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Extraction Equilibria between Benzene and Water of Uni- and Bivalent Metal Picrates with Lariat 16-Crown-5: Effect of the Side Arms on the Extraction Ability and Selectivity

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Abstract. The overall extraction constants (K_{ex}) of uni- and bivalent metal picrates with 15-(2,5-dioxahexyl)-15-methyl-16-crown-5 (L16C5) were determined between benzene and water at 25°C. The K_{ex} values were analyzed into the constituent equilibrium constants, i.e., the extraction constant of picric acid, the distribution constant of the crown ether, the stability constant of the metal ion–crown ether complex in water, and the ion-pair extraction constant of the complex cation with the picrate anion. The K_{ex} value decreases in the orders $Ag^+ > Na^+ > Tl^+ > K^+ > Li^+$ and $Pb^{2+} > Ba^{2+} > Sr^{2+}$ for the uni- and bivalent metals, respectively, which are the same as those observed for 16C5. The extraction selectivity was found to be governed by the selectivity of the ion-pair extraction of the L16C5–metal picrate complex rather than by that of the complex formation in water. The extraction ability of L16C5 is smaller for all the metals than that of 16C5, which is mostly attributed to the higher lipophilicity of L16C5. Differences in the extraction selectivity between L16C5 and 16C5 were observed for the bivalent metals but little for the univalent metals. The side-arm effect on the extraction selectivity was interpreted on the basis of the negative correlation between the effect on the complex stability constant in water and that on the ion-pair extraction constant.

Key words: solvent extraction, constituent equilibria, ion-pair extraction constant, lariat 16-crown-5, uni- and bivalent metal picrates, side-arm effect.

1. Introduction

Lariat ethers, which possess cation-ligating side arms, were originally designed to enhance the cation-binding ability of the parent crown ethers [1]. Higher abilities in complexation and extraction of cations have been reported for some of them [2-4]. On the other hand, it has been shown that the complex-stability constants of 15-(2,5-dioxahexyl)-15-methyl-16-crown-5 (L16C5) (Figure 1) with several uni-

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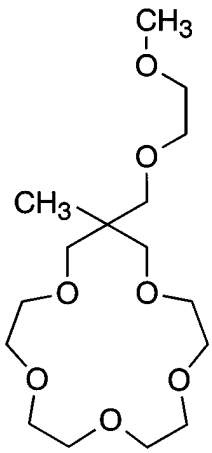

Figure 1. Structure of L16C5.

and bivalent metal ions in water are comparable to the corresponding values of 16-crown-5 (16C5), and that the selectivity is little altered by the side arms [5].

The purpose of this study is to clarify the contribution of the side arms of L16C5 to its extraction ability and selectivity for cations. The overall extraction equilibrium constants of several uni- and bivalent metal picrates with L16C5 between benzene and water are determined, and analyzed into four constituent equilibria. Each of the equilibrium constants is compared with that of 16C5 previously reported [6], and the side-arm effect is discussed in detail.

2. Experimental

2.1. Materials

The preparation of L16C5 has been described elsewhere [4]. Benzene, picric acid, $LiOH{\cdot}H_2O$, NaOH, KOH, $AgNO_3$, $TlNO_3$, $Sr(OH)_2{\cdot}8H_2O$, $Ba(OH)_2{\cdot}8H_2O$, and $Pb(NO_3)_2$ were of analytical grade. The purity of $AgNO_3$ was determined by titration with KCl, and that of $TlNO_3$ and $Pb(NO_3)_2$ with EDTA. The concentrations of metal hydroxides and picric acid in stock solutions were determined by acid–base titrations. Benzene was washed three times with distilled water.

2.2. Extraction of metals

A 10 mL portion of a benzene solution of L16C5 (4.2×10^{-5}–5.3×10^{-2} mol dm^{-3}) and an equal volume of an aqueous solution of picric acid (3.0×10^{-3}–1.0×10^{-2} mol dm^{-3}) and metal hydroxide or nitrate (4.2×10^{-3}–1.7×10^{-1} mol dm^{-3}) were placed in a stoppered glass tube (volume 30 mL). The pH of the aqueous solution was adjusted to 2.5–2.7 for Ag, Tl, and Pb, 5.4–7.0 for Sr, and 6.5–8.1 for Ba with nitric acid to prevent the hydrolysis. The tube was shaken in

a thermostated water bath at 25 ± 0.2°C for 2 h and centrifuged. This shaking time was shown to be sufficient to attain equilibrium. For the extraction of Li, Na, K, Sr, and Ba, the picrate in the benzene phase was completely back-extracted into 2.0×10^{-2} mol dm^{-3} potassium hydroxide solution by 2-h shaking, and the concentration was determined with a UV spectrophotometer ($\lambda_{\text{max}} = 355.5$ nm, $\epsilon = 1.44 \times 10^4$ cm^{-1} dm^3 mol^{-1}). For Ag, Tl, and Pb, the metals in the benzene phase were back-extracted into 0.1 mol dm^{-3} nitric acid solution and the concentrations were determined with an atomic absorption spectophotometer (Seiko SAS-725). Scarcely any metal picrate was extracted into benzene in the absence of L16C5. The pH of the aqueous phase at equilibrium was measured with a glass electrode.

2.3. Distribution of L16C5

A benzene solution (6 mL) of L16C5 (3.4×10^{-3}–1.2×10^{-2} mol dm^{-3}) and an equal volume of distilled water were placed in a glass stoppered tube (No. 0), shaken for 2 h at 25 ± 0.2°C, and centrifuged. A 1 mL portion of the aqueous phase was transferred into another tube (No. 1) where benzene (12 mL) and an aqueous solution (11 mL) containing 0.2–0.5 mol dm^{-3} NaOH and 0.02 mol dm^{-3} picric acid were placed. The benzene and aqueous phases in the No. 1 tube were shaken and centrifuged. A portion $(12 - 2n)$ mL of the aqueous phase in the tube (No. n) and an equal volume of benzene were placed in another tube (No. $n + 1$), shaken and centrifuged; this procedure must be repeated until $n = 3$ to completely extract L16C5 in the aqueous phase of tube No. 1 as a L16C5–sodium picrate 1:1:1 complex. The picrate in the benzene phase in each tube was back-extracted into an equal volume of 0.01 mol dm^{-3} NaOH aqueous solution. The concentration was determined spectrophotometrically. The total amount of the picrate extracted in a series of these extractions was calculated and assumed to be equal to that of L16C5 which was distributed into the 6 mL aqueous phase in tube No. 0. The equilibrium concentration of L16C5 in the benzene phase in tube No. 0 was calculated by subtracting the concentration in the aqueous phase from the initial concentration in the benzene phase. The distribution constant ($K_{\text{D,L}}$) was determined as a ratio of the molarity of L16C5 in the benzene phase to that in the aqueous phase; $K_{\text{D,L}} = 8.58 \pm 0.20$ was obtained as the average of 9 measurements at different initial concentrations of L16C5.

3. Results

The overall extraction equilibrium of a metal cation (M^{m+}) with a crown ether (L) and picric acid (HA) is defined as

$$\text{M}^{m+} + \text{L}_\text{o} + m\text{HA}_\text{o} \rightleftharpoons \text{MLA}_{m,\text{o}} + m\ \text{H}^+, \tag{1}$$

and the corresponding extraction equilibrium constant (K_{ex}) is written as

$$K_{\mathrm{ex}} = \frac{[\mathrm{MLA}_m]_{\mathrm{o}}[\mathrm{H}^+]^m}{[\mathrm{M}^{m+}][\mathrm{L}]_{\mathrm{o}}[\mathrm{HA}]_{\mathrm{o}}^m}, \tag{2}$$

where the subscript 'o' and the lack of a subscript denote the species in the organic and aqueous phases, respectively. The overall extraction constant can be expressed using the distribution constant of the crown ether, the extraction constant of picric acid ($K_{\mathrm{ex,HA}} = [\mathrm{HA}]_{\mathrm{o}}[\mathrm{H}^+]^{-1}[\mathrm{A}^-]^{-1}$), the formation constant of a metal ion–crown ether complex in the aqueous phase ($K_{\mathrm{ML}} = [\mathrm{ML}^{m+}][\mathrm{M}^{m+}]^{-1}[\mathrm{L}]^{-1}$), and the ion-pair extraction constant of the complex cation with the picrate anion ($K_{\mathrm{ex,ip}} = [\mathrm{MLA}_m]_{\mathrm{o}}[\mathrm{ML}^{m+}]^{-1}[\mathrm{A}^-]^{-m}$):

$$K_{\mathrm{ex}} = K_{\mathrm{ML}} K_{\mathrm{ex,ip}} K_{\mathrm{D,L}}^{-1} K_{\mathrm{ex,HA}}^{-m}. \tag{3}$$

Since the concentrations of M^{m+}, ML^{m+} and MA_m in the benzene phase are negligible, the extracted metal species can be regarded as MLA_m alone. Then the distribution ratio of the metal is expressed as

$$D = \frac{[\mathrm{MLA}_m]_{\mathrm{o}}}{[\mathrm{M}^{m+}] + [\mathrm{ML}^{m+}] + [\mathrm{MLA}_m]}. \tag{4}$$

Assuming that $[\mathrm{M}^{m+}] \gg [\mathrm{ML}^{m+}] + [\mathrm{MLA}_m]$, Equation (4) can be transformed into

$$D \fallingdotseq \frac{[\mathrm{MLA}_m]_{\mathrm{o}}}{[\mathrm{M}^{m+}]} = K_{\mathrm{ex}} K_{\mathrm{ex,HA}}^m [\mathrm{L}]_{\mathrm{o}}[\mathrm{A}^-]^m. \tag{5}$$

From the mass balance equations, the concentrations, $[\mathrm{M}^{m+}]$, $[\mathrm{L}]_{\mathrm{o}}$ and $[\mathrm{A}^-]$, are calculated as follows:

$$[\mathrm{M}^{m+}] = [\mathrm{M}]_{\mathrm{t}} - [\mathrm{MLA}_m]_{\mathrm{o}}, \tag{6}$$

$$[\mathrm{L}]_{\mathrm{o}} = ([\mathrm{L}]_{\mathrm{t}} - [\mathrm{MLA}_m]_{\mathrm{o}})/(1 + K_{\mathrm{D,L}}^{-1}), \tag{7}$$

$$[\mathrm{A}^-] = ([\mathrm{HA}]_{\mathrm{t}} - m[\mathrm{MLA}_m]_{\mathrm{o}})/\{1 + (K_{\mathrm{HA}} + K_{\mathrm{ex,HA}})[\mathrm{H}^+]\}, \tag{8}$$

where the subscript 't' denotes the total concentration and $K_{\mathrm{HA}} = [\mathrm{HA}] \times [\mathrm{H}^+]^{-1}[\mathrm{A}^-]^{-1}$. The values of $K_{\mathrm{ex,HA}}$, and K_{HA} at 25°C are 247 [7] and 1.9_5 [8], respectively.

Plots of $\log(D/[\mathrm{A}^-])$ vs. $\log [\mathrm{L}]_{\mathrm{o}}$ for the univalent ions and those of $\log(D/[\mathrm{A}^-]^2)$ vs. $\log[\mathrm{L}]_{\mathrm{o}}$ for the bivalent ions are shown in Figure 2. Each plot gives a straight line with a slope of unity, as expected from Equation (5), proving that the metals are extracted as MLA_m complexes.

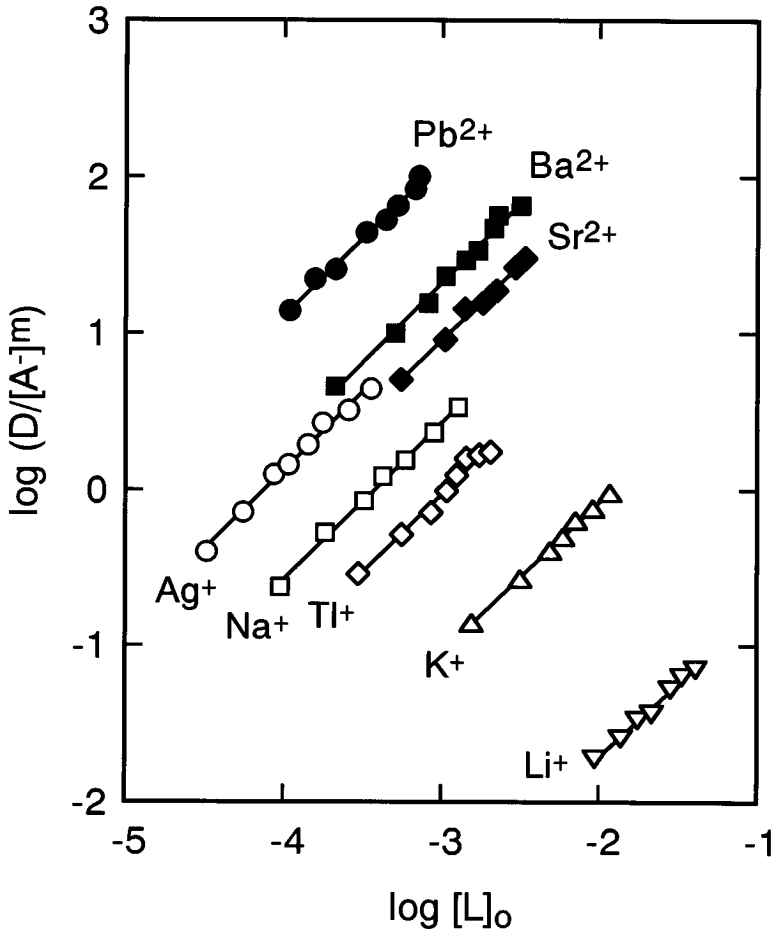

Figure 2. Plots of $\log(D/[\mathrm{A}^-]^m)$ vs. $\log\,[\mathrm{L}]_\mathrm{o}$ for solvent extraction of uni- ($m = 1$) and bivalent ($m = 2$) metal picrates with L16C5. The open symbols denote the univalent metals, and the filled ones the bivalent metals.

For all the systems except for Li^+, in order to determine the K_ex value from Equation (2) as accurately as possible, the concentrations $[\mathrm{L}]_\mathrm{o}$ and $[\mathrm{M}^{m+}]$ were evaluated by solving the following simultaneous equations in which the formation of ML^{m+} in the aqueous phase is considered:

$$[\mathrm{L}]_\mathrm{o} = ([\mathrm{L}]_\mathrm{t} - [\mathrm{MLA}_m]_\mathrm{o})/(1 + K_\mathrm{D,L}^{-1} + K_\mathrm{ML}K_\mathrm{D,L}^{-1}\mathrm{M}^{m+}]), \tag{9}$$

$$[\mathrm{M}^{m+}] = ([\mathrm{M}]_\mathrm{t} - [\mathrm{MLA}_m]_\mathrm{o})/(1 + K_\mathrm{ML}K_\mathrm{D,L}^{-1}[\mathrm{L}]_\mathrm{o}). \tag{10}$$

Table I. Summary of the equilibrium constants in the extraction of metal picrates with L16C5 between benzene and water at 25 °C.

Cation	log K_{ex}	(Δ log K_{ex})*	log K_{ML}†	(Δ log K_{ML})*	log $K_{ex,ip}$	(Δ 1og $K_{ex,ip}$)*
Li^+	-2.13 ± 0.02	(−0.39)				
Na^+	1.00 ± 0.01	(−0.47)	0.65	(−0.13)	3.68	(1.00)
K^+	-0.48 ± 0.01	(−0.52)	0.3	(−0.1)	2.5	(0.9)
Ag^+	1.72 ± 0.01	(−0.52)	1.12	(0.02)	3.93	(0.80)
Tl^+	0.53 ± 0.02	(−0.43)	0.56	(−0.17)	3.30	(1.08)
Sr^{2+}	-0.85 ± 0.02	(−0.85)	2.18	(0.10)	2.69	(0.39)
Ba^{2+}	-0.50 ± 0.01	(−0.57)	1.84	(0.00)	3.38	(0.77)
Pb^{2+}	0.30 ± 0.04	(−0.86)	1.27	(0.53)	4.75	(−0.06)

*Deviation from the value of 16C5 [6]: $\Delta \log K_{ex} = \log\{K_{ex}(\text{L16C5})/K_{ex}(\text{16C5})\}$; $\Delta \log K_{ML} = \log\{K_{ML}(\text{L16C5})/K_{ML}(\text{16C5})\}$; $\Delta \log K_{ex,ip} = \log\{K_{ex,ip}(\text{L16C5})/K_{ex,ip}(\text{16C5})\}$.
†Cited from the literature [5].

The K_{ML} values used are shown in Table I. For the Li^+ system, where the K_{ML} value was not available, the values of $[M^{m+}]$ and $[L]_o$ were calculated from Equations (6) and (7), respectively. The $[HA]_o$ value was calculated as

$$[\text{HA}]_\text{o} = ([\text{HA}]_\text{t} - m[\text{MLA}_m]_\text{o})/\{1 + ([\text{H}^+]^{-1} + K_\text{HA})K_{\text{ex,HA}}^{-1}\}. \tag{11}$$

The K_{ex} and $K_{ex,ip}$ values obtained are summarized in Table I.

4. Discussion

4.1. Extraction selectivity of L16C5

In Figure 3, the log K_{ex}, log $K_{ex,ip}$, and log K_{ML} values are plotted against the crystal ionic radii [9] of the metals. The K_{ex} value decreases in the order $Ag^+ > Na^+ > Tl^+ > K^+ > Li^+$ for the univalent metals and $Pb^{2+} > Ba^{2+} > Sr^{2+}$ for the bivalent metals, which are the same as those observed for 16C5. Assuming that the cavity size of L16C5 is comparable to that of 16C5 (cavity radius = 0.9 È [10]), the size-fit concept, i.e., the metal which is more closely fitted into the crown cavity is more extractable, can successfully explain the K_{ex} order for the alkali metals, $Na^+ > K^+ > Li^+$, but not the order $Ag^+ > Na^+$, $Tl^+ > K^+$, $Pb^{2+} > Sr^{2+}$, and $Ba^{2+} > Sr^{2+}$.

According to Equation (3), the extraction selectivity expressed as a difference in log K_{ex} between two metals is determined by the differences in log K_{ML} and in log $K_{ex,ip}$. The K_{ML} value decreases in the orders $Ag^+ > Na^+ > Tl^+ > K^+$ and $Sr^{2+} > Ba^{2+} > Pb^{2+}$. The sequence of K_{ML} for the univalent metals is consistent with that of K_{ex} but opposite for the bivalent metals. The $K_{ex,ip}$ value decreases as $Ag^+ > Na^+ > Tl^+ > K^+$ for the univalent metals and $Pb^{2+} > Ba^{2+} > Sr^{2+}$ for the bivalent metals. The sequences of $K_{ex,ip}$ for the univalent and bivalent metals are both consistent with those of K_{ex}. Therefore, the K_{ex} order for the bivalent metals is

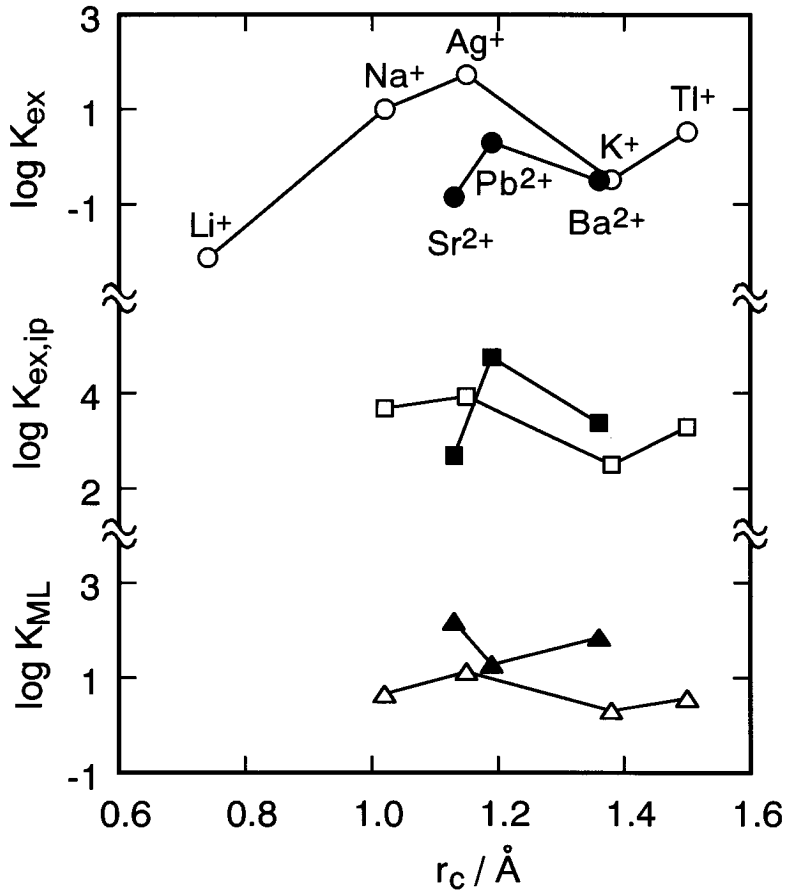

Figure 3. Plots of log K_{ex}, log $K_{ex,ip}$, and log K_{ML} vs. crystal ionic radius. ○ ●: K_{ex}; □ ■: $K_{ex,ip}$; △ ▲: K_{ML}. The open symbols denote the univalent metals, and the filled ones the bivalent metals.

governed by the $K_{ex,ip}$ order alone. Although the K_{ex} order for the univalent metals depends on both the K_{ML} and $K_{ex,ip}$ orders, the difference in log K_{ex} between the metals, except for the case of Ag^+/Na^+, is more dependent on the difference in log $K_{ex,ip}$ than that in log K_{ML}. In conclusion, the extraction selectivity for the uni- and bivalent metals is governed by the selectivity of the ion-pair extraction of the L16C5–metal picrate complex rather than by that of the complex formation in water.

4.2. Comparison of L16C5 with 16C5

The differences in log K_{ex} for a given metal between L16C5 and 16C5, $\log\{K_{ex}(\text{L16C5})/K_{ex}(\text{16C5})\}$, are shown in Table I. The values decrease in the order $Li^+ > Tl^+ > Na^+ \geqslant Ag^+ = K^+ > Ba^{2+} > Sr^{2+} \sim Pb^{2+}$; they are all negative,

and comparable (-0.39 to -0.57) except for Sr^{2+} (-0.85) and Pb^{2+} (-0.86), indicating that the extraction ability of L16C5 is lower for all the metals than that of 16C5 and that the selectivity of L16C5 for the univalent metals is similar to that of 16C5. Since the side arm's effect on the extractability is more pronounced for Sr^{2+} and Pb^{2+} as compared to that observed for Ba^{2+}, the extraction selectivity of L16C5 becomes higher for Ba^{2+}/Sr^{2+} but lower for Pb^{2+}/Ba^{2+} than that of 16C5.

The difference in log K_{ex} between two crown ethers, L1 and L2, can be expressed by the following relationship derived from Equation (3):

$$\log \frac{K_{ex}(L1)}{K_{ex}(L2)} = \log \frac{K_{ML}(L1)}{K_{ML}(L2)} + \log \frac{K_{ex,ip}(L1)}{K_{ex,ip}(L2)} - \log \frac{K_{D,L}(L1)}{K_{D,L}(L2)}. \tag{12}$$

Irrespective of the metal considered, Table I shows that the $\log\{K_{D,L}(L16C5)/K_{D,L}(16C5)\}$ value (1.33) is always greater than the $\log\{K_{ML}(L16C5)/K_{ML}(16C5)\}$ + $\log\{K_{ex,ip}(L16C5)/K_{ex,ip}(16C5)\}$ value. It can be concluded from this that the systematic diminution of the K_{ex} value of L16C5, as compared to those displayed by 16C5, is completely attributed to the much higher lipophilicity of L16C5 due to the side arms.

The $\log\{K_{ML}(L16C5)/K_{ML}(16C5)\}$ value, which shows the effect of the side arms on the stability of the complexes ML^{m+}, is negative for Na^+, K^+, and Tl^+, nearly zero for Ag^+ and Ba^{2+}, and positive for Sr^{2+} and Pb^{2+}; the value decreases in the order $Pb^{2+} > Sr^{2+} > Ag^+ \sim Ba^{2+} > K^+ \geqslant Na^+ > Tl^+$. The $\log\{K_{ML}(L16C5)/K_{ML}(16C5)\}$ values are very small (-0.17 to 0.10), except for Pb^{2+} (0.53). Detailed discussions on the K_{ML} values of L16C5 and 16C5 have been presented in our previous paper [5]. The side-arm effect on log $K_{ex,ip}$, expressed by $\log\{K_{ex,ip}(L16C5)/K_{ex,ip}(16C5)\}$, is always positive except for the case of Pb^{2+}; the value decreases in the order $Tl^+ > Na^+ > K^+ > Ag^+ \geqslant Ba^{2+} > Sr^{2+} > Pb^{2+}$. The order of $\log\{K_{ex,ip}(L16C5)/K_{ex,ip}(16C5)\}$ for the metals is almost the reverse of that of $\log\{K_{ML}(L16C5)/K_{ML}(16C5)\}$, but identical with that of $\log\{K_{ex}(L16C5)/K_{ex}(16C5)\}$. Therefore, as can be seen from Equation (12), the order of $\log\{K_{ex}(L16C5)/K_{ex}(16C5)\}$ is governed by that in $\log\{K_{ex,ip}(L16C5)/K_{ex,ip}(16C5)\}$.

The $K_{ex,ip}$ value is expressed as a product of the ion-pair formation constant in the aqueous phase ($K_{MLA} = [MLA_m][ML^{m+}]^{-1}[A^-]^{-m}$) and the distribution constant of the extractable complex ($K_{D,MLA} = [MLA_m]_o[MLA_m]^{-1}$). Then the difference in log $K_{ex,ip}$ between two crown ethers, L1 and L2, can be expressed as follows:

$$\log \frac{K_{ex,ip}(L1)}{K_{ex,ip}(L2)} = \log \frac{K_{MLA}(L1)}{K_{MLA}(L2)} + \log \frac{K_{D,MLA}(L1)}{K_{D,MLA}(L2)}. \tag{13}$$

Although the $\log\{K_{D,MLA}(Ll6C5)/K_{D,MLA}(16C5)\}$ values are unknown, they are expected to be positive from the large positive $\log\{K_{D,L}(Ll6C5)/K_{D,L}(16C5)\}$ value. The previous studies [5, 6] on the transfer activity coefficients (${}^{S}\gamma^{W}$) of

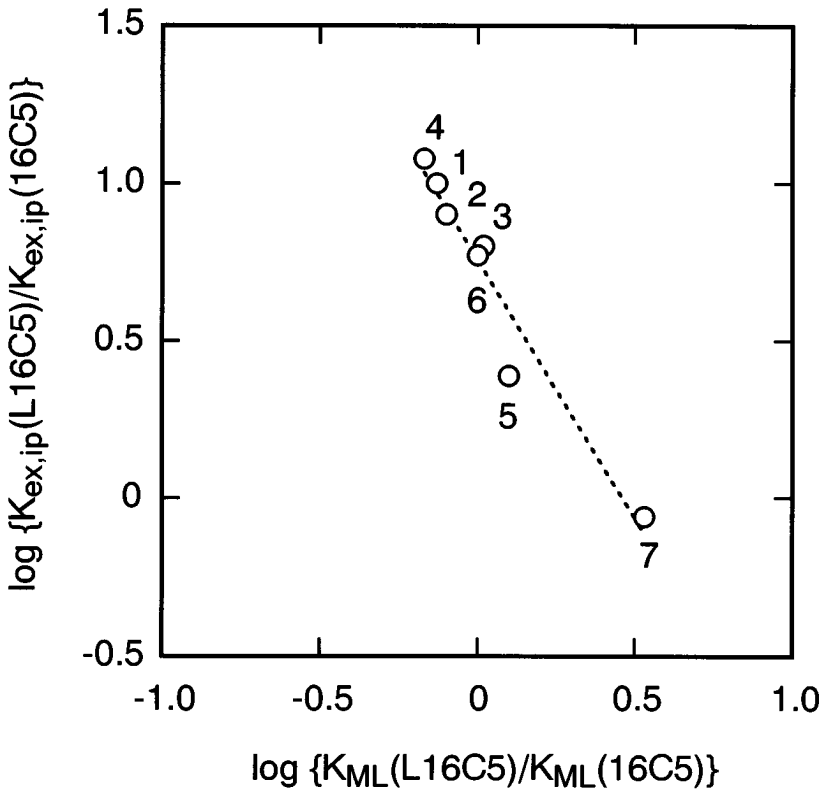

Figure 4. Correlation between the side-arm effects on K_{ML} and $K_{ex,ip}$. Cations: (1) Na^+; (2) K^+; (3) Ag^+;(4) Tl^+; (5) Sr^{2+}; (6) Ba^{2+}; (7) Pb^{2+}.

the alkali metal complexes with L16C5 and 16C5 between water (W) and polar organic solvents (S) indicated that the ${}^{S}\gamma^{W}$(L16C5)/ ${}^{S}\gamma^{W}$(16C5) ratios for the K^+ complexes are nearly equal to those for the Na^+ complexes. This result suggests that the $K_{D,MLA}$(Ll6C5)/$K_{D,MLA}$(16C5) ratios are also comparable regardless of the central metals. It follows from this that the differences in $K_{ex,ip}$ among the metals are largely dependent on those in K_{MLA}. If the dioxahexyl arm of L16C5 ligates to the central metal, the arm may sterically hinder the approach of a picrate anion to the central metal and weaken the electrostatic interaction between the metal and the picrate ion. In Figure 4, the value of log$\{K_{ex,ip}$(L16C5)/$K_{ex,ip}$(16C5)$\}$ is plotted against that of log$\{K_{ML}$(L16C5)/K_{ML}(16C5)$\}$. A good negative correlation is observed. The differences in log$\{K_{ML}$(L16C5)/K_{ML}(16C5)$\}$ among the metal ions would reflect those in the interaction of the dioxahexyl arm of L16C5 with the central metal. Therefore, the negative correlation suggests that the interaction of the central metal with the side arm decreases the stability of the ion-pair significantly. It appears from Figure 4 that, corresponding to the trend in K_{ML}, the side-arm effect

decreasing K_{MLA} is larger for the bivalent metals than for the univalent metals and largest for Pb^{2+}.

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