

CROWN ETHER-BASED EXTRACTION PHOTOMETRIC REAGENTS FOR ALKALI METALS

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We have studied the synthesis and the application of chromogenic crown ethers, 1b and 3, and reported that they are useful to the extraction photometric determination of alkali or alkaline earth metals.^{1,2)} The 15-crown-5 type reagent 1b extracted lithium ion selectively, even though 15-crown-5 itself prefers to sodium ion to complex. In this study, we wish to report the synthesis of 12-crown-4 type new reagent 1a with a hope to obtain a photometric reagent with much higher selectivity to lithium. Syntheses of fluorimetric reagents 2a,b are also reported.

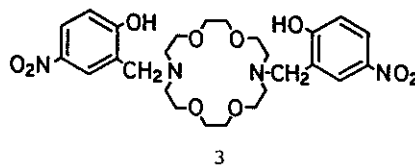
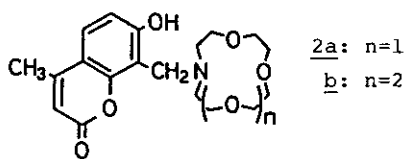
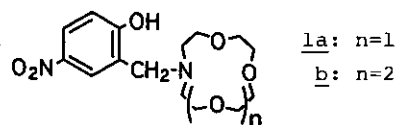
The compound 1a, N-(2-hydroxy-5-nitrobenzyl)-aza-12-crown-4 was synthesized from aza-12-crown-4 and 2-hydroxy-5-nitrobenzylbromide. 2a, N-(7-hydroxy-4-methyl-2H-benzopyrane-2-one-8-yl)methyl-aza-12-crown-4 and its 15-crown-5 (2b) derivative were readily synthesized from 4-methylumbelliferone, formaldehyde and corresponding aza-crown ethers, by Mannich reaction. The

structures were fully supported by elemental, ir and ¹H nmr analyses. These are monobasic reagents (HL), and they can extract alkali metal cations to the organic solvent (1,2-dichloroethane) as their 1:1 complex (ML).

The extraction of alkali cations by 1a, 2a and 2b were studied spectrophotometrically.

The metal selectivity in the extraction by 1a, 2a and 2b is as follows: Li⁺ > Na⁺ > K⁺. The

alkali metal complexes of 2a and 2b show strong fluorescence around 440 nm by the irradiation at 380 nm, and they can be used to the fluorimetric determination of alkali metals.



REFERENCES

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- 2) H. Nishida, M. Tazaki, M. Takagi and K. Ueno, Mikrochim. Acta, I, 281 (1981)