathrm{K^+}$, ▼; $\mathrm{Cs^+}$.

Table 1. The Logarithmic Thermodynamic Constants of the Distribution and the Ion-Pair Formation of Alkali Metal Picrate and the Interionic Distance, a, in a Water-Saturated MIBK

Metal	$\log K^{\circ}_{\mathrm{dist,MP}}$	$\log K^{\circ}_{\mathrm{ip,MP,o}}$	$\log\,(K^{\circ}_{\mathrm{d,M}} \cdot K^{\circ}_{\mathrm{d,P}})$	a/Å
$\mathrm{Li^+}$	0.69	3.35	−2.66	3.8
$\mathrm{Na^+}$	0.76	3.59	−2.83	3.4
$\mathrm{K^+}$	1.00	3.55	−2.55	3.5
$\mathrm{Cs^+}$	1.01	3.57	−2.56	3.4

Distribution of Alkali Metal Picrate with DEO*n*. Based on the assumption of the formation of the 1 : 1 complex of alkali metal ion with DEO*n* in the organic phase, the distribution equilibria of alkali metal picrate with DEO*n* are expressed by

$$\mathrm{M^+ + Pic^- + S_o} \xrightleftharpoons{K_{\mathrm{dist,o}}} \mathrm{SM^+{\cdot}Pic_o^-} \xrightleftharpoons{K^{-1}_{\mathrm{ip,SMP,o}}} \mathrm{SM_o^+ + Pic_o^-}. \qquad (7)$$

The thermodynamic constants of the distribution of the ion pair ($\mathrm{SM^+{\cdot}Pic^-}$), $K^{\circ}_{\mathrm{dist,SMP}}$, and the ion-pair formation, $K^{\circ}_{\mathrm{ip,SMP,o}}$, are defined as

$$K^{\circ}_{\mathrm{dist,SMP}} = \frac{[\mathrm{SM^+{\cdot}Pic^-}]_\mathrm{o}}{[\mathrm{M^+}][\mathrm{Pic^-}][\mathrm{S}]_\mathrm{o}f_\pm^2}, \qquad (8)$$

$$K^{\circ}_{\mathrm{ip,SMP,o}} = \frac{[\mathrm{SM^+{\cdot}Pic^-}]_\mathrm{o}}{[\mathrm{SM^+}]_\mathrm{o}[\mathrm{Pic^-}]_\mathrm{o}f_{\pm,\mathrm{o}}^2}. \qquad (9)$$

The distribution ratio of picrate, D', is defined by

$$D' \equiv \frac{c'_{\mathrm{Pic,o}}}{c_{\mathrm{Pic}}} = \frac{[\mathrm{SM^+{\cdot}Pic^-}]_\mathrm{o} + [\mathrm{Pic^-}]_\mathrm{o}}{[\mathrm{Pic^-}]}, \qquad (10)$$

where $c'_{\mathrm{Pic,o}}$ is the concentration of the picrate ion in the organic phase corrected for the partition of the ion pair of uncomplexed alkali metal picrate ($c'_{\mathrm{Pic,o}} = c_{\mathrm{Pic,o}} - [\mathrm{M^+{\cdot}Pic^-}]_\mathrm{o}$). From Eqs. 8, 9, and 10, we obtain

$$\log D' = \log k^{\circ}_{\mathrm{dist,SMP}} + \log\,[\mathrm{M^+}] + \log\,[\mathrm{S}]_\mathrm{o}$$
$$+ 2\log f_\pm + \log F, \qquad (11)$$

where the function F is the same as Eq. 6, in which $K^{\circ}_{\mathrm{ip,MP,o}}$ is substituted by $K^{\circ}_{\mathrm{ip,SMP,o}}$.

Plots of $\log D'$ vs. $\log c'_{\rm Pic,o}$ of the Na•Pic system are shown in Fig. 2 as an example. The experimental results were analyzed in the same manner as in the preceding section. The fact that the experimental results depicted in Fig. 2 show a good agreement with the calculated curve confirms the equilibria of Eq. 7, i.e. the distribution and dissociation of the ion pair $SM^+\cdot Pic^-$, in which similar equilibria and ion-pair composition were elucidated in 1,2-DCE.[12] The results of other metal–ion systems also show good agreement with the calculated curves. The thus-obtained values of $K^\circ_{\rm dist,SMP}$ and $K^\circ_{\rm ip,SMP,o}$ are summarized in Table 2.

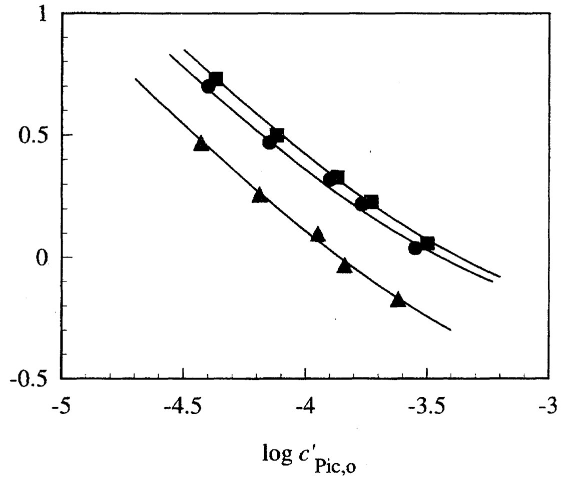


Fig. 2. The distribution of the ion pair of the DEO*n*–Na^+ complex with picrate ion into MIBK. Plots of $\log D'$ vs. $\log c'_{\rm Pic,o}$. Symbols: ●; DEO4, ▲; DEO6, ■; DEO8.

Discussion

Distribution of Alkali Metal Picrate. The distribution of the ion pair, $M^+\cdot Pic^-$, is described by the steps in partitioning individual ions (M^+ and Pic^-) and the formation of ion pairs in the organic phase (Scheme 1).[8,11] Thus, the distribution constant of ion pairs, $M^+\cdot Pic^-$, is given by

$$K^\circ_{\rm dist,MP} = K^\circ_{\rm d,M}\cdot K^\circ_{\rm d,P}\cdot K^\circ_{\rm ip,MP,o}, \tag{12}$$

where $K^\circ_{\rm d,M}$ ($\equiv [M^+]_o f_{\pm,o}/[M^+]f_\pm$) and $K^\circ_{\rm d,P}$ ($\equiv [Pic^-]_o f_{\pm,o}/[Pic^-]f_\pm$) are the partition coefficients of M^+ and Pic^-, respectively. Thus, the partition coefficients of $M^+\cdot Pic^-$ are given by

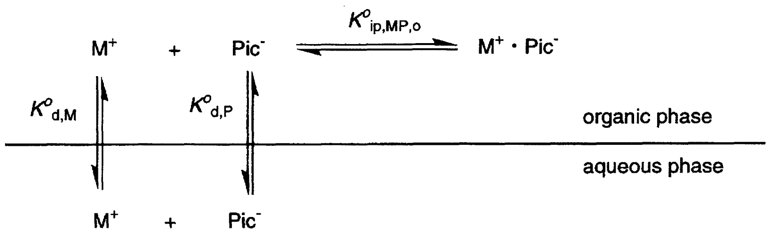
$$\log K^\circ_{\rm d,M}\cdot K^\circ_{\rm d,P} = \log K^\circ_{\rm dist,MP} - \log K^\circ_{\rm ip,MP,o}. \tag{13}$$

The values of $\log K^\circ_{\rm d,M}\cdot K^\circ_{\rm d,P}$ calculated from Eq. 13 are listed in Table 1 and are plotted in Fig. 3 as a function of the ionic radius of alkali metal ions. The results of the distribution of alkali metal picrates form water to the inert solvent, 1,2-DCE,[11] are also plotted in Fig. 3 for a comparison. Because the value of $\log K^\circ_{\rm d,P}$ is common for any metal picrates, the differences of the values of $\log K^\circ_{\rm d,M}\cdot K^\circ_{\rm d,P}$ among the metal ions correspond to those of $\log K^\circ_{\rm d,M}$.

As can be seen from Fig. 3, the plot of $\log K^\circ_{\rm d,M}\cdot K^\circ_{\rm d,P}$ of the MIBK system shows different features from that of the 1,2-DCE system, although the dielectric constants do not differ much between these two solvents. The large value of the partition coefficient of $M^+\cdot Pic^-$ of the MIBK system may be mainly attributed to the coordinating ability of MIBK.

Table 2. The Logarithmic Thermodynamic Constants of the Distribution and Ion-Pair Formation of Alkali Metal Ion Complexes of POE Compounds with Picrate Ion and the Interionic Distance, *a*, of the Ion Pair in a Water-Saturated MIBK

POE	Metal	$\log K^\circ_{\rm dist,SMP}$	$\log K^\circ_{\rm ip,SMP,o}$	a/Å	$\log K^\circ_{\rm comp,o}$
DEO4	Li^+	1.99	3.04	4.6	1.61
	Na^+	2.32	3.07	4.5	2.08
	K^+	2.73	2.97	4.9	2.31
	Cs^+	2.64	3.06	4.6	2.14
DEO6	Li^+	2.29	2.90	5.2	2.05
	Na^+	3.04	3.04	4.6	2.83
	K^+	3.71	2.99	4.8	3.27
	Cs^+	3.28	2.92	5.0	2.92
DEO8	Li^+	2.43	2.91	5.1	2.18
	Na^+	3.35	3.04	4.6	3.14
	K^+	4.08	2.86	5.4	3.77
	Cs^+	3.82	2.80	5.7	3.58



Scheme 1.

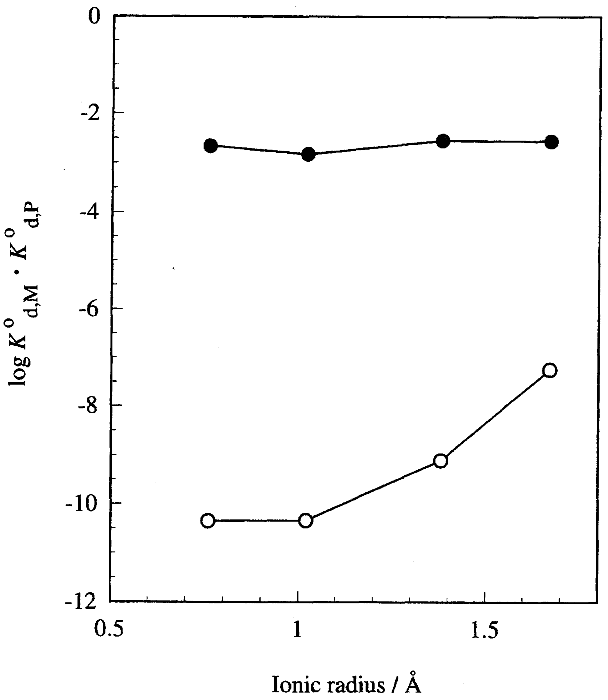


Fig. 3. Plots of $\log K^{\circ}_{\mathrm{d,M}}K^{\circ}_{\mathrm{d,P}}$ as a function of an ionic radius of alkali metals. Filled and open symbols refer to the MIBK and the 1,2-DCE systems, respectively.

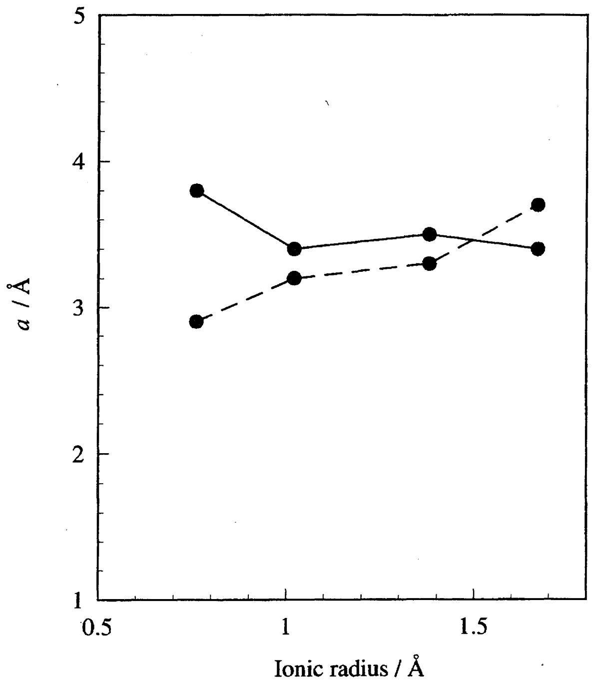


Fig. 4. Plots of the interionic distance, *a*, of the ion pair of alkali metal picrates ($M^+\cdot Pic^-$) as a function of an ionic radius of alkali metals. The solid line and the broken line refer to the MIBK (water-saturated) and the MIBK ($c_{\mathrm{H2O}} = 0.1$ mol dm^{-3}) systems, respectively.

The small differences of $\log K^{\circ}_{\mathrm{d,M}}$ among metal ions in the MIBK system (within 0.3 unit) might be explained by the difference in the hydration of metal ions. Recently, we obtained the hydration number of alkali metal ions in water-saturated MIBK, in which these values were determined to be; $Li^+ = 6.2$, $Na^+ = 3.8$, $K^+ = 1.0$, $Cs^+ = 0.9$.[19] As can be seen from the 1,2-DCE system, a small-size ion is generally unfavorable to partition into an inert solvent because of its large hydration energy in the aqueous phase.[11] Nevertheless, in the case of partition into MIBK, the disadvantage of small metal ions must be compensated by a partition of the hydrated species.

The interionic distance, *a*, of the ion pair, $M^+\cdot Pic^-$, in MIBK was estimated from the ion-pair formation constant by using Bjerrum's equation[20] (Table 1). These values are plotted in Fig. 4 (solid line) as a function of the ionic radius of alkali metal, where the values, *a*, in a low water concentration MIBK (0.1 mol dm^{-3}), determined by means of conductometry, are also depicted by the broken line for a comparison.[21] The a value of $Li^+\cdot Pic^-$ in water-saturated MIBK is larger than that of any other alkali metal picrates in spite of the smallest crystal ionic radius of the lithium ion. The *a* value of $Li^+\cdot Pic^-$ at a low water concentration is apparently smaller than that in water-saturated MIBK, and is smaller than that of any other alkali metal picrates. These facts suggest that the hydrated lithium ion forms an ion pair with the picrate ion in the high water concentration MIBK, i.e., the water-separated ion pair.

Distribution and Formation of POE Compound—Alkali Metal Ion Complexes. The thermodynamic distribution constant ($K^{\circ}_{\mathrm{dist,SMP}}$) of ion pairs of POE compound-alkali metal ion complexes with the picrate ion are plotted in Fig. 5 as a function of the ionic radius of alkali metal (filled symbols) together with results of the 1,2-DCE system (open symbols).[10] As can be seen from Fig. 5, the thermodynamic distribution constant shows a maximum at the potassium ion, and the extractability decreases in the order of $K^+ > Cs^+ > Na^+ > Li^+$ irrespective of the number of oxyethylene units (EO unit) of POE compounds in both solvents. Although the $\log K^{\circ}_{\mathrm{dist,SMP}}$ of MIBK are larger than those of 1,2-DCE in any system, the difference of $\log K^{\circ}_{\mathrm{dist,SMP}}$ is not so large between two solvents.

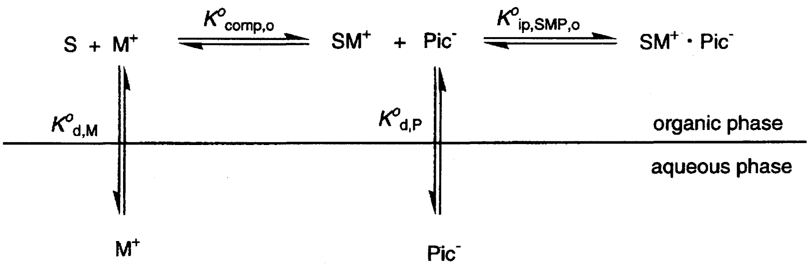
As shown in a previous paper,[11] the distribution equilibrium of an ion pair, $SM^+\cdot Pic^-$, is rationalized by Scheme 2, i.e., the partition of alkali metal ion ($K^{\circ}_{\mathrm{d,M}}$) and picrate ion ($K^{\circ}_{\mathrm{d,P}}$), the formation of SM^+ complex ($K^{\circ}_{\mathrm{comp,o}}$), and the $SM^+\cdot Pic^-$ ion-pair formation ($K^{\circ}_{\mathrm{ip,SMP,o}}$). According to this process, the thermodynamic formation constant of an alkali metal ion complex with a POE compound in MIBK,

$$K^{\circ}_{\mathrm{comp,o}} = \frac{[\mathrm{SM^+}]_o}{[\mathrm{S}]_o[\mathrm{M^+}]_o}, \tag{14}$$

is given by

$$K^{\circ}_{\mathrm{comp,o}} = K^{\circ}_{\mathrm{dist,o}}\cdot K^{\circ\,-1}_{\mathrm{ip,SMP,o}}\cdot K^{\circ\,-1}_{\mathrm{d,M}}\cdot K^{\circ\,-1}_{\mathrm{d,P}}. \tag{15}$$

The values of $K^{\circ}_{\mathrm{comp,o}}$ obtained by Eq. 15 are listed in Table 2, and are plotted in Fig. 6 as a function of the ionic radius of the alkali metal (filled symbols) together with the results in 1,2-DCE[11] (open symbols). The complex formation of a POE compound has been investigated mainly in methanol.[21—23] The formation constants of alkali metal ions with bis(methyl



Scheme 2.

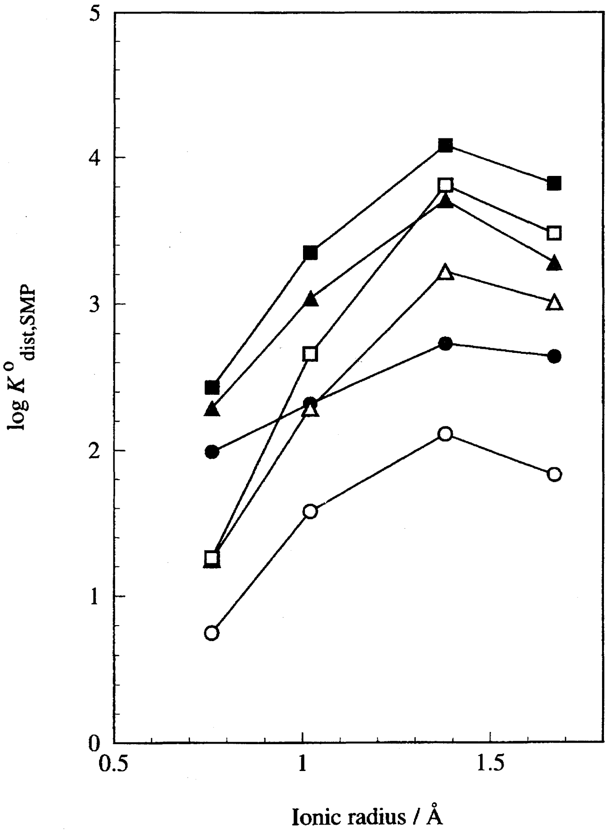


Fig. 5. Plots of $\log K^{\circ}_{\mathrm{dist,SMP}}$ as a function of an ionic radius of alkali metals. Symbols: ●; DEO4, ▲; DEO6, ■; DEO8. Filled and open symbols refer to the MIBK and the 1,2-DCE systems, respectively.

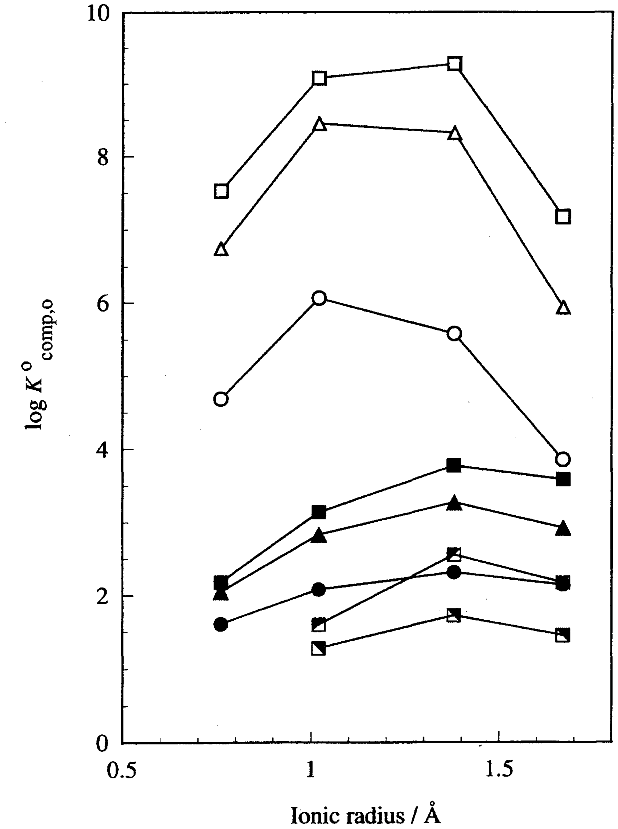


Fig. 6. Plots of $\log K^{\circ}_{\mathrm{comp,o}}$ as a function of an ionic radius of alkali metals. Symbols: ●; DEO4, ▲; DEO6, ■; DEO8, ◪; bis(methyl ether) of tetraethylene glycol, ◩; bis(methyl ether) of hexaethylene glycol. Filled, open, and half-filled symbols refer to the MIBK, the 1,2-DCE and the methanol systems, respectively.

ether) of tetraethylene glycol ($n = 4$) and bis(methyl ether) of hexaethylene glycol ($n = 6$) in methanol[22] are plotted in Fig. 6 for a comparison.

As can be seen from Fig. 6, the values of $K^{\circ}_{\mathrm{comp,o}}$ are much smaller than those in 1,2-DCE, and their difference among the metal ion in MIBK is small. The values of $K^{\circ}_{\mathrm{comp,o}}$ in MIBK is comparable to those in methanol and its order among the metal ions ($\mathrm{Li}^+ < \mathrm{Na}^+ < \mathrm{K}^+ > \mathrm{Cs}^+$) is the same as that in methanol. Although the dielectric constant of MIBK is much smaller than that of methanol ($\varepsilon = 32.6$), the coordinating ability of MIBK is almost the same as that of methanol ($DN = 19.0$).[13] On the other hand, 1,2-DCE is a non-coordinating solvent, whereas the dielectric constant of 1,2-DCE is comparable to that of MIBK. Consequently, the donating ability of the solvent is considered to be the dominant factor to determine the stability of the complexes. The dielectric constant of the solvent might not be so effective for complex formation. H. Honda et al. reported on the solvent effect on the POE compound-M$^+$ complex formation in polar solvents, and concluded that the stability of the complex was mainly governed by DN.[25] Consequently, the nature of the solvent effect of low dielectric constant solvent systems is the same as that of polar solvent systems.

The values of $\log K^{\circ}_{\mathrm{comp,o}}$ increase by increasing the number of EO units of POE compounds in any system. This fact is fundamentally explained by an increase in the number of oxygen atoms binding to the central metal ion.[10,24] The effect of the EO number on $K^{\circ}_{\mathrm{comp,o}}$ in MIBK is much smaller than that in 1,2-DCE. Since the free metal ion is quite unstable in a non-coordinating solvent, the metal ions

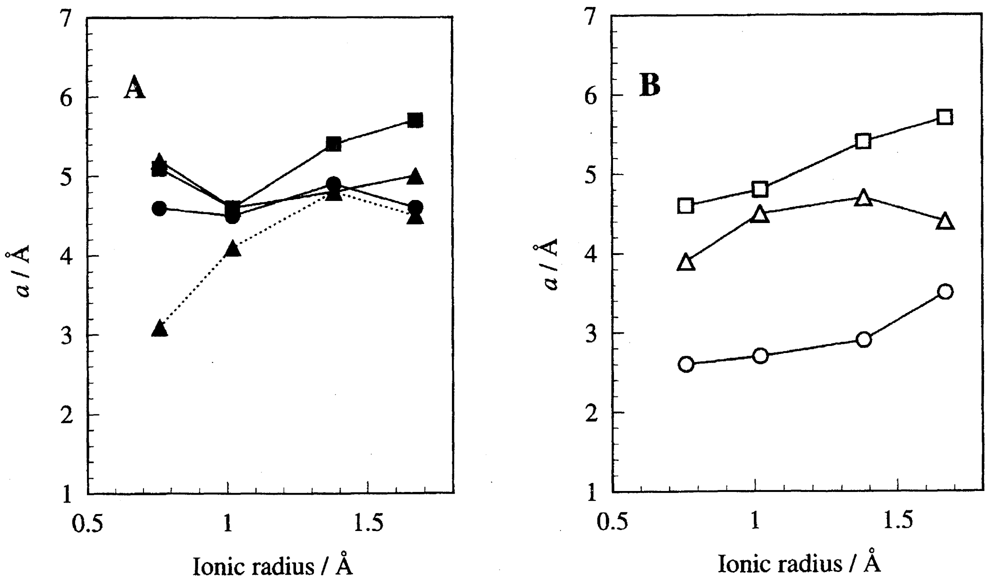


Fig. 7. Plots of the interionic distance, *a*, of the ion pair of the POE compound-M$^+$ complex with picrate ion as a function of an ionic radius of alkali metals in the MIBK system (A) and the 1,2-DCE system (B). The broken line in A refers to the low water MIBK ($c_{\mathrm{H2O}} = 0.1$ mol dm^{-3}) system. Symbols: see Fig. 5.

in 1,2-DCE are strongly stabilized by the coordination of the EO chain. Thus, complex formation in a non-coordinating solvent is distinctively affected by the number of EO units and the kind of metal ion. On the other hand, in a solvating solvent, MIBK, the free metal ions are relatively stable by solvation and hydration; thus, stabilization by the coordination of POE compounds is not so large and the formation constants, $K^{\circ}_{\mathrm{comp,o}}$, do not differ very much by a change in the POE compound and metal ion.

The hydration number of the lithium ion in the POE compound complex in the water-saturated MIBK was determined to be six,[19] i.e., the hydration number of Li$^+$ does not change due to coordination of the POE compound. This result suggests that the hydrated metal ion is surrounded by the EO chain in the complex.[26,27] The ion size of the hydrated lithium ion is larger than the suitable size of the EO chain cavity. Thus, the stability constant of the lithium complex, $K^{\circ}_{\mathrm{comp,o}}$ is smaller than that of the cesium ion in MIBK, whereas that of Li$^+$ is larger than that of Cs$^+$ in 1,2-DCE.

Interionic Distance of the Ion Pair with Picrate Ion. The interionic distance, *a*, of the ion pair of the POE compound-M$^+$ complex with Pic$^-$ was estimated from the ion-pair formation constant in water-saturated MIBK (Table 2). The value of *a* is plotted in Fig. 7A (solid lines) together with the results in a water-saturated 1,2-DCE (Fig. 7B).[10]

The interionic distance of the ion pair in MIBK are almost the same as that of the corresponding ion pair in 1,2-DCE, except for the lithium and DEO4 complexes. These results indicate that those cationic complexes have identical structures in both solvents. The metal ion is surrounded by the EO chain, and the increase in the interionic distance by increasing in EO unit is interpreted by a steric hindrance of the EO chain.[10,26,27]

In the MIBK system, the *a* value of ion pair of lithium ion complex is larger than that of the sodium ion complex for any POE compound. This result corroborates the above discussion, i.e., the lithium ion in the complex is relatively large due to hydration. The dissociation constants of the ion pairs of alkali metal ion complexes of DEO6 with the picrate ion in a low water concentration MIBK ($c_{\mathrm{H2O}} = 0.1$ mol dm^{-3}) were determined by means of conductometry.[21] The interionic distance evaluated from these constants are depicted by the dotted line in Fig. 7A for a comparison. As can be seen from Fig. 7A, the interionic distance of the lithium ion complex in the low water MIBK is distinctively smaller than that of any other ion pairs of DEO6 complexes and that of lithium complex in the water-saturated MIBK. Thus, the structure of the complexes of a small-size metal ion is substantially changed by hydration.

The *a* values of DEO4 complexes in 1,2-DCE are much smaller than those of other POE compounds and close to the interionic distance of the contact ion pair of metal picrates. Because the number of EO units of DEO4 is not sufficient to fully surround the metal ion, the picrate ion can approach the metal ion without the disturbance of the EO chain. The values of *a* of ion pairs of DEO4 complexes in a water-saturated MIBK are relatively large and comparable to those of DEO6 complexes. These results indicate that the picrate ion in the ion pair of DEO4 complexes in water-saturated MIBK is separated by the water and/or solvent molecule coordinating to the metal ion.

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