The Solvent Extraction of Several Univalent Metal Picrates by 15-Crown-5 and 18-Crown-6

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(Received November 24, 1978)

The overall extraction equilibrium constants (K_{ex}) for 1:1:1 complexes of 15-crown-5 (15C5) and 18-crown-6 (18C6) with several univalent metal picrates between benzene and water have been determined at 25 °C. The K_{ex} sequences of the univalent metal ion with 15C5 and 18C6 are $Ag^+ > Na^+ > Tl^+ \gg K^+ > Rb^+ > Cs^+ > Li^+$ and $Tl^+ > K^+ > Rb^+ > Ag^+ > Cs^+ > Na^+ \gg Li^+$ respectively. The K_{ex} series for each same crown ether reflects the stability and the extractability of the univalent metal ion–crown ether complex in the aqueous phase. The K_{ex} sequences for the 15C5 system depends entirely on the extractability of the univalent metal ion–crown ether complex. In the case of the 18C6 system this largely depends on the stability of the univalent metal ion–crown ether complex.

It has been reported that crown ethers form stoichiometrically stable complexes with a variety of cations, especially those of the alkali and alkaline earths, and that the stability of the complexes, in which the cation is held in the center of the crown ether cavity, depends primarily on the ratio of the ionic size to the cavity size of the crown ether.[1)]

Solvent extraction is an available and convenient method for investigating the complexing ability of crown ethers for various cations, and several extraction studies have been reported to date.[2)] In some of the studies the extractability of the metal cation–crown ether complex as well as that of the metal cation have been discussed in detail.[2b,d)]

In this paper, the overall extraction equilibrium constant values for the univalent metal cation–15-crown-5 (15C5) and 18-crown-6 (18C6) systems have been determined and the overall extraction equilibria analyzed by constituent equilibria. Since a large anion is readily extracted into nonpolar solvents,[2d)] the picrate anion has been used as the counter ion. Benzene has been used as the solvent on account of its nonpolarity.

Experimental

Materials. 15C5 and 18C6 were purchased from Nisso Co., Ltd. and used without further purification. Analytical-grade benzene, HNO_3, $LiOH \cdot H_2O$, NaOH, KOH, and reagent-grade $TlNO_3$ were obtained from Wako-Pure Chemicals Ltd. $AgNO_3$ and picric acid were analytical grade reagents obtained 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 $AgNO_3$ and $TlNO_3$, and the concentrations of the alkali metal hydroxides and picric acid solutions were determined by means of KCl, EDTA, acid and basic titrations, respectively. Benzene was washed twice with distilled water.

Apparatus and Procedure. The organic phase of the crown ether (6.0×10^{-5}—6.6×10^{-2} M; 1 M=1 mol dm^{-3}) and the aqueous phase of the univalent metal hydroxide or nitrate (9.9×10^{-4}—3.2×10^{-2} M) and the picric acid (1.0×10^{-3}—1.1×10^{-2} M) in stoppered glass tubes (30 ml) were shaken in a thermostated water bath for approx. 30 min at 25±0.2 °C and centrifuged. The initial volume of each phase was 10 ml in all cases. A portion of the aqueous phase 8 ml was transferred to a 10 ml beaker and the hydrogen ion concentration determined by a Hitachi-Horiba F-5 pH meter. For the univalent metal hydroxide and nitrate systems the extractions were conducted at pH 9.7—12.1 and pH 2.3—2.8, respectively. For the systems of the alkali metals–15C5 and 18C6, a portion of the organic phase 8 ml was transferred to a 50 ml beaker and allowed to evaporate over several days. The residue was dissolved in 0.01 M NaOH aqueous solution 8 ml and the picrate concentration determined at 356 nm by a Shimadzu UV-200 spectrophotometer ($\varepsilon = 1.45 \times 10^4$ cm^{-1} M^{-1}). For the systems of Ag and Tl–15C5 and 18C6, the metal in the organic phase was back-extracted into 1 M nitric acid aqueous solution 8 ml and the metal concentration in the aqueous phase determined by a Seiko SAS-725 atomic absorption spectrophotometer. In control experiments in the absence of either the crown ether or picric acid, for the alkali metals and Tl–15C5 and 18C6 system, and for the Ag–15C5 and 18C6 system it was found that there was no extraction and a little extraction, respectively.

The Distribution Coefficient of the Crown Ether. A portion 13 ml of benzene solution containing the crown ether and an equal volume of distilled water were placed in a stoppered glass tube and shaken under the same conditions as above. The range of concentration of 15C5 and 18C6 were from 5.1×10^{-2} to 3.3×10^{-1} M and from 2.8×10^{-2} to 3.1×10^{-1} M, respectively. After centrifuging, a portion 12 ml of the organic phase was transferred to a 10 ml beaker, allowed to evaporate over several days, and the residue weighed. The average distribution coefficients determined in this way are given in Table 1.

Results

In an equilibrium between an aqueous solution of a univalent metal ion, M^+, a picrate ion, A^-, and a benzene solution of a crown ether, L, the equilibrium constants may be defined by the following equations:

$$K_{ex} = [MLA]_0[H^+]/[M^+][L]_0[HA]_0 \quad (1)$$

$$K_{D,L} = [L]_0/[L] \quad (2)$$

$$K_{ex}(HA) = [HA]_0/[H^+][A^-] \quad (3)$$

$$K_{ML} = [ML^+]/[M^+][L] \quad (4)$$

$$K_{ex'} = [MLA]_0/[ML^+][A^-] \quad (5)$$

where the subscript "0" and the lack of subscript designates the organic phase and the aqueous phase, respectively: square brackets indicate the molar concentrations. Thus K_{ex} can be written as follows:

$$K_{ex} = K_{D,L}^{-1}K_{ex}(HA)^{-1}K_{ML}K_{ex'} \quad (6)$$

From the mass balance, $[L]_0$, $[M^+]$, and $[A^-]$ may be given by;

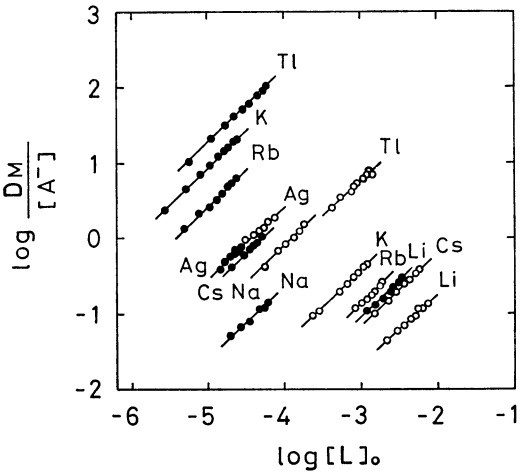

Fig. 1. Plots of log (D_M/[A$^-$]) *vs.* log[L]$_0$ for the 15C5 and 18C6 systems at 25 °C. ○: 15C5, ●: 18C6.

$$[L]_0 = ([L]_t - [MLA]_0)/(\alpha+\beta[M^+]) \quad (7)$$

$$[M^+] = ([M]_t - [MLA]_0)/(1+\beta[L]_0) \quad (8)$$

$$[A^-] = ([HA]_t - [MLA]_0)/\{1+(K_{HA}+K_{ex}(HA))[H^+]\} \quad (9)$$

where the subscript "t" denotes the total concentration, $\alpha=1+K_{D,L}^{-1}$, and $\beta=K_{ML}K_{D,L}^{-1}$. The value of K_{ex} (HA) has spectrophotometrically been determined as 247 using the association constant of picric acid ($K_{HA}=1.9_5$[3]). Substitution of Eq. 8 into Eq. 7 gives:

$$[L]_0 = [-\{\alpha+\beta([M]_t-[L]_t)\} + \sqrt{\{\alpha+\beta([M]_t-[L]_t)\}^2-4\alpha\beta([MLA]_0-[L]_t)}]/2\alpha\beta \quad (10)$$

The distribution ratio of the univalent metal may be represented by

$$D_M = [MLA]_0/([M^+] + [ML^+]) \quad (11)$$

In the case of $[M^+] \gg [ML^+]$, Eq. 11 becomes

$$D_M = K_{ex}K_{ex}(HA)[L]_0[A^-] \quad (12)$$

The log(D_M/[A$^-$]) *vs.* log[L]$_0$ plot in Fig. 1 shows a linear relationship with a slope of 1 in every case, indicating that the crown ether forms a 1:1 complex with the univalent metal ion. The values of [L]$_0$ and [A$^-$] in Eq. 12 were calculated from Eqs. 10 and 9, respectively. For the Li$^+$–15C5 and 18C6 systems, however, the value of [L]$_0$ has been calculated from Eq. 7, neglecting the term, β[M$^+$]. The equilibrium constants obtained from these data are summarized in Table 1, together with the literature values.

Discussion

From Table 1, the log K_{ex} series for 15C5 and 18C6 for the alkali metal ions are given by Na$^+ \gg$K$^+$>Rb$^+$>Cs$^+$>Li$^+$ and K$^+$>Rb$^+$>Cs$^+$>Na$^+ \gg$Li$^+$, respectively, indicating that the extractability of the alkali metal ion depends on the ratio of the ionic size to the cavity size of the crown ether, as can be seen in Table 2. Although the crystal radii of the Ag$^+$ and Tl$^+$ ions are nearly equal to that of the K$^+$ ion (Table 2), for the 15C5 system the log K_{ex} values for Ag$^+$ and Tl$^+$ are much larger than that for K$^+$, and for the 18C6 system the log K_{ex} value for K$^+$ is much larger than that for Ag$^+$ and a little smaller than that for Tl$^+$ (Table 1).

Table 1. Summary of equilibrium constants at 25 °C

Crown ether	$K_{D,L}$	Cation	log K_{ex}	log $K_{ex'}$	log K_{ML}[4]
15C5	0.15_6	Li$^+$	−1.10	—	—
		Na$^+$	1.51	2.40	0.70
		K$^+$	0.19	1.04	0.74
		Rb$^+$	−0.25	0.72	0.62
		Cs$^+$	−0.49	0.30	0.8
		Ag$^+$	2.06	2.71	0.94
		Tl$^+$	1.41	1.77	1.23
18C6	0.063_4	Li$^+$	−0.47	—	—
		Na$^+$	1.00	1.39	0.80
		K$^+$	3.58	2.74	2.03
		Rb$^+$	3.04	2.67	1.56
		Cs$^+$	1.99	2.19	0.99
		Ag$^+$	2.05	1.74	1.50
		Tl$^+$	3.91	2.83	2.27

Table 2. Crystal ionic radii of univalent metals and cavity radii of crown ethers (Å)

Cation	Crystal ionic radius[5]	Crown ether	Cavity radius[6]
Li$^+$	0.60	15-crown-5	0.85-1.1
Na$^+$	0.95	18-crown-6	1.3-1.6
K$^+$	1.33		
Rb$^+$	1.48		
Cs$^+$	1.69		
Ag$^+$	1.26		
Tl$^+$	1.40		

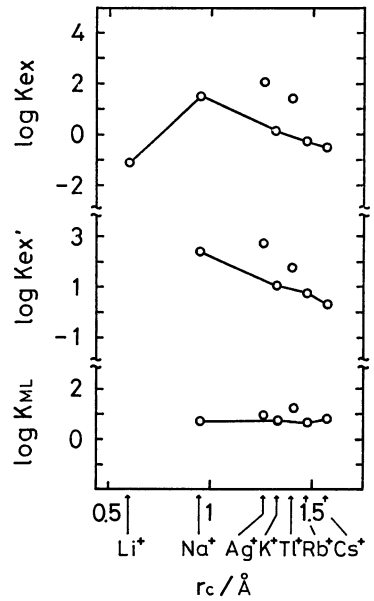

Fig. 2. Plots of logK_{ex}, log$K_{ex'}$, and logK_{ML} *vs.* crystal ionic radius, r_c, of univalent metal for the 15C5 system.

In the case of Ag$^+$ and Tl$^+$, it may be seen from Tables 1 and 2 that the univalent metal ion which has a more optimum size for the crown ether cavity shows a greater extractability, which is the same tendency for the alkali metal ions reported above.

It may be seen from Table 1 that the log $K_{ex'}$ se-

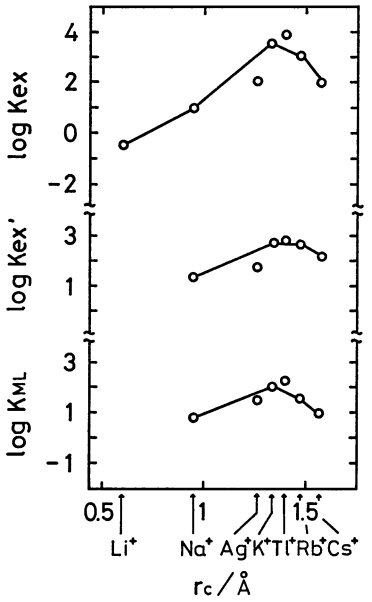

Fig. 3. Plots of $\log K_{ex}$, $\log K_{ex'}$, and $\log K_{ML}$ *vs.* crystal ionic radius of univalent metal for the 18C6 system.

quences of the alkali metal ions with 15C5 and 18C6 are $Na^+ \gg K^+ > Rb^+ > Cs^+$ and $K^+ \geq Rb^+ > Cs^+ > Na^+$, respectively. For the 15C5 system the $\log K_{ex'}$ value for Ag^+ is larger than that for Tl^+, and on the contrary for the 18C6 system (Table 1). The results show that the more closely the univalent metal ion fits into the crown ether cavity, the more extractable is the univalent metal ion–crown ether complex (Table 2). Consequently, the extractability of the univalent metal ion–crown ether complex is affected by the chemical nature of the univalent metal ion held in the cavity of the crown ether.

Equation 6 shows that the series for K_{ex} for the same crown ether for different univalent metal ions reflects the stability and the extractability of the univalent metal ion–crown ether complex in the aqueous phase. Plots of $\log K_{ex}$, $\log K_{ex'}$, and $\log K_{ML}$ *vs.* the crystal ionic radius for the 15C5 and 18C6 systems are given in Figs. 2 and 3, respectively. It may be seen from Figs. 2 and 3 that the $\log K_{ex}$ sequences for the 15C5 system depend completely on the $\log K_{ex'}$ sequences. On the other hand those for the 18C6 system largely depend on the $\log K_{ML}$ ones.

The authors would like to thank Mr. Fujio Takahashi of this laboratory for experimental assistance.

References

1) a) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967); b) C. J. Pedersen, *ibid.*, **92**, 386 (1970).

2) a) C. J. Pedersen, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **27**, 1305 (1968); b) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 4684 (1971); c) A. Sadakane, T. Iwachido, and K. Tōei, *Bull. Chem. Soc. Jpn.*, **48**, 60 (1975); d) P. R. Danesi, H. Meider-Gorican, R. Chiarizia, and G. Scibona, *J. Inorg. Nucl. Chem.*, **37**, 1479 (1975); e) M. Jawaid and F. Ingman, *Talanta*, **25**, 91 (1978).

3) "Dissociation Constants of Organic Acids in Aqueous Solution," ed by G. Kortün, W. Vogel, and K. Andrussov, Butterworths, London (1961).

4) R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, *J. Am. Chem. Soc.*, **98**, 7620 (1976).

5) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell Univ. Press (1960).

6) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 600 (1971).