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Solvent Extraction of Alkali Metal Picrates with Poly- and Bis(benzo-12-crown-4)s

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Solvent extractions of alkali metal picrates were carried out using newly synthesized poly- and bis(crown ether)s containing benzo-12-crown-4 moieties in a water–chloroform system. The extraction equilibrium constants(K_e) and the complexation constants (K_c) in the chloroform phase were determined at 25 °C. The K_e values for the alkali metal cations decreases as follows: $Na^+ > K^+ > Rb^+ \geq Cs^+$ with the poly(benzo-12-crown-4) and K^+, Rb^+, $Cs^+ > Na^+$ with the bis(benzo-12-crown-4). The poly(benzo-12-crown-4) improved the sodium-ion selectivity of the corresponding monocyclic analog because of the easy formation of 2:1 crown ether unit-cation complexes assisted by the cooperative action of two adjacent crown ether units, while the bis(benzo-12-crown-4) did not. A separate extraction experiment was also undertaken in a water–dichloromethane system in order to compare the extractability of these benzo-12-crown-4 derivatives with that of 12-crown-4.

It is known that 12-crown-4 has a relatively small cavity, which seems to be suitable for forming stable complexes with Li^+ or Na^+. However, only a few papers have been published on the solvent extraction of metal cations using 12-crown-4 and its derivatives.[1,2] On the other hand, our previous work concerning the cation-binding ability of benzo-15-crown-5 and benzo-18-crown-6 derivatives has made it clear that poly- and bis(crown ether)s have much greater extractabilities and selectivities than their monocyclic analogs, especially for the cations which form 2:1 crown ether unit-cation complexes with them.[3—6] Some cooperative effects of adjacent crown ether units of the crown ethers were thought to bring about these results. This observation induced us to synthesize poly- and bis(crown ether)s containing benzo-12-crown-4 moieties and then to investigate their binding properties for alkali metal cations.

In this paper, we will consider the solvent extraction of alkali metal picrates with newly synthesized poly- and bis(crown ether)s **2**(n=1), **3** and their monocyclic analogs **1**(n=1), **4** in water–chloroform and water–dichloromethane systems.

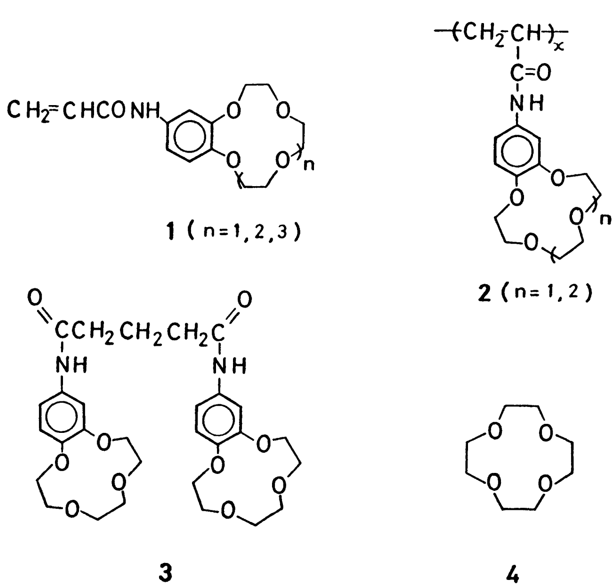

Fig. 1. Crown ether derivatives used in this study.

Experimental

Materials. 12-Crown-4 was obtained from Wako Pure Chemical Industries, Ltd., and used without further purification. Benzo-12-crown-4 was prepared according to Liotta's method.[7] The monocyclic crown ether **1**(n=1) and poly- and bis(crown ether)s **2**(n=1) and **3** were derived from benzo-12-crown-4 in the manner described elsewhere.[3] The analytical data of **1**(n=1) and **3** are as follows: **1**(n=1): mp 105.0—106.5 °C; M^+ 293. Found: C, 61.18; H, 6.70; N, 4.34%. Calcd for $C_{15}H_{19}O_5N$: C, 61.42; H, 6.53; N, 4.78%. **3**: Mp 170.0—171.0 °C; M^+ 574. Found: C, 60.20; H, 6.85; N, 4.88%. Calcd for $C_{29}H_{38}O_{10}N_2$: C, 60.62 H, 6.67; N, 4.88%. Poly(crown ether) **2**(n=1) was purified by reprecipitation in chloroform–diethyl ether system. The alkali metal picrates were synthesized according to Fuoss' method.[8] Tetrahydrofuran (THF) was dried over sodium. Chloroform and dichloromethane were purified by distillation just before use.

Optical Spectra. Optical spectral changes in the above crown ether–cation complexes were measured by adding the crown ethers to 2.5×10^{-5} M(1 M=1 mol dm^{-3}) THF solutions of alkali metal picrates. Measurements were carried out with a Hitachi 340 recording spectrophotometer.

Extraction. Equal volumes (10 ml) of organic and aqueous solutions were shaken in a stoppered flask for 40 min at 25±0.1 °C.

Chloroform was chosen primarily as the organic phase for extraction. However, in order to compare the extractabilities and cation selectivities of the crown ethers **1**, **2** (n=1), and **3** with those of **4**, solvent extractions were also carried out with a dichloromethane solution of the crown ethers (1.4×10^{-2} M or 3.5×10^{-3} M for crown ether units) and an aqueous solution of alkali metal hydroxide (1.0×10^{-2} M) and picric acid(7.0×10^{-4} M), because the chloroform solution containing **4** often became turbid.

Extraction equilibrium constants with **1**, **2**(n=1), and **3** were calculated in a water–chloroform system. In this system, the concentrations of the crown ether in the organic phase were $(1.0—5.0) \times 10^{-4}$ M for **2** (n=1) and $(1.0—5.0) \times 10^{-3}$ M for **1** (n=1) and **3**, while that of the alkali metal picrate in the aqueous phase was 1.0×10^{-2} M. After the complete phase separation, a 2-ml portion of acetonitrile was added to 2 ml of the chloroform phase, and the concentration of the picrate was determined spectrophotometrically[λ_{max}=374 nm, ε: Na^+ 1.86, K^+ 1.87, Rb^+ 1.88, Cs^+ 1.86 ($\times 10^4$ M^{-1} cm^{-1})]. The distribution constants of the picrates in the absence of crown ethers, K_d, have been obtained previously [Na^+ 1.20, K^+ 2.67 Rb^+ 3.66, Cs^+ 6.66 ($\times 10^{-3}$ M^{-1})].[4)]

Extraction Equilibrium Constant and Complexation Constant for the Organic Phase. The overall extraction equilibrium may be written as:

$$M^+ + Pi^- + nCr^* \rightleftharpoons M(Cr)_nPi^*$$

$$K_e = [M(Cr)_nPi^*]/[M^+][Pi^-][Cr^*]^n \qquad (1)$$

where M^+, Pi^-, and Cr denote an alkali metal cation, a picrate anion, and a crown ether unit, respectively. The asterisk refers to the species in the organic phase.[9)] This equilibrium consists of the following equilibria:[10)]

$$M^+ + Pi^- \rightleftharpoons MPi^*$$

$$K_d = [MPi^*]/[M^+][Pi^-], \qquad (2)$$

$$MPi^* + nCr^* \rightleftharpoons M(Cr)_nPi^*$$

$$K_c = [M(Cr)_nPi^*]/[MPi^*][Cr^*]^n. \qquad (3)$$

K_c represents the complexation constant in the organic phase, which can be calculated with Eq. 4;

$$K_c = K_e/K_d. \qquad (4)$$

In the same way as has been described in the previous paper, the following relations can be derived;[4,11)]

$$D = K_e(M^\circ - A)(Cr^\circ - A), \qquad (5)$$

$$D = K_e(M^\circ - A)(Cr^\circ - 2A)^2, \qquad (6)$$

$$D = K_e(M^\circ - A)(Cr^\circ - 2A), \qquad (7)$$

where D is the distribution ratio of the metal between the two phases. M°, Cr°, and A denote the initial concentrations of metal cations and crown ether units, and the concentrations of the picrates extracted into the organic phase as the counter anions, respectively. Equation 5 is applied when 1:1 crown ether unit-cation complexes are formed. When 2:1 crown ether unit-cation complexes are formed by monomeric crown ethers, Eq. 6 is used. However, in the system of poly- and bis(crown ether)s, which may be thought to form intramolecular 2:1 crown ether unit-cation complexes, Eq. 7 can be applied.

Results and Discussion

Optical Spectra of Alkali Metal Picrates and Their Crown Ether Complexes. Optical spectral changes of alkali metal picrates in THF accompanying an increase in the concentration of crown ether units suggest the stoichiometry of the crown ether unit-cation complexes qualitatively.[6,12)] The maxima of the main absorption band, λ_{max}, for alkali metal picrates are found to be at 351 nm (Na^+), 358 nm (K^+), 359 nm (Rb^+), and 361 nm (Cs^+). In their complexes with crown ethers, the increase in the distance between cations and counter anions causes bathochromic shifts of the spectrum. When 1:1 crown ether unit-cation complexes are formed, cations and their counter anions are close to each other, forming tight ion-pairs. In this case, the bathochromic shift is not very large. On the other hand, in 2:1 crown ether unit-cation complexes, cations are forced to separate from their counter anions, which results in the large spectral shift to nearly 380 nm. Figure 2 shows some typical optical spectra for the 1:1 and 2:1 crown ether unit-cation complexes. In the **3**–Na^+ system, the addition of a large excess of crown ethers (the molar ratio of crown ether unit to picrate salt is 100) causes a spectral shift to only 353 nm, which suggests that 1:1 crown ether unit-cation complexes are formed. On the contrary, in the system of **2**(n=1)–Na^+, the absorption maximum shifts to 378 nm, showing the formation of 2:1 crown ether unit-cation complexes. However, a much higher concentration of crown ether units is needed for the pronounced bathochromic shift of the spectrum in the **2**(n=1)–Na^+ system than for that in the system of **2**(n=2)–K^+, which suggests that the complexation constant of the **2**(n=1)–Na^+ complex is quite small. From the results of similar experiments for other systems, the stoichiometry of these complexes was determined to be as follows: for Na^+ through Cs^+, only **2**(n=1) forms 2:1 crown ether unit-cation complexes; **1**(n=1) and **3** form 1:1 complexes.

Extraction Equilibria. Table 1 shows a considerable difference in the extractability for Na^+ between **1**(n=1) and **4**, although they have the same number of oxygen atoms. For the system of **4**, the extractability apparently depends on the relation between the cation size and the cavity size of **4**. For the sys-

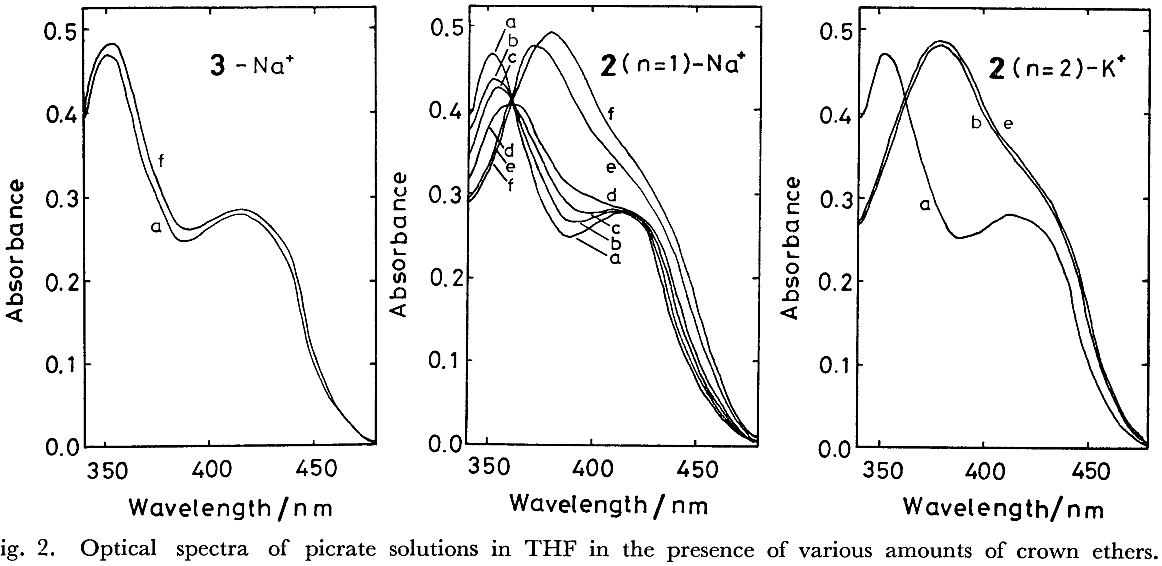

Fig. 2. Optical spectra of picrate solutions in THF in the presence of various amounts of crown ethers. [Metal picrates]=2.5×10^{-5} M, [crown ether unit]/[metal picrate]: a; 0, b; 3, c; 5, d; 10, e; 50, f; 100.

TABLE 1. EXTRACTION OF ALKALI METAL PICRATES WITH 12-CROWN-4 DERIVATIVES IN H_2O-CH_2Cl_2 SYSTEM[a)]

Crown	Picrate salt extracted (%)			
	Na^+	K^+	Rb^+	Cs^+
1(n=1)	5.81	9.10	10.1	10.3
2(n=1)	78.3 (36.1)	63.3 (25.3)	53.6 (20.5)	50.6 (18.7)
3	17.2	19.4	18.8	19.4
4	18.6	6.90	4.30	3.50

a) [Picric acid] = 7×10^{-4} M, [metal hydroxide] = 1×10^{-2} M, [crown ether unit] = 1.4×10^{-2} M(3.5×10^{-3} M in parentheses).

TABLE 2. DISTRIBUTION RATIOS OF ALKALI METAL CATIONS IN H_2O-$CHCl_3$ SYSTEM[a)]

Crown	D ($\times10^{-3}$)			
	Na^+	K^+	Rb^+	Cs^+
1(n=1)	(0.670)	(1.85)	(2.20)	(2.55)
2(n=1)	7.15	6.67	4.68	4.43
3	(5.03)	(6.19)	(5.76)	(5.44)
1(n=2)	5.26[b)]	16.7	9.72	0.708[b)]
1(n=3)	6.16[b)]	53.2	47.3	46.9

a) [Picrate] = 1×10^{-2} M, [crown ether unit] = 5×10^{-4} M (5×10^{-3} M in parentheses). b) Taken from Ref. 4.

tem of **1**(n=1), the distribution of picrate itself from the aqueous phase to the dichloromethane phase, the order of which can be expected to be the same as that in chloroform ($Cs^+>Rb^+>K^+>Na^+$, see Experimental), might contribute significantly to the extractability compared to the complexing ability, probably because the benzene ring decreases the basicity of the oxygen atoms adjacent to aromatic carbons,[13)] which seems to lower the complexing ability. Poly(crown ether) **2**(n=1) has a much greater extractability for Na^+ than the others. Because of the extremely strong hydration, very little Li^+ was extracted [*e.g.*, <1% for **1**(n=1)], so no further investigation was made with respect to Li^+. Values of distribution ratios, D, are useful for comparing the extractability of the crown ethers for these cations. Since **1**(n=1) and **3** have much smaller extractabilities than **2**(n=1) and **1**(n=2, 3), the concentrations of **1**(n=1) and **3** in extractions were ten times higher than those of **2**(n=1) and **1**(n=2, 3). It should be noted that poly(crown ether) **2**(n=1) has a larger extractability and selectivity for Na^+ than **1**(n=2, 3) does.

The plots of logarithms of both sides in Eqs. 5—7 gave straight lines with a slope of 1, indicating that the stoichiometry of the complexes and the assumptions used for the derivation of these equations are reasonable. Figure 3 shows the plots for the **2**(n=1) systems as the examples. The values of $\log K_e$, which are obtained from the intercepts of the lines, and those of $\log K_c$, which are calculated from Eq. 4, are listed in Tables 3 and 4. There is a close correlation between the D and K_e values. **1**(n=1) and **3** have very small $\log K_e$ values for all the cations. The order of $\log K_e$ values for alkali metal ions with **1**(n=1) and **3** are $Cs^+>Rb^+>K^+>Na^+$ and K^+, Rb^+, $Cs^+>Na^+$, respectively. On the other hand, a relatively high selectivity for Na^+ was observed with poly(crown ether) **2**(n=1).

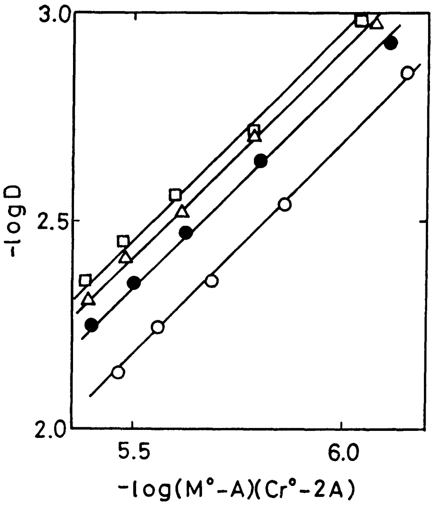

Fig. 3. Plots of $-\log D$ *vs.* $-\log(M^\circ-A)(Cr^\circ-2A)$ for poly(crown ether) **2**(n=1) systems.
○: Na^+, ●: K^+, △: Rb^+, □: Cs^+.

TABLE 3. EXTRACTION EQUILIBRIUM CONSTANTS IN H_2O-$CHCl_3$ SYSTEM AT 25 °C

Crown	$\log K_e$[a)]			
	Na^+	K^+	Rb^+	Cs^+
1(n=1)	1.12	1.56	1.64	1.70
2(n=1)	3.30	3.16	3.08	3.04
3	2.00	2.10	2.07	2.05
1(n=2)[b)]	3.10	(7.10)	(6.54)	(5.59)
1(n=3)[b)]	3.16	5.22	4.64	4.24

a) The unit of K_e is M^{-2} (M^{-3} in parentheses). b) Taken from Ref. 4.

TABLE 4. COMPLEXATION CONSTANTS IN CHLOROFORM PHASE AT 25 °C

Crown	$\log K_c$[a)]			
	Na^+	K^+	Rb^+	Cs^+
1(n=1)	4.04	4.13	4.08	3.88
2(n=1)	6.22	5.73	5.52	5.22
3	4.92	4.67	4.51	4.23
1(n=2)[b)]	6.02	(9.67)	(8.98)	(7.77)
1(n=3)[b)]	6.08	7.79	7.08	6.42

a) The unit of K_c is M^{-1} (M^{-2} in parentheses). b) Taken from Ref. 4.

The stoichiometry of the crown ether unit-cation complexes is likely to have a correlation with these results. When we compare the relative size of the cavity of 12-crown-4 and alkali metal cations (cavity radius: 12-crown-4 0.5—0.65 Å[1)], ionic radius: Na^+ 0.95 Å, K^+ 1.33 Å, Rb^+ 1.48 Å, Cs^+ 1.69 Å[14)]), **1**, **2**(n=1), and **3** may be anticipated to form 2:1 crown ether unit-cation complexes. Nevertheless, the formation of the 2:1 crown ether unit-cation complexes was observed only with **2**($n=1$) (see the optical measurement section). For the systems of **1**($n=1$) and **3**, the comparison of the values of $\log K_e$ and $\log K_c$ shows a large difference in the sequence between them, which suggests that the extractability for the cations depends mainly on the value of K_d and not on that of K_c. However, poly(crown ether) **2**($n=1$), which may be thought to have a close proximity of adjacent crown ether moieties induced by the rigidity of its comformation, may be able to form 2:1 crown ether unit-cation complexes more easily than **1**($n=1$) and **3**. Therefore, the suitable structure of the crown ether to form the 2:1 crown ether unit-cation complex with Na^+ may result in the selective binding of **2**($n=1$) for Na^+. Moreover, the large lipophilicity of **2**($n=1$) may also be thought to bring about its high extractability for Na^+, which is comparable to that of **1**(n=2,3). In this case, the values of $\log K_e$ reflect those of $\log K_c$. That is to say, the extractability of **2**($n=1$) for the cations depends mainly on the values of K_c and not on those of K_d, as was observed in our previous work with benzo-15-crown-5 and benzo-18-crown-6 derivatives.[4,5]

In conclusion, the newly synthesized poly(crown ether) **2**($n=1$) forms 2:1 crown ether unit-cation complexes with alkali metal cations, and the cooperative effect of two adjacent crown ether units of **2**($n=1$) in forming the 2:1 complexes brings about the selectivity and the large extractability for Na^+.

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