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Compositional Variation of Ionizable Crown Ether-Alkali Metal Ion Complexes in the Solvent Extraction Using Several Extraction Solvents

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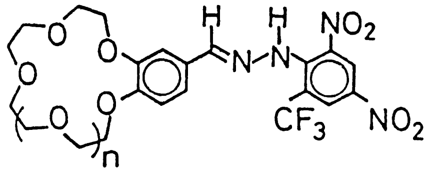
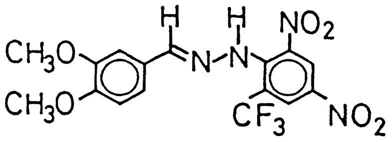
Novel benzo-15-crown-5 and 18-crown-6 derivatives bearing an ionizable hydrazone group were synthesized and complex formation equilibria of the compounds with alkali metal ions in solvent extraction were evaluated spectrophotometrically. Formation of 2:2 complexes of the crown ethers with metal ions was observed using chloroform as an extraction solvent.

Several chromogenic crown ether derivatives, which possess a proton-dissociable group as not only a chromophore but a cooperating site, have been investigated as analytical reagents for colorimetry and metal-ion detector.$^{1,2)}$ Benzocrown ether derivatives bearing a potential anionic site are known to form ion-pair complexes with alkali metal ions selectively under basic conditions.$^{2)}$ This paper is concerned in more detail with the complex formation of alkali metal ions and tetramethylammonium ion (TMA^+) by using the benzo-15-crown-5 and -18-crown-6 derivatives with a substituted hydrazone group, being a proton-dissociable chromogenic one, on the solvent extraction systems. It was realized that the composition of the complex extracted was dependent on the dielectric constant of the extraction solvent.

The reactions of (2,4-dinitro-6-trifluoromethylphenyl)hydrazine with appropriate 4'-formylbenzocrown ethers$^{3)}$ or 3,4-dimethoxybenzaldehyde (ethanol, acetic acid, reflux) afforded the corresponding hydrazones, 1,



1 n = 1
2 n = 2



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2, and 3, which were purified by reprecipitation from ethanol. Alkali metal ions in aqueous solution were extracted with 1,2-dichloroethane, dichloromethane or chloroform solutions containing the hydrazones. The extraction was carried out at 25 °C and was evaluated spectrophotometrically.

The ion-selectivities for both 1 and 2 in the solvent extraction using 1,2-dichloroethane under the conditions where the aqueous solutions contained the metal ions in 0.1 mol dm^{-3} each and were adjusted to pH 8.88 and 9.85, respectively, were decreased in the order $K^+ > Rb^+ > Cs^+ > Na^+$, $TMA^+ > Li^+$. The extraction equilibrium constants were determined by varying the metal ion concentration at appropriate pH value adjusted with LiOH and a buffer solution, and by keeping the hydrazone concentration constant in the organic solution. Their values were calculated according to the following equations by a non-linear least-squares method from the absorbance at the wavelength of maximal absorption of the organic phase.

$$(HL)_{org} + (M^+) \rightleftharpoons (ML)_{org} + (H^+), \qquad K^{ex}_{ML} = \frac{[ML]_o[H^+]}{[HL]_o[M^+]}$$

$$2(HL)_{org} + (M^+) \rightleftharpoons (MLHL)_{org} + (H^+), \qquad K^{ex}_{MLHL} = \frac{[MLHL]_o[H^+]}{[HL]_o^2[M^+]}$$

$$2(HL)_{org} + 2(M^+) \rightleftharpoons (MLML)_{org} + 2(H^+), \qquad K^{ex}_{MLML} = \frac{[MLML]_o[H^+]^2}{[HL]_o^2[M^+]^2}$$

It is shown in Table 1 that alkali metal ions were extracted into 1,2-dichloroethane solution as a mixture of 1:1 (ML) and 2:1 (MLHL) complexes with 15-crown-5 derivative 1, and the ion-selectivity of the crown ether was observed on extraction of 2:1 complex, being more lipophilic and stable than the 1:1 complex. When the alkali metal ions are extracted as 1:1 complexes with 1, the cation-complexing ability of the crown ether moiety might be in competition with the hydration of the cation. Extraction equilibrium constant of TMA^+ for 1 is in agreement with those for 18-crown-6 derivative 2 and dimethoxyphenyl one 3 without crown ether ring. It is probably because TMA^+ has high lipophilicity and low complexing ability with the crown ether.

On the other hand, 18-crown-6 derivative 2 formed overwhelmingly 1:1 complexes with the cations, except for Cs^+, using 1,2-dichloroethane (dielectric constant: $\varepsilon = 10.65$) as an extraction solvent. It implies that the cation-extractabilities of 2 are attributed to the high cation-binding ability of the benzo-18-crown-6 moiety.4) Use of dichloromethane,

Table 1. Extraction equilibrium constants[a)] (-log K_{ex}) of benzo-15-crown-5, -18-crown-6 and dimethoxyphenyl hydrazone, 1, 2, and 3, for cations by using the chlorinated hydrocarbons as extraction solvent

Solvent (dielectric constant)	Species	Extraction equilibrium constant (-log K_{ex})				
		Na^+	K^+	Rb^+	Cs^+	TMA^+
	Benzo-15-crown-5 hydrazone 1 (pK_a = 7.46[b)])					
CH_2ClCH_2Cl (10.65[c)])	ML	10.9	11.3	11.2	10.6	9.5
	MLHL	7.5	5.0	5.5	6.8	-
	MLML	-	-	-	-	-
CH_2Cl_2 (7.74[d)])	ML	11.3	-	12.0	11.4	
	MLHL	6.6	5.2	6.7	-	
	MLML	-	-	-	-	
$CHCl_3$ (4.80[c)])	ML	12.6	-	12.7	>13.0	
	MLHL	-	6.0	7.9	-	
	MLML	19.8	-	-	-	
	Benzo-18-crown-6 hydrazone 2 (pK_a = 7.45[b)])					
CH_2ClCH_2Cl (10.65[c)])	ML	9.4	7.4	7.9	8.1	9.5
	MLHL	-	-	-	4.0	-
	MLML	-	-	-	-	-
CH_2Cl_2 (7.74[d)])	ML	10.1	8.0	8.4	8.9	10.1
	MLHL	-	-	-	-	-
	MLML	-	-	-	-	-
$CHCl_3$ (4.80[c)])	ML	11.8	9.4	9.9	10.1	11.5
	MLHL	-	-	-	-	-
	MLML	19.0	12.9	13.9	15.3	-
	Dimethoxyphenyl hydrazone 3 (pK_a = 7.48[b)])					
CH_2ClCH_2Cl (10.65[c)])	ML	-	-	-	-	9.5

a) Average of measurements for three distinct crown ether concentrations. organic phase: [crown ether] = 4.0×10^{-6}, 2.0×10^{-5} and 1.0×10^{-4} mol dm^{-3}; aqueous phase: [cation] = 1.0×10^{-3} - 2.0 mol dm^{-3}, pH = 10.0.
b) $pK_a = -\log K_a$, $K_a = [H^+][L^-]/[HL]$ in water - 1,4-dioxane (8/2 v/v).
c) At 20 °C. d) At 10 °C.

which possesses the lower dielectric constant ε = 7.74, instead of 1,2-dichloroethane resulted in remarkable decrease in the extractabilities of <u>1</u> for alkali metal ions and TMA^+ uniformly.

Especially, when chloroform, which has the lowest dielectric constant ε = 4.80, was used as an extraction solvent, <u>2</u> formed mixtures of 1:1 and 2:2 complexes with Na^+, K^+, Rb^+, and Cs^+. While the 2:2 complexes of Na^+ and K^+ were predominantly formed under the conditions depicted in the note of Table 1, the extractability of TMA^+ extracted as 1:1 ion-pair complex was only more decreased than in the case using dichloromethane. Such a high extractability of 2:2 complex into chloroform solution is attributed to higher lipophilicity of 2:2 complex than that of 1:1 complex.5) In the extraction of Na^+ with <u>1</u> into chloroform solution, the formation of 2:2 complex was also observed. These phenomena were established by the relationship between metal distribution constant and reagent concentration.6)

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6) If 2:2 complex (MLML) of crown ether with cation is in large excess of 1:1 (ML) and/or 2:1 (MLHL) complexes in the organic phase on the solvent extraction, the relationship between metal distribution constant (D_M) and the reagent concentration in the organic phase ($[HL]_o$) can be expressed as the following equation: $\log(D_M/[M^+]) = \log K^{ex}_{MLML} + 2\log[HL]_o + 2pH + \log 2$, where as $[M^+]$ is a great excess of the other species in the aqueous phase, it is regarded as a constant.

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