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The Solvent Extraction of Alkali Metal Picrates by 12-Crown-4

Yasuyuki Takeda

Department of Chemistry, Faculty of Science, Chiba University, Yayoi-chō, Chiba 260

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Synopsis. The overall extraction equilibrium constants (K_{ex}) for 1 : 1 : 1 complexes of 12-crown-4 (12C4) with alkali metal picrates between benzene and water have been determined at 25 °C. The K_{ex} series for the 12C4 for the alkali metal ions are given by $Na^+ > Li^+ > K^+ > Rb^+ \geq Cs^+$.

Solvent-extraction studies of crown ether complexes with various metal ions, particularly with the alkali and alkaline earth metal ions, have been reported.[1)] In some of the studies, the overall extraction equilibria have been analyzed by means of the constituent equilibria, and the extractability of the crown ether complex as well as that of the metal ion has been discussed in detail.[1b),1c),1d)] Moreover, crown ethers have been used for extraction analysis.[2)]

In this paper, the overall extraction equilibrium constant values for the 12-crown-4 (12C4)–alkali metal picrate system have been determined between benzene and water at 25 °C, and these extraction constant values have been compared with those of 15-crown-5 (15C5), in order to clarify the role of 12C4 in the extraction process.

Experimental

Materials. The 12C4 was obtained from Wako-Pure Chemicals, Ltd., and was used without further purification. The concentrations of the alkali metal hydroxides and picric acid solutions were determined by means of acid and basic titrations respectively. The benzene (analytical-grade) was washed twice with distilled water.

Apparatus and Procedure. The organic phase of the crown ether (1.2×10^{-2}—2.5×10^{-1} M; 1 M = 1 mol dm^{-3}) and the aqueous phase of the alkali metal hydroxide (1.1—1.7×10^{-2} M) and the picric acid (6.0×10^{-3}—1.1×10^{-2} M) in stoppered glass tubes (30 ml) were shaken in a thermostated water bath for approx. 35 min at 25±0.2 °C and then centrifuged. The initial volume of each phase was 10 ml in all cases. A portion of the aqueous phase (8 ml) was transferred into a 10-ml beaker, and the hydrogen-ion concentration determined by means of a Hitachi-Horiba F-5 pH meter. The extractions were conducted at pH 9.1—11.9. The picrate in the organic phase was back-extracted into 8 ml of a 0.01 M NaOH aqueous solution, and the picrate concentration was determined at 356 nm by means of a Shimadzu UV-200 spectrophotometer ($\varepsilon = 1.45 \times 10^4$ cm^{-1} M^{-1}). In blank experiments, no detectable extraction was found in the absence of 12C4.

The Distribution Coefficient of 12C4. A portion (13 ml) of a benzene solution containing 12C4 and an equal volume of distilled water were placed in a stoppered glass tube and shaken under the conditions given above. The range of concentration of the 12C4 was from 1.3×10^{-1} to 2.3×10^{-1} M. After centrifuging, a portion (12 ml) of the organic phase was transferred to a 20-ml beaker, and allowed to evaporate over several days, and the residue weighed. Since 12C4 is very hygroscopic, the water content of the residue was determined by Karl Fischer titration. The average distribution coefficient, determined in this way, was 0.15.

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:

$$K_{ex} = [MLA]_o[H^+]/[M^+][L]_o[HA]_o \tag{1}$$

$$K_{D,L} = [L]_o/[L] \tag{2}$$

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

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

$$K_{ex'} = [MLA]_o/[ML^+][A^-] \tag{5}$$

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

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

The distribution ratio of the univalent metal may be represented by:

$$D_M = [MLA]_o/([M^+]+[ML^+]) \tag{7}$$

In the case of $[M^+] \gg [ML^+]$, Eq. 7 becomes:

$$D_M = K_{ex}K_{ex}(HA)[L]_o[A^-]. \tag{8}$$

The $-\log(D_M/[A^-])$ *vs.* $-\log[L]_o$ plot in Fig. 1 shows a linear relationship with a slope of 1 in every case, indicating that 12C4 forms the 1 : 1 complex with the alkali metal ion. The values of $[L]_o$ and $[A^-]$ in Eq. 8 were calculated by means of Eqs. 9 and 10 respectively:

$$[L]_o = ([L]_t - [MLA]_o)/(1 + K_{D,L}{}^{-1}) \tag{9}$$

$$[A^-] = ([HA]_t - [MLA]_o)/\{1 + (K_{HA} + K_{ex}(HA))[H^+]\} \tag{10}$$

Table 1. Equilibrium constants at 25 °C, crystal ionic radii of alkali metals, and cavity radii of crown ethers

Crown ether	Cavity radius (Å)[4)]	$K_{D,L}$	Cation	Crystal ionic radius(Å)[5)]	$\log K_{ex}$
12C4	0.5—0.65	0.15			
			Li^+	0.60	−1.62
			Na^+	0.95	−1.44
			K^+	1.33	−1.82
			Rb^+	1.48	−2.10
			Cs^+	1.69	−2.18
15C5	0.85—1.1	0.15_6[1d)]			
			Li^+	0.60	−1.10[1d)]
			Na^+	0.95	1.51[1d)]
			K^+	1.33	0.19[1d)]
			Rb^+	1.48	−0.25[1d)]
			Cs^+	1.69	−0.49[1d)]

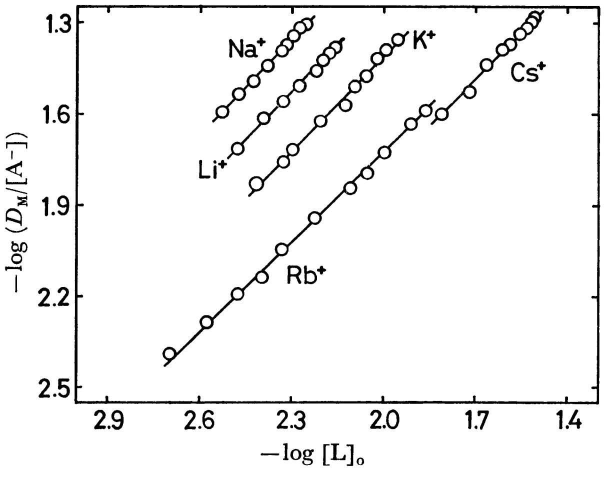

Fig. 1. Plots of $-\log(D_{\mathrm{M}}/[\mathrm{A}^-])$ *vs.* $-\log[\mathrm{L}]_0$ for the alkali metals–12C4 system at 25 °C.

where the subscript "t" denotes the total concentration. The value of $K_{\mathrm{ex}}(\mathrm{HA})$ was spectrophotometrically determined to be 247 by using the association constant of picric acid ($K_{\mathrm{HA}}=1.9_5$[3]). The equilibrium constants obtained from these data are summarized in Table 1, together with the literature values.

Discussion

The $\log K_{\mathrm{ex}}$ series for the 12C4 for the alkali metal ions are given by $\mathrm{Na^+} > \mathrm{Li^+} > \mathrm{K^+} > \mathrm{Rb^+} \geq \mathrm{Cs^+}$, indicating that the nearer the crystal radius of the alkali metal ion approaches to the cavity radius of 12C4, the more extractable the alkali metal ion is except for $\mathrm{Li^+}$ (Table 1). In a previous paper,[1d] we have demonstrated that, in each case of 15C5 and 18-crown-6 (18C6), the alkali metal ion which has the optimum size for the crown ether cavity and the corresponding alkali metal ion–crown ether complex are the most extractable of all the alkali metal ions and the alkali metal ion–crown ether complexes respectively. In the case of 12C4, $\mathrm{Na^+}$ is more extractable than $\mathrm{Li^+}$, although $\mathrm{Li^+}$ fits more closely into the 12C4 cavity than $\mathrm{Na^+}$. This may be attributed to the fact that $\mathrm{Li^+}$ is much more strongly hydrated than $\mathrm{Na^+}$. 14-Crown-4 (14C4) and 12C4 have four donor oxygen atoms. 14C4 has a slightly larger cavity radius (0.6—0.75 Å[4]) than 12C4. However, $\mathrm{Li^+}$ is the most favorable fit for the 14C4 cavity of all the alkali metal ions. It is interesting that 14C4 extracted $\mathrm{Li^+}$ most effectively among the alkali metal ions.[1a] 15C5 and 18C6 show the most remarkable selectivity for $\mathrm{Na^+}$ and $\mathrm{K^+}$ respectively among the alkali metal ions.[1d] On the other hand, 12C4 displays no pronounced selectivity for any alkali metal ion.

Equation 6 shows that the series for K_{ex} for the same univalent metal ion for different crown ethers reflects the magnitude of $K_{\mathrm{D,L}}$, the stability, and the extractability of the univalent metal ion–crown ether complex in the aqueous phase. It may be noted from Table 1 that the $\log K_{\mathrm{ex}}$ value of 12C4 for the same alkali metal ion is smaller than that of 15C5. Since the $K_{\mathrm{D,L}}$ value of 12C4 is nearly equal to that of 15C5, this may be due to the fact that the size of the 12C4 complex with the same alkali metal ion is smaller than that of the 15C5 complex and that the ability of 12C4, which has fewer donor oxygen atoms (four) than 15C5 (five), to form the complex with the same alkali metal ion in the aqueous phase is poorer than that of 15C5.

References

1) 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) Y. Takeda and H. Katō, *Bull. Chem. Soc. Jpn.*, **52**, 1027 (1979); d) Y. Takeda and H. Gotō, *ibid.*, **52**, 1920 (1979); e) Y. Takeda, *ibid.*, **52**, 2501 (1979).

2) a) H. Sumiyoshi, K. Nakahara, and K. Ueno, *Talanta*, **24**, 763 (1977); b) M. Takagi, H. Nakamura, and K. Ueno, *Anal. Lett.*, **10**, 1115 (1977); c)T. Kimura, K. Iwashima, T. Ishimori, and H. Hamaguchi, *Chem. Lett.*, **1977**, 563; d) Y. Takeda, S. Suzuki, and Y. Ohyagi, *ibid.*, **1978**, 1377; e) Y. Takeda, K. Oshio, and Y. Segawa, *ibid.*, **1979**, 601.

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

4) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem. Int. Ed.*, **11**, 16 (1972).

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