SHORT COMMUNICATIONS

CHROMOGENIC CROWN ETHER REAGENT SELECTIVE TO SODIUM¹⁾Hiroshi NAKAMURA, Hiroshi NISHIDA, Makoto TAKAGI, and Keihei UENO[®]Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

ABSTRACT: A new type of chromogenic crown ethers, 2-hydroxy-5-(4-nitrophenylazo)phenoxy-methyl-15-crown-5 and -18-crown-6 were synthesized. The 15-crown-5 type reagent extracts a sodium ion most effectively, and is the first chromogenic reagent suitable to the determination of ppm level sodium.

In the previous papers, a series of new chromogenic crown ethers selective to potassium (1)²⁻⁴⁾ and lithium (2)⁵⁾ were reported. These monobasic reagents (HL), dissolved in organic solvents, extracted alkali metal ions selectively through a proton - metal ion exchange, and served as a photometric tool in the determination of these metals. However, the dyes with high selectivity to sodium have yet remained undeveloped. In the present communication, another new type of crown ether dyes (3) are introduced, which overcome the previous difficulties in obtaining the selectivity to sodium.

1

3a: n = 1

3b: n = 2

2

In the extraction with **1**, the structure of the extracted metal complex is essentially an intramolecular ion-pair,^{3,6)} and the strongly hydrated sodium is reluctant to extraction. On the other hand, for the reagent **2**, in which the pendent phenolic group locates in a position favorable to coordinate to the crown ether-bound metal ion,⁵⁾ the selectivity to lithium exceeded that of sodium. This is probably due to the higher coordinating tendency of lithium with anionic ligands.⁵⁾ Thus, the structural features just between these two extremes are needed to attain the selectivity to sodium. In the structure of **3**, the phenolic group can come close to the

encapsulated metal ion, but its coordination to the metal is somewhat hampered by the increased freedom of the pendent chain.

The reagent **3** was synthesized via three reaction steps from guaiacol glyceryl ether which is commercially available. The overall yield was 20~40 %. The details will be reported elsewhere. The extraction procedure was as follows. In a stoppered glass tube, a 1,2-dichloroethane solution of **3** (1×10^{-4} M) and an equal volume of aqueous solution containing 0.1 - 0.2 M alkali metal chloride and pH-buffering salts (tetramethylammonium salt of tartaric acid, Tricine or boric acid) were shaken for 10 min at 25°C. The absorption spectra of the organic phase were measured after centrifugation.

The extraction of alkali metal ions is schematically shown below. The extraction constant K_{ML}^{ex} , which is a measure of the ease of extraction, is defined in Eq. 1. The metal-free reagent **3** in the organic phase had an absorption maximum at 400 nm, while the metal complexes showed maxima around 580 nm. Since the distribution of the reagent species into the aqueous phase could be neglected, the values of K_{ML}^{ex} were readily calculated from the spectral data of the organic phase obtained at various pH conditions of the aqueous solution. The extraction took place only under 1:1 (metal: reagent) stoichiometry according to Eq. 1. The acid dissociation constant of the phenolic proton is defined in Eq. 2, and was obtained in water containing 10 % v/v dioxane at 25°C and $\mu = 0.1$ (tetramethylammonium bromide).

The acid dissociation constants and extraction constants obtained in this study are summarized in Table 1 along with the relevant data for **1** and **2**. In the table, the smaller the figure, the larger is the extent of the acid dissociation or the metal extraction.

The 15-crown-5 type reagent **3a** and the 18-crown-6 type reagent **3b** show the highest selectivity to sodium and potassium, respectively. This is simply a reflection of a well documented metal selectivity of crown ethers according to the size of the macrocycle. However, it is emphasized that this "size selectivity" was revealed for **2** and **3**, but not for **1**. The picrylamino-type reagent **1** in the 18-crown-6 structure extracts potassium most readily as expected (Table 1). However, the reagent in the 15-crown-5 structure again preferred the extraction of potassium, because the reagent now forms a 1 : 2 complex with the metals of larger ionic radius than sodium.^{3,4)} In the extraction with **2** and **3**, a chelate-forming interaction of the anionic pendent group with the crown ether-bound metal obviously excluded such a 1 : 2 complex.

Table 1. Equilibrium Constants

Reagent	pK_a	$-\log K_{ML}^{ex}$				
		Li	Na	K	Rb	Cs
1 ^{a)}	10.58	--	12.5	10.52	10.90	11.28
2 ^{b,c)}	5.79 ^{d)} , 9.69 ^{e)}	9.15	9.76	9.86	-- ^{f)}	-- ^{f)}
3a ^{c)}	7.51	9.8	8.40	9.20	9.55	>10
3b ^{c)}	7.54	8.8	8.32	7.11	7.75	>10

a) quoted from ref. 4; solvent, chloroform b) quoted from ref. 5

c) solvent, 1,2-dichloroethane d) pK_{a1} e) pK_{a2} f) no extraction

formation.

The extraction constants for **3** are generally much higher than those of the previous reagents. The two factors contribute to the low extraction efficiency by **1** and **2**. The charge-separated structure of the metal complex derived from **1** is not favorable for the solvent extraction. A low proton dissociation constant of **2** inevitably leads to the low extraction constant, though the expression in Eq. 1 does not involve the proton dissociation constant explicitly.

The high extraction constant of **3** makes the application of these reagents to an extraction photometry easier. The larger bathochromic shift associated with metal extraction and the higher molar absorptivity of the extracted species (ϵ , 35,000) are the additional advantage of the reagent. In fact, **3a** and **3b** were successfully used for the determination of ppm-level sodium and potassium, respectively, in the synthetic samples. Since the procedure for the alkali metal determination with chromogenic crown ethers is well studied and established,¹⁻⁵⁾ **3a** seems to be a promising photometric reagent for sodium determination.⁷⁾

In summary, the crown ether dyes **3a** and **3b** proved that the basic idea in the molecular design of a sodium-selective reagent was correct. Now, photometry of alkali metals is possible for the first three of the five alkali metals. However, in order for the photometric method to be of practical importance, the extraction constants and the selectivity among the neighboring metals must be still further improved. More rigid macrocyclic structures (maybe bicyclic), in which the proton-dissociable chromophore is an integral part of the crown ether skeleton, seems to have to be invoked for the further development.

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References

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- 7) A photometric method of determining sodium was developed only recently by us (M. Takagi, H. Nakamura, Y. Sanui, K. Ueno: Anal. Chim. Acta, 1981, 126, 185). It used an ion-pair extraction of the cryptand - complexed sodium with an anionic dye. Much more work is needed to expand the scope and prove the versatility of the photometric method.

Keyword phrases

colorimetric reagent; determination of alkali metal; crown ether; crown ether complex; alkali metal extraction.

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