STRUCTURE AND CATION SELECTIVITY OF UNSYMMETRICAL BIS(CROWN ETHER)S

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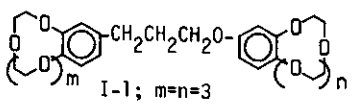
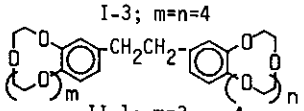
Structure-cation selectivity relationship of crown ethers has been actively investigated. Bis(crown ether)s having two same crown ether units are known to show both increased ability of complexation and selectivity for large alkali metal cations as compared to the corresponding monomeric analogs,[1] and are considered to give a basis for complexation behaviour of the polymers carrying crown ether units. Type and length of the binding chain in the symmetrical bis(benzocrown ether)s affected the degree of complexation, but not cation selectivity.[2] Now we present some interesting behaviours of unsymmetrical bis(benzocrown ether)s consisting of crown ethers of different ring size.

Two type of unsymmetrical bis(benzocrown ether)s (I and II) were synthesized using Pd(II)-Cu(I) catalyzed coupling of iodobenzocrown ether with suitable acetylenic compound as a key step.[3] The typical results obtained in the solvent extraction (CH_2Cl_2-H_2O) of alkali metal picrates are shown in figure 1 and 2. Increased selectivity to Rb^+ ion was obtained with trimetyleneoxy linked unsymmetrical bis(benzocrown ether) consisting of 15C5 and 18C6 units, while similar dimetylene linked unsymmetrical bis(benzocrown ether)s showed variety of cation selectivities depending on the combination of two crown ether units. The present results show the fact that unsymmetrical bis(benzocrown ether)s afford new cation selectivity which may be unable to expect in symmetrical bis(benzocrown ether)s.



I-1; m=n=3
I-2; m=3, n=4
I-3; m=n=4



II-1; m=3, n=4
II-2; m=3, n=5
II-3; m=4, n=5

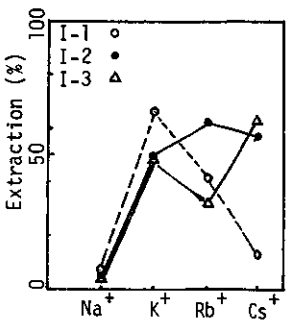


Fig 1 Solvent Extraction of I

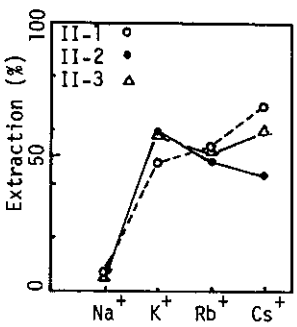


Fig 2 Solvent Extraction of II

References
1) K. Kimura, T. Maeda, T. Shono, Talanta, 26, 945 (1979).
2) F. Wada, Y. Wada, T. Goto, K. Kikukawa, T. Matsuda, Chem. Lett., 1980, 1189.
3) K. Kikukawa, A. Abe, F. Wada, and T. Matsuda, Bull. Chem. Soc. Jpn., 56, 961 (1983).