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Solvent Extraction of Thallium(I) Picrate into Benzene with Mixtures of Crown Ethers and Tributyl Phosphate

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Synopsis. Thallium(I) picrate was extracted into benzene at 25 °C with crown ether (15-crown-5 (15C5) and benzo-15-crown-5 (B15C5)) and/or tributyl phosphate (TBP). The crown ether complex with thallium picrate (1:1:1) accepts one TBP molecule. The thallium picrate complex with B15C5 and TBP is more stable than the corresponding 15C5 complex in benzene.

Solvent extraction of metal ions by crown compounds is widely studied in various fields.[1] Numerous basic data about extraction process have been reported to date, and furthermore, crown compounds have been used as extraction reagents for separation and determination of metal ions, particularly alkali and alkaline earth metal ions.

There are many factors which influence extractability and extraction-selectivity of crown compounds for metal ions; namely, (1) distribution of a crown compound itself, (2) stability of a crown compound complex with a metal ion in an aqueous solution, (3) extraction of a crown compound complex with a metal ion, (4) a counter anion which forms an ion pair with a cationic crown compound complex, (5) diluent, (6) coexisting species in an aqueous phase, (7) coexisting another ligand in an organic phase, and (8) structure of a crown compound. As for the factor (7), extractability of crown ethers for alkali and alkaline earth metal ions is enhanced by the addition of donor solvents such as tributyl phosphate (TBP), trioctylphosphine oxide, and bis(2-ethylhexyl)hydrogenphosphate.[1,2] This synergistic increase is due to the fact that crown ether–metal ion complexes form adducts with the donor solvents. The stoichiometry of the adduct complex with an alkali metal ion is metal ion : crown ether : donor solvent = 1 : 1 : 1.[1,2]

In the present work, since scarcely any data on synergistic extractions of crown ether–Tl^+ complexes with donor solvents have been reported, extraction of thallium(I) picrate was conducted in the presence of crown ether and/or TBP at 25 °C between benzene and water. Compositions of the extracted complexes and adduct-formation constants in benzene have been determined. The synergistic extraction-behavior of Tl^+ was compared with that of Rb^+, which is a s-block element and nearly equal to Tl^+ in size. The crown ethers used in this study were 15-crown-5 (15C5) and benzo-15-crown-5 (B15C5). Their cavities (0.85—1.1 Å[1] (radius)) are smaller than Tl^+.

Experimental

Materials. 15-Crown-5 (Nisso Co., Ltd.) and analytical-grade TBP (Wako Pure Chemicals, Ltd.) were used without further purification. Benzo-15-crown-5 (Merck Japan Ltd.) was dissolved in heptane, and filtered while hot. It was recrystallized from heptane twice and, prior to use, dried at 40 °C in vacuo. The purity of $TlNO_3$ and concentrations of picric acid solutions were determined by EDTA and alkaline titrations, respectively. Analytical-grade benzene was washed twice with distilled water.

Procedure. All the experiments were conducted at 25±0.2 °C. The experimental procedures were similar to those in the previous paper.[2] Concentrations of $TlNO_3$, picric acid, TBP, 15C5, and B15C5 were 4.2×10^{-5}—4.2×10^{-3}, 4.4×10^{-4}—4.9×10^{-3}, 8.0×10^{-2}—9.7×10^{-1}, $(1.4$—$2.9)\times10^{-2}$, and 6.5×10^{-4}—1.6×10^{-1} mol dm^{-3}, respectively. All the extractions were carried out in the pH range of 1.9—5.7. Concentrations of thallium(I) extracted into benzene phase were determined by atomic absorption spectrometry.

Results and Discussion

Equilibrium constants can be defined by the following equations:

$$K_{ex}(MLL'A) = [MLL'A]_o[H^+]/[M^+][L]_o[L']_o[HA]_o, \quad (1)$$

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

$$K_{ex}(HA) = [HA]_o/[H^+][A^-], \quad (3)$$

$$K_{MLL'A,o} = [MLL'A]_o/[MLA]_o[L']_o, \quad (4)$$

where the subscript "o" and the lack of a subscript refer to the organic and the aqueous phase, respectively; M^+, A^-, L, and L′ denote a monovalent metal ion, a picrate ion, crown ether, and another neutral ligand, respectively. All the activity coefficients of chemical species have been assumed as unity. The $K_{ex}(HA)$

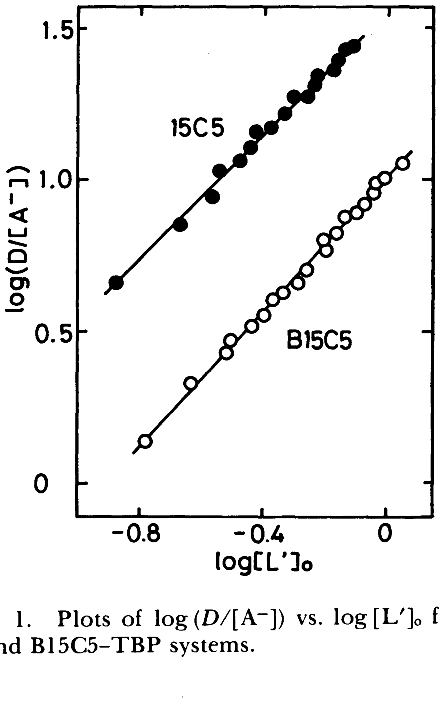

Fig. 1. Plots of log $(D/[A^-])$ vs. log $[L']_o$ for 15C5- and B15C5–TBP systems.

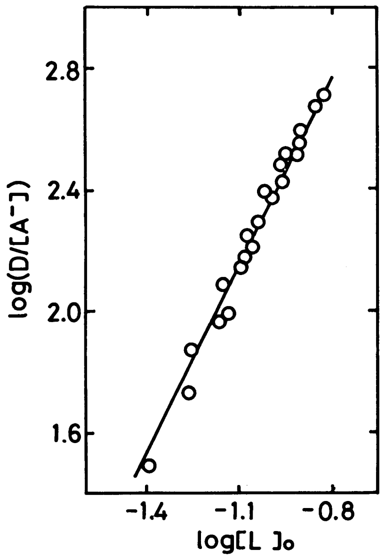

Fig. 2. Plots of $\log(D/[\mathrm{A}^-])$ vs. $\log[\mathrm{L}]_o$ for the B15C5 system.

value was spectrophotometrically determined to be 247.

When both L and L′ is in the benzene phase, the distribution ratio (D) is represented by

$$D = [\mathrm{MLL'A}]_o/[\mathrm{M}^+]. \tag{5}$$

Substitution of Eqs. 1 and 3 into Eq. 5 gives

$$D = K_{ex}(\mathrm{MLL'A})K_{ex}(\mathrm{HA})[\mathrm{L}]_o[\mathrm{L'}]_o[\mathrm{A}^-]. \tag{6}$$

$\log(D/[\mathrm{A}^-])$ vs. $\log[\mathrm{L'}]_o$ plots for 15C5- and B15C5–TBP systems are shown in Fig. 1. The plots for 15C5 and B15C5 in Fig. 1 have a slope of 1. $\log(D/[\mathrm{A}^-])$ vs. $\log[\mathrm{L}]_o$ plots for the 15C5- and B15C5-TBP systems were similar (a straight line with a slope of 1), and so have been omitted. $\log(D/[\mathrm{A}^-])$ vs. $\log[\mathrm{L}]_o$ plots for the B15C5 system in Fig. 2 show a straight line with a slope of 2, where L=L′=B15C5. This indicates that B15C5 forms a 2:1 complex with Tl^+. Thus, $K_{ex}(\mathrm{MLL'A})$ can be described by Eq. 1. When L′=TBP, the value of $[\mathrm{L'}]_o$ in Eq. 6 was supposed to be nearly equal to that of $[\mathrm{L'}]_t$, and those of $[\mathrm{L}]_o$ and $[\mathrm{A}^-]$ were calculated from Eqs. 7 and 8 respectively:

$$[\mathrm{L}]_o = ([\mathrm{L}]_t - [\mathrm{MLL'A}]_o - [\mathrm{MLA}]_o)/(1 + K_{D,L}^{-1}), \tag{7}$$

$$[\mathrm{A}^-] = ([\mathrm{HA}]_t - [\mathrm{M}]_{o,t})/\{1 + (K_{HA} + K_{ex}(\mathrm{HA}))[\mathrm{H}^+]\}, \tag{8}$$

where the subscript "t", $[\mathrm{M}]_{o,t}$, and K_{HA} denote the total concentration, the total concentration of thallium in the organic phase, and the association constant of picric acid ($K_{HA}=1.95_3$[3]). When both L and L′ are B15C5, values of $[\mathrm{B15C5}]_o$ and $[\mathrm{A}^-]$ in Eq. 6 were calculated from Eqs. 9 and 8, respectively:

$$[\mathrm{L}]_o = ([\mathrm{L}]_t - 2[\mathrm{M}]_{o,t})/\{1 + K_{D,L}^{-1} - K_{ex}(\mathrm{HA})K_{ex}(\mathrm{MLA})[\mathrm{M}^+][\mathrm{A}^-]\}, \tag{9}$$

where $K_{ex}(\mathrm{MLA})=[\mathrm{MLA}]_o[\mathrm{H}^+]/[\mathrm{M}^+][\mathrm{L}]_o[\mathrm{HA}]_o$ ($K_{ex}(\mathrm{MLA})=6.9$[4]) and $[\mathrm{M}^+]=[\mathrm{M}]_t-[\mathrm{M}]_{o,t}$. The equilibrium constants obtained from these data are summarized in Table 1.

Table 1. Equilibrium Constants at 25 °C

	15C5		B15C5	
$K_{D,L}$	0.15$_6$[5]		20[6]	
	L	L′	Tl^+	Rb^+
$\log K_{ex}(\mathrm{MLL'A})$	15C5	TBP	1.58	0.56[7]
	B15C5	TBP	1.17	0.37[6]
	B15C5	B15C5	1.95	1.22[6]
$\log K_{\mathrm{MLL'A},o}$[a]	15C5	TBP	0.17	0.81[7]
	B15C5	TBP	0.33	1.32[6]
	B15C5	B15C5	1.11	2.17[6]

a) $K_{\mathrm{MLL'A},o}=[\mathrm{MLL'A}]_o/[\mathrm{MLA}]_o[\mathrm{L'}]_o$.

By way of example, for the crown ether–TBP mixed system, D values of Tl(I) are 4.6×10^{-3} ($[\mathrm{15C5}]_t=2.9\times10^{-2}$ M (1 M=1 mol dm^{-3}), $[\mathrm{Tl}]_t=2.0\times10^{-3}$ M, $[\mathrm{HA}]_t=5.6\times10^{-4}$ M, $[\mathrm{TBP}]_t=3.2\times10^{-1}$ M) and 2.1×10^{-3} ($[\mathrm{B15C5}]_t=4.0\times10^{-3}$ M, $[\mathrm{Tl}]_t=2.0\times10^{-3}$ M, $[\mathrm{HA}]_t=4.5\times10^{-4}$ M, $[\mathrm{TBP}]_t=3.3\times10^{-1}$ M). This shows that only a slight amount of Tl(I) ((0.2—0.5)%) is extracted into a benzene phase.

Ionic radius of Tl^+ (1.50 Å[8]) is nearly equal to that of Rb^+ (1.49 Å[8]). Thallium(I), however, is much more extracted into benzene than Rb^+ with mixtures of crown ether and TBP. Mixtures of 15C5 and TBP are more effective for extraction of Tl^+ than those of B15C5 and TBP.

The crown ether complex with thallium picrate (1:1:1) accepts one TBP molecule. From the structure of the crown ether complex with Tl^+ held in the cavity, a picrate anion- and a TBP molecule-contact are possible in respective directions perpendicular to the plane of the ring.

$K_{\mathrm{MLL'A},o}$ designates adduct-formation constant of a MLA complex with L′ in a benzene solution. It is seen from $\log K_{\mathrm{MLL'A},o}$ values in Table 1 that extractability of Tl^+ is slightly enhanced by the addition of TBP. Since Tl^+ and Rb^+ have nearly equal sizes, 15C5 and B15C5 complexes with Tl^+ are expected to be similar in size and shape to those with Rb^+, respectively; in addition, free energy of hydration of Tl^+ (343 kJ mol^{-1}[9]) is much the same as that of Rb^+ (320 kJ mol^{-1}[9]); however, $\log K_{\mathrm{MLL'A},o}$ values of Tl^+ are relatively smaller than those of Rb^+. This cannot clearly be explained at the present time.

When L′=TBP, $\log K_{\mathrm{MLL'A},o}$ value of Tl^+ for B15C5 is larger than that for 15C5. The same tendency was observed for Rb^+ and Cs^+.[6] Benzo-15-crown-5 has two aromatic ether oxygen atoms. It thus appears that electron density in the B15C5 cavity is lower than that in the 15C5 cavity. Consequently, surface charge density of an exposed part of the metal ion trapped in the cavity may be lower for 15C5 than for B15C5. This is responsible for the larger $\log K_{\mathrm{MLL'A},o}$ value of B15C5 than that of 15C5. A $\mathrm{Tl(B15C5)_2A}$ complex is more stable than a Tl(B15C5)(TBP)A complex in a benzene solution. This may be attributed to the fact that B15C5 has more donor oxygen atoms than TBP.

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