

HIGHLY LITHIUM-SELECTIVE CROWN ETHER DYES FOR EXTRACTION PHOTOMETRY

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Lipophilic 14-crown-4 derivatives bearing a chromogen such as nitrophenol and azophenol residues prove to be excellent extraction-photometric reagents for lithium ion. The lithium selectivities are extremely high, the extraction equilibrium constants for lithium being increased about two orders of magnitude over those for sodium.

Several crown ether dyes have been so far designed for Li^+ -selective photometric reagents.¹⁻³⁾ Some of them are applicable to Li^+ extraction photometry, where a crown ether bearing a proton-dissociable chromogen selectively extracts the ion from an aqueous sample under basic condition and thereafter serves as a photometric reagent for determination of the ion.^{1,3)} The Li^+ selectivities, however, are far from excellent. Here, we wish to report extremely high Li^+ selectivities of lipophilic 14-crown-4 derivatives incorporating a nitrophenol or azophenol residue as the extraction-photometric reagent.

Lipophilic crown phenol 1 was synthesized by the reaction of 2-dodecyl-2-(2'-methoxybenzyl)propane-1,3-diol with 3,7-dioxanonane-1,9-diyl bistoluene *p*-sulfonate in refluxing dioxane in the presence of NaH, followed by demethylation. Nitration of the crown phenol afforded *p*-nitrophenol 2, *o*-nitrophenol 3, and dinitrophenol 4 derivatives. Conventional azo-coupling of the crown phenol with *N,N*-dimethyl *p*-aminobenzene sulfonamide yielded crown azophenol 5.

Extraction of alkali and alkaline-earth metal ions was carried out from an aqueous solution containing an appropriate amount of tetramethylammonium hydroxide as the base into 1,2-dichloroethane. When the metal ions are extracted into the organic phase by complex formation with the crown ether dyes, the color of the organic phase⁴⁾ changes from colorless or pale yellow to deep yellow in the crown nitrophenols and from yellow to orange in the crown azophenol.

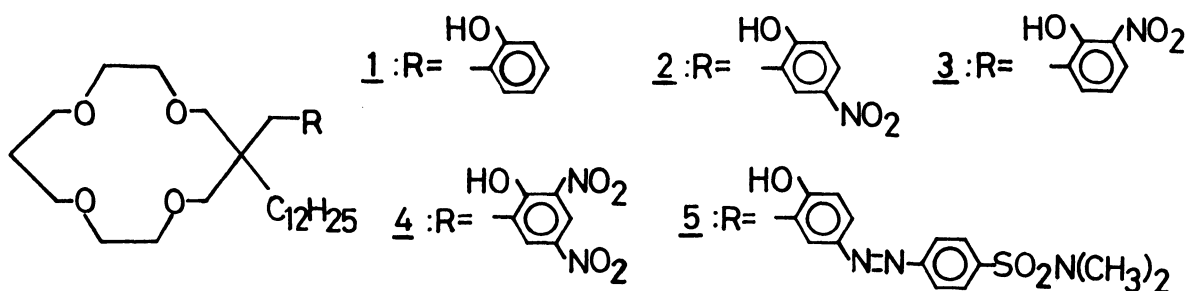
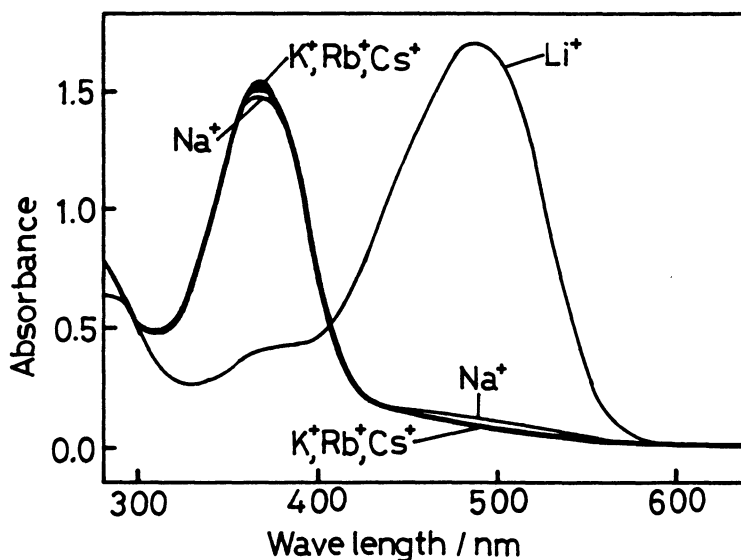


Fig. 1. Spectral changes in organic phase on extraction of alkali metal ions with crown azophenol 5. 7.5×10^{-5} M crown ether in $\text{ClCH}_2\text{CH}_2\text{Cl}$; 1 M metal ion and 2.2×10^{-1} M $(\text{CH}_3)_4\text{NOH}$ in H_2O , at 25 °C. (1 M = 1 mol dm^{-3})



The typical spectral change of the organic phase in the extraction of the metal ions with 5 illustrates distinguishing Li^+ selectivity of the crown ether dye (Fig. 1). Only Li^+ can be extracted efficiently with 5, whereas the spectrum changes very slightly in the Na^+ extraction. There was hardly any detectable spectral change in the extraction of other metal ions. Such drastic difference in spectral change between Li^+ and other metal ions was also found in the extraction systems of crown nitrophenols 2 through 4. The selectivity ratios of Li^+ over Na^+ in the extraction equilibrium constant ($K_{\text{ML}}^{\text{ex}}$)⁵⁾ were determined as 240 for 2 and 87 for 4,⁶⁾ exceeding by far the values (below 5) for the previous crown ether dyes for Li^+ extraction photometry.^{1,3)} The high Li^+ selectivities of the present crown ether dyes are definitely reflected in that of the 14-crown-4 cycle.⁷⁾

Thus, the 14-crown-4 derivatives incorporating the chromogens are quite promising for extraction-photometric determination of Li^+ in aqueous samples possessing high background of other alkali and alkaline-earth metal ions.

References

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- 2) K. Nakashima, S. Nakatsuji, S. Akiyama, T. Kaneda, and S. Misumi, *Chem. Lett.*, **1982**, 1781.
- 3) Y. P. Wu and G. E. Pacey, *Anal. Chim. Acta*, **162**, 285 (1984).
- 4) λ_{max} for the uncomplexed crown ether dyes (HL): 316 nm (ϵ 8070) for 2, 292 nm (ϵ 6910) for 3, 272 nm (ϵ 19200) for 4, and 366 nm (ϵ 21800) for 5; λ_{max} for the complexed one (ML, M=Li): 413 nm (ϵ 19300) for 2, 424 nm (ϵ 5610) for 3, 374 nm (ϵ 13600) for 4, and 488 nm (ϵ 31800) for 5.
- 5) $K_{\text{ML}}^{\text{ex}} = ([\text{ML}_o][\text{H}_a^+]) / ([\text{HL}_o][\text{M}_a^+])$, where subscripts "o" and "a" stand for the organic and the aqueous phases, respectively.
- 6) In the 3 and 5 systems, the $K_{\text{NaL}}^{\text{ex}}$ values could not be determined.
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