



Extraction of Alkali Metal (Li, Na, K) Picrates with Benzo-15-crown-5 into Various Organic Solvents. Elucidation of Fundamental Equilibria Determining the Extraction-ability and -selectivity

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Abstract

To quantitatively elucidate the effects of the benzo group on the extraction-selectivity and -ability of benzo-15-crown-5 (B15C5) for alkali metal ions, the constants of the overall extraction (K_{ex}), the distribution for various diluents having low dielectric constants ($K_{\text{D,MLA}}$), and the aqueous ion-pair formation (K_{MLA}) of B15C5-alkali metal (Li, Na, K) picrate 1:1:1 complexes (MLA) were determined at 25 °C. The partition constants of B15C5 were also measured at 25 °C. The $\log K_{\text{MLA}}$ values for Li^+ , Na^+ , and K^+ are -0.32 ± 0.22 , 2.66 ± 0.19 , and 0.71 ± 0.47 , respectively. In going from 15-crown-5 (15C5) to B15C5, the benzo group considerably decreases the K_{MLA} value for the same alkali metal ion. The distribution behavior of B15C5 and its 1:1:1 complexes with the alkali metal picrates closely obeys regular solution theory, omitting chloroform. Molar volumes and solubility parameters of B15C5 and the 1:1:1 complexes were determined. For every diluent, the K_{ex} value for B15C5 increases in the order $\text{Li}^+ < \text{K}^+ < \text{Na}^+$. $K_{\text{D,MLA}}$ makes an unfavorable contribution to the Na^+ extraction-selectivity of B15C5 because of the smallest molar volume of the $\text{Na}(\text{B15C5})\text{A}$ complex. The Na^+ extraction-selectivity of B15C5 is determined completely by much the highest $K_{\text{Na}(\text{B15C5})\text{A}}$ value. The extraction-ability and -selectivity of B15C5 for the alkali metal picrates are compared with those of 15C5 on the basis of the underlying equilibrium constants.

Introduction

The extraction-selectivity order of benzo-15-crown-5 (B15C5) for alkali metal picrates between benzene and water is $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Li}^+ > \text{Cs}^+$, which is somewhat different from that of 15-crown-5 (15C5); the extractability of B15C5 for lithium picrate is comparable to that of 15C5, however, that for the other alkali metal picrates is lower compared with 15C5 [1–3]. The benzo group changes the extraction-selectivity and -ability. To completely elucidate the benzo-group effect on molecular grounds, it is necessary to analyze the overall extraction equilibrium by the fundamental equilibria. In the previous studies [4–6], the overall extraction equilibria for 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6, and alkali metal picrates were analyzed by the four underlying equilibria, and the effects of the benzo group on the extraction-efficiencies and -selectivities for the 18-crown-6 analogues were quantitatively clarified.

The benzo group causes B15C5 to have a larger size, higher lipophilicity, and a more rigid and less symmetrical

structure compared with 15C5. In this study, to quantitatively elucidate the effect of the benzo group on the extraction-selectivity and -ability of B15C5 for alkali metal picrates, the overall extraction and fundamental equilibrium constants for B15C5 were determined, and the overall extraction equilibrium constants were analyzed by the four underlying equilibrium constants. The equilibrium constants for B15C5 were compared with those for 15C5.

Experimental

Materials

Benzo-15-crown-5 (Merck Japan Ltd.) was dissolved in heptane, and filtered while hot. Then it was recrystallized from heptane and, prior to use, dried at 40 °C in a vacuum oven (mp 78.4–79.8 °C). $\text{LiOH}\cdot\text{H}_2\text{O}$, NaOH , KOH , and picric acid were analytical-grade reagents; the concentrations of their aqueous solutions were determined by neutralization titration. All of the organic solvents were analytical grade. They were washed three times with deionized

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Table 1. Solvent parameters at 25 °C

No.	Solvent ^a	δ^b	V^c	$\mu^{d,e}$	ϵ_r^e
1	DCM	9.7	63.9	1.14	8.93
2	CF	9.3	80.7	1.15	4.81 ^f
3	1,2-DCE	9.8	79.4	1.86	10.36
4	CBu	8.4	104	1.90	7.39 ^f
5	BZ	9.16	89.4	0.0	2.275
6	TE	8.93	106.9	0.31	2.379
7	<i>mX</i>	8.80	123.5	0.30	2.4
8	CB	9.5	102.1	1.54	5.62
9	BB	9.87	105	1.55	5.40
10	<i>o</i> -DCB	10.0	112.8	2.27	9.93
11	Water	17.55 ^g	18.1	1.85	–

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

^b Solubility parameter (cal^{1/2} cm^{-3/2}). Ref. [8] and A.F.M. Barton, *Chem. Rev.* **75**, 731 (1975).

^c Molar volume (cm³ mol⁻¹). The molar volumes were calculated using the densities in D.R. Lide, *Handbook of Chemistry and Physics*, 75th edn., CRC Press, Boca Raton, FL, 1994–1995.

^d Dipole moment (Debye).

^e J.A. Riddick and W.B. Bunger, *Organic Solvents*, 3rd edn., Wiley-Interscience, New York, 1970.

^f 20 °C.

^g T. Wakabayashi, S. Oki, T. Omori and N. Sukuki, *J. Inorg. Nucl. Chem.* **26**, 2255 (1964).

water prior to use. The solvent parameters are compiled in Table 1.

Determination of distribution constants of B15C5

A 10 mL portion of an aqueous solution of B15C5 (8.2×10^{-4} – 1.0×10^{-2} M; $1 \text{ M} = 1 \text{ mol dm}^{-3}$) and an equal volume of an organic solvent in a stoppered glass tube (volume 30 mL) were shaken in a thermostated water bath for 2 h at 25 ± 0.2 °C and centrifuged. The B15C5 concentration in the aqueous phase was spectrophotometrically determined at 273 nm ($\epsilon = 2.51 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$). The distribution constants of B15C5 are summarized in Table 2.

Extraction of alkali metal picrates with B15C5

The experimental procedures were almost the same as those described in the previous papers [6,7]. Extractions were conducted at pH values > 11.0 at 25 ± 0.2 °C. Concentration ranges of B15C5, alkali metal hydroxides, and picric acid were 3.0×10^{-5} – 8.1×10^{-1} , $(1.7$ – $9.0) \times 10^{-2}$, and 4.2×10^{-3} – 2.4×10^{-2} M, respectively. 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 3.3×10^{-2} and 9.9×10^{-2} M throughout the extraction experiments. In blank experiments, there was no extraction in the absence of B15C5.

Table 2. Distribution constants for B15C5 and 1:1:1 B15C5-alkali metal picrate complexes at 25 °C

No.	Solvent ^a	$K_{D,L}^b$	$\log K_{D,L}$	$\log K_{D,MLA}$		
				Li	Na	K
1	DCM	$(2.64 \pm 0.08) \times 10^2$	2.422	3.7 ₀	3.1 ₃	5.0 ₅
2	CF	$(2.52 \pm 0.05) \times 10^2$	2.401	3.0 ₄	2.7 ₆	3.5 ₉
3	1,2-DCE	$(8.12 \pm 0.06) \times 10$	1.910	3.4 ₄	2.7 ₃	4.6 ₉
4	CBu	4.19 ± 0.09	0.622	1.1 ₂	0.7 ₆	1.8 ₂
5	BZ	$(1.43 \pm 0.03) \times 10$	1.155	1.6 ₄	1.4 ₂	1.9 ₉
6	TE	8.30 ± 0.23	0.92	1.3 ₄	1.1 ₆	1.6 ₅
7	<i>mX</i>	4.99 ± 0.12	0.70	1.0 ₇	0.9 ₀	1.4 ₃
8	CB	$(2.18 \pm 0.04) \times 10$	1.338	2.2 ₄	2.0 ₃	2.8 ₇
9	BB	$(2.29 \pm 0.08) \times 10$	1.360	2.2 ₀	2.0 ₆	2.7 ₈
10	<i>o</i> -DCB	$(2.30 \pm 0.01) \times 10$	1.362	2.4 ₉	2.1 ₅	3.6 ₂

^aFor abbreviations, see footnote to Table 1.

^bEach value is the average of 16–24 determinations. The uncertainty is the standard deviation.

Theory and results

When an aqueous phase of an alkali metal picrate (MA) and an organic phase of a crown ether (L) are equilibrated, the equilibrium constants are defined as

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

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

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

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

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

$$K_{\text{MA}} = [\text{MA}] / [\text{M}^+] [\text{A}^-], \quad (6)$$

where the subscript “o” and the lack of a subscript denote the organic and aqueous phase, respectively. The aqueous phase is always under strong alkaline conditions. The dissociation of MLA into ML^+ and A^- in the organic phases is neglected because of the low dielectric constants (ϵ_r) of the organic solvents used in this study. The overall extraction equilibrium constant (K_{ex}) can be written as

$$K_{\text{ex}} = K_{D,L}^{-1} K_{\text{ML}} K_{\text{MLA}} K_{D,MLA}, \quad (7)$$

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

$$D = [\text{MLA}]_o / ([\text{M}^+] + [\text{MA}] + [\text{ML}^+] + [\text{MLA}]). \quad (8)$$

When $[\text{M}^+] \gg [\text{MA}] + [\text{ML}^+] + [\text{MLA}]$, Equation (8) leads to

$$D = K_{\text{ex}}[L]_o[A^-]. \quad (9)$$

From the mass balances, $[M^+]$, $[L]_o$, and $[A^-]$ are given by

$$[M^+] = ([M]_t - [MLA]_o) / \{1 + a[L]_o + (K_{MA} + b[L]_o)[A^-]\}, \quad (10)$$

$$[L]_o = ([L]_t - [MLA]_o) / \{c + (a + b[A^-])[M^+]\}, \quad (11)$$

$$[A^-] = ([HA]_t - [MLA]_o) / \{1 + (K_{MA} + b[L]_o)[M^+]\}, \quad (12)$$

where $a = K_{D,L}^{-1}K_{ML}$, $b = K_{D,L}^{-1}K_{ML}K_{MLA}$, $c = 1 + K_{D,L}^{-1}$, and the subscript "t" designates the total concentration. As a first approximation, it was assumed that $1 \gg a[L]_o + (K_{MA} + b[L]_o)[A^-]$ (Equation (10)), $c + a[M^+] \gg b[M^+][A^-]$ (Equation (11)), and $1 + K_{MA}[M^+] \gg b[L]_o[M^+]$ (Equation (12)). The $[L]_o$ and $[A^-]$ values of Equation (9) were calculated on this assumption. Plots of $\log(D/[A^-])$ vs. $\log[L]_o$ always give a straight line with a slope of 1 in every case, showing that B15C5 forms a 1:1 complex with the M^+ ion and that the assumptions are valid. The first approximate K_{ex} for each system was determined on these assumptions.

The partition constants of the crown ether ($K_{D,L}$) and a neutral ion-pair complex MLA ($K_{D,MLA}$) are estimated by Equations (13) and (14) derived from the regular solution theory [8]:

$$RT \ln K_{D,L}/(\delta_w - \delta_o) = V_L(\delta_w - 2\delta_L) + V_L\delta'_o, \quad (13)$$

$$RT \ln K_{D,MLA}/(\delta_w - \delta_o) = V_{MLA}(\delta_w - 2\delta_{MLA}) + V_{MLA}\delta'_o, \quad (14)$$

where $\delta'_o = \delta_o + RT(1/V_o - 1/V_w)/(\delta_w - \delta_o)$; δ_w , δ_o , δ_L , and δ_{MLA} denote the solubility parameters of water, the organic solvent, the crown ether, and MLA, respectively; V_L , V_o , V_w , and V_{MLA} designate the molar volumes of the crown ether, the organic solvent, water, and MLA, respectively. Combining Equations (13) and (14) leads to

$$\log K_{D,MLA} = \{V_{MLA}(\delta_w + \delta'_o - 2\delta_{MLA})/V_L(\delta_w + \delta'_o - 2\delta_L)\} \log K_{D,L}. \quad (15)$$

By adding $\log K_{MLA}$ to both sides of Equations (15), Equation (16) is obtained [9].

$$\log K_{\text{ex,ip}} = \{V_{MLA}(\delta_w + \delta'_o - 2\delta_{MLA})/V_L(\delta_w + \delta'_o - 2\delta_L)\} \log K_{D,L} + \log K_{MLA}. \quad (16)$$

When δ_{MLA} is nearly equal to δ_L , Equation (16) leads to

$$\log K_{\text{ex,ip}} = (V_{MLA}/V_L) \log K_{D,L} + \log K_{MLA}. \quad (17)$$

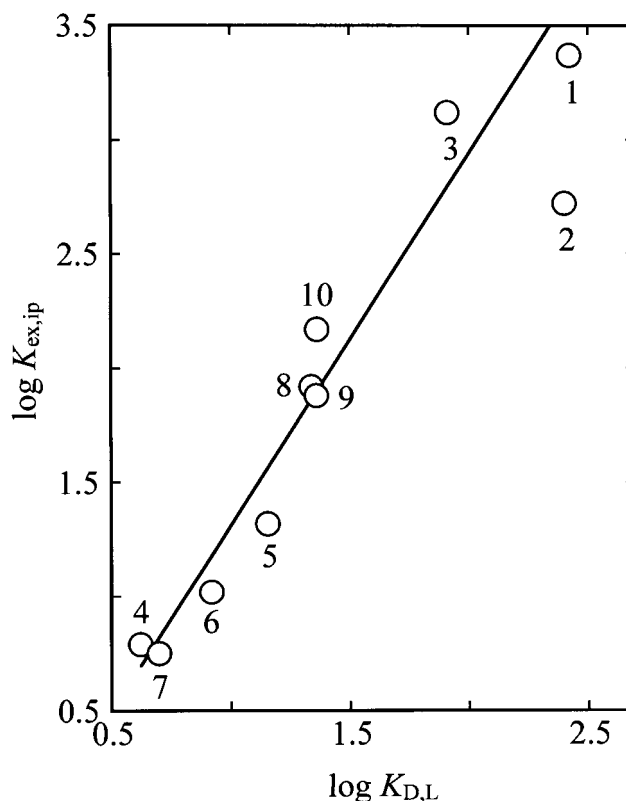


Figure 1. Plots of $\log K_{\text{ex,ip}}$ versus $\log K_{D,L}$ for the B15C5-lithium picrate system. The numbers for different solvents are given in Table 1.

Plots of the first approximate $\log K_{\text{ex,ip}}$ against $\log K_{D,L}$ show a good linear relationship for the respective alkali metals, except for CF (Figures 1–3). The first approximate $\log K_{MLA}$ values were obtained from the intercepts of the $\log K_{\text{ex,ip}}$ vs. $\log K_{D,L}$ plots. The second approximate $[A^-]$ value was calculated from Equation (12) by using the first approximate values of $[M^+]$, $[L]_o$, and K_{MLA} . The final $[M^+]$, $[L]_o$, $[A^-]$, K_{MLA} , and K_{ex} values were calculated from Equations (1), (7), (10), (11), (12), and (17) by the successive-approximation method. The $\log K_{\text{ex}}$ and $\log K_{MLA}$ values are listed in Tables 3 and 4, respectively. A good linear relationship is also observed for the plots of the final $\log K_{\text{ex,ip}}$ vs. $\log K_{D,L}$ for the respective alkali metals except for CF. The correlation coefficients for the Li, Na, and K systems are 0.976, 0.976, and 0.948, respectively.

Discussion

The $RT \ln K_{D,L}/(\delta_w - \delta_o)$ against δ'_o plots for B15C5 in Figure 4 show a good linear relationship, except for CF. The correlation coefficient $r = 0.960$ for B15C5 is much higher than that for 15C5, $r = 0.869$ [10]. This is ascribed to the greatly decreased specific interaction of B15C5 with water and some of the diluents by the benzo group and to the more rigid structure of B15C5 compared with 15C5. The positive deviation of CF is lower for B15C5 than for 15C5 [10], reflecting the reduced hydrogen bonding with CF by the benzo group from 15C5 to B15C5. From the slope and the intercept, the V and δ values of B15C5 obtained are 237 ± 26

Table 3. Extraction equilibrium constants for 1:1 B15C5-alkali metal picrate complexes at 25 °C

No.	Solvent ^a	log K_{ex}^b			log $K_{ex,ip}$		
		Li	Na	K	Li	Na	K
1	DCM	1.720 ± 0.006	3.821 ± 0.009	3.73 ± 0.03	3.3 ₇	5.7 ₈	5.7 ₇
2	CF	1.090 ± 0.010	3.485 ± 0.014	2.29 ± 0.03	2.7 ₂	5.4 ₂	4.3 ₁
3	1,2-DCE	1.982 ± 0.011	3.943 ± 0.013	3.88 ± 0.03	3.1 ₂	5.3 ₉	5.4 ₁
4	CBu	0.940 ± 0.016	3.261 ± 0.006	2.30 ± 0.02	0.7 ₉	3.4 ₂	2.5 ₄
5	BZ	0.932 ± 0.004	3.378 ± 0.010	1.93 ± 0.01	1.3 ₂	4.0 ₈	2.7 ₁
6	TE	0.865 ± 0.006	3.357 ± 0.006	1.83 ± 0.04	1.0 ₂	3.8 ₂	2.3 ₇
7	<i>m</i> X	0.815 ± 0.010	3.322 ± 0.004	1.83 ± 0.01	0.7 ₅	3.5 ₆	2.1 ₅
8	CB	1.345 ± 0.002	3.813 ± 0.011	2.63 ± 0.04	1.9 ₂	4.6 ₉	3.5 ₉
9	BB	1.291 ± 0.011	3.821 ± 0.008	2.52 ± 0.01	1.8 ₈	4.7 ₂	3.5 ₀
10	<i>o</i> -DCB	1.575 ± 0.012	3.908 ± 0.008	3.36 ± 0.02	2.1 ₇	4.8 ₁	4.3 ₄

^a For abbreviations, see footnote to Table 1.

^b Each value is the average of 10–20 determinations. The uncertainty is the standard deviation.

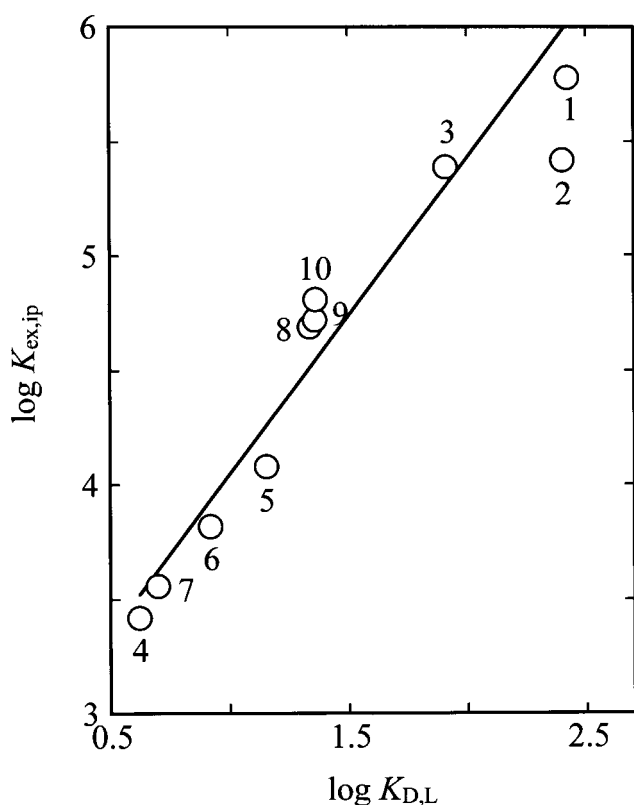


Figure 2. Plots of log $K_{ex,ip}$ versus log $K_{D,L}$ for the B15C5-sodium picrate system. The numbers for different solvents are given in Table 1.

and 11.4 ± 0.1 , respectively. The experimental V_{B15C5} value is consistent with the calculated one, $232 \text{ cm}^3 \text{ mol}^{-1}$, from molar volume group contributions [11]. The experimental V_L value is larger for B15C5 than for 15C5 ($189 \text{ cm}^3 \text{ mol}^{-1}$ [10]). The log $K_{D,L}$ value of B15C5 is always much greater than that of 15C5 [10] for the diluents used in this study. Equation (13) is transformed into

$$RT \ln(K_{D,B15C5}/K_{D,15C5}) = (\delta_w - \delta_o)\{(V_{B15C5} - V_{15C5})(\delta'_o - 5.25) + 2(\delta_{15C5} - \delta_{B15C5})V_{15C5}\}. \quad (18)$$

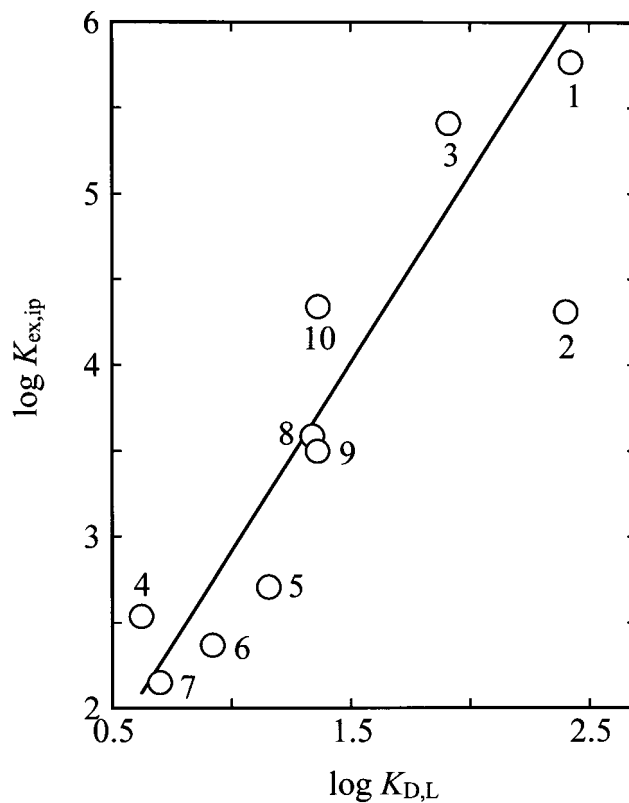


Figure 3. Plots of log $K_{ex,ip}$ versus log $K_{D,L}$ for the B15C5-potassium picrate system. The numbers for different solvents are given in Table 1.

Owing to the benzo group, the V and δ values are larger and smaller, respectively, for B15C5 than for 15C5. The δ'_o value of the diluent employed in this study is greater than 5.25 ($= -\delta_w + 2\delta_L = -\delta_w + 2\delta_{MLA}$). Therefore, it can be seen from Equation (18) that the lipophilicity is higher for B15C5 than for 15C5 ($\delta_w \gg \delta_o$ (Table 1)).

The log $K_{D,MLA}$ values for B15C5 calculated by Equation (7) are summarized in Table 2. For respective Figures 5–7, a good linear relationship is observed between $RT \ln K_{D,MLA}/(\delta_w - \delta_o)$ and δ'_o , except for CF in Figures 5 and 6. Except for CF, the correlation coefficients for Li, Na, and K are 0.958, 0.981, and 0.925, respectively. The size-matched Na(B15C5)A complex obeys the regular solu-

Table 4. Fundamental equilibrium constants in water at 25 °C

	M		
	Li	Na	K
$\log K_{MA}^a$	1.13	1.38	1.64
L = B15C5			
$\log K_{MLA}$	-0.32 ± 0.22	2.66 ± 0.19	0.71 ± 0.47
$\log K_{ML}$	0.76^b	0.45^b	0.38^c
L = 15C5			
$\log K_{MLA}^d$	–	4.43 ± 0.27	3.27 ± 0.42
$\log K_{ML}^e$	–	0.70	0.74

The uncertainty is the standard deviation.

^aT. Iwachido, *Bull. Chem. Soc. Jpn.* **45**, 432 (1972).

^bY. Takeda, M. Tanaka, H. Yamada and S. Katsuta, *J. Coord. Chem.* (2002) in press.

^cR.M. Izatt, R.E. Terry, D.P. Nelson, Y. Chan, D.J. Eatough, J.S. Bradshaw, L.D. Hansen and J.J. Christensen, *J. Am. Chem. Soc.* **98**, 7626 (1976).

^dRef. [3].

^eR.M. Izatt, R.E. Terry, B.L. Haymore, L.D. Hansen, N.K. Dalley, A.G. Avondet and J.J. Christensen, *J. Am. Chem. Soc.* **98**, 7620 (1976).

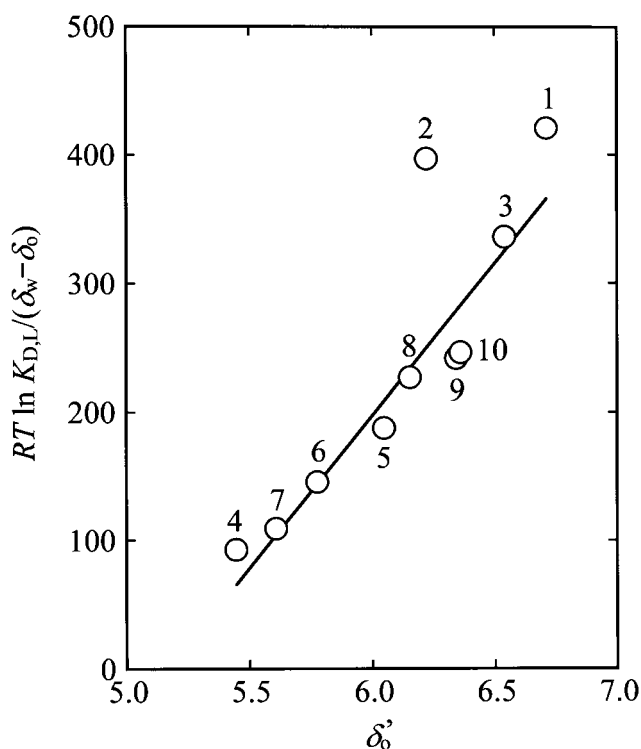


Figure 4. Plots of $RT \ln K_{D,L}/(\delta_w - \delta_0)$ versus δ'_0 for B15C5. The numbers for different solvents are given in Table 1.

tion theory better than the size-mismatched Li(B15C5)A and K(B15C5)A complexes. Because the Na^+ ion is most effectively shielded by B15C5 from surrounding solvents, specific solute-solvent interaction other than dispersion force is most greatly decreased. The M(B15C5)A complex follows the regular solution theory better than the corresponding M(15C5)A one ($r(\text{Na}) = 0.921$, $r(\text{K}) = 0.880$ [3]). This is due to the greatly reduced specific interaction of the MLA complex with water and some of the diluents by the benzo group from L = 15C5 to L = B15C5 and to the more rigid

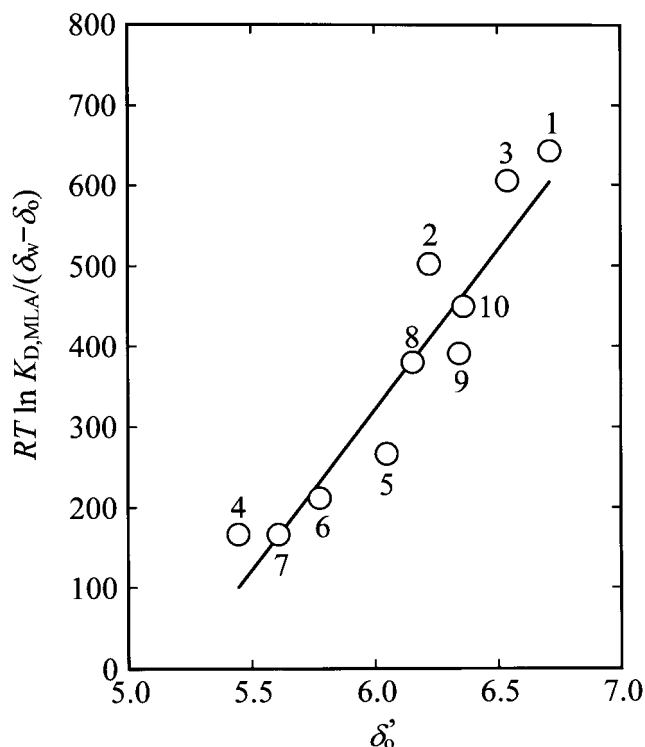


Figure 5. Plots of $RT \ln K_{D,MLA}/(\delta_w - \delta_0)$ versus δ'_0 for a B15C5-lithium picrate complex. The numbers for different solvents are given in Table 1.

Table 5. Molar volumes and solubility parameters for B15C5, 15C5, and their 1:1:1 complexes with alkali metal picrates at 25 °C

L	MLA			
	Li	Na	K	
L = B15C5				
V	237 ± 26	398 ± 45	346 ± 26	533 ± 83
δ	11.4 ± 0.1	11.4 ± 0.1	11.4 ± 0.1	11.4 ± 0.1
L = 15C5 ^a				
V	189 ± 34	–	210 ± 34	374 ± 76
δ	12.0 ± 0.1	–	12.0 ± 0.1	12.0 ± 0.1

The uncertainty is the standard deviation.

^a Ref. [3].

MLA structure of B15C5 compared with 15C5. Except for CF, the V and δ values for the M(B15C5)A complex were determined from the slope and the intercept, respectively. They are compiled in Table 5. The δ values of B15C5 and the M(B15C5)A complexes are identical. The validity of Equation (17) is verified.

Table 2 shows that the M(B15C5)A complex is always more lipophilic than B15C5 itself. This is entirely attributable to the larger V value of M(B15C5)A compared with B15C5 because $\delta_w > \delta_0$ and the δ'_0 value of every diluent used in this study is higher than 5.25 [12]. The $V_{M(B15C5)A}$ -value order is $\text{Na}^+ < \text{Li}^+ \ll \text{K}^+$. The $V_{M(B15C5)A}$ value is smaller for the most size-matched Na^+ ion than for the size-mismatched alkali metal ions. The same trend is found for 15C5 [3]. For every diluent, the $K_{D,M(B15C5)A}$ -value order is $\text{Na}^+ < \text{Li}^+ < \text{K}^+$ (Figure 8). This is completely determined by the $V_{M(B15C5)A}$ -value order ($\text{Na} < \text{Li} \ll \text{K}$), because $\delta_w > \delta_0$ and the δ'_0 value of the diluent is larger than 5.25

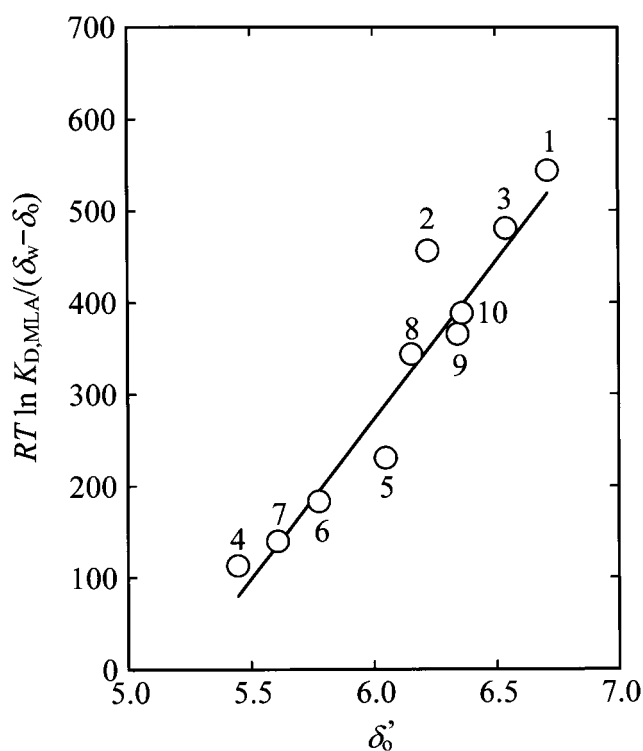


Figure 6. Plots of $RT \ln K_{D,MLA}/(\delta_w - \delta_0)$ versus δ'_0 for a B15C5-sodium picrate complex. The numbers for different solvents are given in Table 1.

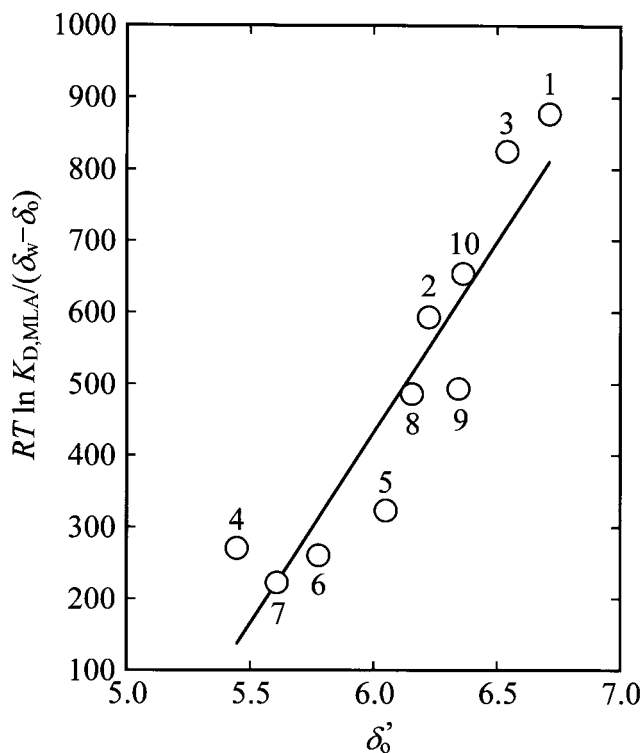


Figure 7. Plots of $RT \ln K_{D,MLA}/(\delta_w - \delta_0)$ versus δ'_0 for a B15C5-potassium picrate complex. The numbers for different solvents are given in Table 1.

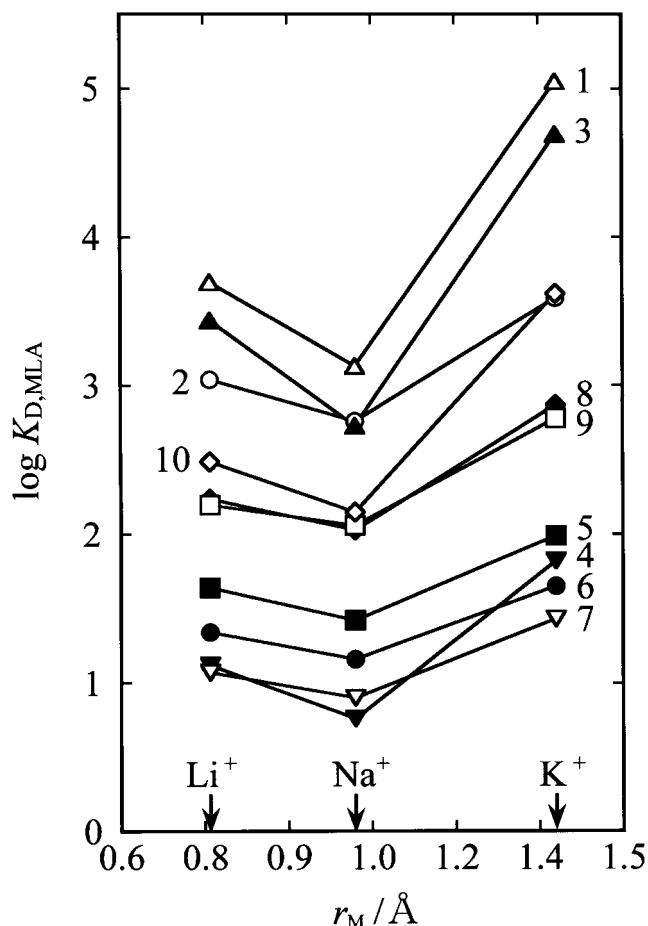


Figure 8. Plots of $\log K_{D,MLA}$ versus effective ionic radii (r_M) of alkali metals for the B15C5 system. The numbers for different solvents are given in Table 1.

[13]. Except for CF and CBU, the $\log K_{D,KLA}/\log K_{D,LiLA}$ and $\log K_{D,LiLA}/\log K_{D,NaLA}$ values of B15C5 are 1.21–1.45 and 1.07–1.26, respectively. The former and the latter are consistent with the V_{KLA}/V_{LiLA} (1.34) and V_{LiLA}/V_{NaLA} (1.15) values of B15C5, respectively [13]. For the same alkali metal ion, the benzo group increases the V_{MLA} value, and decreases the δ_{MLA} value from 15C5 to B15C5. This results in the fact that the $K_{D,M(B15C5)A}$ value is much greater than the corresponding $K_{D,M(15C5)A}$ one [14]. Among all the $M(B15C5)A$ complexes, the V_{MLA} value of the most size-matched Na^+ ion which has the greatest K_{MLA} value is the smallest. The same holds also for 15C5 [3].

Table 4 shows that the order of increasing K_{MA} value is $Li^+ < Na^+ < K^+$. Stronger hydration of the alkali metal ion causes a smaller K_{MA} value. The $K_{M(B15C5)A}$ value increases in the order $Li^+ < K^+ \ll Na^+$. The $K_{M(B15C5)A}$ value of the most size-matched Na^+ ion is the greatest. It has been reported that the better the alkali metal ion fits into the 15C5 cavity, the more water molecules bound to the cation are liberated [3]. This is also true for the case of B15C5. The largest $K_{Na(B15C5)A}$ value is due to the most effective dehydration of the Na^+ ion upon complexation. This is supported by the fact that, for Na^+ , the $\log K_{M(B15C5)A}$ value is larger than the $\log K_{MA}$ one, but the reverse is true for Li^+ and K^+ . In the cases of Li^+ and K^+ , owing to the remaining water

molecules bound to the cation in the B15C5 cavity and the hindrance caused by the benzo group, the $K_{M(B15C5)A}$ value is lower than the corresponding K_{MA} value. The $V_{M(B15C5)A}$ value is larger for Li and K than for Na. There exists a close relation between the magnitude of V_{MLA} and that of K_{MLA} in cases where the conformations of the MLA complexes of the same crown ether are similar. From 15C5 to B15C5, the benzo group considerably decreases the K_{MLA} value for the same alkali metal ion.

The $K_{D,B15C5}$ and $K_{D,M(B15C5)A}$ values increase in the order, B15C5: CBU < mX < TE < BZ < CB \leq BB \approx *o*-DCB < 1,2-DCE < CF \leq DCM, Li(B15C5)A: $mX \approx$ CBU < TE < BZ < BB \approx CB < *o*-DCB < CF < 1,2-DCE < DCM, Na(B15C5)A: CBU < mX < TE < BZ < CB \approx BB \leq *o*-DCB < 1,2-DCE \approx CF < DCM, K(B15C5)A: mX < TE < CBU < BZ < BB \leq CB < CF \approx *o*-DCB < 1,2-DCE < DCM.

Equations (13) and (14) are transformed into Equations (19) and (20), respectively.

$$RT \ln K_{D,L} = V_L\{(\delta_w - \delta_L)^2 - (\delta_o - \delta_L)^2 + RT(V_o^{-1} - V_w^{-1})\}, \quad (19)$$

$$RT \ln K_{D,MLA} = V_{MLA}\{(\delta_w - \delta_{MLA})^2 - (\delta_o - \delta_{MLA})^2 + RT(V_o^{-1} - V_w^{-1})\}. \quad (20)$$

The nearer to the value of δ_L or δ_{MLA} the δ_o value is and the smaller the V_o value, the larger the value of $K_{D,L}$ or $K_{D,MLA}$. The δ_o values of DCM and 1,2-DCE are not as similar to the δ_{B15C5} and $\delta_{M(B15C5)A}$ values as those of *o*-DCB and BB. However, the B15C5 and M(B15C5)A complexes are most distributed into DCM and 1,2-DCE, except for the partition into CF of B15C5 and Na(B15C5)A. This is attributable to the fact that DCM and 1,2-DCE have the largest δ_o values omitting *o*-DCB and BB and the smallest V_o values (Table 1). For the same alkali metal, the $K_{D,M(B15C5)A}$ value of BB is nearly equal to that of CB. The same is true for the $K_{D,B15C5}$ values. This is caused by the slightly larger δ_o and V_o values of BB compared with CB and their nearly equal μ values. Although the V_o value is smaller for BZ than for CB and BB, the $K_{D,B15C5}$ and $K_{D,M(B15C5)A}$ values are lower for BZ than for CB and BB. This is ascribed to the smaller δ_o value of BZ compared with CB and BB. The δ_o and V_o values of mX , TE, and BZ increase in the order $mX \leq$ TE < BZ and BZ < TE < mX , respectively, resulting in the order of the increasing $K_{D,B15C5}$ and $K_{D,M(B15C5)A}$ values mX < TE < BZ. From B15C5 to M(B15C5)A, the polarity is expected to become greater. The more size-mismatched the alkali metal ion is, the more the M(B15C5)A complex is expected to be polarized; the B15C5 complex with the size-mismatched larger K^+ ion is considered to be more polarized compared with the Li^+ and Na^+ complexes. It thus appears that the highly polarized M(B15C5)A complex is more stabilized in the order Na < Li < K by CBU with the second largest dipole moment (Table 1). This is responsible for the following facts. For CBU, mX , and TE, both the $K_{D,B15C5}$ -

and $K_{D,Na(B15C5)A}$ -value orders are CBU < mX < TE; however, the $K_{D,M(B15C5)A}$ -value orders for Li and K are $mX \approx$ CBU < TE and mX < TE < CBU, respectively. Both the δ_o and V_o values of BB are close to those of *o*-DCB; the $K_{D,M(B15C5)A}$ value of the same alkali metal for BB is nearly equal to (Na) or smaller than that for *o*-DCB (Li, K); the difference in the $K_{D,M(B15C5)A}$ value between BB and *o*-DCB increases in the order Na < Li < K. The $K_{D,B15C5}$ values for BB and *o*-DCB are equal. The additional stabilization of the M(B15C5)A complex by dipole-dipole interaction is also found for the *o*-DCB-Li and -K systems, particularly, remarkable for the latter. The dipole moment of *o*-DCB is the highest (Table 1). Similar trends for CBU and *o*-DCB are observed for some cases of 15C5 [3], 16-crown-5 [15], and 18-crown-6 [6]. The $RT \ln K_{D,M(B15C5)A}/(\delta_w - \delta_o)$ value of the increment, which is caused by the dipole-dipole interaction, to the $RT \ln K_{D,M(B15C5)A}$ value estimated based on the regular solution theory is much greater for *o*-DCB than for CBU because the dipole moment is higher for *o*-DCB than for CBU and the $\delta_w - \delta_o$ value is smaller for *o*-DCB (7.6) than for CBU (9.2) (Equation (14)). Therefore, the slope of the $RT \ln K_{D,M(B15C5)A}/(\delta_w - \delta_o)$ vs. δ'_o plots becomes unexpectedly steep owing to the larger δ'_o value of *o*-DCB compared with CBU, resulting in the greater than expected $V_{M(B15C5)A}$ value. This is responsible for the fact that the V value of the K(B15C5)A complex which is considered to be most polarized is unexpectedly much the largest. The greater $V_{M(B15C5)A}$ value of Li is caused by the higher polarization of Li(B15C5)A and the higher hydration of $Li(B15C5)^+$ compared with Na. The latter is supported by the fact that $K_{Li(B15C5)A} \ll K_{Na(B15C5)A}$.

Every alkali metal picrate is most extracted into 1,2-DCE with B15C5 among all the diluents. This is due to the highest $\log K_{D,MLA} - \log K_{D,L}$ value of 1,2-DCE because both K_{ML} and K_{MLA} are independent of the diluent. The signs of $\log K_{D,B15C5}$ and $\log K_{D,M(B15C5)A}$ for a given diluent are the same. Equation (7) shows that $K_{D,B15C5}$ and $K_{D,M(B15C5)A}$ related to partition behavior cancel each other. Thus, the magnitude of $\log K_{ex}$ for Na is determined largely by the $\log K_{M(B15C5)A}$ value; that for Li is mainly by the $\log K_{D,M(B15C5)A} - \log K_{D,B15C5}$ value or by both the $\log K_{D,M(B15C5)A} - \log K_{D,B15C5}$ and $\log K_{M(B15C5)}$ values; that for K is largely by the $\log K_{D,M(B15C5)A} - \log K_{D,B15C5}$ value or by both the $\log K_{D,M(B15C5)A} - \log K_{D,B15C5}$ and $\log K_{M(B15C5)A}$ values.

For every diluent, the K_{ex} and $K_{D,MLA}$ values of B15C5 increase in the order $Li^+ < K^+ < Na^+$ and $Na^+ < Li^+ < K^+$, respectively. K_{ML} and K_{MLA} values of B15C5 increase in the order $K^+ \leq Na^+ < Li^+$ and $Li^+ < K^+ \ll Na^+$, respectively. The $K_{D,MLA}$ makes an unfavorable contribution to the Na^+ extraction-selectivity of B15C5 because of the smallest $V_{Na(B15C5)A}$ value; K_{ML} makes a small contribution and an unfavorable one to the extraction selectivity of B15C5 for Na^+ over K^+ and Li^+ , respectively. The Na^+ extraction-selectivity of B15C5 is determined completely by much the highest $K_{Na(B15C5)A}$ value (Figure 9).

The Na^+ extraction-selectivity of B15C5 varies with the diluent (Table 3). The highest Na^+ extraction-selectivity is

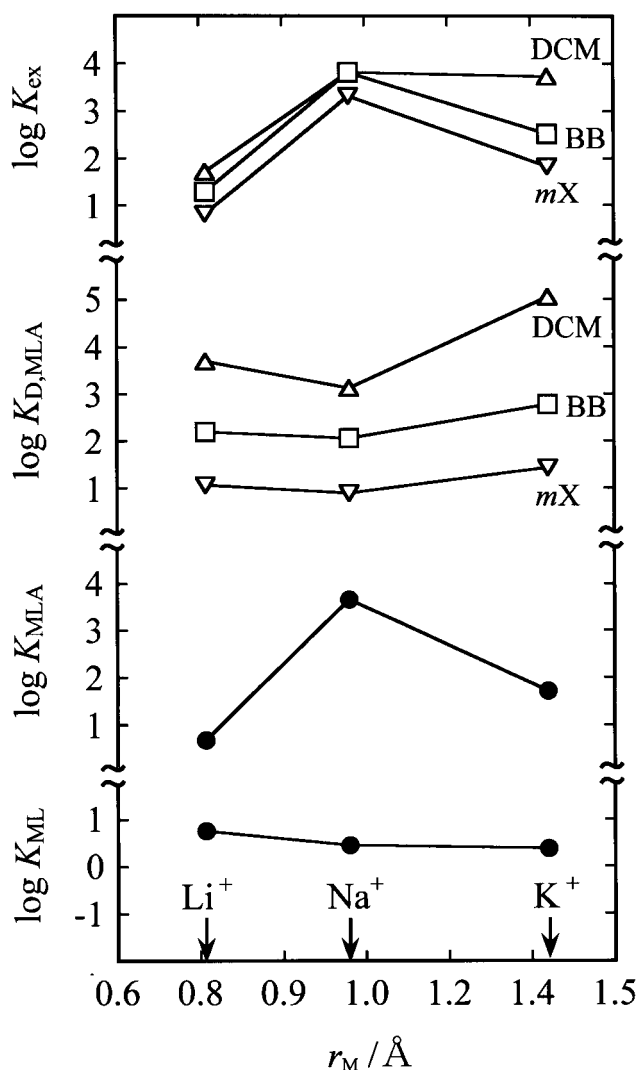


Figure 9. Plots of $\log K_{\text{ex}}$, $\log K_{\text{D,MLA}}$, $\log K_{\text{MLA}}$, and $\log K_{\text{ML}}$ versus effective ionic radii (r_{M}) of alkali metals for the B15C5 system.

observed for TE and *mX*, and the lowest for 1,2-DCE and DCM. Equation (21) is derived from Equation (14).

$$RT \ln(K_{\text{D,MLA}}/K_{\text{D,NaLA}}) = (\delta_{\text{w}} - \delta_{\text{o}})(V_{\text{MLA}} - V_{\text{NaLA}})(\delta'_{\text{o}} - 5.25), \quad (21)$$

where M = Li or K. Tables 1 and 5 show that $\delta_{\text{w}} - \delta_{\text{o}} > 0$, $V_{\text{MLA}} - V_{\text{NaLA}} > 0$, and $\delta'_{\text{o}} - 5.25 > 0$. The diluent having the smaller δ'_{o} value such as TE and *mX* decreases the $K_{\text{D,MLA}}/K_{\text{D,NaLA}}$ value, resulting in the enhancement of the Na^+ extraction-selectivity of B15C5 because the formation processes in water of the complex ion ML^+ and the ion pair MLA are common to every overall extraction system. The opposite holds for the diluent having a larger δ'_{o} value such as 1,2-DCE and DCM.

$$\begin{aligned} & \{\log K_{\text{ex}}(\text{Na}) - \log K_{\text{ex}}(\text{K})\}_{\text{B15C5}} - \{\log K_{\text{ex}}(\text{Na}) \\ & \quad - \log K_{\text{ex}}(\text{K})\}_{15\text{C5}} \\ & = 0.90 + \{[\log K_{\text{D,Na(B15C5)A}} - \log K_{\text{D,K(B15C5)A}}] \\ & \quad - [\log K_{\text{D,Na(15C5)A}} - \log K_{\text{D,K(15C5)A}}]\} \\ & = 0.90 + (\delta_{\text{w}} - \delta_{\text{o}})[\{V_{\text{Na(B15C5)A}} - V_{\text{K(B15C5)A}}\}(\delta'_{\text{o}} \\ & \quad - 5.25) - \{V_{\text{Na(15C5)A}} - V_{\text{K(15C5)A}}\}(\delta'_{\text{o}} \\ & \quad - 6.45)]/2.303RT \\ & = 0.90 + (\delta_{\text{w}} - \delta_{\text{o}})\{-187(\delta'_{\text{o}} - 5.25) + 164(\delta'_{\text{o}} - 5.25) \\ & \quad - 164 \times 1.20\}/2.303RT, \end{aligned} \quad (22)$$

where $0.90 = \{\log K_{\text{Na(B15C5)}} - \log K_{\text{K(B15C5)}}\} - \{\log K_{\text{Na(15C5)}} - \log K_{\text{K(15C5)}}\} (=0.11) + \{\log K_{\text{Na(B15C5)A}} - \log K_{\text{K(B15C5)A}}\} - \{\log K_{\text{Na(15C5)A}} - \log K_{\text{K(15C5)A}}\} (=0.79)$ and $\{\log K_{\text{ex}}(\text{Na}) - \log K_{\text{ex}}(\text{K})\}_{\text{B15C5}}$ (or 15C5) denotes the difference in the $\log K_{\text{ex}}$ value between Na and K for B15C5 (or 15C5). The $\log K_{\text{ex}}(\text{Na}) - \log K_{\text{ex}}(\text{K})$ value for every diluent used in this study, omitting CF, is lower for B15C5 than for 15C5 [3]; the Na^+ extraction-selectivity over K^+ of B15C5 is inferior to that of 15C5. The value of $\{\log K_{\text{D,Na(B15C5)A}} - \log K_{\text{D,K(B15C5)A}}\} - \{\log K_{\text{D,Na(15C5)A}} - \log K_{\text{D,K(15C5)A}}\}$ varies with the diluent from -1.71 to -1.33 , except for CF. Both the values of $\{\log K_{\text{Na(B15C5)}} - \log K_{\text{K(B15C5)}}\} - \{\log K_{\text{Na(15C5)}} - \log K_{\text{K(15C5)}}\}$ and $\{\log K_{\text{Na(B15C5)A}} - \log K_{\text{K(B15C5)A}}\} - \{\log K_{\text{Na(15C5)A}} - \log K_{\text{K(15C5)A}}\}$ cause higher Na^+ extraction-selectivity over K^+ of B15C5 compared with 15C5. However, they are canceled by the value of $\{\log K_{\text{D,Na(B15C5)A}} - \log K_{\text{D,K(B15C5)A}}\} - \{\log K_{\text{D,Na(15C5)A}} - \log K_{\text{D,K(15C5)A}}\}$, resulting in the lower Na^+ extraction-selectivity of B15C5 compared with 15C5, except for CF. Equation (22) shows that, in going from 15C5 to B15C5, the decreased Na^+ extraction-selectivity over K^+ is completely attributed to the decreased δ_{MLA} and the increased $|V_{\text{NaLA}} - V_{\text{KLA}}|$ values because the δ_{o} and δ'_{o} values of the diluent used in this study are always smaller and larger than the δ_{w} value and 5.25, respectively.

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9. The right-hand side of Equation (16) 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, and $C_{\text{o,L}}$ 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.
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12. $RT \ln(K_{D,MLA}/K_{D,L}) = (V_{MLA} - V_L)(\delta_w - \delta_o)(\delta_w + \delta'_o - 2\delta)$,
where $\delta = \delta_L = \delta_{MLA}$.
13. $RT \ln K_{D,MLA} = V_{MLA}(\delta_w - \delta_o)(\delta'_o - 5.25)$.
14. $RT \ln\{K_{D,M(B15C5)A}/K_{D,M(15C5)A}\} = (\delta_w - \delta_o)[\{V_{M(B15C5)A} - V_{M(15C5)A}\}(\delta'_o - 5.25) + 2\{\delta_{M(15C5)A} - \delta_{M(B15C5)A}\}V_{M(15C5)A}]$,
where the δ_o and δ'_o values of every diluent used in this study are smaller and larger than the δ_w value and 5.25, respectively.
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