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On the Extractability of Univalent Cation as Dibenzo-18-crown-6 Complexes with Picrate Ion

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The solvent extractions of alkali metal(I) with dibenzo-18-crown-6 (the nomenclature recommended by IUPAC is 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene) as the picrate into chloroform and benzene were studied at 25°C and compared with those of other univalent ions. The extraction constants of the metal ions ($K_{ex0}=[ME^+A^-]_{org}[M^+]^{-1}[E]_{org}^{-1}[A^-]^{-1}$), are in the sequence of $Tl^+\simeq K^+>Rb^+>NH_4^+\geq Ag^+>Cs^+>Na^+$, but the extraction constants of the metal complexes ($K_{ex}=[ME^+A^-]_{org}\times[ME^+]^{-1}[A^-]^{-1}$) are $NH_4^+\simeq Tl^+\simeq Rb^+\simeq K^+>Cs^+\simeq Ag^+>Na^+$.

The effects of the ionic size, the diluent, and the counter ion on the solvent extraction of univalent metal ions as cyclic polyether complexes were studied previously[1-5] and also recently.[6-10]

Although some early studies[4,11] pointed out that the extraction of metal ions with crown ethers is closely connected with the extractability of the complexes formed, not much has been reported about the extraction of metal ions with crown ethers in connection with the extractability of the complex formed in aqueous solutions. The present work was undertaken in order to learn the relation between the extraction of metal ions and the extractability of the complex. For this purpose, the extraction of alkali dibenzo-18-crown-6 (DBC) complexes with picrate ion was studied and the results were compared with those of thallium(I),[8] silver(I) and ammonium ions.[10]

Experimental

All of the procedures were performed at 25±0.5 °C, as done previously.[8,10] A seven milliliter portion of an aqueous solution containing lithium picrate and one of the alkali metal ions was equilibrated in a stoppered glass tube with an equal volume of chloroform or benzene containing DBC. The concentrations of the metal ions which were back-extracted from the organic phase into 0.1 mol dm^{-3} perchloric acid and that in the equilibrated aqueous phase were determined by flamephotometry. In the cases of sodium(I) and potassium(I), blank tests were necessary to correct the measured concentration of the back-extracts. The distribution ratio, D, was defined as:

$$D=\frac{\text{the total concentration of M(I) in the organic phase}}{\text{the total concentration of M(I) in the aqueous phase}}.$$

Results and Discussion

The statistical treatment was reported previously.[8,10] The extraction constants for the cation and the complex are defined as (here E is DBC and A$^-$ picrate ion):

$$K_{ex0} = [ME^+A^-]_{org}[M^+]^{-1}[E]_{org}^{-1}[A^-]^{-1}, \quad (1)$$

$$K_{ex} = [ME^+A^-]_{org}[ME^+]^{-1}[A^-]^{-1}. \quad (2)$$

When $[M^+]\gg[ME^+]$, the distribution ratio can be written as

$$D = [ME^+A^-]_{org}/[M^+] = K_{ex0}[E]_{org}[A^-]$$
$$\text{and } K_{ex}\beta_1[E][A^-], \quad (3)$$

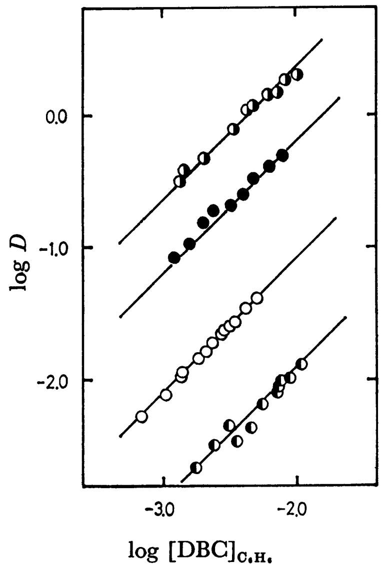

Fig. 1. Distribution ratio K$^+$ (◑), Rb$^+$ (●), Cs$^+$ (○), and Na$^+$ (◐) as a function of DBC concentration in benzene. The picrate concentration was 1×10^{-2} mol dm^{-3}. The solid lines were calculated using K_{ex0} values in Table 1.

where $\beta_1=[ME^+][M^+]^{-1}[E]^{-1}$. Then $K_{ex}=K_{ex0}K_d\beta_1^{-1}$ where $K_d=[E]_{org}/[E]$.

Figure 1 shows the distribution ratio of alkali metal ions in the benzene system as a function of the DBC concentration and Fig. 2 shows those in the chloroform system; the slope of the curves is always unity in these figures. The slope was also found to be unity for the curves obtained as a function of the picrate concentration at a constant DBC concentration. These results show that the stoichiometry in the extracted species in the organic phase should be 1 : 1 : 1 with respect to the metal ion, DBC, and picrate anion. Thus no correction for Eq. 3 due to the dissociation of the complexes was necessary. The extraction constants K_{ex0} and K_{ex} calculated from these data are listed in Table 1, together with those previously reported. Figure 3 shows the correlation of the values of log K_{ex0} and log K_{ex} with the ionic diameters of the cations.

When these metal ions are extracted with DBC, the more stable the complexes, the better the extraction which is expected. The marked difference in the extraction of the metal ions which is seen from the

Table 1. Summary of constants for univalent metals

	Na^+	K^+	Rb^+	Cs^+	Ag^+[10]	Tl^+[8]	NH_4^+[10]
Diameter/nm[12]	0.19	0.27	0.29	0.33	0.25	0.29	0.29
log $K_{ex0}(C_6H_6)$	2.1	4.4	3.8	2.9	3.6	4.5	3.6
log K_{ex} (C_6H_6)	3.8	5.6	5.6	5.0	5.1	5.9	6.2
log $K_{ex0}(CHCl_3)$	2.1	4.6	4.2	3.2	3.3	4.7	3.7
log K_{ex} $(CHCl_3)$	4.8	6.8	7.0	6.3	5.8	7.1	7.3
log β_1[12]	1.2	1.7	1.1	0.8	1.4	1.5	*ca.* 0.3

log K_d: 2.9(C_6H_6),[5] 3.9($CHCl_3$).[10]

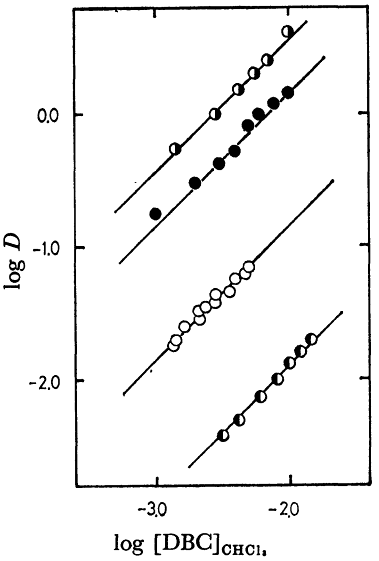

Fig. 2. Distribution ratio of K^+ (◑), Rb^+ (●), Cs^+ (○), and Na^+ (◐) as a function of DBC concentration in chloroform. The picrate concentration was 1×10^{-2} mol dm^{-3}. The solid lines were calculated using K_{ex0} values in Table 1.

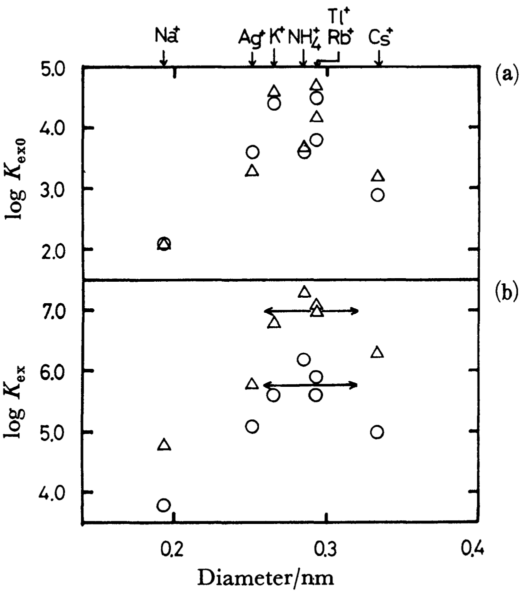

Fig. 3. Extraction constants of univalent metal ions (a) and the complexes (b) with DBC *vs.* the diameters of the ions in benzene system (○), and in chloroform (△). The arrow lines show the hole size of DBC.[2]

values of K_{ex0} in Table 1 should primarily be caused by the difference in the stability of the complexes formed in the aqueous phase. However, the extraction of the metal ions should also be affected by the extractability of the complexes. This property is represented by K_{ex} in Eq. 2. The factors affecting the extractability include:

i) Larger ion-pairs should be extracted better for otherwise identical systems. This hydrophobic tendency, however, is similar for the ion-pairs in the present study because the crown ether is always DBC and the counterion picrate.

ii) Stronger attractions of water molecules to the complex should cause poorer extraction. The poorer extractions of sodium(I), silver(I), and caesium(I) complexes, as seen from the K_{ex} values in Table 1, may be attributed to stronger hydrations of them (most probably of the central metal ion). The sodium(I) complex is especially poorly extracted. At present, the authors can not make any reasonable explanation for this markedly strong hydration, although Frensdorff[2] also pointed out that the extractability of sodium–dicyclohexyl-18-crown-6 complex is almost two decades lower than that of potassium complex, when the anion was picrate and the solvent was dichloromethane.

The hydration of a metal ion should be reduced by complexation with crown ethers.[3,4,11] When the size of the central metal ion is larger than the hole, the ion may project over the polyether ring. In such a case, the hydration should be stronger than that of a central metal ion fitting better with the crown ether, for example, potassium(I) for DBC. The lower K_{ex} value of the caesium(I)–DBC complex may be explained by this type of stronger hydration and thus both the instability and the stronger hydration of the caesium(I)–complex should cause the poorer extraction of caesium(I) (represented by K_{ex0}). Hydration of extracted crown ether complexes of alkali metal in nitrobenzene was previously reported.[13] The present authors have no clear explanation for these high K_{ex} values of the ammonium complex, which is much less stable than the other complexes. One possible reason for this may be inaccuracy of the stability constant of the ammonium–DBC complex which was used for the estimation of the K_{ex} values; this value was noted to be somewhat inaccurate.[12]

iii) The extraction of the free crown ether is better into chloroform than into benzene. This may be explained in terms of stronger interactions of the former diluent molecules with DBC. The same tendency is also observed among the metal–DBC complexes and the diluent effect is somewhat larger with the complexes than with the reagent, except for sodium and silver. The relatively better extraction of the silver complex into benzene than the other metal complexes was explained in terms of the stronger interactions of benzene with the central silver ion due to the π-electrons.(10)

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