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Synergistic Solvent Extraction of Crown Ether Complexes with Alkali Metal Picrates by Neutral Donor Solvents

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The solvent extraction of rubidium and caesium picrates has been studied at 25 °C with mixtures of crown ether and tributyl phosphate (TBP) or trioctylphosphine oxide (TOPO) in benzene, and the adduct-formation constants in the benzene solution have been calculated. The crown ethers used in this work were 12-crown-4 (12C4), 15-crown-5 (15C5), and benzo-15-crown-5 (B15C5). The stoichiometric composition of any extracted complex under the present experimental conditions is alkali metal ion : crown ether : TBP or TOPO : picrate ion = 1 : 1 : 1 : 1. The TOPO complex is more extractable than the corresponding TBP complex. The extractability of the Rb^+ complex is larger than that of the corresponding Cs^+ complex. For both TBP and TOPO, the adduct-formation constant value sequences of Rb^+ and Cs^+ are B15C5 > 12C4 > 15C5 and 12C4 > B15C5 > 15C5, respectively.

Extractions of crown ether complexes with metal picrates are enhanced by the addition of a neutral donor solvent such as tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO).[1–3] This enhancement is attributed to the fact that the crown ether complexes with the metal picrates form adducts with the neutral donor solvents. The crown ether complex (metal ion : crown ether : picrate ion = 1 : 1 : 1) accepts one or two neutral donor solvents. The magnitude of the adduct-formation constant in the organic phase reflects the chemical nature of the metal ion trapped in the crown ether cavity.

At present, only a few quantitative data have been reported on the synergistic solvent extraction study for crown ethers.

In the present study, the solvent extraction of rubidium and caesium picrates has been investigated at 25 °C with mixtures of crown ether and TBP or TOPO in benzene. The compositions of the extracted complexes have been determined and the adduct-formation constants in a benzene solution have been calculated. The crown ethers used in this work were 12-crown-4 (12C4), 15-crown-5 (15C5), and benzo-15-crown-5 (B15C5). Since it is known that TOPO forms more stable adducts than TBP, TOPO was chosen in the hope that the higher extractabilities for alkali metal ions compared with TBP could be obtained.

Experimental

Materials. 12-Crown-4 and TBP were obtained from Wako-Pure Chemicals, Ltd., 15C5 from Nisso Co., Ltd., and TOPO from Dojin-Do Co., Ltd. They were used without further purification. The method of the purification of B15C5 (Merck Japan Ltd.) was described elsewhere.[1] Analytical-grade benzene was washed three times with distilled water.

Procedure. An aqueous phase contained alkali metal hydroxide ($(2.0\text{—}6.5)\times10^{-3}$ M; 1 M = 1 mol dm^{-3}) and picric acid ($(1.0\text{—}8.9)\times10^{-3}$ M). A benzene phase contained one of the extractants (TBP: 9.0×10^{-2}—6.5×10^{-1} M, TOPO: 2.4×10^{-2}—1.8×10^{-1} M, crown ether: 1.4×10^{-3}—1.3×10^{-1} M), or both TBP (8.8×10^{-2}—6.6×10^{-1} M) or TOPO (2.4×10^{-2}—1.8×10^{-1} M) and crown ether (1.4×10^{-3}—1.3×10^{-1} M). The two phases in stoppered glass tubes (30 ml) were shaken in a thermostated water bath for 45 min at 25±0.2 °C and then centrifuged. The initial valume of each phase was 10 ml in all cases. The extractions were carried out at pH 5.8—6.2. The alkali metal in the benzene phase was back-extracted into 8 ml of a 0.1 M HNO_3 aqueous solution, and the alkali metal concentration was determined by atomic absorption spectrometry.

Results

The equilibrium constants for this solvent extraction system can be defined by the following equations:

$$K\text{ex}(\text{MLL}'\text{A}) = [\text{MLL}'\text{A}]_\text{o}[\text{H}^+]/[\text{M}^+][\text{L}]_\text{o}[\text{L}']_\text{o}[\text{HA}]_\text{o}, \tag{1}$$

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

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

$$K_{\text{MLL}'\text{A,o}} = [\text{MLL}'\text{A}]_\text{o}/[\text{MLA}]_\text{o}[\text{L}']_\text{o}, \tag{4}$$

where the subscript "o" and the lack of a subscript denote the organic and the aqueous phase, respectively; M^+, A^-, L, and L′ refer to an alkali metal ion, a picrate ion, crown ether, and another neutral ligand, respectively. The all activity coefficients of the chemical species in this study have been assumed as unity. The Kex(HA) value was spectrophotometrically determined to be 247.

When the benzene phase contains both L and L′, the distribution ratio is represented by

$$D = [\text{MLL}'\text{A}]_\text{o}/[\text{M}^+]. \tag{5}$$

The substitution of Eqs. 1 and 3 into Eq. 5 gives

$$D = K\text{ex}(\text{MLL}'\text{A})K\text{ex}(\text{HA})[\text{L}]_\text{o}[\text{L}']_\text{o}[\text{A}^-]. \tag{6}$$

The log ($D/[\text{A}^-]$) *vs.* log $[\text{L}]_\text{o}$ plots for the 15C5-TOPO system are given in Fig. 1. The log($D/[\text{A}^-]$) *vs.* log$[\text{L}']_\text{o}$ plots for the 15C5-TOPO system are illustrated in Fig. 2. The plots of the other systems (12C4-TBP, 12C4-TOPO, and B15C5-TOPO) were similar, and so have been omitted. For each system, the plots of both Rb and Cs have a slope of 1 (*e.g.*, Figs. 1 and 2). Thus, the Kex(MLL′A) in this study can be described by Eq. 1. The value of $[\text{L}']_\text{o}$ in Eq. 6 was presumed to be nearly equal to that of $[\text{L}']_\text{t}$, and those of $[\text{L}]_\text{o}$ and $[\text{A}^-]$ were calculated from Eqs. 7 and 8 respectively:

$$[\text{L}]_\text{o} = ([\text{L}]_\text{t} - [\text{MLL}'\text{A}]_\text{o})/(1 + K_{\text{D,L}}^{-1}), \tag{7}$$

$$[\text{A}^-] = [\text{HA}]_\text{t} - [\text{MLL}'\text{A}]_\text{o}, \tag{8}$$

where the subscript "t" denotes the total concentration. The equilibrium constants obtained from these data

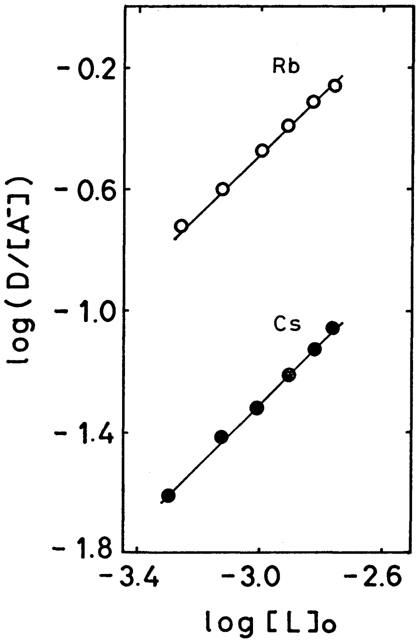

Fig. 1. Plots of log (D/[A^-]) *vs.* log $[L]_o$ for the 15C5-TOPO system (L=15C5).

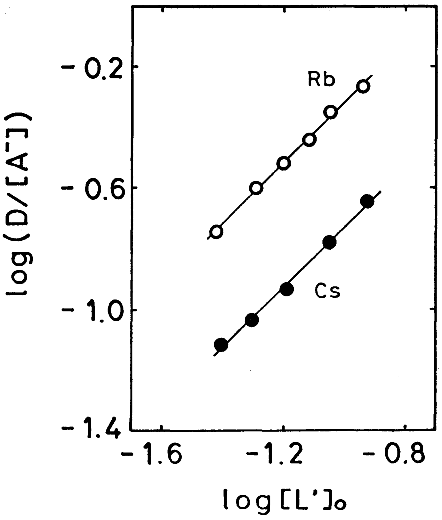

Fig. 2. Plots of log (D/[A^-]) *vs.* log $[L']_o$ for the 15C5-TOPO system (L'=TOPO).

are listed in Table 1.

Table 1. EQUILIBRIUM CONSTANTS AT 25 °C

$K_{\mathrm{D,L}}$	12C4 0.15[4]	15C5 0.15_6[5]	B15C5 20[1]	
	L	L'	Rb^+	Cs^+
log Kex(MLL'A)	12C4	TBP	−0.84	−0.99
		TOPO	−0.34	−0.57
		12C4	−0.29[2]	−0.64[2]
	15C5	TBP	0.56[2]	0.19[2]
		TOPO	1.25	0.78
		15C5	2.15[2]	1.48[2]
	B15C5	TBP	0.37[1]	−0.15[1]
		TOPO	0.88	0.21
		B15C5	1.22[1]	0.41[1]
log $K_{\mathrm{MLL'A,o}}$	12C4	TBP	1.26	1.19
		TOPO	1.76	1.61
		12C4	1.81[2]	1.54[2]
	15C5	TBP	0.81[2]	0.68[2]
		TOPO	1.50	1.27
		15C5	2.40[2]	1.97[2]
	B15C5	TBP	1.32[1]	1.16[1]
		TOPO	1.83	1.52
		B15C5	2.17[1]	1.72[1]

Discussion

In the case of the same crown ether, the extractability of the same alkali metal ion increases in the order TBP<TOPO<crown ether except $Cs(12C4)_2A$ (Table 1). For the same L and L' system, Rb^+ is more extractable than Cs^+, and extraction-selectivity for Rb^+ compared to Cs^+ is enhanced in the order TBP<TOPO<crown ether (Table 1).

$K_{\mathrm{MLL'A,o}}$ represents the formation constant for the MLL'A complex in a benzene solution. For each of Rb^+ and Cs^+, the log $K_{\mathrm{MLL'A,o}}$ value of the same crown ether increases in the order TBP<TOPO<crown ether except for the case of $Cs(12C4)_2A$. The reason why the TOPO complex is more stable than the TBP complex may be attributed to the higher basicity of TOPO compared with that of TBP. It is interesting that, although the number of donor oxygen atoms is much larger for 12C4 than for TOPO, the $Cs(12C4)_2A$ complex is slightly less stable than the Cs(12C4)(TOPO)A complex. The fact that the other sandwich complexes with two crown ethers are more stable than the corresponding TOPO complexes may reflect the larger number of donor oxygen atoms of the crown ether compared to that of TOPO.

For both TBP and TOPO, the log $K_{\mathrm{MLL'A,o}}$ value sequences of Rb^+ and Cs^+ are B15C5>12C4>15C5 and 12C4>B15C5>15C5, respectively. It thus appears that the electron density in the crown ether cavity is one of the most important factors in determining the stabilities of the TBP- and TOPO-adducts.[1] In each case of the ML(TOPO)A and ML(TBP)A complexes, the stability for Rb^+ is larger than that for Cs^+. This is probably due to the higher charge density of Rb^+ compared to Cs^+.

The MLA complex in the series of our synergistic solvent extraction studies[1,2] accepts a TBP or a TOPO molecule in a benzene solution, while, a dibenzo-18-crown-6 complex with silver picrate accepts two TOPO molecules in a $CHCl_3$ solution.[3]

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