



Extraction of Alkali Metal (Na—Cs) Picrates with Dibenzo-18-crown-6 into Various Organic Solvents. Elucidation of Fundamental Equilibria which Govern the Extraction-Ability and -Selectivity

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Abstract. In order to quantitatively investigate effects of the size, the structural rigidity, and the lipophilicity of dibenzo-18-crown-6 (DB18C6) on its extraction-ability and -selectivity for alkali metal ions, constants of the overall extraction (K_{ex}), the distribution for various diluents of low dielectric constants ($K_{D,MLA}$), and the aqueous ion-pair formation (K_{MLA}) of DB18C6-alkali metal (Na—Cs) picrate 1:1:1 complexes were determined at 25 °C; the partition constants of DB18C6 itself were also measured at 25 °C. The log K_{MLA} of Na, K, Rb, and Cs are -0.14 ± 0.11 , 1.30 ± 0.10 , 1.00 ± 0.09 , and 0.24 ± 0.11 , respectively. The partition behavior of DB18C6 and its 1:1:1 complexes with the alkali metal picrates can be clearly explained by regular solution theory, except for chloroform. The molar volumes and solubility parameters of DB18C6 and the 1:1:1 complexes were determined. A relation between molar volumes of the complexes and K_{MLA} is discussed. The magnitude of K_{ex} is largely determined by that of $K_{D,MLA}$. For every diluent, the extraction selectivity of DB18C6 increases in the order Na < Cs < Rb < K. The K extraction-selectivity of DB18C6 over Na is the highest among all the combinations of the two neighboring alkali metals in the periodic table. The extraction-ability and -selectivity for the alkali metal picrates and their change with the diluent of DB18C6 were completely elucidated by the four fundamental equilibria and regular solution theory.

Key words: solvent extraction, extractability, selectivity, fundamental equilibria, ion-pair formation constants in water, distribution constants, solvent effects, regular solution theory, molar volume, solubility parameter, dibenzo-18-crown-6, alkali metal picrates, complexes.

1. Introduction

It can be considered that the overall extraction equilibrium of a monovalent metal salt (MA) with an electroneutral ligand (L) into an organic solvent of low dielectric constant consists of four fundamental equilibria; (1) $L \rightleftharpoons L_o$, (2) $M^+ + L \rightleftharpoons ML^+$ in water, (3) $ML^+ + A^- \rightleftharpoons MLA$ in water, (4) $MLA \rightleftharpoons MLA_o$, where the subscript “o” denotes an organic phase. Regarding crown ethers, their distribution constants and complex-formation constants with metal ions in water can be measured in

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some cases, whereas the determination of ion-pair formation constants in water and the distribution constants of the complexes with metal salts (MLA) is difficult in most cases. However, the method of determining the ion-pair formation constant in water by solvent extraction has been established [1]. Moreover, the determination method with an ion-selective electrode has been reported [2]. By the ion-pair formation constant in water, the distribution constant of the ion-pair complex can be calculated from the other two fundamental equilibrium constants and the overall extraction constant. The distribution constants enable us to develop the field of liquid-liquid partition study of crown ether-metal salt complexes. The extraction-ability and -selectivity and the change in those with the diluent of a crown ether for metal salts can be quantitatively elucidated by the fundamental equilibrium constants. In the previous studies [1, 3, 4], constants of the overall extraction, the distribution, and the aqueous ion-pair formation of 18-crown-6 (18C6)- and benzo-18-crown-6 (B18C6)-alkali metal picrate 1:1:1 complexes were determined; partition constants of 18C6 and B18C6 were also measured. For both 18C6 and B18C6, the relatively large difference in the aqueous ion-pair formation constant between light (Li, Na) and heavy alkali metals (K, Rb, Cs) reflects the difference in the structure of the crown ether-alkali metal ion 1:1 complex between light and heavy alkali metals. The partition behavior of 18C6 and B18C6 and their 1:1:1 complexes with alkali metal picrates was clearly explained by regular solution theory [5]. Solvent effects on and the underlying equilibria governing the extraction-ability and -selectivity of 18C6 and B18C6 for alkali metal picrates were clarified.

In this study, in order to quantitatively investigate effects of the larger size, the higher structural rigidity and the greater lipophilicity of dibenzo-18-crown-6 (DB18C6) compared with 18C6 and B18C6 on the extraction-ability and -selectivity for alkali metal ions, constants of the overall extraction and the fundamental equilibria, except for the complex-formation constants in water, were determined and the overall extraction equilibrium constant was analyzed by the four underlying equilibrium constants.

2. Experimental

2.1. MATERIALS

Dibenzo-18-crown-6 (Nisso Co., Ltd.) was recrystallized more than twice from acetone and, prior to use, dried in a vacuum over diphosphorus pentoxide. The purity was checked by the melting point (157.1–161.1 °C). LiOH·H₂O, NaOH, KOH, and picric acid were analytical-grade reagents; the concentrations of their solutions were determined by neutralization titration. Rubidium and caesium hydroxides were of reagent grade; the concentrations of their solutions were determined by atomic absorption spectrophotometry. All of the organic solvents were analytical-grade reagents. 1,2-Dichloroethane was purified by distillation, but the others were not purified. They were washed three times with deionized water prior to use.

2.2. DETERMINATION OF DISTRIBUTION CONSTANTS OF DB18C6

A 5 to 10 mL portion of an organic solution of DB18C6 and 10 to 20 mL deionized water were placed in a stoppered glass tube (volume 30 mL), and shaken in a thermostated water bath for 2 h at 25 ± 0.2 °C. The concentration range of DB18C6 used for the determination of all the distribution constants was from 4.0×10^{-5} M (1 M = 1 mol dm⁻³) to 6.3×10^{-2} M. After centrifugation, DB18C6 in the aqueous phase was extracted into chloroform. A certain amount of the chloroform phase was transferred to a beaker and left until evaporation was complete. The residue in the beaker was dissolved in acetonitrile and the DB18C6 concentration was determined spectrophotometrically at 275 nm ($\epsilon = 5.89 \times 10^3$ cm⁻¹ M⁻¹). The distribution constants of DB18C6 are summarized in Table III.

2.3. EXTRACTION OF ALKALI METAL PICRATES WITH DB18C6

A 10 mL portion of an aqueous solution of alkali metal hydroxide (2.1×10^{-3} – 7.3×10^{-2} M) and picric acid (8.2×10^{-4} – 2.7×10^{-2} M) and an equal volume of an organic solution of DB18C6 (5.7×10^{-5} – 1.3×10^{-2} M) in a stoppered glass tube were agitated in a thermostated water bath at 25 ± 0.2 °C for 2 h and centrifuged. 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 5.8×10^{-2} and 7.6×10^{-2} M throughout the extraction experiments. The extractions were performed at pH 11.5–12.9. The picrate in the organic phase was back extracted into a 0.01 M NaOH aqueous solution. The picrate concentration was determined at 356 nm by spectrophotometry ($\epsilon = 1.44 \times 10^4$ cm⁻¹ M⁻¹). In blank experiments, no extraction was found in the absence of DB18C6.

3. Theory and Results

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

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

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

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

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

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

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

Table I. Solvent parameters at 25 °C

No.	Solvent ^a	δ^b	V^c	ϵ_r^d
1	DCM	9.7	63.9	8.93
2	CF	9.3	80.7	4.81 ^e
3	1,2-DCE	9.8	79.4	10.36
4	CBu	8.4	104	7.39 ^e
5	BZ	9.16	89.4	2.275
6	TE	8.93	106.9	2.379
7	<i>mX</i>	8.80	123.5	2.4
8	CB	9.5	102.1	5.62
9	BB	9.87	105	5.40
10	<i>o</i> -DCB	10.0	112.8	9.93
11	DBE	7.76	170.4	3.1
12	CTC	8.6	97.1	2.24 ^e
13	H ₂ O	17.55 ^f	18.1	–

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

^b Solubility parameter (cal^{1/2} cm^{-3/2}). Ref. [5]. A. F. M. Barton: *Chem. Rev.* **75**, 731 (1975).

^c Molar volume (cm³ mol⁻¹). D. R. Lide: *Handbook of Chemistry and Physics*, 75th edn., CRC Press, Boca Raton (1994–1995) (density).

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

^e 20 °C.

^f T. Omori, T. Wakahayashi, S. Oki, and N. Suzuki: *J. Inorg. Nucl. Chem.* **26**, 2265 (1964).

the subscript “o” and the lack of a subscript denoting 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

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

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

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

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

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

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. This shows that DB18C6 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 distribution constants of the crown ether ($K_{D,L}$) and a neutral ion-pair complex MLA ($K_{D,MLA}$) are estimated by the following equations derived from the regular solution theory [5]:

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

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

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 Equation (15), Equation (16) [6] is obtained.

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

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

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

Plots of the first approximate $\log K_{ex,ip}$ against $\log K_{D,L}$ show a very good linear relationship for the respective alkali metals, except for CF (Figures 1–4). The correlation coefficients for the Na, K, Rb, and Cs systems are 0.997, 0.996, 0.997, and 0.997, respectively. The first approximate $\log K_{MLA}$ values were obtained from

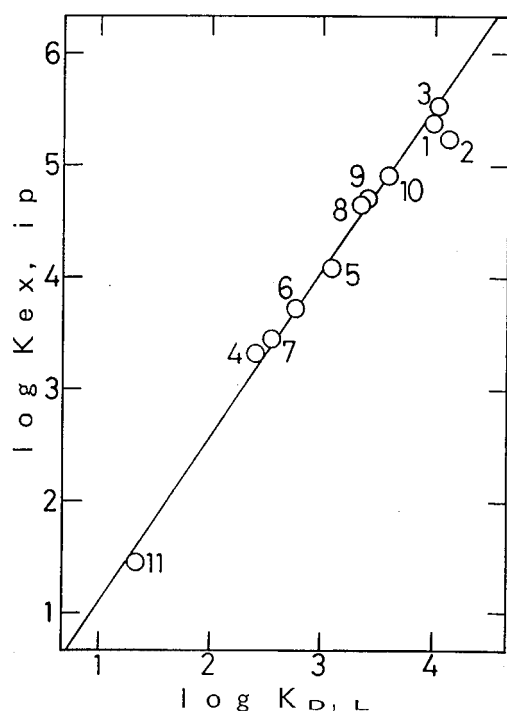


Figure 1. Plots of the first approximate $\log K_{ex,ip}$ vs. $\log K_{D,L}$ for the DB18C6-sodium picrate system. The numbers correspond to those in Table I.

the intercepts of the $\log K_{ex,ip}$ 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} were calculated from Equations (1), (7), (10), (11), (12), and (17) by the successive-approximation method. The $\log K_{ex}$ and $\log K_{MLA}$ values are summarized in Tables II and V, respectively. A very good linear relationship is also observed for the plots of the final $\log K_{ex,ip}$ vs. $\log K_{D,L}$ for the respective alkali metals except for CF. The correlation coefficients for the Na, K, Rb, and Cs systems are 0.996, 0.996, 0.998, and 0.997, respectively.

4. Discussion

Plots of $RT \ln K_{D,L}/(\delta_w - \delta_o)$ against δ'_o for DB18C6 in Figure 5 show a good linear relationship, except for CF (the correlation coefficient $r = 0.986$). The correlation coefficient approximates more and more closely to unity in the direction 18-crown-6 (18C6) ($r = 0.858$ [3]) \rightarrow benzo-18-crown-6 (B18C6) ($r = 0.948$ [4]) \rightarrow DB18C6; namely, the crown ether more closely obeys the regular solution theory with an increase in the number of benzo groups. The nearest r to unity of DB18C6 is attributed to the highest rigidity of the structure, the weakest specific interaction

Table II. Extraction equilibrium constants for 1:1:1 DB18C6-alkali metal picrate complexes at 25 °C

No.	Solvent	log K_{ex}^a				log $K_{ex,ip}$			
		Na	K	Rb	Cs	Na	K	Rb	Cs
1	DCM	2.990 ± 0.007	4.989 ± 0.005	4.662 ± 0.014	4.251 ± 0.013	5.81	7.30	7.56	7.40
2	CF	2.421 ± 0.014	4.700 ± 0.012	4.396 ± 0.004	3.828 ± 0.007	5.38	7.15	7.44	7.12
3	1,2-DCE	3.091 ± 0.011	5.031 ± 0.022	4.652 ± 0.018	4.338 ± 0.013	5.96	7.39	7.60	7.54
4	CBu	2.219 ± 0.016	4.327 ± 0.007	3.757 ± 0.008	3.217 ± 0.020	3.48	5.077	5.10	4.80
5	BZ	2.290 ± 0.012	4.471 ± 0.013	3.942 ± 0.013	3.393 ± 0.019	4.22	5.89	5.95	5.65
6	TE	2.251 ± 0.007	4.475 ± 0.007	3.867 ± 0.015	3.208 ± 0.015	3.86	5.58	5.56	5.15
7	<i>m</i> X	2.200 ± 0.009	4.415 ± 0.005	3.756 ± 0.019	2.972 ± 0.011	3.59	5.295	5.23	4.69
8	CB	2.599 ± 0.005	4.886 ± 0.010	4.420 ± 0.009	3.689 ± 0.016	4.80	6.58	6.70	6.22
9	BB	2.587 ± 0.011	4.906 ± 0.007	4.377 ± 0.015	3.730 ± 0.021	4.84	6.646	6.71	6.31
10	<i>o</i> -DCB	2.628 ± 0.010	4.925 ± 0.007	4.421 ± 0.009	3.961 ± 0.016	5.04	6.83	6.91	6.70
11	DBE	1.744 ± 0.013	3.577 ± 0.009	2.912 ± 0.020	2.141 ± 0.016	1.91	3.237	3.16	2.64

For abbreviations, see footnote to Table I. ^aEach value is the average of 10–21 measurements. The uncertainties are the standard deviations.

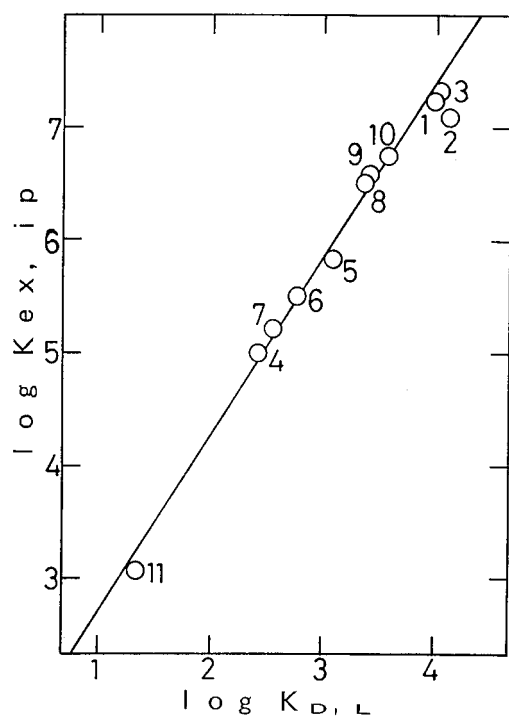


Figure 2. Plots of the first approximate $\log K_{ex,ip}$ vs. $\log K_{D,L}$ for the DB18C6-potassium picrate system. The numbers correspond to those in Table I.

of DB18C6 with some of the organic solvents and the smallest variation with the organic solvent of the number of water molecules attached to DB18C6. It can be seen from Figure 5 that CF shows the largest positive deviation due to the hydrogen bond between DB18C6 and CF. The deviation is smaller for DB18C6 than for 18C6 [3] and B18C6 [4], which reflects the greater decreased specific interaction with CF of DB18C6 by the two benzo groups. The V and δ of DB18C6 obtained from the slope and the intercept are 288 ± 16 and 10.9 ± 0.1 , respectively. The experimental V_{DB18C6} is almost identical with the calculated one ($296 \text{ cm}^3 \text{ mol}^{-1}$) from molar volume group contributions [7]. The experimental V_L value increases in the order V_{18C6} ($214 \text{ cm}^3 \text{ mol}^{-1}$ [3]) $< V_{B18C6}$ ($252 \text{ cm}^3 \text{ mol}^{-1}$ [4]) $< V_{DB18C6}$; the difference ($36 \text{ cm}^3 \text{ mol}^{-1}$) between V_{DB18C6} and V_{B18C6} is nearly equal to that ($38 \text{ cm}^3 \text{ mol}^{-1}$) between V_{B18C6} and V_{18C6} , as is to be expected. The differences are comparable to the difference ($25\text{--}30 \text{ cm}^3 \text{ mol}^{-1}$) in molar volume between a benzo group and an ethylene group [7]. $\log K_{D,L}$ is always much greater for DB18C6 than for 18C6 [3] and B18C6 [4]. Equation (13) is transformed into

$$\ln K_{D,L} = V_L(\delta_w - \delta_o)(\delta_w + \delta'_o - 2\delta_L)/RT. \quad (18)$$

Tables I and IV show that the $\delta_w - \delta_o$ and $\delta_w + \delta'_o - 2\delta_{DB18C6}$ values are both positive for every diluent; the smallest δ_{DB18C6} causes the greatest $\delta_w + \delta'_o - 2\delta_{DB18C6}$

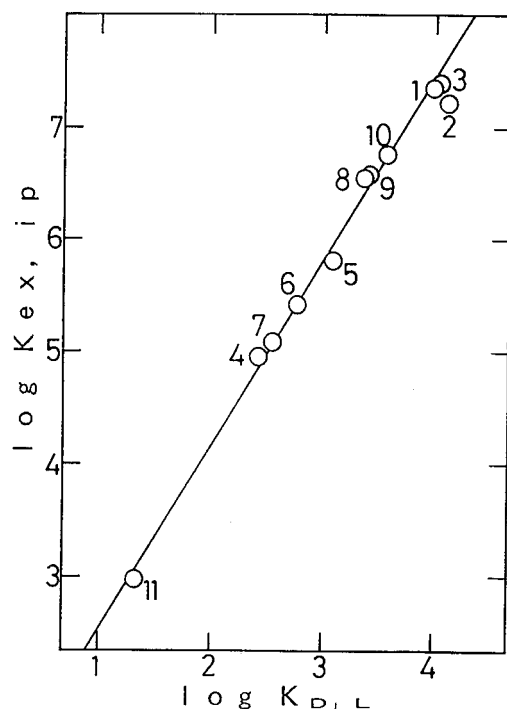


Figure 3. Plots of the first approximate $\log K_{ex,ip}$ vs. $\log K_{D,L}$ for the DB18C6-rubidium picrate system. The numbers correspond to those in Table I.

($\delta_{18C6} = 12.2$ [3], $\delta_{B18C6} = 11.4$ [4]); the V_{DB18C6} is the largest, resulting in the highest lipophilicity of DB18C6 (Equation (18)).

The $\log K_{D,MLA}$ values calculated from the $\log K_{ex,ip}$ and $\log K_{MLA}$ values are listed in Table III. From Figures 6–9, a good linear relationship is observed between $RT \ln K_{D,MLA}/(\delta_w - \delta_o)$ and δ'_o for the respective alkali metals. For K, Rb, and Cs, the largest deviation from the straight line is found for CF; for Na, it is for 1,2-DCE. The deviation of CF for the M(DB18C6)A system is smaller than that for the corresponding M(18C6)A [3] or M(B18C6)A system [4]. The specific interaction between MLA and CF is reduced with an increase in the number of benzo groups. Except for CF, the correlation coefficients (r) of Na, K, Rb, and Cs for the $RT \ln K_{D,M(DB18C6)A}/(\delta_w - \delta_o)$ vs. δ'_o plots are 0.983, 0.987, 0.987, and 0.984, respectively. The r value for the same alkali metal approximates more and more closely to unity in the direction M(18C6)A \rightarrow M(B18C6)A \rightarrow M(DB18C6)A [3, 4], similar to the case of free 18C6, B18C6, and DB18C6. The explanation for this is the same as that described above. The r value for M(DB18C6)A is almost constant regardless of the alkali metal, whereas that for M(18C6)A varies with the alkali metal (Na 0.919, K 0.949, Rb 0.920, Cs 0.943 [3]). This reflects the higher rigidity of DB18C6, and similar and more effective shielding of the alkali metal ion in the DB18C6 cavity compared with 18C6. The V and δ values for M(DB18C6)A were determined

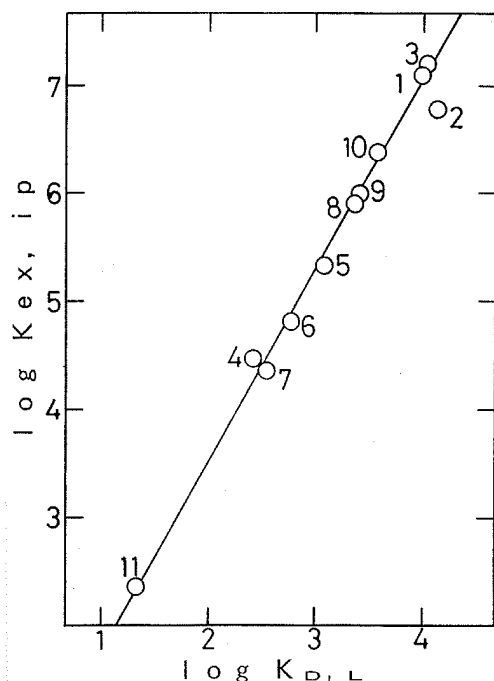


Figure 4. Plots of the first approximate $\log K_{ex,ip}$ vs. $\log K_{D,L}$ for the DB18C6-caesium picrate system. The numbers correspond to those in Table I.

from the slope and the intercept, respectively, except for CF. They are compiled in Table IV. The δ values of DB18C6 and the M(DB18C6)A complexes are the same, showing that the validity of Equation (17) is verified.

As is to be expected, V is much greater for the M(DB18C6)A complex than for uncomplexed DB18C6; V_{MLA} is larger for DB18C6 than for B18C6 and 18C6 [3, 4]. $K_{D,MLA}$ is always much larger for DB18C6 than for 18C6 [3] and B18C6 [4]. Equation (14) is transformed into

$$\ln K_{D,MLA} = V_{MLA}(\delta_w - \delta_o)(\delta_w + \delta'_o - 2\delta_{MLA})/RT. \quad (19)$$

From Tables I and IV, $\delta_w - \delta_o$ and $\delta_w + \delta'_o - 2\delta_{M(DB18C6)A}$ of Equation (19) are both positive for every diluent; the $\delta_w + \delta'_o - 2\delta_{M(DB18C6)A}$ value is the largest owing to the smallest $\delta_{M(DB18C6)A}$ value; $V_{M(DB18C6)A}$ is the greatest. These result in the highest lipophilicity of the M(DB18C6)A complex (Equation (19)). The M(DB18C6)A complex is more lipophilic than DB18C6. This is due to the larger $V_{M(DB18C6)A}$ than V_{DB18C6} because $\delta_{M(DB18C6)A} = \delta_{DB18C6}$.

$V_{M(DB18C6)A}$ increases in the order $Na < K < Rb < Cs$. Except for Na, the larger size-mismatched the alkali metal ion, the greater is $V_{M(DB18C6)A}$. A similar tendency is observed for 18C6 [3] and B18C6 [4]. Among the alkali metals, V_{NaLA} is the smallest for DB18C6, the second smallest for B18C6, and the third smallest for 18C6. This reflects the difference in conformation of the crown ether between

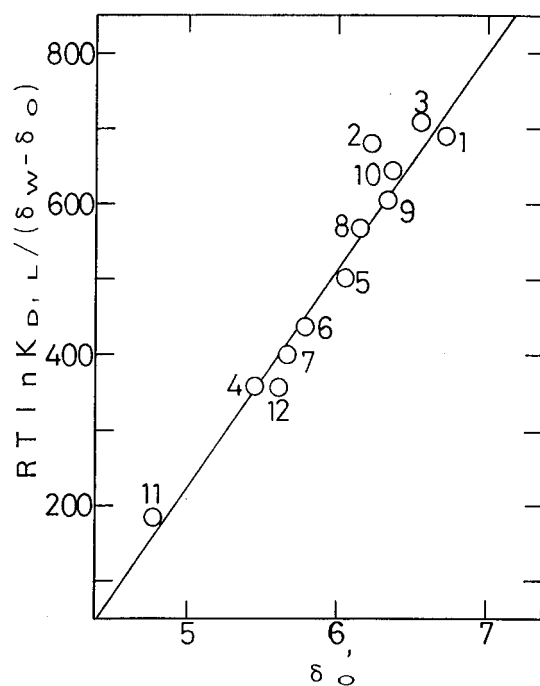


Figure 5. Plots of $RT \ln K_{D,L} / (\delta_w - \delta_o)$ vs. δ_o' for DB18C6. The numbers correspond to those in Table I.

Table III. Distribution constants for DB18C6 and 1:1:1 DB18C6 – alkali metal picrate complexes at 25 °C

No.	Solvent	$K_{D,L}^a$	$\log K_{D,L}$	$\log K_{D,MLA}$			
				Na	K	Rb	Cs
1	DCM	$(9.56 \pm 0.96) \times 10^3$	3.98	5.96	6.00	6.56	7.16
2	CF	$(1.34 \pm 0.22) \times 10^4$	4.12	5.53	5.85	6.43	6.87
3	1,2-DCE	$(1.06 \pm 0.05) \times 10^4$	4.026	6.11	6.09	6.60	7.30
4	CBu	$(2.66 \pm 0.09) \times 10^2$	2.424	3.63	3.78	4.09	4.56
5	BZ	$(1.22 \pm 0.03) \times 10^3$	3.087	4.37	4.59	4.95	5.41
6	TE	$(5.92 \pm 0.16) \times 10^2$	2.77	4.01	4.27	4.55	4.91
7	<i>m</i> X	$(3.54 \pm 0.05) \times 10^2$	2.548	3.74	3.99	4.22	4.45
8	CB	$(2.30 \pm 0.06) \times 10^3$	3.362	4.95	5.28	5.70	5.98
9	BB	$(2.58 \pm 0.07) \times 10^3$	3.410	4.99	5.35	5.70	6.07
10	<i>o</i> -DCB	$(3.75 \pm 0.13) \times 10^3$	3.57	5.19	5.52	5.91	6.46
11	DBE	$(2.12 \pm 0.04) \times 10$	1.327	2.06	1.94	2.16	2.40
12	CTC	$(2.17 \pm 0.05) \times 10^2$	2.335	–	–	–	–

For abbreviations, see footnote to Table I.

^aEach value is the average of 8–12 measurements. The uncertainties are the standard deviations.

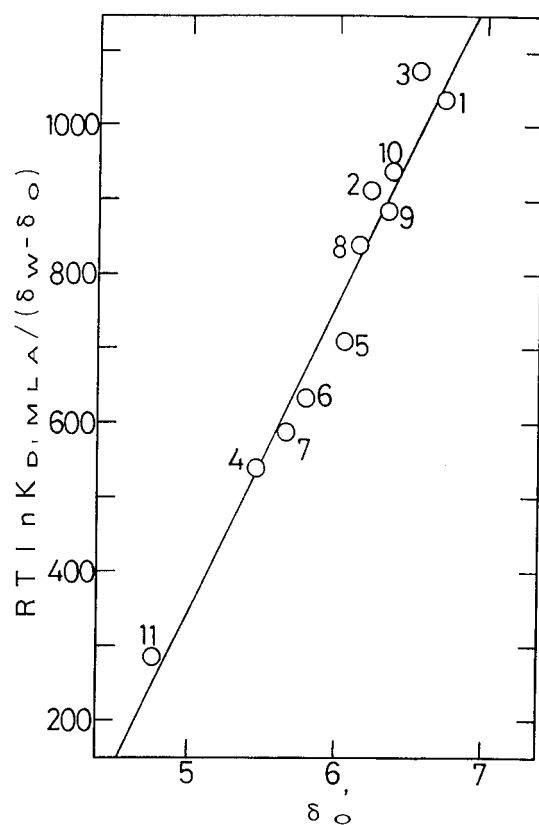


Figure 6. Plots of $RT \ln K_{D,MLA}/(\delta_w - \delta_o)$ vs. δ_o' for the DB18C6-sodium picrate complex. The numbers correspond to those in Table I.

Table IV. Molar volumes and solubility parameters for DB18C6, B18C6, 18C6, and their 1:1:1 complexes with alkali metal picrates

	L	MLA			
		Na	K	Rb	Cs
L = DB18C6					
V	288 ± 16	416 ± 27	432 ± 24	466 ± 26	505 ± 32
δ	10.9 ± 0.1	10.9 ± 0.1	10.9 ± 0.1	10.9 ± 0.1	10.9 ± 0.1
L = B18C6 ^a					
V	252 ± 28	366 ± 34	354 ± 32	393 ± 35	—
δ	11.4 ± 0.1	11.4 ± 0.1	11.4 ± 0.1	11.4 ± 0.1	—
L = 18C6 ^b					
V	214 ± 47	294 ± 48	248 ± 29	267 ± 43	336 ± 45
δ	12.2 ± 0.2	12.1 ± 0.1	11.8 ± 0.1	11.9 ± 0.1	12.0 ± 0.1

^aRef. [4]. ^bRef. [3].

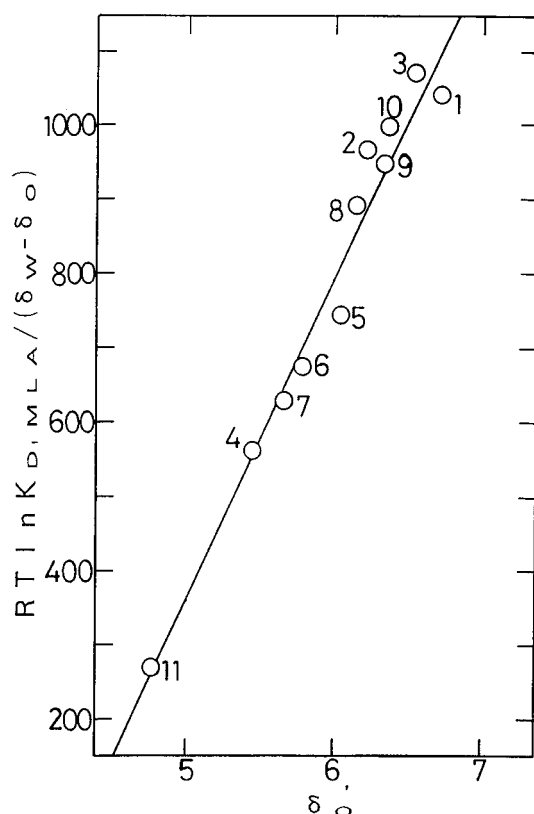


Figure 7. Plots of $RT \ln K_{D,MLA}/(\delta_w - \delta_o)$ vs. δ_o' for the DB18C6-potassium picrate complex. The numbers correspond to those in Table I.

NaLA and the other MLA. It has been reported that there exists an intimate relation between V_{MLA} and K_{MLA} where the conformations of MLA complexes of the same crown ether are similar; namely, for the same crown ether, the smaller V_{MLA} is, the larger is K_{MLA} [3, 8, 9]. The same holds also for the $M(DB18C6)A$ complexes except for Na; $\log K_{M(DB18C6)A}$ decreases in the order $K > Rb > Cs$ (Table V). $\log K_{MLA}$ of DB18C6 is always smaller than the corresponding $\log K_{MA}$. The opposite holds for 18C6 and B18C6 ($\log K_{MLA} > \log K_{MA}$). $\log K_{MLA}$ for a given alkali metal increases in the order DB18C6 < B18C6 < 18C6. The smaller $\log K_{MLA}$ of DB18C6 is caused by the two benzo groups. The two benzo groups prevent a picrate ion from approaching the size-mismatched smaller Na^+ ion in the DB18C6 cavity, resulting in the lowest $\log K_{Na(DB18C6)A}$ among the alkali metals.

Except for the case that the $\log K_{D,Cs(DB18C6)A}$ value is slightly higher for CBU than for mX , $\log K_{D,MLA}$ of DB18C6 for the same alkali metal decreases in the order 1,2-DCE > DCM > *o*-DCB > BB > CB > BZ > TE > mX > CBU > DBE. The same order of decreasing $K_{D,L}$ for the diluents is also observed for

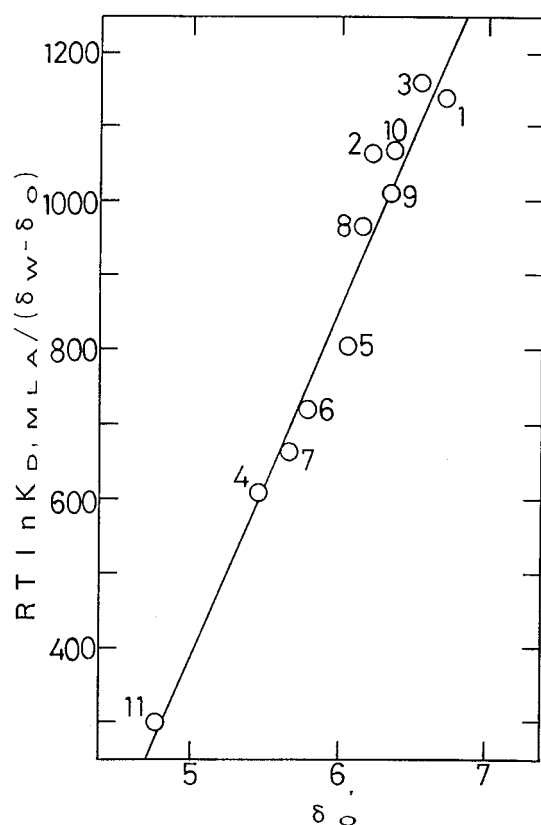


Figure 8. Plots of $RT \ln K_{D,MLA}/(\delta_w - \delta_o)$ vs. δ_o' for the DB18C6-rubidium picrate complex. The numbers correspond to those in Table I.

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

	M			
	Na	K	Rb	Cs
L = DB18C6				
$\log K_{MLA}$	-0.14 ± 0.11	1.30 ± 0.10	1.00 ± 0.09	0.24 ± 0.11
$\log K_{ML}$ ^a	1.16	1.667	1.08	0.83
L = B18C6				
$\log K_{MLA}$ ^b	1.54 ± 0.16	3.30 ± 0.20	3.11 ± 0.24	–
$\log K_{ML}$ ^c	1.38	1.744	1.15	–
L = 18C6				
$\log K_{MLA}$ ^d	3.29 ± 0.23	4.76 ± 0.27	4.62 ± 0.36	4.49 ± 0.36
$\log K_{ML}$	0.73 ^e	2.034 ^f	1.56 ^g	0.99 ^g
$\log K_{MA}$ ^h	1.38	1.64	1.94	2.07

^aRef. [10]. ^bRef. [4]. ^cRef. [11]. ^dRef. [3]. ^eRef. [12]. ^fRef. [13]. ^gRef. [14]. ^hRef. [15].

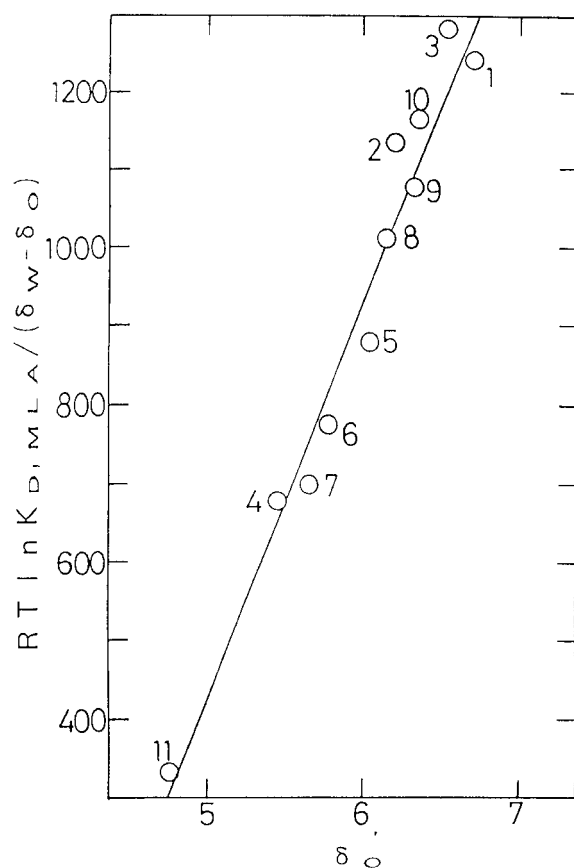


Figure 9. Plots of $RT \ln K_{D,MLA} / (\delta_w - \delta_o)$ vs. δ_o for the DB18C6-caesium picrate complex. The numbers correspond to those in Table I.

DB18C6 itself. Equations (13) and (14) are transformed into Equations (20) and (21), respectively.

$$RT \ln K_{D,L} = V_L \{ (\delta_w - \delta_L)^2 - (\delta_o - \delta_L)^2 + RT(V_o^{-1} - V_w^{-1}) \} \quad (20)$$

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

Equations (20) and (21) show that the closer to δ_L or δ_{MLA} the δ_o value is and the smaller the V_o value, the larger the $K_{D,L}$ value or the $K_{D,MLA}$ value. The δ_o values of 1,2-DCE and DCM are not so close to δ_{DB18C6} and $\delta_{M(DB18C6)A}$ as the δ_o values of *o*-DCB and BB. But DB18C6 and its MLA complexes are most distributed into 1,2-DCE and DCM among all the diluents. This is attributed to the fact that 1,2-DCE and DCM have the smallest V_o and the greatest δ_o except for *o*-DCB and BB.

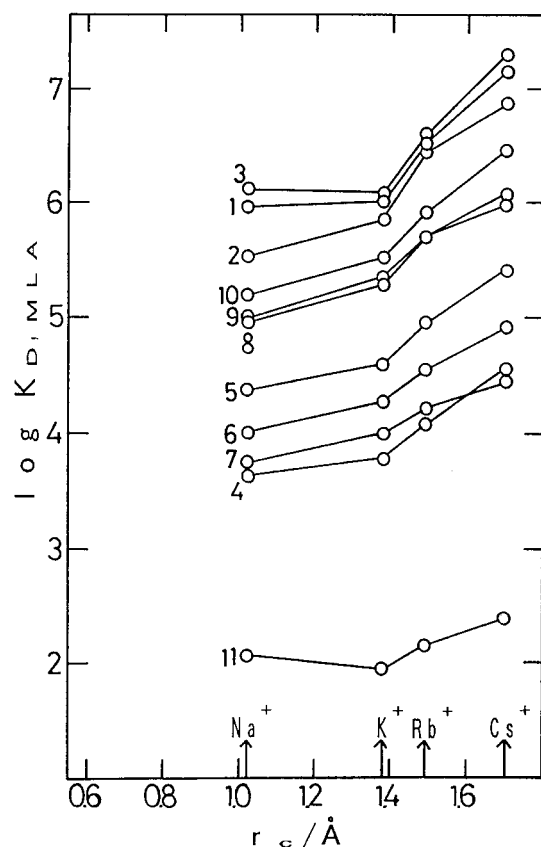


Figure 10. Plots of $\log K_{D,MLA}$ vs. crystal ionic radii (r_c) of alkali metals.

The much lower distribution constants of DB18C6 and its MLA complexes into DBE are ascribed to the much larger V_o and the much smaller δ_o of DBE compared with all the other diluents.

$\log K_{D,MLA}$ for the same diluent increases in the order $\text{Na} < \text{K} < \text{Rb} < \text{Cs}$ except for the cases of Na and K for 1,2-DCE and DBE (Table III and Figure 10). $\log K_{D,MLA}$ increases with an increase in V_{MLA} . This is consistent with the expectation from Equation (19) ($\delta_{M(DB18C6)A}$ of all the alkali metals are equal).

Equation (7) shows that $K_{D,L}$ and $K_{D,MLA}$ related to distribution behavior cancel each other. Equation (22) can be obtained from Equations (13) and (14).

$$\ln K_{D,MLA} - \ln K_{D,L} = (RT)^{-1}(V_{MLA} - V_L)\{-(\delta_o - \delta)^2 + (\delta_w - \delta)^2 + RT(V_o^{-1} - V_w^{-1})\}, \quad (22)$$

where $\delta = \delta_L = \delta_{MLA}$. From Equations (7) and (22), the closer δ_o is to δ of DB18C6 and $M(DB18C6)A$, and the smaller V_o is, the larger K_{ex} is because both K_{ML} and K_{MLA} are independent of the diluent. This is the reason why the alkali

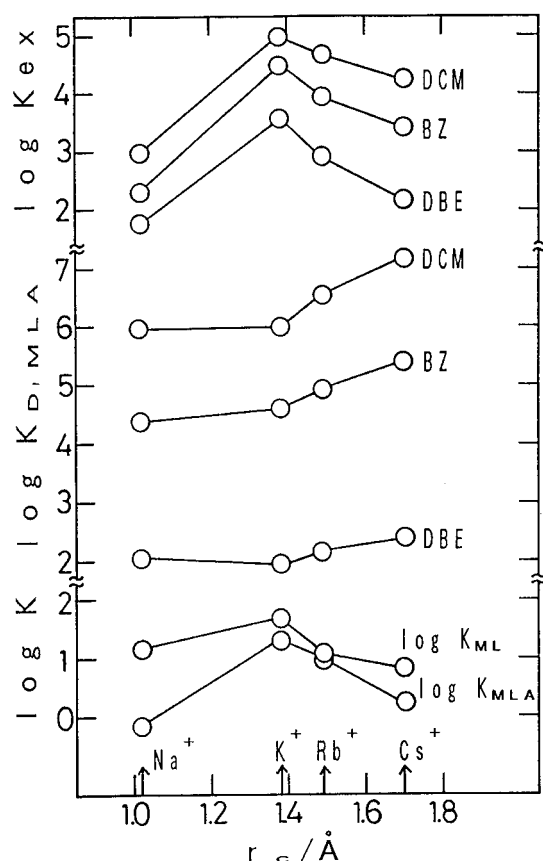


Figure 11. Plots of $\log K_{ex}$, $\log K_{D,MLA}$, $\log K_{ML}$, and $\log K_{MLA}$ vs. crystal ionic radii (r_c) of alkali metals.

metal picrate is extracted with DB18C6 most into 1,2-DCE and DCM, but least into DBE. For the same diluent, $\log K_{D,MLA} - \log K_{D,L}$ of a given alkali metal is larger for DB18C6 than for B18C6 [4] and 18C6 [3]; namely, the contribution of the distribution of electroneutral L and MLA to K_{ex} is greater for DB18C6 than for B18C6 and 18C6 (Equation (7)). This is ascribed to the smaller δ_L and δ_{MLA} and the larger $V_{MLA} - V_L$ of DB18C6 compared with B18C6 and 18C6 (Equation (22)). The δ_L and δ_{MLA} of DB18C6 are greater than δ_o of the diluents used in this study (Table I). For 18C6, K_{ex} is determined mostly by K_{MLA} [3]. For B18C6, K_{ex} of K and Rb depend largely on K_{MLA} , and that of Na mainly on both K_{ML} and K_{MLA} [4]. For DB18C6, $K_{D,MLA}$ contributes most favorably to K_{ex} . This is due to the much smaller $\log K_{MLA}$, the larger V_{MLA} , and the smaller δ_{MLA} of DB18C6 compared with B18C6 and 18C6. Differences in $\log K_{ML}$ for the same alkali metal among 18C6, B18C6, and DB18C6 are not large (less than 0.58) compared with $\log K_{MLA}$ and $\log K_{D,MLA}$.

Plots of $\log K_{ex}$ and $\log K_{D,MLA}$ for some representative diluents, $\log K_{ML}$, and $\log K_{MLA}$ vs. the crystal ionic radii of alkali metals are shown in Figure 11. For every diluent, the extraction selectivity of DB18C6 for the alkali metals decreases in the order $K > Rb > Cs > Na$. Except for Na, both K_{ML} and K_{MLA} decrease in the order $K > Rb > Cs$, but the reverse is true for $K_{D,MLA}$ ($Cs > Rb > K$). The extraction-selectivity order of DB18C6 for K, Rb, and Cs is determined by the order of both K_{ML} and K_{MLA} , whereas $K_{D,MLA}$ lowers the extraction selectivity (Figure 11). The difference between K and Rb in $\log K_{ML}$ is always larger than that in $\log K_{D,MLA}$. The difference between Rb and Cs in $\log K_{MLA}$ is always greater than that in $\log K_{D,MLA}$. K_{ML} and K_{MLA} contribute most to the extraction selectivity of DB18C6 for K over Rb and for Rb over Cs, respectively, among the three fundamental equilibrium constants. The K extraction-selectivity of DB18C6 over Na is the highest among all the combinations of the two neighboring alkali metals in the periodic table, which is completely determined by the contribution of K_{MLA} . Moreover, K_{ML} makes an additional contribution to the K extraction selectivity of DB18C6 over Na, and so does $K_{D,MLA}$ except for only DCM, 1,2-DCE, and DBE. This greatly enhances the K extraction selectivity.

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