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NEW PHOTOMETRIC REAGENTS FOR ALKALI METAL IONS BASED ON CROWN ETHER COMPLEX FORMATION

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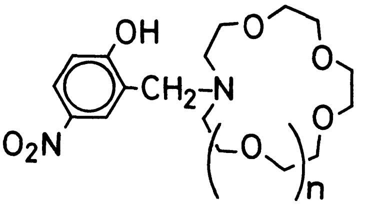
Two chromogenic crown ethers, N-(2-hydroxy-5-nitrobenzyl)-aza-15-crown-5(1) and N-(2-hydroxy-5-nitrobenzyl)-aza-18-crown-6(2), were synthesized for the extraction photometry of alkali metal ions. The extraction selectivity followed the order: 1, $Li^+ > Na^+ > K^+ >> Rb^+$, Cs^+ and 2, $K^+ > Na^+ > Rb^+ > Li^+ > Cs^+$. 1 is useful for determining 10 - 100 ppm Li^+ as well as for concentrating Li^+ from a dilute solution.

In the previous papers,[1)] 4'-picrylaminobenzo-crown ethers were reported for the first alkali metal-selective photometric reagents. In the present communication, a different type of crown ether chromogenic reagents are described which show a different selectivity from the former reagents.

The compound 1, N-(2-hydroxy-5-nitrobenzyl)-aza-15-crown-5, and its aza-18-crown-6 derivative (2) were synthesized from the corresponding aza-crown ethers[2)] through condensation with 2-hydroxy-5-nitrobenzyl bromide.[3)] They have two acidic dissociation constants (Table 1).

Alkali metal ions were extracted from an aqueous solution into 1,2-dichloroethane. The extraction equilibria are illustrated in Fig. 1 and the extraction constant is defined by Eq. 1. The partitions of 1, 2, and their alkali metal complexes are strongly in favor of the organic phase, and the color of the organic solution changes from pale yellow (λ_{max} 310 nm) to deep yellow (λ_{max} 411-417 nm) on extraction of metals. The extraction took place only through a 1:1 (reagent : metal) complex for both 1 and 2. The extraction constants are summarized in Table 2 along with the corresponding values for 4'-picrylaminobenzo-18-crown-6 (3).[1)]

The 18-crown-6-type compound 2 extracts a K^+ ion most effectively, the extractability of alkali metal ions being in the order, $K^+ > Na^+ > Rb^+ > Li^+ > Cs^+$. The selectivity of 2 for K^+ against Na^+ is less than that of 3, but the value of the extraction constant for K^+ is 39 fold greater. The increased extraction by 2 may be attributed to the presence of a phenolate anion in such a position that allows the coordination to the metal ion in the crown ether ring. In the case of 1, which has a 15-crown-5-type structure, the extractability follows the order, $Li^+ > Na^+ > K^+ >> Rb^+, Cs^+$. The high selectivity of 1 toward lithium is very unusual, since lithium complexes of monocyclic crown ethers



1: n = 1
2: n = 2

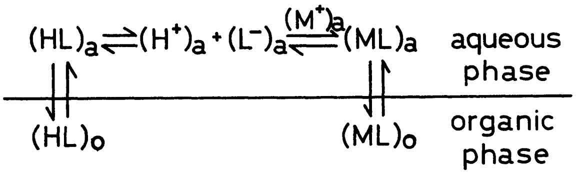


Fig. 1. Extraction Equilibria of 1 or 2

$$K_{ex} = \frac{[(ML)o]\,[(H^+)a]}{[(HL)o]\,[(M^+)a]} \quad \cdots\cdots\cdots (1)$$

are usually much less stable than those of the other alkali metals except for an extremely rigid Spherand.[4)]

15-Crown-5 and its homologues, whose hole size is too small for K^+, Rb^+, and Cs^+, frequently extract these metals by forming 2:1 (reagent : metal) complexes, however, 1 forms only 1:1 complexes. This is probably due to the presence of the additional phenolate oxygen, effectively completing the octahedral coordination around the encapsulated metal ion, and the covalent character of Li-O bond of the phenolate complex is presumably contributing to the facile extraction of Li^+ with 1.

Table 1. Acid Dissociation Constants, 25 °C[a)]

compound	$-\log K_1$	$-\log K_2$
1	5.79	9.69
2	5.77	9.59

a) dissociation of phenolic(K_1) and ammonium (K_2) protons in water, $\mu=0.1$ ($(CH_3)_4NCl$)

These newly synthesized reagents were applicable to the photometric determination of alkali metals. The conditions were similar to those described previously.[1)] The compound 2 was used for the purpose similar to that of 3, while 1 was useful for Li^+ as well as for preconcentrating lithium from a dilute sample.[5)]

Table 2. Extraction Constants of Alkali Metal Ions, 25 °C

metal	$-\log K_{ex}$		
	1[a)](ε_{ML}, λ_{max} 411 nm[b)])	2[a)](ε_{ML}, λ_{max} 417 nm[c)])	3[d)]
Li^+	9.15 (19,400)	10.29 (24,600)	---[e)]
Na^+	9.76 (18,600)	9.46 (22,500)	12.5
K^+	9.86 (16,700)	8.93 (22,600)	10.52
Rb^+	---[e)]	9.63 (20,600)	10.90
Cs^+	---[e)]	10.62 (21,800)	11.28

a) solvent, 1,2-dichloroethane b) ε_{HL}(1,2-dichloroethane) 9,170; λ_{max} 325 nm
c) ε_{HL}(1,2-dichloroethane) 9,270; λ_{max} 327 nm d) solvent, chloroform
e) no extraction

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References

1) H. Nakamura, M. Takagi, and K. Ueno, Anal. Chem., 52, 1668 (1980), and the literatures cited therein.

2) G. W. Gokel and B. J. Garcia, Tetrahedron Lett., 317 (1977).

3) 1. Yield 91%, NMR ($CDCl_3$): 6.85 (1H), 7.8-8.25 (2H, aromatic-H), 3.90 ($Ar-CH_2$), 3.5-3.85 ($O-CH_2$), 2.81 ($N-CH_2$).

2. Yield 89%, NMR ($CDCl_3$): 6.82 (1H), 7.8-8.2 (2H, aromatic-H), 3.92 ($Ar-CH_2$), 3.4-3.85 ($O-CH_2$), 2.85 ($N-CH_2$).

4) D. J. Cram, T. Kaneda, R. C. Helgeson, and G. M. Lein, J. Am. Chem. Soc., 101, 6752 (1979).

5) A solution of 1×10^{-6} M ($M=mol\cdot dm^{-3}$) LiCl was concentrated to 1.5×10^{-5} M by a single extraction with an equal volume of a 0.01 M solution of 1 at pH 12.0, followed by back extraction with an acid.

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