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The Solvent Extraction of Uni- and Bivalent Metal Picrates by Dibenzo-24-crown-8

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The overall extraction equilibrium constants (K_{ex}) for the 1:1:1 and 1:1:2 complexes of dibenzo-24-crown-8 (DB24C8) with several uni- and bivalent metal picrates between benzene and water have been determined at 25 °C. The K_{ex} sequences of the uni- and bivalent metal ions with DB24C8 are $\text{Tl}^+ > \text{Cs}^+ > \text{Ag}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ \gg \text{Li}^+$ and $\text{Ba}^{2+} \gg \text{Pb}^{2+} \gg \text{Sr}^{2+} > \text{Ca}^{2+}$, respectively. DB24C8 shows the highest selectivity for Ba^{2+} among all the alkali and alkaline earth metal ions, but no selectivity for the alkali metal ions. The extractability of DB24C8 for the alkali metal ions is not sensitive to the ratio of the ionic size to the cavity size of DB24C8. The plots of log K_{ex} values *vs.* reciprocal crystal ionic radii of the alkali and alkaline earth metals give straight lines, indicating that these straight lines are related to Born's formula of solvation free energy.

Dibenzo-24-crown-8 (DB24C8) forms stoichiometric complexes with alkali metal ions; the alkali metal ion in the complex is trapped in the cavity of the DB24C8 ring by ion-dipole forces.[1] Since DB24C8 is a flexible crown ether and has a large cavity size (>4.0 Å[2]) compared to the alkali metal ionic size, in its complex with the alkali metal ion it is partially wrapped around the alkali metal ion.[1a] Accordingly, when the complex reaction between DB24C8 and metal ions occurs, the metal ion may be expected to require almost complete desolvation, as found in the NMR studies of nonactin.[3] Dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6), which are rigid crown ethers, show pronounced cation selectivities,[1b,4] while DB24C8 does not.[1b,4a] Some solvent extraction studies of alkali metal ions with DC18C6 and DB18C6 have been reported and these data show that the extractability of the metal ion is very sensitive to the ratio of the ionic size to the cavity size of the crown ether.[5] However, there is only one paper about the solvent extraction study of DB24C8 up to date and in this paper the extraction equilibria have not been discussed in detail.[2] Therefore, the present study was undertaken to determine the extraction constant values of the DB24C8-uni- and bivalent metal picrates and to compare these extraction constant values with those of DB18C6, in order to clarify the role of DB24C8 in the extraction process. Since a large anion is easily extracted into nonpolar solvents, the picrate anion was used as the counter ion. Benzene was used as the solvent because of its nonpolarity.

Experimental

Materials. DB24C8 was obtained from Nisso Co., Ltd. It was dissolved in hexane, and filtered while hot. Then it was recrystallized from hexane and, before use, dried at 50 °C in a vacuum oven. Analytical-grade benzene, HNO_3, $\text{LiOH}\cdot\text{H}_2\text{O}$, NaOH, KOH, $\text{Ca(NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{Sr(NO}_3)_2$, $\text{Ba(NO}_3)_2$, $\text{Pb(NO}_3)_2$, and reagent-grade TlNO_3 were purchased from Wako-Pure Chemicals Ltd. AgNO_3 and picric acid were analytical grade from Koso Chemical Co., Ltd. Reagent-grade RbOH and CsOH were obtained from Mitsuwa Pure Chemicals Ltd. and Kanto Chemical Co., Inc., respectively. The purities of TlNO_3 and the bivalent metal nitrates were determined by means of EDTA titration, and the concentrations of AgNO_3, the picric acid, and the alkali metal hydroxide solutions were determined by means of KCl, basic, and acid ones, respectively. Benzene was washed twice with distilled water.

Apparatus and Procedures. The organic phase of DB24C8 (9.2×10^{-5}—2.1×10^{-2} M) and the aqueous phase of the univalent metal hydroxide or nitrate (9.9×10^{-4}—2.9×10^{-2} M), or the bivalent metal nitrate (2.0×10^{-3}—1.1×10^{-1} M) and the picric acid (8.8×10^{-4}—2.7×10^{-2} M) were placed in a stoppered glass tube (volume 30 ml), shaken in a thermostated water bath for about 30 min at 25±0.2 °C, and separated by centrifugation. The initial volume of each phase was 10 ml in all cases. A portion of the aqueous phase about 8 ml was transferred to a 10 ml beaker and the hydrogen ion concentration was determined by a Hitachi-Horiba F-5 pH meter. In the cases of the univalent metal hydroxide, the univalent metal nitrate, and the bivalent metal nitrate, the extractions were carried out at pH 10.0—12.1, 2.3—2.6, and 1.6—2.7, respectively. For the systems of Ag, Tl, and the bivalent metals, the metal in the organic phase was back-extracted into 8 ml of 1 M nitric acid aqueous solution. The Ba concentration of this aqueous phase was determined by flame photometry and the others by atomic absorption spectroscopy using a Seiko SAS-725 atomic absorption spectrophotometer. For the systems of the alkali metals, the picrate in the organic phase was back-extracted into 8 ml of 0.01 M NaOH aqueous solution and the picrate concentration was determined at 356 nm by a Shimadzu UV-200 spectrophotometer ($\varepsilon=1.45\times10^4\ \text{cm}^{-1}\,\text{M}^{-1}$). In blank experiments, for the alkali metals no detectable extraction was found in the absence of DB24C8, and for Ag and Tl a little detectable extraction was found in the absence of either DB24C8 or picric acid. It was impossible to extract any Mg and Hg into the organic phase.

The Distribution Coefficient of DB24C8. A 100 ml portion of a benzene solution containing DB24C8 and an equal volume of distilled water were placed in a 300 ml separatory funnel and shaken under the same conditions as given above. The concentration range of DB24C8 was from 5.0×10^{-3}—1.0×10^{-2} M. After centrifugation, DB24C8 in the aqueous phase was extracted into chloroform (90 ml). A 80 ml portion of the organic phase was transferred to a 200 ml beaker and left until evaporation was complete. The residue in the beaker was dissolved by chloroform (10 ml) and the DB24C8 concentration was determined spectrophotometricall at 277 nm ($\varepsilon=5.25\times10^3\ \text{cm}^{-1}\,\text{M}^{-1}$). The average value of the distribution coefficient determined in this way is 1.1×10^3.

Results

When equilibrium takes place between an aqueous solution of a metal ion, M^{m+}, and a picrate ion, A^-, and a benzene solution of a crown ether, L, the equilibrium constants may be defined by the following equations:

$$K_{\rm ex} = [{\rm MLA}_m]_{\rm o}[{\rm H}^+]^m/[{\rm M}^{m+}][{\rm L}]_{\rm o}[{\rm HA}]_{\rm o}^m \tag{1}$$

$$K_{\rm D,L} = [{\rm L}]_{\rm o}/[{\rm L}] \tag{2}$$

$$K_{\rm ex}({\rm HA}) = [{\rm HA}]_{\rm o}/[{\rm H}^+][A^-] \tag{3}$$

$$K_{\rm ML} = [{\rm ML}^{m+}]/[{\rm M}^{m+}][{\rm L}] \tag{4}$$

$$K_{\rm ex'} = [{\rm MLA}_m]_{\rm o}/[{\rm ML}^{m+}][{\rm A}^-]^m \tag{5}$$

where the subscript "o" and the lack of a subscript designates the organic and the aqueous phase, respectively; square brackets indicate the molar concentrations. The distribution ratio of the metal may be represented by

$$D_{\rm M} = [{\rm MLA}_m]_{\rm o}/([{\rm M}^{m+}] + [{\rm ML}^{m+}]) \tag{6}$$

In the case of $[{\rm M}^{m+}] \gg [{\rm ML}^{m+}]$, Eq. 6 may be transformed into

$$D_{\rm M} = K_{\rm ex}K_{\rm ex}({\rm HA})^m[{\rm L}]_{\rm o}[{\rm A}^-]^m \tag{7}$$

For the univalent metal ion system the $\log(D_{\rm M}/[{\rm A}^-])$ *vs.* $\log[{\rm L}]_{\rm o}$ plot in Fig. 1 shows a straight line with a slope of 1 in every case, indicating that DB24C8 forms the 1:1 complex with the univalent metal ion. For the bivalent metal ion system the $\log(D_{\rm M}/[{\rm A}^-]^2)$ *vs.* $\log[{\rm L}]_{\rm o}$ plot in Fig. 2 and the $\log(D_{\rm M}/[{\rm L}]_{\rm o})$ *vs.* $\log[{\rm A}^-]$ plot in Fig. 3 always show lines with slopes of 1 and 2, respectively, indicating that DB24C8 forms the 1:1:2 complex with the bivalent metal ion and the picrate ion. The values of $[{\rm L}]_{\rm o}$ and $[{\rm A}^-]$ in Eq. 7 were calculated from Eqs. 8 and 9 respectively.

$$[{\rm L}]_{\rm o} = [{\rm L}]_{\rm t} - [{\rm MLA}_m]_{\rm o} \tag{8}$$

$$[{\rm A}^-] = ([{\rm HA}]_{\rm t} - m[{\rm MLA}_m]_{\rm o})/\{1 + (K_{\rm HA}+K_{\rm ex}({\rm HA}))[{\rm H}^+]\} \tag{9}$$

where the subscript "t" denotes the total concentration. The value of $K_{\rm ex}({\rm HA})$ was spectrophotometrically determined to be 247 by using the association constant of picric acid ($K_{\rm HA}=1.9_5$[6]). The equilibrium constants obtained from these data are summarized in Table 1, together with those from the literature.

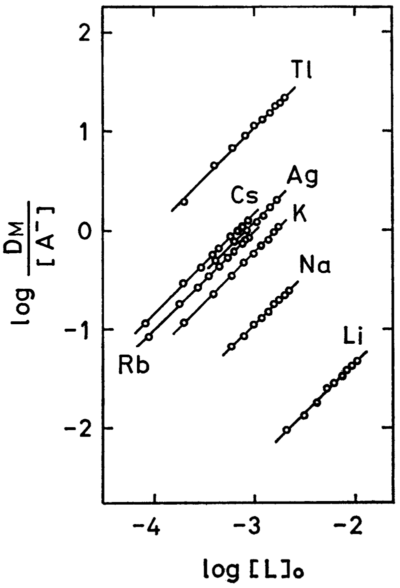

Fig. 1. Plots of $\log(D_{\rm M}/[{\rm A}^-])$ *vs.* $\log[{\rm L}]_{\rm o}$ for the univalent metals-DB24C8 system at 25 °C.

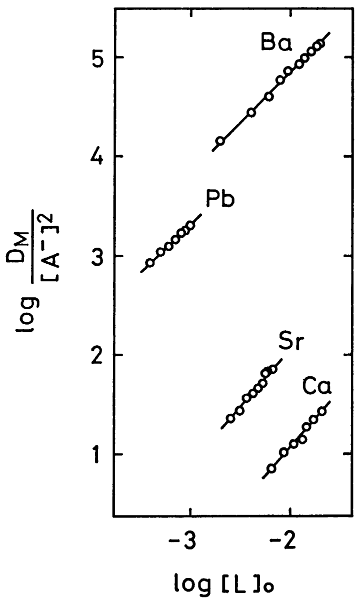

Fig. 2. Plots of $\log(D_{\rm M}/[{\rm A}^-]^2)$ *vs.* $\log[{\rm L}]_{\rm o}$ for the bivalent metals-DB24C8 system at 25 °C.

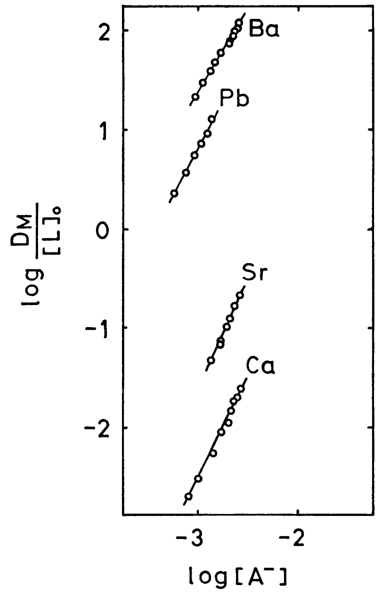

Fig. 3. Plots of $\log(D_{\rm M}/[{\rm L}]_{\rm o})$ *vs.* $\log[{\rm A}^-]$ for the bivalent metals-DB24C8 system at 25 °C.

Discussion

The plots of $\log K_{\rm ex}$ value *vs.* crystal ionic radius for the DB24C8 and the DB18C6 systems are given in Fig. 4. Table 1 shows that the $\log K_{\rm ex}$ value sequences for the alkali metal and the alkaline earth metal ions with DB24C8 are $\rm Cs^+ > Rb^+ > K^+ > Na^+ \gg Li^+$ and $\rm Ba^{2+} \gg Sr^{2+} > Ca^{2+}$ respectively, indicating that in both cases the nearer the crystal radius of the metal ion approaches to the cavity radius of DB24C8 (>2.0 Å[2]), the more extractable the metal ion is, as can

Table 1. Equilibrium constants at 25 °C

Crown ether	$K_{D,L}$	Cation	$\log K_{ex}$
DB24C8	1.1×10^{3}	Li$^+$	−1.72
		Na$^+$	−0.34
		K$^+$	0.40
		Rb$^+$	0.61
		Cs$^+$	0.76
		Ag$^+$	0.70
		Tl$^+$	1.67
		Ca^{2+}	−1.72
		Sr^{2+}	−0.80
		Ba^{2+}	2.07
		Pb^{2+}	1.53
DB18C6	8×10^{2} [5c]	Na$^+$	−0.18[5c]
		K$^+$	2.26[5c]
		Rb$^+$	1.36[5c]
		Cs$^+$	0.68[5c]

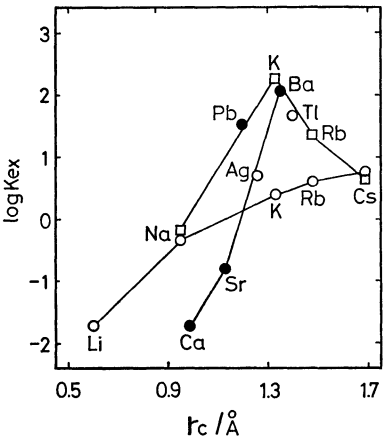

Fig. 4. Plots of $\log K_{ex}$ *vs.* crystal ionic radii, r_c, of uni- and bivalent metals for the DB24C8 and DB18C6 systems. ○: DB24C8-univalent metal, ●: DB24C8-bivalent metal, □: DB18C6-univalent metal.

be seen in Fig. 4. DB18C6, which is a rigid ligand,[1b] shows the highest selectivity for K$^+$ of all the alkali metal ions, and the extractability of DB18C6 for the alkali metal ions is very sensitive to the ratio of the crystal ionic radius to the cavity radius (1.3—1.6 Å[4a]). On the other hand, DB24C8, which is a flexible ligand,[1b] displays no peak selectivity for any alkali metal ion. The extractability of DB24C8 for the alkali metal ions is not sensitive to the ratio of the crystal ionic radius to the cavity radius (Fig. 4), and in the case of DB24C8 the difference in the $\log K_{ex}$ values of the neighboring alkali metal ions decreases gradually with an increase in the ionic size (Table 1). It may be noted from Fig. 4 that DB24C8 reveals the highest selectivity for Ba^{2+} among all the alkali and alkaline earth metal ions. It is very noticeable that the difference in the $\log K_{ex}$ values of Ba^{2+} and Sr^{2+} with DB24C8 (2.87) is markedly larger than those with 15-crown-5 (−0.50[9]) and 18-crown-6 (0.00[9]). This fact suggests that DB24C8 will be an useful reagent for separating a small amount of Ba from large amounts of Sr by a solvent extraction method.

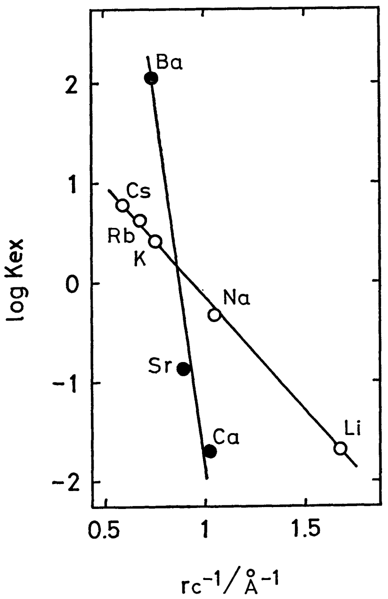

Fig. 5. Plots of $\log K_{ex}$ *vs.* reciprocal crystal ionic radii of alkali and alkaline earth metals for the DB24C8 system.

As can be seen from Fig. 4, the crystal radii of Ag$^+$ (1.26 Å[7]) and Tl$^+$ (1.40 Å[7]) are nearly equal to that of K$^+$ (1.33 Å[7]) and those of K$^+$ and Rb$^+$ (1.48 Å[7]) respectively. However, the $\log K_{ex}$ value of DB24C8 for Ag$^+$ is larger than that for K$^+$ and that for Tl$^+$ is much larger than those for K$^+$ and Rb$^+$. The $\log K_{ex}$ value of DB24C8 for Pb^{2+}, whose crystal radius (1.20 Å[8]) is nearly identical with that of Sr^{2+} (1.13 Å[7]), is much larger than that for Sr^{2+} (Fig. 4). The extractability of DB24C8 for Tl$^+$, whose ionic size is nearer to the cavity size of DB24C8 than is that of Ag$^+$, is much greater than that for Ag$^+$ (Fig. 4). The crystal radii of Ba^{2+} (1.35 Å[7]) and K$^+$ are nearly equal and the $\log K_{ex}$ value of DB24C8 for Ba^{2+} is much larger than that for K$^+$, while Ca^{2+} (0.99 Å[7]) and Na$^+$ (0.95 Å[7]) have nearly identical crystal radii and the $\log K_{ex}$ value of DB24C8 for Ca^{2+} is much smaller than that for Na$^+$ (Fig. 4).

The plot of $\log K_{ex}$ value *vs.* the reciprocal crystal ionic radius for the DB24C8 system is given in Fig. 5. The larger the crystal radii of the alkali and alkaline earth metal ions are, the more extractable these ions are. The plots of $\log K_{ex}$ values *vs.* the reciprocal crystal ionic radii of the alkali and alkaline earth metals give straight lines with slopes of −2.3 and −13.9 respectively, and the slope of the alkaline earth metal ions is about 6 times steeper than that of the alkali metal ions. Thus, it seems that these straight lines in Fig. 5 are related to Born's formula of solvation free energy.

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