Benzocrown Ether Hydrazones as Extractants for Alkali Metal Ions

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Four types of benzo-15-crown-5 and benzo-18-crown-6 derivatives bearing a substituted hydrazone moiety as a proton-dissociable chromogenic group were synthesized and the solvent extraction behaviors of these compounds for alkali metal ions were evaluated spectrophotometrically. Benzo-15-crown-5 and -18-crown-6 hydrazones with 2,4-dinitro-6-(trifluoromethyl)phenyl or 2,6-dinitro-4-(trifluoromethyl)phenyl groups extracted alkali metal ions predominantly as 2 : 1 and 1 : 1 (crown ether : metal ion) complexes, respectively, from an aqueous alkaline solution into 1,2-dichloroethane and these ligands exhibited high K^+-selectivity. The composition of the extracted species and the K^+-selectivity depended on the polarity of the extraction solvent used. In particular, 2 : 2 complexes of several alkali metal ions with benzo-15-crown-5 and -18-crown-6 hydrazones bearing a 2,4-dinitro-6-(trifluoromethyl)phenyl group were readily extracted from an aqueous solution into chloroform.

Crown ether dyes with a proton-dissociable chromogenic group have been investigated as reagents for determination and identification of particular metal ions.[1)] The properties of the crown ether dyes as extractants for alkali and alkaline earth metal ions were estimated in the solvent extraction and then were evaluated from the standpoint of the molecular structure of the compounds.[2—6)] It is well known that the ion selectivities and the complexing abilities of crown ether derivatives are correlated with the structure and/or the metal ion affinity of substituents on the periphery as well as with the relationship between the size of the crown ether cavity and the metal ion diameter.[4,7)] For example, chromoionophores with an identical crown ether ring but with different proton-dissociable chromogenic moieties as substituents exhibit various metal ion selectivities and/or compositional variations of the extracted complexes owing to differences in the basicity and in the structural effect of the anionic site caused by deprotonation of the chromogenic group.

Metal ion complexation and extraction properties of benzo-15-crown-5 and benzo-18-crown-6 derivatives bearing a 2,4,6-trinitrophenylamino moiety were evaluated spectrophotometrically in aqueous homogeneous solutions and for solvent extraction, respectively, by Takagi and co-workers.[8,9)] Benzo-15-crown-5 derivatives formed predominantly 2 : 1 (crown ether : metal ion) complexes extractable into chloroform with cations such as K^+, Rb^+, and Cs^+ that have large ionic diameters compared to the crown ether cavity. These compounds exhibited a high selectivity for K^+.[9)] Analogous benzo-18-crown-6 derivatives preferred formation of 1 : 1 complexes with Na^+, K^+, and Rb^+, except for Cs^+ forming a 2 : 1 complex, and also exhibited K^+ selectivity. Pacey and co-workers also reported that analogous benzo-15-crown-5 dyes exhibited similar extraction behavior for alkali metal ions.[10)] No other detailed study, however, has been reported on the relationship between the ion selectivities and the composition of the extracted complexes of the crown ether dyes in the solvent extraction.

We recently communicated the compositional variation of the extracted complexes of the alkali metal ions with the crown ether hydrazones in the solvent extraction using several solvents.[11)] This paper describes syntheses of four types of benzo-15-crown-5 and benzo-18-crown-6 derivatives bearing a substituted hydrazone moiety as a proton-dissociable chromogenic group and the characteristics of these compounds as chromoionophores for alkali metal ions. In addition, the solvent extraction equilibria of alkali metal ions and tetramethylammonium ion (TMA^+) and the influence of the extraction solvents with different dielectric constants on the extraction behavior, viz., the composition of the extracted complex, extractability, and ion selectivity, were examined for benzo-15-crown-5 hydrazones, **1a** and **1b**, benzo-18-crown-6 hydrazones, **2a** and **2b**, and analogous hydrazones, **3a** and **3b**, without the crown ether moiety which were synthesized for comparison. The structures of the compounds studied are given in Fig. 1.

Experimental

Syntheses of Hydrazone Derivatives. General Procedure for Condensation Reaction of Aldehyde and Hydrazine:[12)] A substituted arylhydrazine was obtained by the reaction of an appropriate aryl chloride (6.0 mmol) and hydrazine monohydrate (6.6 mmol) in 100 cm^3 of refluxing ethanol for 1 h, followed by recrystallization from ethanol. A mixture of aldehyde derivative (2.3 mmol), substituted arylhydrazine (2.5 mmol) and acetic acid (ca. 2 mmol) in 200 cm^3 ethanol was refluxed for 2 h with stirring. After cooling to room temperature, the resulting precipitate was recovered by filtration and then was recrystallized from ethanol to yield the hydrazone derivative.

Benzo-15-crown-5 Hydrazones 1a—1d: The 4′-formylbenzo-15-crown-5 was obtained by the cyclization reaction of 1,11-dichloro-3,6,9-tetraoxaundecane with 3,4-dihydroxybenzaldehyde in 1-butanol in the presence of NaOH under N_2 atmosphere, followed by recrystallization from heptane.[13)] The reactions of the 4′-formylbenzo 15-crown-

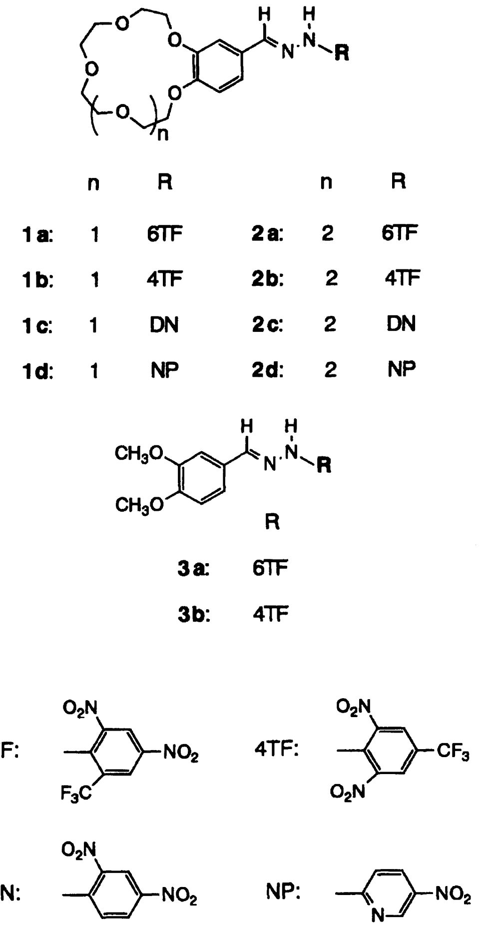

Fig. 1. Hydrazone derivatives employed.

5 obtained and an appropriate arylhydrazine as mentioned above yielded the compounds **1a**—**1d**.

1a: Reddish purple crystals; yield 58%; mp 177—178 °C; MS m/z=544 (M$^+$); IR (KBr) 3270 (N–H), 2870 (C–H), 1640 (C=N), 1540 (NO$_2$), 1320 (C–F), and 1120 cm^{-1} (C–O–C); ^{1}H NMR (CDCl$_3$) δ=3.77—4.29 (16H, m, OCH$_2$CH$_2$O), 6.80—7.37 (3H, m, aromatic H in benzocrown ether), 7.92 (1H, s, CH), 8.75, 9.07 (2H, d, aromatic H in hydrazone moiety), 10.94 (1H, s, NH). Found: C, 48.58; H, 4.23; N, 10.23%. Calcd for C$_{22}$H$_{23}$N$_4$O$_9$F$_3$:, 48.53; H, 4.23; N, 10.29%.

1b: Deep red crystals; yield 56%; mp 187—188 °C; MS m/z=544 (M$^+$); IR (KBr) 3270 (N–H), 2870 (C–H), 1630 (C=N), 1540 (NO$_2$), 1320 (C–F), and 1120 cm^{-1} (C–O–C); ^{1}H NMR (CDCl$_3$) δ=3.77—4.27 (16H, m, OCH$_2$CH$_2$O), 6.78—7.27 (3H, m, aromatic H in benzocrown ether), 7.82 (1H, s, CH), 8.25 (2H, s, aromatic H in hydrazone moiety), 11.16 (1H, s, NH). Found: C, 48.59; H, 4.27; N, 10.27%. Calcd for C$_{22}$H$_{23}$N$_4$O$_9$F$_3$: C, 48.53; H, 4.23; N, 10.29%.

1c: Reddish brown crystals; yield 48%; mp 206—207 °C; MS m/z=476 (M$^+$); IR (KBr) 3280 (N–H), 2870 (C–H), 1620 (C=N), 1510 (NO$_2$), and 1130 cm^{-1} (C–O–C). Found: C, 52.40; H, 5.09; N, 11.43%. Calcd for C$_{21}$H$_{24}$N$_4$O$_9$: C, 52.94; H, 5.07; N, 11.76%.

1d: Yellow crystals; yield 60%; mp 202—203 °C; MS m/z=432 (M$^+$); IR (KBr) 3280 (N–H), 2870 (C–H), 1600 (C=N), 1500 (NO$_2$), and 1130 cm^{-1} (C–O–C). Found: C, 55.13; H, 5.60; N, 12.45%. Calcd for C$_{20}$H$_{24}$N$_4$O$_7$: C, 55.55; H, 5.59; N, 12.96%.

Benzo-18-crown-6 Hydrazones 2a—2d: The compounds **2a**—**2d** were obtained by the condensation reactions of an arylhydrazine and 4′-formylbenzo-18-crown-6. 4′-Formylbenzo-18-crown-6 was synthesized in a similar manner to that for 4′-formylbenzo-15-crown-5.[13]

2a: Reddish orange crystal; yield 56%; mp 151—152 °C; MS m/z=588 (M$^+$); IR (KBr) 3270 (N–H), 2870 (C–H), 1640 (C=N), 1540 (NO$_2$), 1320 (C–F), and 1120 cm^{-1} (C–O–C); ^{1}H NMR (CDCl$_3$) δ=3.77—4.29 (20H, m, OCH$_2$CH$_2$O), 6.80—7.36 (3H, m, aromatic H in benzocrown ether), 7.92 (1H, s, CH), 8.75, 9.06 (2H, d, aromatic H in hydrazone moiety), 10.94 (1H, s, NH). Found: C, 48.95; H, 4.56; N, 9.43%. Calcd for C$_{24}$H$_{27}$N$_4$O$_{10}$F$_3$: C, 48.98; H, 4.62; N, 9.52%.

2b: Deep red crystal; yield 61%; mp 173—174 °C; MS m/z=588 (M$^+$); IR (KBr) 3270 (N–H), 2870 (C–H), 1630 (C=N), 1540 (NO$_2$), 1320 (C–F), and 1120 cm^{-1} (C–O–C); ^{1}H NMR (CDCl$_3$) δ=3.69—4.32 (20H, m, OCH$_2$CH$_2$O), 6.79—7.26 (3H, m, aromatic H in benzocrown ether), 7.86 (1H, s, CH), 8.26 (2H, s, aromatic H in hydrazone moiety), 11.16 (1H, s, NH). Found: C, 49.42; H, 4.77; N, 9.36%. Calcd for C$_{24}$H$_{27}$N$_4$O$_{10}$F$_3$: C, 48.98; H, 4.62; N, 9.52%.

2c: Reddish brown crystals; yield 37%; mp 184—185 °C; MS m/z=520 (M$^+$); IR (KBr) 3280 (N–H), 2870 (C–H), 1620 (C=N), 1510 (NO$_2$), and 1130 cm^{-1} (C–O–C). Found: C, 52.72; H, 5.06; N, 11.57%. Calcd for C$_{23}$H$_{28}$N$_4$O$_{10}$: C, 53.04; H, 5.07; N, 10.77%.

2d: Yellow crystals; yield 63%; mp 158—159 °C; MS m/z=476 (M$^+$); IR (KBr) 3280 (N–H), 2870 (C–H), 1600 (C=N), 1500 (NO$_2$), and 1130 cm^{-1} (C–O–C). Found: C, 55.66; H, 5.97; N, 11.65%. Calcd for C$_{22}$H$_{28}$N$_4$O$_8$: C, 55.45; H, 5.92; N, 11.76%.

3,4-Dimethoxybenzaldehyde Hydrazones 3a and 3b: The 3,4-dimethoxybenzaldehyde hydrazones were synthesized by the reaction of 3,4-dimethoxybenzaldehyde with a substituted arylhydrazine.

3a: Reddish orange crystals; yield 61%; mp 192—193 °C; MS m/z=414 (M$^+$); IR (KBr) 3280 (N–H), 2870 (C–H), 1640 (C=N), 1540 (NO$_2$), 1320 (C–F), and 1120 cm^{-1} (C–O–C); ^{1}H NMR (CDCl$_3$) δ=3.38 (3H, s, CH$_3$), 4.58 (3H, s, CH$_3$), 6.79—7.26 (3H, m, aromatic H), 7.86 (1H, s, CH), 8.26 (2H, d, aromatic H in hydrazone moiety), 11.16 (1H, s, NH). Found: C, 46.36; H, 3.24; N, 13.27%. Calcd for C$_{16}$H$_{13}$N$_4$O$_6$F$_3$: C, 46.38; H, 3.16; N, 13.53%.

3b: Reddish orange crystals; yield 63%; mp 246—247 °C; MS m/z=414 (M$^+$); IR (KBr) 3280 (N–H), 2870 (C–H), 1640 (C=N), 1540 (NO$_2$), 1320 (C–F), and 1120 cm^{-1} (C–O–C); ^{1}H NMR (CDCl$_3$) δ=3.40 (3H, s, CH$_3$), 4.56 (3H, s, CH$_3$), 6.79—7.26 (3H, m, aromatic H), 7.86 (1H, s, CH), 8.26 (2H, s, aromatic H in hydrazone moiety), 11.16 (1H, s, NH). Found: C, 46.55; H, 3.08; N, 13.56%. Calcd for C$_{16}$H$_{13}$N$_4$O$_6$F$_3$: C, 46.38; H, 3.16; N, 13.53%.

Acidity Constant. The acidity constants of the hydrazone derivatives were determined spectrophotometrically at 25±0.2°C. Aqueous 1,4-dioxane (20 vol%) solution was chosen as the solvent because most of the hydrazones used are slightly soluble in water. The pH value of the solution (25 cm^3) containing 2.0×10^{-5} M (1 M=1 mol dm^{-3}) hydrazone (4.0×10^{-5} M for **1b**, **2b**, and **3b**) and 0.1 M teramethylammonium chloride (TMACl) for obtaining constant ionic strength was adjusted using TMAOH and was measured with a TOA pH Meter HM-30S equipped with a TOA GST-5311C glass electrode. The absorption spectra were obtained at each pH on a Hitachi Spectrophotometer 150-20 with 1-cm quartz cells.

Solvent Extraction. In order to evaluate the metal ion selectivities of the hydrazones, **1a**—**3a** and **1b**—**3b**, solvent extraction experiments were carried out as follows: In a 50 cm^3 separatory funnel were placed a 1,2-dichloroethane solution (10 cm^3) of 2.0×10^{-5} M crown ether hydrazone and 0.1 M alkali metal ion aqueous solution (10 cm^3). The pH of the aqueous solution was controlled with LiOH and buffers of 2-(cyclohexylamino)ethanesulfonic acid (CHES) or 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS) and LiOH. The mixture was shaken for 15 min at 25±0.2°C. After standing for 12 h to attain complete phase separation, the absorbance of the organic phase was measured as mentioned above unless otherwise noted.

For the determination of extraction constants of the hydrazones for alkali metal and TMA^+ ions, the extraction experiments were carried out by varying the alkali metal and TMA^+ ion concentration (1.0×10^{-3}—2.0 M) at appropriate pH values in the aqueous solution and keeping the hydrazone concentration constant in the organic solution. The hydrazone concentrations were 4.0×10^{-6}, 2.0×10^{-5}, and 1.0×10^{-4} M when 1,2-dichloroethane was used, and 1.7×10^{-5} and 1.5×10^{-4} M when both dichloromethane and chloroform were used as the extraction solvents. The pH values of the aqueous solution were adjusted to 10.75, 12.75, 8.90, 12.23, 11.05, and 13.19 using LiOH and buffers for **1a**, **1b**, **2a**, **2b**, **3a**, and **3b**, respectively, unless otherwise specified.

Results and Discussion

Acidity Constant. Proton dissociation of the imino group of the crown ether hydrazones and their analogues was spectrophotometrically studied in water-1,4-dioxane (80/20 vol%) by titration with a standard tetramethylammonium hydroxide (TMAOH) solution. The acidity constant, K_a, was obtained by calculation from the following equation: $[H^+]A=-K_aA+\varepsilon_{L^-}K_a[HL]_t$, where A and ε_{L^-} are, respectively, the absorbance and the molar absorptivity of the proton-dissociated species at a wavelength, where the undissociated species has no absorbance; $[HL]_t$ is the total concentration of the hydrazone derivative. The spectral data and the acidity constants calculated for the hydrazone derivatives are summarized in Table 1.

Table 1. Acidity Constants and Spectral Data of the Hydrazone Derivatives

Compound	pK_a[a]	$\varepsilon_{HL}/M^{-1}\,cm^{-1}$ (λ_{max}/nm)	$\varepsilon_{L^-}/M^{-1}\,cm^{-1}$ (λ_{max}/nm)
1a	7.46	24600 (399)	33800 (498)
1b	10.05	21300 (330)	7100 (567)
1c	11.70	29400 (403)	32000 (470)
1d	11.57	30500 (400)	39600 (506)
2a	7.45	24200 (399)	33400 (498)
2b	10.04	21900 (330)	8400 (568)
2c	11.69	29000 (403)	31500 (470)
2d	11.56	30100 (400)	39100 (507)
3a	7.48	25700 (399)	35900 (498)
3b	10.06	20200 (330)	8600 (568)

a) $pK_a=-\log K_a$, $K_a=[H^+][L^-]/[HL]$, water–1,4-dioxane (80/20 vol%), Ionic strength=0.1 (TMACl).

Benzo-15-crown-5 hydrazone **1a** with 2,4-dinitro-6-(trifluoromethyl)phenyl group exhibited a significantly low pK_a value compared to the analogous compound **1b** bearind 2,6-dinitro-4-(trifluoromethyl)phenyl group.[10,14] The proton-dissociated species (L^-) of **1a** gave much larger molar absorptivity than that of **1b**. Compounds **1c** and **1d**, carrying 2,4-dinitrophenyl and 5-nitro-2-pyridyl groups, respectively, had large molar absorptivities for the proton-dissociable species, while the proton-dissociation abilities were less than those of **1a** and **1b**.

Benzo-18-crown-6 hydrazones, **2a**—**2d**, and 3,4-dimethoxybenzaldehyde hydrazones, **3a** and **3b**, bearing the corresponding hydrazone moieties exhibited similar spectral properties and proton-dissociation abilities as observed for benzo-15-crown-5 hydrazones, **1a**—**1d**.

Solvent Extraction of Alkali Metal and TMA^+ Ions. The solvent extraction of alkali metal and TMA^+ ions with hydrazone derivatives was carried out using 1,2-dichloroethane as the extraction solvent. Spectral change in the organic solution of benzo-18-crown-6 hydrazone **2a** for different alkali metal ions is shown in Fig. 2. The ion extractability of **2a** was decreased in the order $K^+>Rb^+>Cs^+>Na^+\gg Li^+$, and similar extractability was observed for the benzo-15-crown-5 analogue **1a**. Because it has been known that 15-crown-5 derivatives frequently form 2 : 1 complexes with alkali metal ions,[9,15] the extraction constants of 1 : 1 and 2 : 1 complexes, K_{ML}^{ex} and K_{MLHL}^{ex}, respectively, were defined according to the following equi-

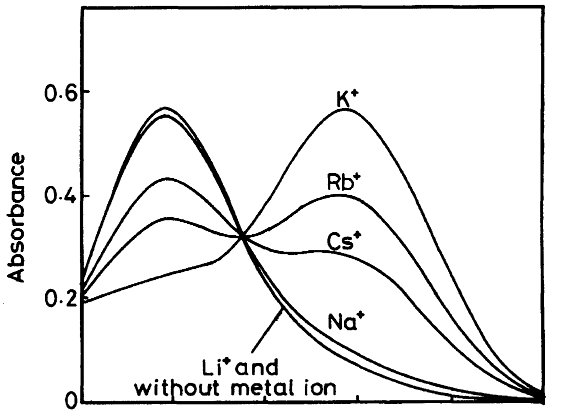

Fig. 2. Spectral change in the organic phase in the extraction of alkali metal ions with benzo-18-crown-6 hydrazone **2a**. Organic phase: $[\mathbf{2a}]=2.0\times10^{-5}$ M in 1,2-dichloroethane; aqueous phase: [metal ion]=0.1 M at pH 8.88.

librium equations.

$$(\mathrm{HL})_\mathrm{o} + \mathrm{M}^+ \rightleftharpoons (\mathrm{ML})_\mathrm{o} + \mathrm{H}^+ \qquad (1)$$

$$2(\mathrm{HL})_\mathrm{o} + \mathrm{M}^+ \rightleftharpoons (\mathrm{MLHL})_\mathrm{o} + \mathrm{H}^+ \qquad (2)$$

$$K_\mathrm{ML}^\mathrm{ex} = \frac{[\mathrm{ML}]_\mathrm{o}[\mathrm{H}^+]}{[\mathrm{HL}]_\mathrm{o}[\mathrm{M}^+]} \qquad (3)$$

$$K_\mathrm{MLHL}^\mathrm{ex} = \frac{[\mathrm{MLHL}]_\mathrm{o}[\mathrm{H}^+]}{[\mathrm{HL}]_\mathrm{o}^2[\mathrm{M}^+]} \qquad (4)$$

where M^+, HL, ML, and MLHL are the metal ion, undissociated hydrazone, 1 : 1 and 2 : 1 complexes of hydrazones with the metal ion, respectively. The subscript "o" and the lack of a subscript denote an organic and an aqueous phase, respectively. Since the distribution of the hydrazones to the aqueous phase is negligible owing to their high lipophilicity, the total concentrations of the metal (C_M) and the ligand (C_L) are respectively represented as

$$C_\mathrm{M} = [\mathrm{M}^+] + [\mathrm{ML}]_\mathrm{o} + [\mathrm{MLHL}]_\mathrm{o} \qquad (5)$$

$$C_\mathrm{L} = [\mathrm{HL}]_\mathrm{o} + [\mathrm{ML}]_\mathrm{o} + 2[\mathrm{MLHL}]_\mathrm{o} \qquad (6)$$

Because the concentrations of ML and MLHL are much lower than that of M^+, Eq. 5 can be rewritten as

$$C_\mathrm{M} = [\mathrm{M}^+] \qquad (7)$$

The absorbance (A) of the organic phase is given by

$$A = \varepsilon_\mathrm{HL}[\mathrm{HL}]_\mathrm{o} + \varepsilon_\mathrm{ML}[\mathrm{ML}]_\mathrm{o} + \varepsilon_\mathrm{MLHL}[\mathrm{MLHL}]_\mathrm{o} \qquad (8)$$

where ε_HL, ε_ML, and $\varepsilon_\mathrm{MLHL}$ are the molar absorptivities of the species represented by the subscripts. Because the value of ε_HL is known, the values of ε_ML, $\varepsilon_\mathrm{MLHL}$, $K_\mathrm{ML}^\mathrm{ex}$ and $K_\mathrm{MLHL}^\mathrm{ex}$ can be obtained simultaneously by minimizing the error square sum (U) defined by

$$U = \sum (A_{\mathrm{obs},i} - A_{\mathrm{cal},i})^2 \qquad (9)$$

where A_obs and A_cal are the experimentally observed and the calculated absorbances at a selected wavelength, respectively.

The solid lines in Fig. 3(a) and (b), which can be fitted well to the absorbance obtained in the extraction experiments for K^+ ion with benzo-15-crown-5 and -18-crown-6 hydrazones, **1a** and **2a**, respectively, demonstrate the validity of all the constants determined. The broken lines in Fig. 3(a) denote the absorbances of the species calculated from the extraction constants of the complexes, KL and KLHL. The extraction constants of K^+, Rb^+, and Cs^+ with benzo-15-crown-5 derivatives bearing a proton-dissociable group have so far been reported only for 2 : 1 complexes.[9,10,16] It is, however, seen in Fig. 3(a) that benzo-15-crown-5 hydrazone **1a** bearing a 2,4-dinitro-6-(trifluoromethyl)phenyl group simultaneously forms 1 : 1 and 2 : 1 complexes with K^+, KL and KLHL, respectively, in the solvent extraction.

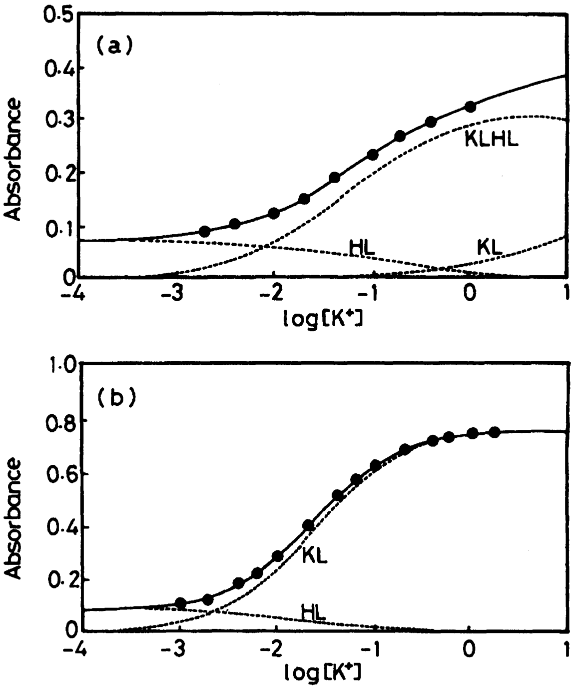

Fig. 3. Plots of absorbance at 496 nm in the organic phase vs. $\log[\mathrm{K}^+]$ in the aqueous phase in the extraction of K^+ with (a) benzo-15-crown-5 hydrazone **1a** and (b) benzo-18-crown-6 hydrazone **2a**. Organic phase: [crown hydrazone]=2.0×10^{-5} M in 1,2-dichloroethane; aqueous phase: (a) at pH 10.75; (b) at pH 9.00. Solid line: calculated from the absorbance in the organic phase. Broken line: calculated from the absorbances of species extracted into the organic phase.

The extraction constants of alkali metal and TMA^+ ions with the hydrazone derivatives are summarized in Table 2. It can be seen from Table 2 that benzo-15-crown-5 hydrazone **1a** simultaneously forms 1 : 1 and 2 : 1 complexes with Na^+, Rb^+, and Cs^+ as well as with K^+ and that the $K_\mathrm{ML}^\mathrm{ex}$ values of **1a** for the metal ions are nearly equal in the magnitude while the $K_\mathrm{MLHL}^\mathrm{ex}$ values are inconsistent. It is known that both the stabilities of 1 : 1 complexes of 15-crown-5 with alkali metal ions in the gas phase and the hydration energies of those metal ions in the aqueous phase decrease in the order $\mathrm{Na}^+ > \mathrm{K}^+ > \mathrm{Rb}^+ > \mathrm{Cs}^+$.[17,18] The hydration of metal ions is hence in competition with the formation of 1 : 1 complexes of the crown ether moiety with the metal ions to prevent the appearance of ion selectivity in the formation of 1 : 1 complexes of the crown ether when the alkali metal ions are extracted with benzo-15-crown-5 derivatives from the aqueous into the organic phase.[19] The ion selectivity in the solvent extraction using **1a** is dependent on the capability of forming the 2 : 1 complex of the compound with an alkali metal ion, because the 2 : 1 complex is much more lipophilic and stable than the 1 : 1 complex.[20—22]

Benzo-15-crown-5 hydrazone **1b** with 2,6-dinitro-4-

Table 2. Extraction Constants[a)] of Hydrazones and Spectral Properties of 1 : 1 Complexes of Benzo-18-crown-6 Hydrazones, **2a** and **2b**, with K^+

Compound	pK^{ex} [b)]	Na^+	K^+	Rb^+	Cs^+	TMA^+	$\varepsilon_{KL}/M^{-1}\,cm^{-1}$ (λ_{max}/nm)
1a	pK^{ex}_{ML}	10.9	11.3	11.2	10.6	9.5	
	pK^{ex}_{MLHL}	7.5	5.0	5.5	6.8	—	
1b	pK^{ex}_{ML}	13.1	14.0	13.8	13.7	12.9	
	pK^{ex}_{MLHL}	—	7.7	8.3	9.6	—	
2a	pK^{ex}_{ML}	9.4	7.4	7.9	8.1	9.5	38200±300
	pK^{ex}_{MLHL}	—	—	—	4.0	—	(498)
2b	pK^{ex}_{ML}	13.0	10.8	11.3	11.6	12.9	6680±50
	pK^{ex}_{MLHL}	—	—	—	8.2	—	(568)
3a	pK^{ex}_{ML}	—	—	—	—	9.5	
	pK^{ex}_{MLHL}	—	—	—	—	—	
3b	pK^{ex}_{ML}	—	—	—	—	12.9	
	pK^{ex}_{MLHL}	—	—	—	—	—	

a) Average of measurements at three distinct concentrations of the hydrazone. The errors of these values are within ±0.2. Organic phase: [hydrazone]$=4.0\times10^{-6}$, 2.0×10^{-5}, and 1.0×10^{-4} M in 1,2-dichloroethane; aqueous phase: [cation]$=1.0\times10^{-3}-2.0$ M.
b) $pK^{ex}=-\log K^{ex}$

(trifluoromethyl)phenyl group exhibited ion selectivity similar to that of **1a**, while the extractability of **1b** for the alkali metal and TMA^+ ions was diminished compared to **1a** due to a lower proton-dissociation ability of the former. Similar differences in the cation extractabilities based on proton-dissociation properties of the substituents were observed between **2a** and **2b** and between **3a** and **3b**.

Benzo-18-crown-6 hydrazones, **2a** and **2b**, predominantly formed 1 : 1 complexes with the alkali metal ions except for Cs^+, being extracted as a mixture of 1 : 1 and 2 : 1 complexes, and gave high K^+ selectivities. (see Fig. 3(b) for the extraction of K^+) The selectivity ratios of K^+ over Na^+ ($K^{ex}_{KL}/K^{ex}_{NaL}=[KL]_o[Na^+]/[NaL]_o[K^+]$) for **2a** and **2b** were 100 and 160, respectively. The differences among the extraction constants of the benzo-18-crown-6 hydrazones for the alkali metal ions imply that the cation extractabilities of **2a** and **2b** are attributed primarily to the capability of the benzo-18-crown-6 moiety to form 1 : 1 complexes.[22,23]

3,4-Dimethoxybenzaldehyde hydrazones, **3a** and **3b** without a crown moiety, appreciably extracted TMA^+ ion as a 1 : 1 ion-pair complex with the hydrazone anion formed by dissociation of the proton on the imino group, although no extraction of alkali metal ions was observed. The extraction constants of **3a** and **3b** for TMA^+ are in agreement with those of the analogous benzo-15-crown-5 and -18-crown-6 hydrazones bearing the corresponding substituents, probably because TMA^+ has high lipophilicity but poor affinity for the crown ether unit.[24]

The crown ether hydrazones, **1c**, **1d**, **2c**, and **2d** bearing 2,4-dinitrophenyl or 5-nitro-2-pyridyl groups, have too high solubility in alkaline solutions and too poor extractability of alkali metal and TMA^+ ions for the determination of the extraction constants to be made.

Effects of Solvents on the Extraction of Alkali Metal and TMA^+ Ions. Four organic solvents with different dielectric constants, i.e., 1,2-dichloroethane (dielectric constant, 10.65 at 20 °C), dichloromethane (7.74 at 10 °C), chloroform (4.80 at 20 °C) and benzene (2.27 at 25 °C), were used to study the effects of solvents on the extraction of alkali metal and TMA^+ ions with crown ether hydrazones, **1a** and **2a**. In the solvent extraction using benzene with the lowest dielectric constant, no extraction of the cations was observed for any hydrazone derivative.

Compared with the solvent extraction using 1,2-dichloroethane, the extractabilities of alkali metal ions with both **1a** and **2a** were uniformly diminished while the compositions of the extracted complexes were not appreciably changed, when dichloromethane, which has a dielectric constant lower than that of 1,2-dichloroethane, was used as an extraction solvent.

When formation of 2 : 1 and 1 : 1 complexes of **2a** with a metal ion in the extraction using chloroform is assumed, the absorbances calculated from the extraction constants are systematically deviated from the measured values. Therefore, we added the following assumption of the extraction equilibrium to those mentioned above:

$$2(HL)_o + 2M^+ \rightleftharpoons (MLML)_o + 2H^+ \qquad (10)$$

$$K^{ex}_{MLML} = \frac{[MLML]_o[H^+]^2}{[HL]_o^2[M^+]^2} \qquad (11)$$

where MLML and K^{ex}_{MLML} denote the 2 : 2 complex and its extraction constant, respectively. On the assumption that the crown hydrazone does not dimerize even in the organic phase under the experimental conditions employed here, the total concentrations of metal (C_M) and ligand (C_L), respectively, can be represented as

$$C_M = [M^+] + [ML]_o + [MLHL]_o + 2[MLML]_o \qquad (12)$$

$$C_L = [HL]_o + [ML]_o + 2[MLHL]_o + 2[MLML]_o \qquad (13)$$

Because the metal ion (M^+) is in large excess compared with ML, MLHL, and MLML, the Eq. 12 can be rewritten as Eq. 7. The absorbance (A) of the organic solution at an appropriate wavelength is expressed as

$$\begin{aligned} A &= \varepsilon_{HL}[HL]_o + \varepsilon_{ML}[ML]_o \\ &\quad + \varepsilon_{MLHL}[MLHL]_o + \varepsilon_{MLML}[MLML]_o \end{aligned} \qquad (14)$$

where ε_{MLML} is the molar absorptivity of a 2 : 2 complex. The extraction constants and molar absorptivities of the extracted complexes were calculated in the same manner as described above. The formation of 1 : 1, 2 : 1, and 2 : 2 complexes were investigated using the organic solution containing 1.5×10^{-4} M crown hydrazone, and the extraction constants were calculated. The extraction constants obtained were refined by the extraction data for the organic solution containing 1.7×10^{-5} M crown hydrazone. In the extraction of K^+ with **2a** using chloroform as an extraction solvent, the absorbance change in the chloroform solution of 1.5×10^{-4} M **2a** could be satisfactorily interpreted by considering the formation of a 2 : 2 complex alone. The K^{ex}_{KLKL} value obtained was then recalculated by the absorbance change in the organic phase containing 1.7×10^{-5} M **2a** and the K^{ex}_{KL} value was also consequently obtained. The absorbances calculated from the extraction constants obtained are in agreement with the experimental data Fig. 4(a and b)). From a comparison of the broken lines in Fig. 4(a) and those in Fig. 4(b), which depict absorbances of the species HL, KL, and KLKL, it is also seen that the extraction of the 2 : 2 complex of **2a** with K^+ from the aqueous into the organic phase is significantly increased with an increase in the **2a** concentration.

The extraction constants calculated are summarized in Table 3. It is evident in Table 3 that **2a** formed a mixture of 1 : 1 and 2 : 2 complexes with Na^+, K^+, Rb^+, and Cs^+ to be extracted into chloroform, and that the 2 : 2 complex with **2a** was preferred to the 1 : 1 complex in the extraction of Na^+, K^+, and Rb^+, because the 2 : 2 complex has higher lipophilicity and stability than the 1 : 1 complex.[25] The fact that the molar absorptivity of the 2 : 2 complex of **2a** with K^+ ($\varepsilon_{KLKL}=74100$ $M^{-1}\,cm^{-1}$ at $\lambda_{max}=494$ nm) was in fair accord with twice that of the 1 : 1 complex ($\varepsilon_{KL}=38200$ $M^{-1}\,cm^{-1}$ at $\lambda_{max}=498$ nm) leads us to propose a structure of the 2 : 2 complex as shown in Fig. 5. This figure shows that K^+ bound with the crown ether moiety of one **2a** associates with a hydrazone anion formed by deprotonation of another **2a** to form a 2 : 2 complex with a structure of the so-called head-to-tail type.[26]

From the extraction constants of the 2 : 2 complexes of Na^+ and K^+ with **2a**, the selectivity ratio of K^+ over Na^+ is calculated to be 1.1×10^3, which is much larger than that (1.0×10^2) of the 1 : 1 complex in the extraction of K^+ with **2a** using 1,2-dichloroethane. In the actual extraction of K^+ from an aqueous solution containing both Na^+ and K^+ into chloroform, however, the selectivity of K^+ over Na^+ did not always correspond to the theoretical value because the 2 : 2 complexes accompanied a small amount of the 1 : 1 complexes of K^+ and Na^+ over a wide concentration range of the metal ions.

The extractability of TMA^+ as a 1 : 1 ion-pair complex with **2a** was further diminished compared to that

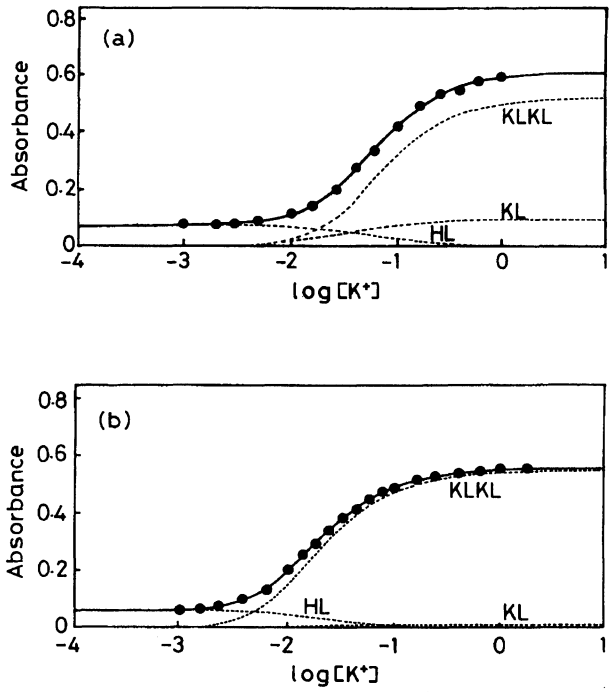

Fig. 4. Plots of absorbance at 494 nm in the organic phase vs. log $[K^+]$ in the aqueous phase in the extraction of K^+ with benzo-18-crown-6 hydrazone **2a** using chloroform as an extraction solvent. Aqueous phase: at pH 10.0; organic phase: (a) [crown hydrazone]=1.7×10^{-5} M (b) [crown hydrazone]=1.5×10^{-4} M. The light path lengths of the quartz cells used were (a) 1.0 cm and (c) 0.1 cm. Solid line: calculated from the absorbance in the organic phase. Broken line: calculated from the absorbances of species extracted into the organic phase.

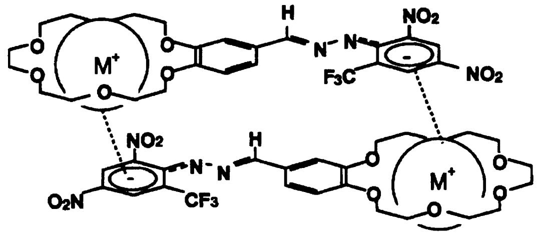

Fig. 5. Postulated structure of the 2 : 2 complex.

Table 3. Extraction Constants[a] of Cations with Benzo-15-crown-5 and -18-crown-6 Hydrazones, **1a** and **2a**, Using the Chlorinated Hydrocarbones as Extraction Solvents

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

a) Average of measurements at two different concentrations of the hydrazone in the case of using dichloromethane and chloroform. Organic phase: [crown hydrazone]=1.7×10^{-5} and 1.5×10^{-4} M in respective solvents; aqueous phase: [cation]=1.0×10^{-3} —2.0 M. b) at 20 °C. c) at 10 °C. d) The errors of the extraction constants for 1 : 1, 2 : 1, and 2 : 2 complexes are within ±0.3, ±0.1, and ±0.1, respectively. e) The errors of the extraction constants for 1 : 1 complexes are within ±0.2.

in the extraction using dichloromethane as an extraction solvent.

Benzo-15-crown-5 hydrazone **1a** exhibited lower extractabilities of alkali metal and TMA^+ ions than those with dichloromethane as the extraction solvent, and extracted the 2 : 2 complex for Na^+ alone.

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