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FLUORESCENT CROWN ETHER REAGENT FOR ALKALI AND ALKALINE EARTH METAL IONS

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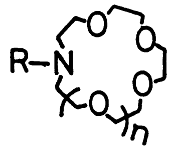
N-(4-methylumbelliferone-8-methylene)-monoaza-15-crown-5 (**1**) and -18-crown-6 (**2**) extracted most efficiently lithium and potassium, respectively, from aqueous solution to 1,2-dichloroethane. The similar fluorescent crown ether derived from diaza-18-crown-6 (**3**) was selective to calcium. The fluorimetric determination of lithium and calcium was feasible by using **1** and **3**, respectively.

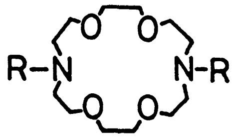
Ordinary crown ethers are not fluorescent nor are their metal complexes. Benzo- or naphto-type crown ethers fluoresce appreciably but do not reflect the complex formation with a sufficient sensitivity except for some heavy metal complexes such as lead - cryptand 2B22, where the fluorescence was quenched through a heavy atom effect in the complex.$^{1)}$ Moreover, the fluorescence is limited in the ultraviolet region, and its observation is more susceptible to the matrix variables than in the visible region.

In the previous papers, we designed and synthesized proton-dissociable chromogenic crown ethers which selectively extracted alkali and alkaline earth metal ions and served as a photometric tool for the determination of these metal ions.$^{2,3)}$ In the present communication, the principle of extraction photometry was further extended to incorporate fluorimetry which can essentially be more sensitive than absorption photometry. An intensely fluorescent, new type of crown ethers **1**, **2**, and **3** were now synthesized for this purpose.



1 (n = 1)

2 (n = 2)



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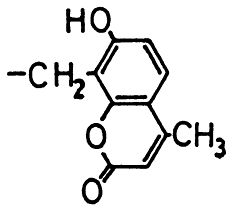

The crown ethers **1**, **2** (HL), and **3** (H_2L) were readily synthesized from 4-methylumbelliferone, formaldehyde, and the corresponding aza-crown ethers by Mannich reaction.$^{4)}$ Alkali and alkaline earth metal ions in aqueous solutions were extracted with 1,2-dichloroethane solutions of crown ethers **1** - **3**. The extraction reaction and the extraction constant are formulated in equations (1) and (2) for alkali metals. The pH of the aqueous solution was varied, and the corresponding metal extraction at equilibrium was assessed by measuring the absorption and the emission spectra of the organic phase. The maximum of excitation spectra for the intense fluorescence at 440 nm shifted from 326 nm to 380 nm in accord with the complex formation. The spectral data were analyzed according to the established method for the extraction constant.$^{5)}$

$$(\mathrm{HL})_{\mathrm{org}} + (\mathrm{M}^{+})_{\mathrm{aq}} \rightleftharpoons (\mathrm{ML})_{\mathrm{org}} + (\mathrm{H}^{+})_{\mathrm{aq}} \tag{1}$$

$$K_{\mathrm{ex}} = [(\mathrm{ML})_{\mathrm{o}}][(\mathrm{H}^{+})_{\mathrm{a}}] \,/\, [(\mathrm{HL})_{\mathrm{o}}][(\mathrm{M}^{+})_{\mathrm{a}}] \tag{2}$$

Figure 1 shows the absorption and the emission spectra of **1** in the extraction of lithium, the excitation spectra being similar to the absorption spectra. Table 1 summarizes the extraction constants of **1** and **2** for alkali metals. In comparison with the corresponding absorption photometric reagent in which the umbelliferone group is substituted by 2-hydroxy-5-nitrophenyl group,[6] the extraction constants are generally lowered by 1 in log unit. The lower extraction constant required more basic conditions for efficient metal extraction, and this, in effect, compensated the higher sensitivity of fluorimetry in the practical application in the alkali metal determination. The extraction constants of **3** for alkaline earth metal ions were also found to be lower than the corresponding absorption photometric reagent,[2] but the extraction of calcium was so efficient that the fluorimetric determination of ppb-level calcium was feasible.

Table 1 Extraction Constants

metal	- log K_{ex}	
	1	**2**
Li^+	9.70	10.30
Na^+	10.30	10.25
K^+	11.50	10.00
Rb^+	-	10.05

water - 1,2-dichloroethane, 25°C

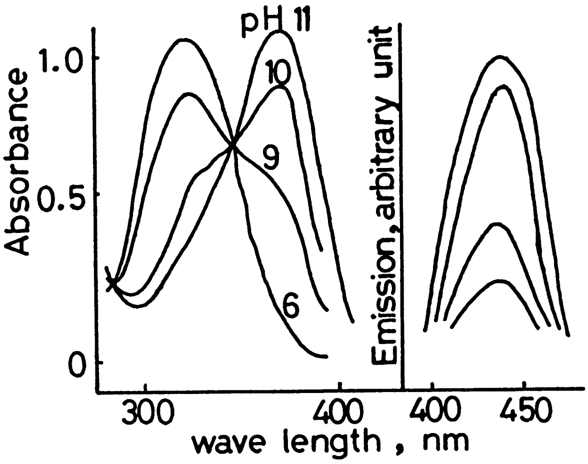

Fig. 1. Absorption and emission spectra of **1** in 1,2-dichloroethane equilibrated with aqueous lithium chloride. [**1**] = 1 x 10^{-4} M (1 M = 1 mol dm^{-3}) (absorption) and 1 x 10^{-5} M (emission), [LiCl] = 1 M

In summation, the crown ether-based fluorimetric reagents have for the first time been introduced for the determination of lithium (**1**) and calcium (**3**). As to the practical usability, the reagents are, however, still to be improved with respect to the metal extraction constant; basic nitrogens have to be eliminated from the molecular framework.[3]

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References

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4) **1** and **2**, yellowish oils, and **3**, yellowish crystals with mp 178-179°C, were purified by column chromatography and identified by conventional instrumental measurements as well as by elemental analysis. **3** was further purified by recrystallization from methanol - water.
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