クラウンエーテルによる重金属イオンの錯生成と溶媒抽出における特異的選択性の解明

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研究組織

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研究成果

　クラウンエーテルなどの大環状化合物は，金属イオンに対して優れた選択能を有することから，分析化学の分野において，錯生成剤や溶媒抽出剤として利用されている。大環状化合物を金属イオンの分離・分析に効率的に利用するためには，均一溶媒系あるいは液液二相系におけるそのイオン選択機構を解明することが非常に重要である。しかし，その解明に役立つ定量的な情報が未だ不充分であり，特に重金属イオンに対する選択性はほとんど研究されていない。そこで本研究では，重金属イオンを含む種々の金属イオンに対するクラウンエーテルの錯化特性および溶媒抽出特性を定量的かつ詳細に解析した。以下にその概要を述べる。

1．クラウンエーテルと重金属イオンの錯生成平衡と溶媒抽出平衡の解析

　ベンゾ-18-クラウン-6 (B18C6) と Zn^{2+} および Cd^{2+} との水中における錯生成定数を電気伝導度法により測定した。さらに，B18C6 とピクラートイオンによる Zn^{2+}, Cd^{2+} の水からベンゼンへの全抽出定数を測定した。これらの平衡定数により，B18C6 の Zn^{2+}, Cd^{2+} に対する錯生成と溶媒抽出における選択性を初めて定量的に明らかにし，従来のサイズ適合説からの予測と異なることを見い出した。さらに，全抽出平衡をその素平衡に分解することにより，抽出選択機構を平衡論的見地から解明した。

2．クラウンエーテル－金属塩抽出系における対イオン効果の解明

　18-クラウン-6－Na^+ 錯イオン (18C6-Na^+) と数種のニトロフェノラートイオンとの水中におけるイオン対生成定数を，Na^+ 選択性電極を用いた電位差法により測定した。さらに，これらのニトロフェノラートイオンによる 18C6-Na^+ の水からベンゼンへのイオン対抽出定数を測定した。イオン対抽出性に及ぼす対イオン（陰イオン）効果を，抽出の素平衡定数（イオン対の水中での生成定数とベンゼン－水間分配定数）に基づいて，初めて定量的に説明した。

３．16-クラウン-5誘導体と種々の金属イオンの水中での錯生成平衡の解析

　分析化学的に注目されている 16-クラウン-5（16C5）と，その誘導体 ［15,15-ジメチル-16-クラウン-5（DM16C5）および 15-(2,5-ジオキサヘキシル)-15-メチル-16-クラウン-5（L16C5）］について，Li^+, Na^+, K^+, Ag^+, Tl^+, Sr^{2+}, Ba^{2+}, Pb^{2+} との水中における錯生成定数を電気伝導度法により測定した。さらに，Li^+, Na^+, K^+ 錯体については，水―非水溶媒間移行活量係数を求めた。これにより，16-クラウン-5 骨格に付加されたメチル基および配位性側鎖（ポリエーテル基）が，水中における錯体の安定性と溶媒和に及ぼす効果を定量的に評価した。

４．16-クラウン-5誘導体―金属ピクリン酸塩抽出系の平衡解析

　DM16C5 とピクラートイオンによる Na^+, K^+, Ag^+, Sr^{2+}, Ba^{2+}, Pb^{2+} の水からベンゼンへの全抽出定数を測定した。これにより，DM16C5 が，先に研究された 16C5 や L16C5 に比べて，抽出能は劣っているものの，抽出選択能においては優れていることを見い出した。さらに，全抽出平衡をその素平衡に分解することにより，16-クラウン-5 骨格に付加されたメチル基および配位性側鎖（ポリエーテル基）が，抽出能・抽出選択能に及ぼす効果を定量的に解明した。

　上記の研究成果は次頁以降に示すように，学術雑誌ならびに学術研究集会における発表や講演にて公表した。

Extraction equilibria between benzene and water of uni- and bivalent metal picrates with 15,15-dimethyl-16-crown-5

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Abstract

The overall extraction constants (K_{ex}) of Na^+, K^+, Ag^+, Sr^{2+}, Ba^{2+}, and Pb^{2+} as picrate salts with 15,15-dimethyl-16-crown-5 (DM16C5) have been determined between benzene and water at 25 °C. The K_{ex} values have been analyzed into the constituent equilibrium constants such as the distribution constant of the crown ether, the formation 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 substituent effects are discussed by comparing the equilibrium constants of DM16C5 with those of 16-crown-5 (16C5) and 15-(2,5-dioxahexyl)-15-methyl-16-crown-5 (L16C5). The K_{ex} value for each metal ion is lower for DM16C5 than for 16C5 and L16C5; this is attributed to the higher lipophilicity and the lower complexing ability in water of DM16C5. The K_{ex} value of DM16C5 decreases in the orders $Ag^+ > Na^+ > K^+$ and $Pb^{2+} > Ba^{2+} > Sr^{2+}$ for the uni- and bivalent metal ions, respectively; the extraction selectivity is governed by the selectivity of the ion-pair extraction rather than by that of the complex-ion formation in water. The K_{ex} orders of DM16C5 are the same as those observed for 16C5 and L16C5, but DM16C5 generally shows the highest extraction selectivity for these metal ions.

Keywords: Solvent extraction; Equilibrium constants; Extraction selectivity; Metal picrates; 16-Crown-5 derivatives; Substituent effects

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1. Introduction

A number of 16-crown-5 derivatives possessing a variety of substituents have been synthesized, and their cation-binding abilities have been evaluated by solvent extraction [1–3]. We previously made a quantitative study of the extraction equilibria between benzene and water of several uni- and bivalent metal picrates with 16-crown-5 (16C5, Fig. 1) [4] and a 16C5 lariat, 15-(2,5-dioxahexyl)-15-methyl-16-crown-5 (L16C5, Fig. 1) [5], with a view to understanding the substituent effects from the standpoint of equilibrium. Despite the introduction of a cation-binding side arm, a decrease in the overall extraction constant from 16C5 to L16C5 was observed for any of the metal picrates; this was mostly explained in terms of the higher lipophilicity of L16C5 compared with 16C5. For further elucidation of this lariat effect, it is needed to evaluate the effect of the methyl group at the 15-position.

The present work deals with the extraction equilibria between benzene and water of the uni- and bivalent metal picrates with 15,15-dimethyl-16-crown-5 (DM16C5, Fig. 1). The overall extraction constants have been determined and analyzed into the constituent equilibrium constants. Each of the equilibrium constants is compared with that of 16C5 or L16C5, and the substituent effects are discussed.

Fig. 1

2. Experimental

2.1. Materials

DM16C5 was prepared by the method reported previously [1]. Analytical-grade benzene was washed three times with deionized water. Analytical-grade picric acid, NaOH, KOH, $AgNO_3$,

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Sr(NO$_3$)$_2$, Ba(OH)$_2$·8H$_2$O, and Pb(NO$_3$)$_2$ were used without further purification; the concentrations of the metal hydroxides and picric acid in stock solutions were determined by acid-base titrations. Water was distilled and further purified with a Milli-Q Labo system (Millipore).

2.2. Extraction of metal picrates with DM16C5

Equal volumes (12 cm^3 each) of a benzene solution of $9.7 \times 10^{-5} - 6.1 \times 10^{-2}$ mol dm^{-3} DM16C5 and an aqueous solution containing $(3.2 - 8.0) \times 10^{-3}$ mol dm^{-3} picric acid and $3.9 \times 10^{-3} - 5.6 \times 10^{-2}$ mol dm^{-3} metal hydroxide or nitrate were placed in a stoppered glass tube, shaken for 2 h at 25 ± 0.2 °C, and centrifuged. The shaking period was confirmed to be sufficient to attain equilibrium. The equilibrium pH of the aqueous phase measured with a glass electrode was more than 12 for Na$^+$ and K$^+$, 8.3 — 9.3 for Ba^{2+} (adjusted with nitric acid), and 2.4 — 2.6 for Ag$^+$, Sr^{2+}, and Pb^{2+}. For the extraction of Na$^+$, K$^+$, and Ba^{2+}, a portion (5 cm^3) of the benzene phase was transferred into a beaker and evaporated to dryness; the residue was dissolved in a 0.01 mol dm^{-3} NaOH aqueous solution (5 cm^3); the picrate concentration was determined with a UV-spectrophotometer (λ_{max} = 356 nm, ε = 1.45×10^4 dm^3 mol^{-1} cm^{-1}). For Ag$^+$, Sr^{2+}, and Pb^{2+}, the metals in the benzene phase were back-extracted into a 0.1 mol dm^{-3} nitric acid aqueous solution; the metal concentrations were determined with an atomic absorption spectrophotometer (Hitachi Z-6100). Scarcely any metal picrate was extracted into benzene in the absence of DM16C5.

2.3. Distribution constant of DM16C5

Equal volumes (12 cm^3 each) of benzene and an aqueous solution of $1.4 \times (10^{-4} - 10^{-3})$ mol dm^{-3} DM16C5 in a stoppered glass tube were shaken for 2 h at 25 ± 0.2 °C and centrifuged. The

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concentration of DM16C5 in the aqueous phase was determined by the following method: a portion (10 cm³) of the aqueous phase was transferred into another tube where dichloromethane (DCM) and an aqueous solution saturated with sodium picrate (10 cm³ each) were placed, and the tube was shaken to completely extract DM16C5 as a DM16C5–sodium picrate 1:1:1 complex into DCM; a portion (4 cm³) of the DCM phase was transferred into a beaker and evaporated to dryness; the residue was dissolved in a 0.01 mol dm⁻³ NaOH aqueous solution (4 cm³), and the picrate concentration was determined spectrophotometrically. The concentration of DM16C5 in the benzene phase was calculated by subtracting the concentration in the aqueous phase from the initial concentration. The distribution constant obtained as the average of 14 measurements is shown in Table 1.
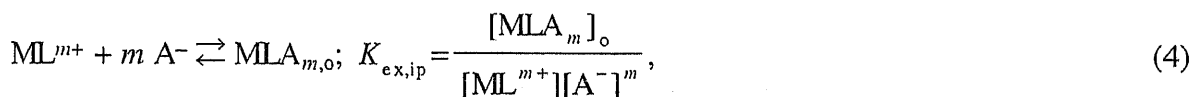
3. Results

When a neutral 1:1:m complex of a metal ion (M^{m+}), a crown ether (L), and a picrate ion (A^-) is extracted into benzene, the overall extraction equilibrium can be defined as

$$M^{m+} + L_o + m\ HA_o \rightleftarrows MLA_{m,o} + m\ H^+;$$
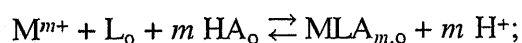
$$K_{ex} = \frac{[MLA_m]_o [H^+]^m}{[M^{m+}][L]_o [HA]_o^{\ m}},$$

(1)

where K_{ex} is the overall extraction constant; the subscript 'o' and the lack of the subscript denote the species in the organic and aqueous phases, respectively. In this study, we considered that the overall extraction equilibrium consists of the following equilibria:

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$$L \rightleftarrows L_o; \quad K_{D,L} = \frac{[L]_o}{[L]}, \tag{2}$$

$$M^{m+} + L \rightleftarrows ML^{m+}; \quad K_{ML} = \frac{[ML^{m+}]}{[M^{m+}][L]}, \tag{3}$$

$$ML^{m+} + m\, A^- \rightleftarrows MLA_{m,o}; \quad K_{ex,ip} = \frac{[MLA_m]_o}{[ML^{m+}][A^-]^m}, \tag{4}$$

$$H^+ + A^- \rightleftarrows HA; \quad K_{HA} = \frac{[HA]}{[H^+][A^-]}, \tag{5}$$

$$HA \rightleftarrows HA_o; \quad K_{D,HA} = \frac{[HA]_o}{[HA]}, \tag{6}$$

where $K_{D,L}$, K_{ML}, $K_{ex,ip}$, K_{HA}, and $K_{D,HA}$ are the distribution constant of the crown ether, the formation constant of a metal ion–crown ether 1:1 complex in water, the ion-pair extraction constant of the complex cation with the picrate anion, the association constant of picric acid in water, and the distribution constant of picric acid, respectively. Thus, K_{ex} can be expressed as

$$K_{ex} = \frac{K_{ML} K_{ex,ip}}{K_{D,L}(K_{HA} K_{D,HA})^m}. \tag{7}$$

Because of the low dielectric constant of benzene, the dissociation of MLA_m and HA in the organic phase is negligible. Neglecting the association of M^{m+} and ML^{m+} with A^- in the aqueous phase, the following equations are derived from the mass balance equations:

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$$[M^{m+}] = ([M]_t - [MLA_m]_o)/(1 + K_{ML}K_{D,L}^{-1}[L]_o), \tag{8}$$

$$[L]_o = ([L]_t - [MLA_m]_o)/(1 + K_{D,L}^{-1} + K_{ML}K_{D,L}^{-1}[M^{m+}]), \tag{9}$$

$$[A^-] = ([HA]_t - m[MLA_m]_o)/\{1 + (K_{HA}K_{D,HA} + K_{HA})[H^+]\}, \tag{10}$$

where the subscript 't' denotes the total concentration. The K_{ML} values of the DM16C5 complexes determined by conductometry at 25 °C [6] are shown in Table 1. The values of K_{HA} and $K_{HA}K_{D,HA}$ at 25 °C are 1.9_5 [7] and 247 [8], respectively. The concentrations, $[M^{m+}]$, $[L]_o$, and $[A^-]$, were calculated from Eqs. (8)—(10) and employed to obtain the K_{ex} values from the equation $K_{ex} = [MLA_m]_o/[M^{m+}][L]_o[A^-]^m (K_{HA}K_{D,HA})^m$. The $K_{ex,ip}$ value was calculated from Eq. (7) by using the other known constants. The equilibrium constants obtained for DM16C5 are summarized in Table 1, together with those for 16C5 [4, 9] and L16C5 [5, 10].

The distribution ratio (D_M) of the metal is expressed as

$$D_M = \frac{[MLA_m]_o}{[M^{m+}] + [ML^{m+}]}$$

$$= \frac{K_{ex}(K_{HA}K_{D,HA})^m [L]_o [A^-]^m}{1 + K_{D,L}^{-1}K_{ML}[L]_o}. \tag{11}$$

Equation (11) can be transformed into

$$\log\{D_M(1 + K_{D,L}^{-1}K_{ML}[L]_o)/[A^-]^m\} = \log K_{ex}(K_{HA}K_{D,HA})^m + \log [L]_o. \tag{12}$$

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Plots of $\log\{D_M(1 + K_{D,L}^{-1}K_{ML}[L]_o)/[A^-]^m\}$ vs. $\log [L]_o$ are shown in Fig. 2. Each plot gives a straight line (correlation coefficient: 0.997—1.000) with a slope of unity (1.00—1.02), as expected from Eq. (12); this verifies the validity of the analysis.

Fig. 2

Table 1

4. Discussion

The K_{ex} value of DM16C5 decreases in the orders $Ag^+ > Na^+ > K^+$ for the univalent metal ions and $Pb^{2+} > Ba^{2+} > Sr^{2+}$ for the bivalent ones, which are the same as those observed for 16C5 and L16C5; thus the extraction-selectivity orders are not altered by the substituents. The following sequences are observed for the K_{ML} and $K_{ex,ip}$ values of DM16C5: $Ag^+ > Na^+ > K^+$ and $Sr^{2+} \geq Ba^{2+} > Pb^{2+}$ for K_{ML}; $Ag^+ > Na^+ > K^+$ and $Pb^{2+} > Ba^{2+} > Sr^{2+}$ for $K_{ex,ip}$. The K_{ex}, K_{ML}, and $K_{ex,ip}$ sequences for the univalent metal ions are identical; however, the difference in $\log K_{ex}$ between the metal ions is generally more dependent on the difference in $\log K_{ex,ip}$ than that in $\log K_{ML}$. For the bivalent metal ions, the sequence of K_{ex} is the same as that of $K_{ex,ip}$ but the reverse of that of K_{ML}. The above results indicate that the extraction selectivity of DM16C5 for the uni- and bivalent metal ions is governed by the selectivity of the ion-pair extraction of the metal ion–DM16C5 complex with the picrate ion rather than by that of the complex-ion formation in water. The same is true for 16C5 [4] and L16C5 [5].

The $\log\{K_{ex}(DM16C5)/K_{ex}(16C5)\}$ and $\log\{K_{ex}(L16C5)/K_{ex}(DM16C5)\}$ values for each metal ion are shown in Table 2. The K_{ex} value is always decreased from 16C5 to DM16C5 ($\log\{K_{ex}(DM16C5)/K_{ex}(16C5)\} < 0$) and unchanged or increased from DM16C5 to L16C5 ($\log\{K_{ex}(L16C5)/K_{ex}(DM16C5)\} \geq 0$). The absolute values of both $\log\{K_{ex}(DM16C5)/K_{ex}(16C5)\}$ and $\log\{K_{ex}(L16C5)/K_{ex}(DM16C5)\}$ decrease in the orders $K^+ > Na^+ \approx Ag^+$ and $Sr^{2+} > Ba^{2+} > Pb^{2+}$.

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This indicates that the negative effect of the methyl groups of DM16C5 and the positive one of the ether side arm ($CH_3OCH_2CH_2O-$) of L16C5 on log K_{ex} are generally greater for the metal ion which is less extractable. Consequently, for any couple of the uni- or bivalent metal ions, $M_1{}^{m+}$ and $M_2{}^{m+}$, the absolute value of log $\{K_{ex}(M_1{}^{m+})/K_{ex}(M_2{}^{m+})\}$ is larger for DM16C5 than for 16C5 and L16C5, except for the case of Ag^+/Na^+. It can be concluded that, among the three crown ethers, DM16C5 has the lowest extraction ability but the highest extraction selectivity for these metal ions. This trend is more pronounced for the bivalent metal ions than for the univalent ones.

For a given metal ion, the difference in log K_{ex} between two crown ethers, L_1 and L_2, is expressed as follows:

$$\log\frac{K_{ex}(L_1)}{K_{ex}(L_2)} = \log\frac{K_{ML}(L_1)}{K_{ML}(L_2)} + \log\frac{K_{ex,ip}(L_1)}{K_{ex,ip}(L_2)} - \log\frac{K_{D,L}(L_1)}{K_{D,L}(L_2)}. \tag{13}$$

The values of log$\{K_X(DM16C5)/K_X(16C5)\}$ and log$\{K_X(L16C5)/K_X(DM16C5)\}$ ($K_X = K_{ML}$, $K_{ex,ip}$, and $K_{D,L}$) are listed in Table 2. Irrespective of the metal ion, the two methyl groups of DM16C5 decrease K_{ML} (log$\{K_{ML}(DM16C5)/K_{ML}(16C5)\} < 0$) and increase $K_{ex,ip}$ (log$\{K_{ex,ip}(DM16C5)/K_{ex,ip}(16C5)\} > 0$). The $K_{D,L}$ value is larger for DM16C5 than for 16C5, being due to the higher lipophilicity of the methyl group than the hydrogen atom. It can therefore be seen from Eq. (13) that the reduced extractability of all the metal ions from 16C5 to DM16C5 results from the reduced stability of the metal ion–crown ether complex in water and the enhanced lipophilicity of the free crown ether; the contribution of the latter is always greater than that of the former. In contrast to the methyl groups, the ether side arm of L16C5 generally increases K_{ML} (log$\{K_{ML}(L16C5)/K_{ML}(DM16C5)\} \geq 0$) and decreases $K_{ex,ip}$ (log$\{K_{ex,ip}(L16C5)/K_{ex,ip}(DM16C5)\} \leq 0$). The $K_{D,L}$ value is smaller for L16C5 than for DM16C5, which is due to hydrogen bonding of

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water to the oxygen atoms in the side arm. The enhanced extractability of K^+, Sr^{2+} and Ba^{2+} from DM16C5 to L16C5 is ascribed to the enhanced stability of the complex ion in water and the reduced lipophilicity of the free crown ether; the contribution of the former is comparable to (K^+) or greater than (Sr^{2+} and Ba^{2+}) that of the latter. In the cases of Na^+, Ag^+, and Pb^{2+}, the contributions of $\log\{K_{ML}(L16C5)/K_{ML}(DM16C5)\}$, $\log\{K_{ex,ip}(L16C5)/K_{ex,ip}(DM16C5)\}$, and $\log\{K_{D,L}(L16C5)/K_{D,L}(DM16C5)\}$ cancel one another, leading to the nearly equal $\log K_{ex}$ values for DM16C5 and L16C5. The substituent effects on the ion-pair extraction are always opposite to those on the overall extraction.

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

$$\log\frac{K_{ex,ip}(L_1)}{K_{ex,ip}(L_2)} = \log\frac{K_{MLA}(L_1)}{K_{MLA}(L_2)} + \log\frac{K_{D,MLA}(L_1)}{K_{D,MLA}(L_2)}. \tag{14}$$

Recently, the K_{MLA} and $K_{D,MLA}$ values have been determined for the extraction system of sodium and potassium picrates with 16C5 and L16C5 into various organic solvents [11,12]; the K_{MLA} value is much smaller for L16C5 than for 16C5, but the reverse is true for the $K_{D,MLA}$ value, resulting in an increase in the $K_{ex,ip}$ value from 16C5 to L16C5. The higher lipophilicity of the MLA complexes for L16C5 than for 16C5 is consistent with the relative lipophilicity of the free crown ethers. For the DM16C5 systems, the K_{MLA} and $K_{D,MLA}$ values have not been determined; however, from the fact that the $K_{ex,ip}$ value is always greater for DM16C5 than for 16C5 and L16C5 as is the $K_{D,L}$ value, it appears that the greater $K_{ex,ip}$ value for DM16C5 largely depends on the higher $K_{D,MLA}$ value for DM16C5 caused by the two methyl groups.

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According to Eq. (13), the difference in $\log\{K_{ex}(L_1)/K_{ex}(L_2)\}$ between the metal ions is equal to the sum of the differences in $\log\{K_{ML}(L_1)/K_{ML}(L_2)\}$ and $\log\{K_{ex,ip}(L_1)/K_{ex,ip}(L_2)\}$. The following discussion is based on the values when $(L_1, L_2) = (DM16C5, 16C5)$ and $(L16C5, DM16C5)$ (Table 2). The differences in $\log\{K_{ML}(L_1)/K_{ML}(L_2)\}$ and $\log\{K_{ex,ip}(L_1)/K_{ex,ip}(L_2)\}$ between the univalent metal ions are zero or nearly zero, resulting in the very small variation of the $\log\{K_{ex}(L_1)/K_{ex}(L_2)\}$ value with the metal ion. For Sr^{2+} and Ba^{2+}, the absolute values of $\log\{K_{ex,ip}(L_1)/K_{ex,ip}(L_2)\}$ are obviously larger for the latter ion, whereas the $\log\{K_{ML}(L_1)/K_{ML}(L_2)\}$ values vary only slightly with the metal ion. Therefore, the differences in $\log\{K_{ex}(L_1)/K_{ex}(L_2)\}$ between Sr^{2+} and Ba^{2+} are almost equal to those in $\log\{K_{ex,ip}(L_1)/K_{ex,ip}(L_2)\}$. This indicates that the substituent effects on the ion-pair extraction are responsible for the much greater extraction selectivity of DM16C5 for Ba^{2+} over Sr^{2+} compared with 16C5 and L16C5.

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Table 1. Summary of equilibrium constants for extraction of metal picrates with 16C5, DM16C5, and L16C5 into benzene at 25 °C

Metal ion	log K_{ex}			log K_{ML}			log $K_{ex,ip}$		
	16C5[a]	DM16C5	L16C5[b]	16C5[c]	DM16C5[d]	L16C5[e]	16C5[a]	DM16C5	L16C5[b]
Na+	1.474	0.942± 0.006	1.00	0.78	0.60	0.65	2.68	3.93	3.68
K+	0.041	−0.70 ± 0.01	−0.48	0.40	0.1	0.3	1.63	2.8	2.5
Ag+	2.235	1.697± 0.008	1.72	1.10	0.92	1.12	3.13	4.37	3.93
Sr2+	0.00	−2.07 ± 0.01	−0.85	2.08	1.1	2.18	2.30	2.8	2.69
Ba2+	0.07	−1.02 ± 0.02	−0.50	1.84	0.9	1.84	2.61	4.1	3.38
Pb2+	1.16	0.347± 0.006	0.30	0.74	0.65	1.27	4.81	5.68	4.75

log $K_{D,L}$		
16C5[a]	DM16C5	L16C5[b]
−0.401	1.197± 0.005	0.933

[a] Ref. [4].
[b] Ref. [5].
[c] Ref. [9].
[d] Ref. [6].
[e] Ref. [10].

Table 2. Differences in log K_{ex}, log K_{ML}, log $K_{ex,ip}$, and log $K_{D,L}$ between crown ethers

Metal ion	log{$K_{ex}(L_1)/K_{ex}(L_2)$}		log{$K_{ML}(L_1)/K_{ML}(L_2)$}		log{$K_{ex,ip}(L_1)/K_{ex,ip}(L_2)$}	
	L_1 = DM16C5 L_2 = 16C5	L16C5 DM16C5	L_1 = DM16C5 L_2 = 16C5	L16C5 DM16C5	L_1 = DM16C5 L_2 = 16C5	L16C5 DM16C5
Na$^+$	−0.532	0.06	−0.18	0.05	1.25	−0.25
K$^+$	−0.74	0.22	−0.3	0.2	1.2	−0.3
Ag$^+$	−0.538	0.02	−0.18	0.2	1.24	−0.44
Sr^{2+}	−2.07	1.22	−1.0	1.1	0.5	−0.1
Ba^{2+}	−1.09	0.52	−0.9	0.9	1.5	−0.7
Pb^{2+}	−0.81	−0.05	−0.09	0.62	0.87	−0.93

log{$K_{D,L}(L_1)/K_{D,L}(L_2)$}

L_1 = DM16C5 L_2 = 16C5	L16C5 DM16C5
1.598	−0.264
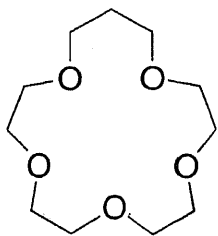
16C5   DM16C5   L16C5
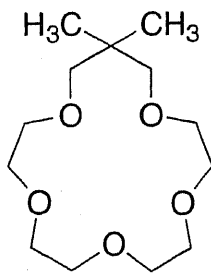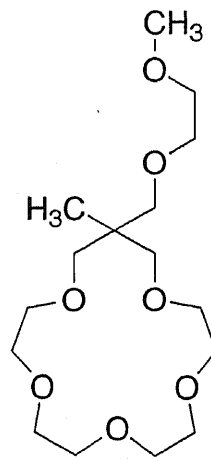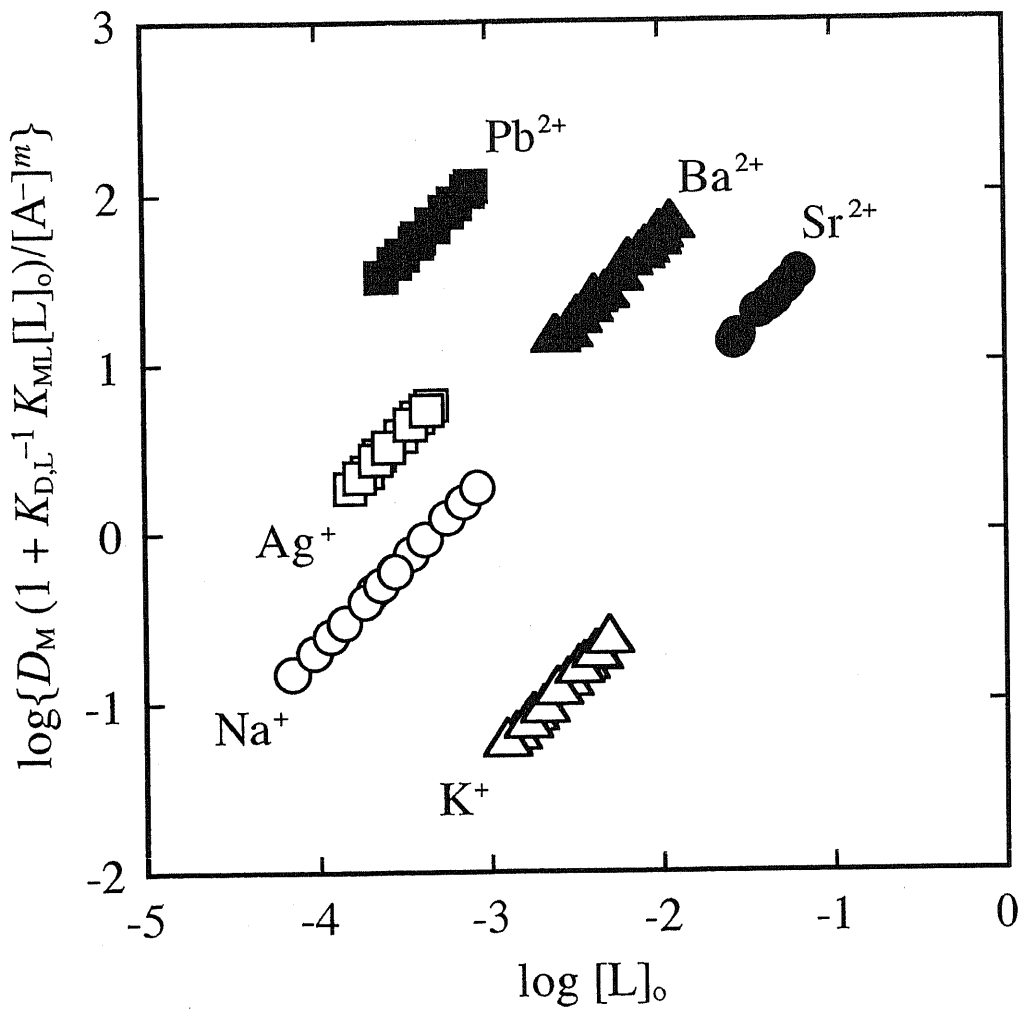
Fig. 1

Fig. 2

Figure captions:

Fig. 1   Structures of 16C5, DM16C5, and L16C5.

Fig. 2.   Plots of $\log\{D_M(1 + K_{D,L}^{-1}K_{ML}[L]_o)/[A^-]^m\}$ vs. $\log [L]_o$ for extraction of uni- ($m = 1$) and

bivalent ($m = 2$) metal picrates with DM16C5 into benzene.