

Extraction of Sodium and Potassium Perchlorates with Dibenzo-18-crown-6 into Various Organic Solvents. Quantitative Elucidation of Anion Effects on the Extraction-Ability and -Selectivity

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Abstract

The constants for overall extraction into various diluents of low dielectric constants (K_{ex}) and aqueous ion-pair formation (K_{MLA}) of dibenzo-18-crown-6 (DB18C6)–sodium and potassium perchlorate 1:1:1 complexes (MLA) were determined at 25 °C. The K_{ex} value was analyzed by the four underlying equilibrium constants. The K_{MLA} values were determined by applying our established method to this DB18C6/alkali metal perchlorate extraction system. The $K_{\text{M(DB18C6)A}}$ value of the perchlorate is much greater for K^+ than for Na^+ , and is much smaller than that of the picrate. The K_{MLA} value makes a negative contribution to the extractability of DB18C6 for MClO_4 , whereas the value of the MLA distribution-constant does a major one. The partition behavior of M(DB18C6)ClO_4 obeys the regular solution theory. However, the M(DB18C6)ClO_4 complexes in the diluent of high dipole moment somewhat undergo the dipole–dipole interaction. DB18C6 always shows high extraction selectivity for KClO_4 over NaClO_4 , which is governed largely by the much greater K_{MLA} value for K^+ than for Na^+ . The K^+ extraction-selectivity of DB18C6 over Na^+ for perchlorate ions is comparable to that for picrate ions. By comparing this perchlorate system with the picrate one, the anion effects on the extraction-efficiency and -selectivity of DB18C6 for Na^+ and K^+ was discussed in terms of the fundamental equilibrium constants.

Introduction

Anions (A^-) play an important role in the three-component extraction system of a crown ether (L) and a metal salt. In order to quantitatively elucidate the anion effect on the extraction-efficiency and -selectivity of a crown ether for monovalent cations (M^+) into a diluent of low dielectric constant on molecular grounds, it is first required to analyze the overall extraction equilibrium into four component equilibria, (i) the distribution of L, (ii) aqueous complex formation of L with M^+ , (iii) aqueous ion-pair formation of the L complex-cation with A^- , and (iv) the partition of the ion-pair complex MLA into the diluent. The dissociation of MLA into ML^+ and A^- in the diluent and the association of A^- with H^+ in the aqueous phase are neglected. The equilibria for (i) and (ii) are independent of the anion effect, whereas those for both (iii) and (iv)

are not. In most cases, it is difficult to measure the equilibrium constants for (iii) and (iv) because of low or moderate stability of ML^+ and MLA in water. However, the method of determining the fundamental equilibrium constants for (iii) and (iv) as well as those for (i) and (ii) has already been established [1]. Consequently, extraction-ability and -selectivity for alkali metal picrates and their change with the diluent of various crown ethers could be quantitatively elucidated by the four underlying equilibrium constants and regular solution theory [2–8]. Furthermore, the established method was successfully applied to the benzo-18-crown-6 (B18C6)/alkali metal perchlorate extraction system, and the anion effect was clarified [9].

In this study, constants of overall extraction equilibrium and the aqueous ion-pair formation for the dibenzo-18-crown-6 (DB18C6)/alkali metal perchlorate system were determined to investigate the anion and substituent effect on the extraction-efficiency and selectivity of DB18C6 for K^+ and Na^+ . Requisite constants of partition and aqueous complex formation with the alkali metal ions of DB18C6 have already been reported [6, 10].

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Experimental

Materials

Dibenzo-18-crown-6 (Tokyo Kasei Kogyo Co., Ltd.) was recrystallized from acetone and, prior to use, dried *in vacuo* for 24 h. The purity was checked by the melting point (160.0–161.2 °C). Alkali metal hydroxides and perchloric acid were analytical-grade reagents. Their aqueous concentrations were determined by acid–base neutralization titration. The organic solvents which were analytical-grade reagents were used without further purification. They were washed three times with deionized water prior to use.

Extraction of alkali metal perchlorates with DB18C6

The experimental procedures were almost the same as those described in the previous paper [9]. The extractions were conducted at pH values ≥ 11.0 at 25 ± 0.2 °C. Concentration ranges of DB18C6, alkali metal hydroxides, and perchloric acid were 6.9×10^{-5} – 1.8×10^{-2} , $(1.8$ – $8.6) \times 10^{-2}$, and 5.5×10^{-3} – 8.0×10^{-2} M (1 M = 1 mol dm⁻³). In order to keep the ionic strength in the aqueous phase as constant as possible, the sum of the initial total electrolyte concentrations was held at between 2.3×10^{-2} and 1.7×10^{-1} M throughout the extraction experiments. In order to determine the concentration of the DB18C6–alkali metal perchlorate complex extracted into the diluent, crystal violet was used as an extractant for the perchlorate ion back-extracted into a 0.01 M NaOH aqueous solution (Crystal Violet method). The ‘Crystal Violet method’ was described in the previous paper [9].

The accuracy of the ‘Crystal Violet method’ was checked; the concentration of the perchlorate ion extracted into chlorobenzene (CB) with a DB18C6-K⁺

complex was directly measured by ion chromatography at 25 ± 0.2 °C, and the overall extraction equilibrium constant (K_{ex}) was determined. The log K_{ex} value is 2.09 ± 0.03 . The value is the average of five measurements and the uncertainty is the standard deviation. It is consistent with the log K_{ex} value determined by the ‘Crystal Violet method’ within the experimental error (log $K_{\text{ex}} = 2.06 \pm 0.02$).

Theory and results

When an aqueous solution of an alkali metal perchlorate (MA) is in equilibrium with an organic solvent of low dielectric constant (ϵ_r) containing a crown ether (L), the equilibrium constants of this extraction system are defined as

$$K_{\text{ex}} = [\text{MLA}]_o / [\text{M}^+][\text{L}]_o [\text{A}^-], \quad (1)$$

$$K_{\text{D,L}} = [\text{L}]_o / [\text{L}], \quad (2)$$

$$K_{\text{ML}} = [\text{ML}^+] / [\text{M}^+][\text{L}], \quad (3)$$

$$K_{\text{MLA}} = [\text{MLA}] / [\text{ML}^+][\text{A}^-], \quad (4)$$

$$K_{\text{D,MLA}} = [\text{MLA}]_o / [\text{MLA}], \quad (5)$$

where the subscript ‘o’ and the lack of a subscript designate the organic and aqueous phases, respectively. The aqueous phase is always under strongly alkaline conditions. It was assumed that $[\text{MLA}]_o \gg [\text{ML}^+]_o$ and $[\text{M}^+] + [\text{ML}^+] + [\text{MLA}] \gg [\text{MA}]$ under the experimental conditions of this study; the dissociation of MLA into ML^+ and A^- in the organic phase and the association between M^+ and A^- in the aqueous phase were neglected. K_{ex} can be written as

Table 1. Solvent parameters at 25 °C

| No. | Solvent ^a | δ ^b | δ_o' | V ^c | μ ^{d,e} | ϵ_r ^e |
|-----|----------------------|-----------------------|------------------|------------------|----------------------|---------------------------|
| 1 | DCM | 9.7 | 6.7 ₁ | 63.9 | 1.14 | 8.93 |
| 2 | 1,2-DCE | 9.8 | 6.5 ₄ | 79.4 | 1.86 | 10.36 |
| 3 | CBu | 8.4 | 5.4 ₅ | 104 | 1.90 | 7.39 ^f |
| 4 | BZ | 9.16 | 6.05 | 89.4 | 0.0 | 2.275 |
| 5 | TE | 8.93 | 5.78 | 106.9 | 0.31 | 2.379 |
| 6 | <i>m</i> X | 8.80 | 5.61 | 123.5 | 0.30 | 2.4 |
| 7 | CB | 9.5 | 6.1 ₅ | 102.1 | 1.54 | 5.62 |
| 8 | BB | 9.87 | 6.34 | 105 | 1.55 | 5.40 |
| 9 | <i>o</i> -DCB | 10.0 | 6.3 ₆ | 112.8 | 2.27 | 9.93 |
| 10 | Water | 17.55 ^g | – | 18.1 | 1.85 | – |

^a DCM – dichloromethane; 1,2-DCE – 1,2-dichloroethane; CBu – chlorobutane; BZ – benzene; TE – toluene; *m*X – *m*-xylene; CB – chlorobenzene; BB – bromobenzene; *o*-DCB – *o*-dichlorobenzene.

^b Solubility parameter (cal^{1/2} cm^{-3/2}), Refs. [11, 12].

^c Molar volume (cm³ mol⁻¹). The molar volumes were calculated using the densities in Ref. [13].

^d Dipole moment (Debye).

^e Ref. [14].

^f 20 °C.

^g Ref. [15].

$$K_{\text{ex}} = K_{\text{D,L}}^{-1} K_{\text{ML}} K_{\text{MLA}} K_{\text{D,MLA}}, \quad (6)$$

where $K_{\text{MLA}} K_{\text{D,MLA}} = [\text{MLA}]_{\text{o}} / [\text{ML}^+][\text{A}^-] = K_{\text{ex,ip}}$ and $K_{\text{ex,ip}}$ expresses ion-pair extraction equilibrium constant of ML^+ and A^- . The distribution ratio (D) of the metal is represented by

$$D = [\text{MLA}]_{\text{o}} / ([\text{M}^+] + [\text{ML}^+] + [\text{MLA}]). \quad (7)$$

When $[\text{M}^+] \gg [\text{ML}^+] + [\text{MLA}]$, Equation (7) leads to

$$D = K_{\text{ex}} [\text{L}]_{\text{o}} [\text{A}^-]. \quad (8)$$

From the mass balances, $[\text{M}^+]$, $[\text{L}]_{\text{o}}$, and $[\text{A}^-]$ are given by

$$[\text{M}^+] = ([\text{M}]_{\text{t}} - [\text{MLA}]_{\text{o}}) / \{1 + (a + b[\text{A}^-])[\text{L}]_{\text{o}}\}, \quad (9)$$

$$[\text{L}]_{\text{o}} = ([\text{L}]_{\text{t}} - [\text{MLA}]_{\text{o}}) / \{c + (a + b[\text{A}^-])[\text{M}^+]\}, \quad (10)$$

$$[\text{A}^-] = ([\text{HA}]_{\text{t}} - [\text{MLA}]_{\text{o}}) / (1 + b[\text{L}]_{\text{o}}[\text{M}^+]), \quad (11)$$

where $a = K_{\text{D,L}}^{-1} K_{\text{ML}}$, $b = K_{\text{D,L}}^{-1} K_{\text{ML}} K_{\text{MLA}}$, $c = 1 + K_{\text{D,L}}^{-1}$, and the subscript 't' denotes the total concentration. As a first approximation, it was presumed that $1 \gg (a + b[\text{A}^-])[\text{L}]_{\text{o}}$ (Equation (9)), $c + a[\text{M}^+] \gg b[\text{M}^+][\text{A}^-]$ (Equation (10)), and $1 \gg b[\text{L}]_{\text{o}}[\text{M}^+]$ (Equation (11)). The $[\text{L}]_{\text{o}}$ and $[\text{A}^-]$ values of Equation (8) were calculated on this assumption. The $\log(D/[\text{A}^-])$ against $\log[\text{L}]_{\text{o}}$ plots give a straight line with a slope of 1 in every case. This proves that DB18C6 forms a 1:1 complex with the M^+ ion and that the assumptions are valid. The first approximate K_{ex} value for each system was determined on these assumptions.

The distribution constants of the crown ether ($K_{\text{D,L}}$) and an ion-pair complex MLA ($K_{\text{D,MLA}}$) are estimated by the following equations derived from the regular solution theory [11]:

$$RT \ln K_{\text{D,L}} / (\delta_{\text{w}} - \delta_{\text{o}}) = V_{\text{L}}(\delta_{\text{w}} - 2\delta_{\text{L}}) + V_{\text{L}}\delta'_{\text{o}}, \quad (12)$$

$$RT \ln K_{\text{D,MLA}} / (\delta_{\text{w}} - \delta_{\text{o}}) = V_{\text{MLA}}(\delta_{\text{w}} - 2\delta_{\text{MLA}}) + V_{\text{MLA}}\delta'_{\text{o}}, \quad (13)$$

where $\delta'_{\text{o}} = \delta_{\text{o}} + RT(1/V_{\text{o}} - 1/V_{\text{w}}) / (\delta_{\text{w}} - \delta_{\text{o}})$; δ_{w} , δ_{o} , δ_{L} , and δ_{MLA} designate the solubility parameters of water, the organic solvent, the crown ether, and MLA, respectively; V_{L} , V_{o} , V_{w} , and V_{MLA} refer to the molar volumes of the crown ether, the organic solvent, water, and MLA, respectively. Combining Equations (12) and (13) leads to

$$\log K_{\text{D,MLA}} = \{V_{\text{MLA}}(\delta_{\text{w}} + \delta'_{\text{o}} - 2\delta_{\text{MLA}}) / V_{\text{L}}(\delta_{\text{w}} + \delta'_{\text{o}} - 2\delta_{\text{L}})\} \log K_{\text{D,L}}. \quad (14)$$

By adding $\log K_{\text{MLA}}$ to both sides of Equation (14), Equation (15) is obtained.

$$\log K_{\text{ex,ip}} = \{V_{\text{MLA}}(\delta_{\text{w}} + \delta'_{\text{o}} - 2\delta_{\text{MLA}}) / V_{\text{L}}(\delta_{\text{w}} + \delta'_{\text{o}} - 2\delta_{\text{L}})\} \log K_{\text{D,L}} + \log K_{\text{MLA}}. \quad (15)$$

When the values of δ_{MLA} and δ_{L} are nearly equal, Equation (15) leads to

$$\log K_{\text{ex,ip}} = (V_{\text{MLA}}/V_{\text{L}}) \log K_{\text{D,L}} + \log K_{\text{MLA}}. \quad (16)$$

The right-hand side of Equation (15) can also be expressed as $\log K_{\text{ex,ip}} = (V_{\text{MLA}}/V_{\text{L}}) \log K_{\text{D,L}} + (2V_{\text{MLA}}/2.303RT)\{(C_{\text{w,L}} - C_{\text{w,MLA}}) - (C_{\text{o,L}} - C_{\text{o,MLA}})\} + \log K_{\text{MLA}}$, where $C_{\text{w,L}}$ and $C_{\text{w,MLA}}$ denote the cohesive energy densities for a mixture of water and L and for water and MLA, respectively; $C_{\text{o,L}}$ and $C_{\text{o,MLA}}$ are the cohesive energy densities for a mixture of an organic solvent and L and for the organic solvent and MLA, respectively. When $\delta_{\text{MLA}} \approx \delta_{\text{L}}$, $(C_{\text{w,L}} - C_{\text{w,MLA}}) - (C_{\text{o,L}} - C_{\text{o,MLA}})$ is nearly equal to zero. Plots of the first approximate $\log K_{\text{ex,ip}}$ values against $\log K_{\text{D,L}}$ values show good linear relationship for sodium and potassium perchlorates with different diluents (Figures 1 and 2). The first approximate $\log K_{\text{MLA}}$ values were determined from the intercepts of $\log K_{\text{ex,ip}}$ versus $\log K_{\text{D,L}}$ plots. The second approximate $[\text{A}^-]$ value was calculated from Equation (11) using the first approximate values of $[\text{M}^+]$, $[\text{L}]_{\text{o}}$, and K_{MLA} . The final $[\text{M}^+]$, $[\text{L}]_{\text{o}}$, $[\text{A}^-]$, K_{MLA} , and K_{ex} values

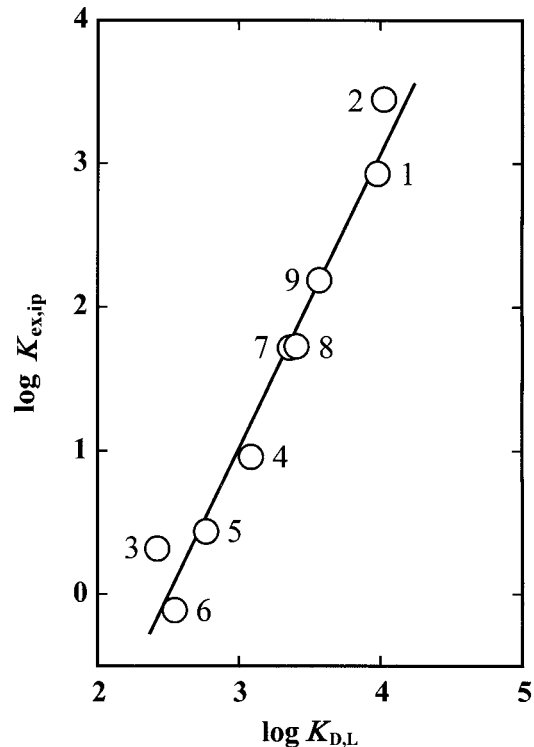


Figure 1. Plots of first approximate $\log K_{\text{ex,ip}}$ values versus $\log K_{\text{D,L}}$ values for the DB18C6– NaClO_4 system. The numbers for different solvents are given in Table 1.

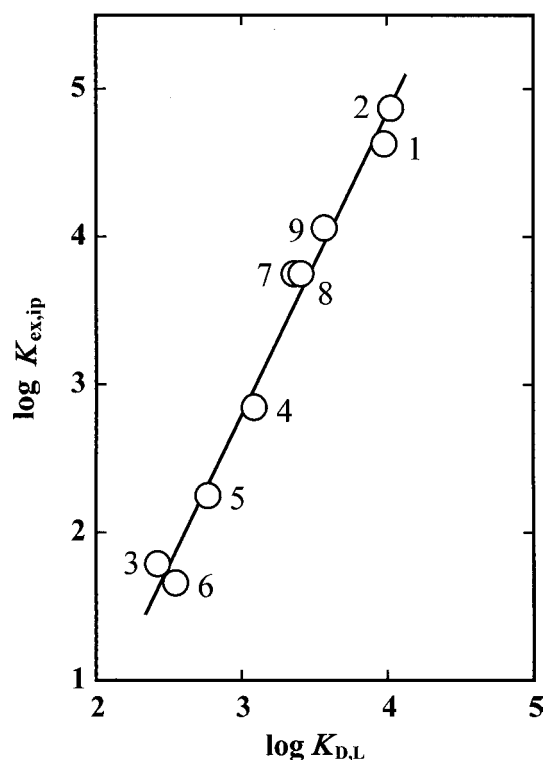


Figure 2. Plots of first approximate $\log K_{\text{ex,ip}}$ values versus $\log K_{\text{D,L}}$ values for the DB18C6-KClO₄ system. The numbers for different solvents are given in Table 1.

were calculated from Equations (1), (6), (9)–(11), and (16) by successive approximation. The $\log K_{\text{ex}}$ and $\log K_{\text{MLA}}$ values are listed in Tables 2 and 5, respectively. A good linear relationship is also observed for the plots of the final $\log K_{\text{ex,ip}}$ versus $\log K_{\text{D,L}}$ for sodium and potassium perchlorates with different diluents. The

correlation coefficients (r) for the Na⁺ and K⁺ systems are 0.978 and 0.991, respectively.

Discussion

The $\log K_{\text{D,MLA}}$ values calculated by Equation (6) are summarized in Table 3. A linear relationship is found for the $RT \ln K_{\text{D,MLA}}/(\delta_{\text{w}} - \delta_{\text{o}})$ versus δ'_{o} plots in Figures 3 and 4. The r values for Na⁺ and K⁺ are 0.957 and 0.971, respectively; for B18C6, they are 0.927 (Na⁺) and 0.936 (K⁺) [9]. The more rigid and hydrophobic the crown ether is and the more nicely the alkali metal ion fits into the crown ether cavity, the more closely the MLCIO₄ complex obeys the regular solution theory. For the same diluents as we used in this study, the r values for the 1:1:1 complexes of DB18C6 with sodium and potassium picrates are 0.976 and 0.975, respectively [9]. The r values for the size-fitted K⁺ complexes of DB18C6 with perchlorate and picrate ions are almost the same. However, for the size-misfitted smaller Na⁺ complex Na(DB18C6)A, the r value of the picrate is closer to unity than that of the perchlorate. The perchlorate complex more strongly receives some specific solute–solvent interaction except for dispersion force than does the picrate one. The V and δ values for M(DB18C6)ClO₄ were determined from the slope and the intercept, respectively. They are compiled in Table 4. The δ values of DB18C6 and the M(DB18C6)ClO₄ complexes are all equal. They were independently determined. The validity of Equation (16) is verified.

From Table 3, the $\log K_{\text{D,M(DB18C6)ClO}_4}$ values of Na⁺ and K⁺ for the same diluent are almost the same. This is due to the fact that $V_{\text{Na(DB18C6)ClO}_4} \approx V_{\text{K(DB18C6)ClO}_4}$ and $\delta_{\text{Na(DB18C6)ClO}_4} = \delta_{\text{K(DB18C6)ClO}_4}$ (Equation (13) and Table 4). Both Equations (17) and (18) are derived from Equation (13).

Table 2. Extraction equilibrium constants for 1:1:1 DB18C6- and B18C6-alkali metal salt complexes at 25 °C

| No. | Solvent ^a | $\log K_{\text{ex}}$ | | | | $\log K_{\text{ex,ip}}$ | | | |
|-----|----------------------|--------------------------------|-------------------|--------------------------------|-------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| | | DB18C6 | | B18C6 ^b | | DB18C6 | | | |
| | | Na ⁺ | | K ⁺ | | Na ⁺ | | K ⁺ | |
| | | ClO ₄ ^{-c} | Pic ^{-d} | ClO ₄ ^{-c} | Pic ^{-d} | ClO ₄ ⁻ | ClO ₄ ⁻ | ClO ₄ ⁻ | ClO ₄ ⁻ |
| 1 | DCM | 0.11 ± 0.02 | 2.990 | 2.32 ± 0.01 | 4.989 | 0.56 | 2.95 | 2.93 | 4.63 |
| 2 | 1,2-DCE | 0.59 ± 0.02 | 3.091 | 2.51 ± 0.01 | 5.031 | 0.99 | 3.29 | 3.45 | 4.87 |
| 3 | CBu | -0.95 ± 0.03 | 2.219 | 1.04 ± 0.01 | 4.327 | -0.46 | 1.88 | 0.32 | 1.79 |
| 4 | BZ | -0.97 ± 0.01 | 2.290 | 1.43 ± 0.02 | 4.471 | -0.82 | 1.59 | 0.96 | 2.85 |
| 5 | TE | -1.17 ± 0.01 | 2.251 | 1.15 ± 0.02 | 4.475 | -0.95 | 1.38 | 0.44 | 2.25 |
| 6 | mX | -1.50 ± 0.02 | 2.200 | 0.78 ± 0.02 | 4.415 | -1.11 | 1.22 | -0.11 | 1.66 |
| 7 | CB | -0.49 ± 0.01 | 2.599 | 2.06 ± 0.02 | 4.886 | -0.09 | 2.47 | 1.72 | 3.75 |
| 8 | BB | -0.52 ± 0.02 | 2.587 | 2.01 ± 0.01 | 4.906 | -0.08 | 2.44 | 1.73 | 3.75 |
| 9 | o-DCB | -0.22 ± 0.01 | 2.628 | 2.16 ± 0.01 | 4.925 | 0.36 | 2.82 | 2.19 | 4.06 |

^aFor abbreviations, see footnote to Table 1.

^bRef. [9].

^cEach value is the average of 8–15 determinations. The uncertainty is the standard deviation.

^dPic⁻ denotes a picrate ion. Ref. [6].

Table 3. Distribution constants for DB18C6, 1:1:1 DB18C6- and B18C6-alkali metal salt complexes at 25 °C

| No. | Solvent ^a | log $K_{D,DB18C6}$ ^b | log $K_{D,MLA}$ | | | | | |
|-----|----------------------|---------------------------------|-------------------------------|---------------------------------|-------------------------------|---------------------------------|-------------------------------|-------------------------------|
| | | | DB18C6 | | | | B18C6 ^c | |
| | | | Na ⁺ | | K ⁺ | | Na ⁺ | K ⁺ |
| | | | ClO ₄ ⁻ | Pic ⁻ . ^b | ClO ₄ ⁻ | Pic ⁻ . ^b | ClO ₄ ⁻ | ClO ₄ ⁻ |
| 1 | DCM | 3.98 | 8.0 ₄ | 5.96 | 7.9 ₅ | 6.00 | 4.2 ₂ | 4.2 ₂ |
| 2 | 1,2-DCE | 4.026 | 8.5 ₆ | 6.11 | 8.1 ₉ | 6.09 | 4.1 ₄ | 4.0 ₅ |
| 3 | CBu | 2.424 | 5.4 ₃ | 3.63 | 5.1 ₁ | 3.78 | 1.0 ₅ | 1.0 ₀ |
| 4 | BZ | 3.087 | 6.0 ₇ | 4.37 | 6.1 ₇ | 4.59 | 1.2 ₆ | 1.2 ₈ |
| 5 | TE | 2.77 | 5.5 ₅ | 4.01 | 5.5 ₇ | 4.27 | 0.8 ₃ | 0.7 ₇ |
| 6 | <i>m</i> X | 2.548 | 5.0 ₀ | 3.74 | 4.9 ₈ | 3.99 | 0.3 ₄ | 0.2 ₇ |
| 7 | CB | 3.362 | 6.8 ₃ | 4.95 | 7.0 ₇ | 5.28 | 2.2 ₁ | 2.3 ₈ |
| 8 | BB | 3.410 | 6.8 ₄ | 4.99 | 7.0 ₇ | 5.35 | 2.1 ₉ | 2.3 ₂ |
| 9 | <i>o</i> -DCB | 3.57 | 7.3 ₀ | 5.19 | 7.3 ₈ | 5.52 | 2.7 ₃ | 2.8 ₀ |

^aFor abbreviations, see footnote to Table 1.

^bRef. [6].

^cRef. [9].

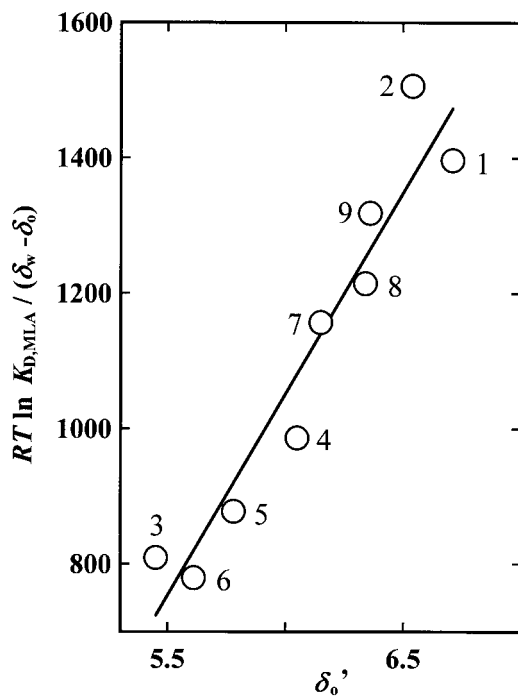


Figure 3. Plots of $RT \ln K_{D,MLA}/(\delta_w - \delta_o)$ versus δ_o' for a DB18C6–NaClO₄ 1:1:1 complex. The numbers for different solvents are given in Table 1.

$$RT \ln(K_{D,Na}(DB18C6)ClO_4/K_{D,Na}(DB18C6)Pic) = 179(\delta_w - \delta_o)(\delta_o' - 4.25). \quad (17)$$

$$RT \ln(K_{D,K}(DB18C6)ClO_4/K_{D,K}(DB18C6)Pic) = 169(\delta_w - \delta_o)(\delta_o' - 4.25). \quad (18)$$

The $K_{D,M}(DB18C6)_A$ value is always greater for the perchlorate than for the corresponding picrate. This is

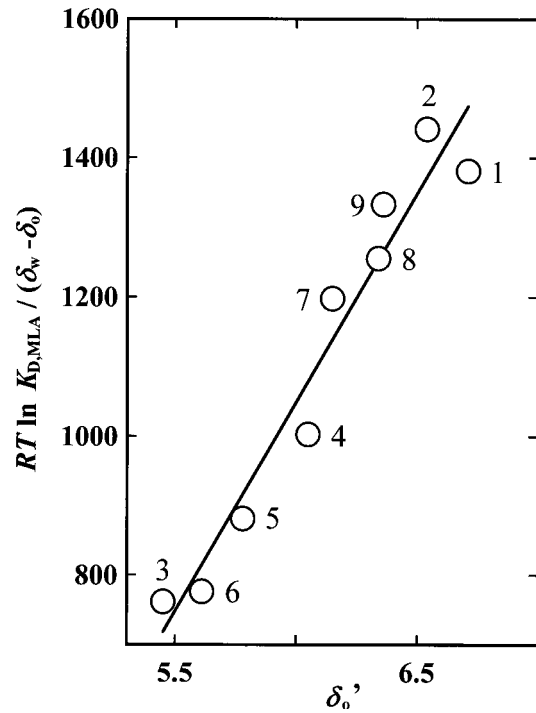


Figure 4. Plots of $RT \ln K_{D,MLA}/(\delta_w - \delta_o)$ versus δ_o' for a DB18C6–KClO₄ 1:1:1 complex. The numbers for different solvents are given in Table 1.

attributed to the fact that the $V_{M(DB18C6)_A}$ value is greater for the perchlorate than for the corresponding picrate, because $\delta_w > \delta_o$, the δ_o' value of the diluent used in this study is larger than 4.25, and the $\delta_{M(DB18C6)_A}$ values of the perchlorates and the picrates are all equal (Tables 1 and 4, Equations (17) and (18)). The $M(DB18C6)ClO_4$ complex is more lipophilic than the $M(B18C6)ClO_4$ one (Table 3). This is ascribed to the fact that $V_{M(DB18C6)ClO_4} > V_{M(B18C6)ClO_4}$ and $\delta_{M(DB18C6)ClO_4} < \delta_{M(B18C6)ClO_4}$.

Table 4. Molar volumes and solubility parameters for DB18C6, 1:1:1 DB18C6- and B18C6-alkali metal salt complexes

| | L | MLA | | | |
|------------|-------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------|
| | | Na ⁺ | | K ⁺ | |
| | | ClO ₄ ⁻ | Pic ⁻ | ClO ₄ ⁻ | Pic ⁻ |
| L = DB18C6 | | | | | |
| <i>V</i> | 288 ± 16 ^a | 595 ± 69 | 416 ± 27 ^a | 600 ± 59 | 432 ± 24 ^a |
| δ | 10.9 ± 0.1 ^a | 10.9 ± 0.1 | 10.9 ± 0.1 ^a | 10.9 ± 0.1 | 10.9 ± 0.1 ^a |
| L = B18C6 | | | | | |
| <i>V</i> | 252 ± 28 ^b | 545 ± 84 ^c | – | 556 ± 79 ^c | – |
| δ | 11.4 ± 0.1 ^b | 11.5 ± 0.1 ^c | – | 11.5 ± 0.1 ^c | – |

The uncertainty is the standard deviation.

^a Ref. [6].

^b Ref. [2].

^c Ref. [9].

Table 5. Fundamental equilibrium constants in water at 25 °C

| M ⁺ = | Na ⁺ | | K ⁺ | |
|-----------------------------|-------------------------------|---------------------------|-------------------------------|--------------------------|
| | ClO ₄ ⁻ | Pic ⁻ | ClO ₄ ⁻ | Pic ⁻ |
| L = DB18C6 | | | | |
| log <i>K</i> _{MLA} | -5.11 ± 0.26 | -0.14 ± 0.11 ^a | -3.30 ± 0.17 | 1.30 ± 0.10 ^a |
| log <i>K</i> _{ML} | | 1.16 ^b | | 1.667 ^b |
| L = B18C6 | | | | |
| log <i>K</i> _{MLA} | -1.95 ± 0.40 ^c | 2.11 ± 0.16 ^c | -0.49 ± 0.42 ^c | 3.30 ± 0.20 ^d |
| log <i>K</i> _{ML} | | 0.81 ^c | | 1.744 ^c |

The uncertainty is the standard deviation.

^a Ref. [6].

^b Ref. [10].

^c Ref. [9].

^d Ref. [2].

^e Ref. [16].

The order of decreasing $K_{D,M(DB18C6)ClO_4}$ value for a given alkali metal is 1,2-DCE > DCM > *o*-DCB > BB ≈ or = CB > BZ > TE > or ≥ CBU > or ≥ *mX*. The same is found for the Cs(DB18C6)Pic complex; for the other M(DB18C6)Pic complexes, omitting CBU, the same order is also observed for the decreasing $K_{D,M(DB18C6)Pic}$ value [6]. Equation (13) is transformed into Equation (19).

$$RT \ln K_{D,MLA} = V_{MLA} \{ (\delta_w - \delta_{MLA})^2 - (\delta_o - \delta_{MLA})^2 + RT(V_o^{-1} - V_w^{-1}) \}. \quad (19)$$

The δ_o values are closer to the $\delta_{M(DB18C6)ClO_4}$ value for *o*-DCB and BB than for 1,2-DCE and DCM. The $K_{D,M(DB18C6)ClO_4}$ values, however, are smaller for *o*-DCB and BB than for 1,2-DCE and DCM. This is caused by the much greater V_o values for *o*-DCB and BB than for 1,2-DCE and DCM (Equation (19)). The largest V_o and the second largest $(\delta_o - \delta_{MLA})^2$ values for *mX* are responsible for the lowest $K_{D,M(DB18C6)ClO_4}$ value among all the diluents (Equation (19)).

Equation (20) is obtained from Equation (13).

$$RT \ln K_{D,M(DB18C6)ClO_4} = V_{M(DB18C6)ClO_4} (\delta_w - \delta_o) (\delta'_o - 4.25). \quad (20)$$

The δ_o and δ'_o values for DCM are smaller and larger, respectively, compared with 1,2-DCE. For BB and *o*-DCB, the δ_o value is lower for the one than for the other, and the δ'_o values are much the same. It follows from this and Equation (20) that the orders of increasing $K_{D,M(DB18C6)ClO_4}$ value for a given alkali metal ion are DCM > 1,2-DCE and BB ≥ *o*-DCB. However, the reverse holds for the experimental $K_{D,M(DB18C6)ClO_4}$ value. The same is true of the picrate (Table 3). This is attributable to the stronger dipole-dipole interaction of M(DB18C6)A (A = ClO₄⁻ or Pic⁻) with 1,2-DCE and *o*-DCB whose polarity is much greater compared with DCM and BB, respectively (Table 1). From the structures of perchlorate and picrate anions, the polarity is expected to be higher for M(DB18C6)ClO₄ than for M(DB18C6)Pic. The difference in the log $K_{D,M(DB18C6)A}$ value between 1,2-DCE and DCM or between *o*-DCB and BB for the perchlorate is greater than or nearly equal to that for the corresponding picrate. This reflects

the higher polarity of $M(\text{DB18C6})\text{ClO}_4$ compared with $M(\text{DB18C6})\text{Pic}$.

The μ value of CBU is nearly equal to that of 1,2-DCE and smaller than that of *o*-DCB. The $\delta_w - \delta_o$ value is larger for CBU (9.2) than for 1,2-DCE (7.8) and *o*-DCB (7.6). It thus appears that the increment caused by the dipole-dipole interaction to the $RT \ln K_{D,MLA}/(\delta_w - \delta_o)$ value estimated based on the regular solution theory is greater for 1,2-DCE and *o*-DCB than for CBU (Equation (13)). Consequently, the experimental slope of the $RT \ln K_{D,M(\text{DB18C6})\text{ClO}_4}/(\delta_w - \delta_o)$ versus δ_o' plots is greater than anticipated based on the regular solution theory because the δ_o' value is larger for 1,2-DCE and *o*-DCB than for CBU (Table 1). This results in the greater $V_{M(\text{DB18C6})\text{ClO}_4}$ values than expected. Furthermore, the much larger $V_{M(\text{DB18C6})\text{A}}$ value for the perchlorate than for the picrate is considered to reflect the difference in the structure between the perchlorate and the picrate. There exists an intimate relation between V_{MLA} and K_{MLA} where the conformation of ML^+ complexes of the same crown ether are similar; the smaller the V_{MLA} value is, the larger is the K_{MLA} value [6, 9]. The same is also found for the $M(\text{DB18C6})\text{A}$ complexes with different anions; $V_{M(\text{DB18C6})\text{ClO}_4} \gg V_{M(\text{DB18C6})\text{Pic}}$, $K_{M(\text{DB18C6})\text{ClO}_4} \ll K_{M(\text{DB18C6})\text{Pic}}$ (Tables 4 and 5). The much higher $K_{M(\text{DB18C6})\text{A}}$ value for the picrate is attributable to the shorter distance between the centers of the positive and negative charges compared with the perchlorate and the enforcement of the hydrogen-bonded structure of water for the picrate ion.

The size-unfitted smaller Na^+ ion in the cavity is more effectively shielded from the surroundings by DB18C6 having two benzo groups than the K^+ ion. DB18C6 itself and water molecules bound to the cation in the cavity prevent the anion from approaching the cation more effectively for Na^+ than for K^+ . This is responsible for the fact that $K_{K(\text{DB18C6})\text{ClO}_4} \gg K_{Na(\text{DB18C6})\text{ClO}_4}$. The $\log K_{ML\text{ClO}_4}$ value for DB18C6 is much smaller than the corresponding one for B18C6, which is caused by the more effective steric hindrance of the two benzo groups.

For DB18C6 and $M(\text{DB18C6})\text{ClO}_4$ having the same δ values, combination of Equations (12) and (13) leads to Equation (21):

$$\ln K_{D,MLA} - \ln K_{D,L} = (RT)^{-1}(V_{MLA} - V_L)\{-(\delta_o - \delta)^2 + (\delta_w - \delta)^2 + RT(V_o^{-1} - V_w^{-1})\}, \quad (21)$$

where $\delta = \delta_L = \delta_{MLA}$. Equation (21) shows that the closer the δ_o value is to the δ value, and the smaller the V_o value is, the larger the K_{ex} value is because both the K_{ML} and K_{MLA} values are independent of the diluent, $\log K_{ex} = \log K_{D,MLA} - \log K_{D,L} + \log K_{ML} + \log K_{MLA}$. This is the reason why DB18C6 extracts the alkali metal perchlorate most into 1,2-DCE, but least into *mX*. The difference in the experimental $\log K_D$ value between $M(\text{DB18C6})\text{ClO}_4$ and DB18C6, \log

$K_{D,M(\text{DB18C6})\text{ClO}_4} - \log K_{D,DB18C6}$, also is the greatest for 1,2-DCE and the smallest for *mX* among all the diluents. Equation (6) shows that the values of $\log K_{D,DB18C6}$ and $\log K_{D,M(\text{DB18C6})\text{ClO}_4}$ whose signs are the same cancel each other. Both the constants are related to distribution behavior. The $\log K_{D,MLA} - \log K_{D,L}$ value, however, makes a major contribution to the extractability of DB18C6 for MClO_4 ; the $\log K_{ML}$ value also contributes to the magnitude of $\log K_{ex}$, whereas the $\log K_{M(\text{DB18C6})\text{ClO}_4}$ value makes a negative contribution to that. Such a negative contribution of $\log K_{M(\text{DB18C6})\text{A}}$ is not found for the picrate [6]. The $\log K_{D,M(\text{DB18C6})\text{A}} - \log K_{D,DB18C6}$ value for the perchlorate more contributes to the magnitude of K_{ex} compared with the picrate because of the much decreased $K_{M(\text{DB18C6})\text{A}}$ and much increased $V_{M(\text{DB18C6})\text{A}}$ values on going from the picrate to the perchlorate. The K_{ex} value for the same diluent is always much smaller for the perchlorate than for the picrate. This is completely ascribed to the much lower $K_{M(\text{DB18C6})\text{A}}$ value for the perchlorate compared with the picrate.

Dibenzo-18-crown-6 always shows high extraction selectivity for KClO_4 over NaClO_4 , which is governed largely by the much greater K_{MLA} value for K^+ than for Na^+ . Furthermore, the larger K_{ML} value for K^+ than for Na^+ also makes a favorable contribution to the high K^+ extraction-selectivity. The difference in the $\log K_{ex}$ value for DB18C6 between KClO_4 and NaClO_4 does not vary much with the diluent (from 1.92 (1,2-DCE) to 2.55 (CB)); namely, the extraction selectivity of DB18C6 for KClO_4 over NaClO_4 is little affected by the diluent. The reason is that $V_{K(\text{DB18C6})\text{ClO}_4} \approx V_{Na(\text{DB18C6})\text{ClO}_4}$ and $\delta_{K(\text{DB18C6})\text{ClO}_4} = \delta_{Na(\text{DB18C6})\text{ClO}_4}$. Table 3 shows that the experimental $\log K_{D,M(\text{DB18C6})\text{ClO}_4}$ values of Na^+ and K^+ for the same diluent are nearly equal. For the same diluent, the difference in the $\log K_{ex}$ value for the perchlorate between K^+ and Na^+ ($\log K_{ex}(\text{K}^+) - \log K_{ex}(\text{Na}^+)$) is approximately equal to that for the picrate; the K^+ extraction-selectivity of DB18C6 over Na^+ for ClO_4^- is comparable to that for Pic^- . This is due to the fact that the $\log K_{K(\text{DB18C6})\text{A}} - \log K_{Na(\text{DB18C6})\text{A}}$ value for the perchlorate (1.8) is close to that for the picrate (1.4) because $V_{K(\text{DB18C6})\text{Pic}} \geq V_{Na(\text{DB18C6})\text{Pic}}$ and $\delta_{K(\text{DB18C6})\text{Pic}} = \delta_{Na(\text{DB18C6})\text{Pic}}$. For the same diluent, KClO_4 extraction-selectivity over NaClO_4 of DB18C6 is slightly lower than or nearly equal to that of B18C6. This is caused by the slightly smaller $\log K_{KL} - \log K_{NaL}$ and $\log K_{KL\text{ClO}_4} - \log K_{NaL\text{ClO}_4}$ values for DB18C6 compared with B18C6.

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