

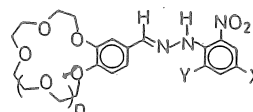
Studies on Separation and Determination of Alkali Metal Ions using Crown Compounds

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Summary

Crown compounds, which are macrocyclic polyethers, are known to complex with particular cations selectively. The objects of this study are to develop novel crown compounds, having selectivities for particular alkali metal ions, with a proton-dissociable chromogenic group and to use the compounds for highly selective and sensitive determination of the cations. In this report, we describe the syntheses of novel chromogenic crown compounds shown in Figure and the solvent extraction behaviors of the compounds for alkali metal ions as the basic information required to obtain high ion-selectivity upon the solvent extraction using crown compounds.

Benzo-15-crown-5 and -18-crown-6, 1a-c and 2a-c, respectively, have substituted



hydrazone groups not only as a chromophore but a potential anionic site. We observed spectrophotometrically that the ion-selectivities for both 1a and 2a on

	n	X	Y		n	X	Y
<u>1a</u> :	1	NO ₂	CF ₃	<u>2a</u> :	2	NO ₂	CF ₃
<u>1b</u> :	1	CF ₃	NO ₂	<u>2b</u> :	2	CF ₃	NO ₂
<u>1c</u> :	1	NO ₂	H	<u>2c</u> :	2	NO ₂	H

the solvent extraction using 1,2-dichloroethane as an extraction solvent were decreased in the order $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. While the mixtures of 1:1 (crown ether: metal ion) and 2:1 complexes of the cations, such as Na^+ , K^+ , Rb^+ and Cs^+ , were extracted by using the benzo-15-crown-5 derivatives 1a and 1b, 2:1 complex was predominantly formed. On the other hand, it was realized that the benzo-18-crown-6 derivative, 2a and 2b, formed only 1:1 complexes with the cations except for Cs^+ . The extraction selectivity ratios of 2a and 2b for K^+ over Na^+ were about 100 and 160, respectively.

When chloroform, which has lower dielectric constant than that of 1,2-dichloroethane, was used as an extraction solvent, 2a formed mixtures of 1:1 and 2:2 complexes with Na^+ , K^+ , Rb^+ and Cs^+ . Especially, K^+ and Rb^+ were extracted as 2:2 complexes overwhelmingly and K^+ selectivity against Na^+ in this case was much higher than that in the case using 1,2-dichloroethane.