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EXCELLENT, pH-SENSITIVE CATION-SELECTIVITIES OF BIS(MONOAZACROWN ETHER) DERIVATIVES IN MEMBRANE CATION TRANSPORT

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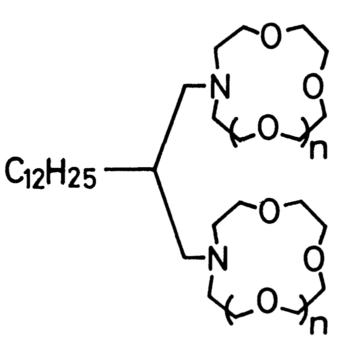
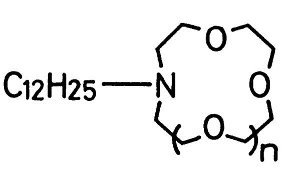
In cation transport through a membrane incorporating a lipophilic bis(monoaza-12-crown-4) derivative, extremely high sodium-selectivity is realized, which can be easily varied by pH values in the aqueous phase.

A strategy for augmenting ion-selectivities of monocyclic crown ethers is to adopt bicyclic structures. Macrobicyclic polyethers containing two crown ether moieties at the end of a short aliphatic chain, called bis(crown ether)s, often exhibit high ion-selectivities compared with their corresponding monocyclic analogs.[1-5] We have further extended this principle to synthesize bis(crown ether)s containing some ring nitrogen atoms, 1 through 3, in order to obtain excellent ionophores of which selectivities can be regulated by proton concentration condition. Here we report extremely high sodium-selectivity of lipophilic bis(monoazacrown ether) 1 and the pH-regulation of the selectivity in cation transport through a liquid membrane.



1: n = 1
2: n = 2
3: n = 3



4: n = 1
5: n = 2
6: n = 3

The reaction of 2-dodecylpropane-1,3-diyl bistoluene *p*-sulfonate with an appropriate monoazacrown ether[6,7] (CH$_3$CN, Na$_2$CO$_3$, reflux) afforded the corresponding bis(monoazacrown ether)s 1 through 3 , which were purified by preparative gel-permeation chromatography. The ionophores dissolved in *o*-nitrophenyl octyl ether (NPOE) were impregnated into microporous polypropylene films (maximum pore size of 0.04 X 0.4 μm, thickness of 25 μm). Competitive transport of alkali metal ions was carried out 25°C using a glass cell which is divided into two compartments by the impregnated membrane.[8] The corresponding monocyclic analogs 4 through 6 were also employed for comparison.

The ion-selectivities in the membrane transport at pH 10 are summarized in Fig. 1, being given as selectivity ratio of a particular metal ion over a most favorably transferred one (ratio of average flux during 10 h). As expected, the bis(monoazacrown ether)s, 1 and 2 , differ significantly from the corresponding monocyclic analogs in the ion-selectivity. The bis(monoaza-18-crown-6) derivative, 3 , however, possesses a similar ion-selectivity to the monocyclic one, 6 . It is probably because little bis(crown ether) effect functions due to the high cation-complexing ability of the monoaza-18-crown-6 ring itself. Emphasis is placed on the excellent sodium-selectivity in the membrane transport system of bis(monoaza-12-crown-4) derivative 1 . Only sodium ion can be transferred efficiently through the 1 membrane under the transport condition, whereas other alkali metal ions can hardly be done.

As the pH value in the aqueous phase[9] decreases, the monoazacrown ether derivatives in the membrane phase are protonated gradually. This in turn leads to suppression of their metal ion complexing due to the electrostatic repulsion between the proton and metal ion. The pH decrease in the aqueous phase brings about pronounced selectivity changes accompanying flux drops in the cation transport through the 1 membrane (Table 1). At pH 8 the transport selectivity varies drastically and then approximates more and more closely to that for an NPOE membrane without any of the ionophores.[10] This means that the pH value in the aqueous phase is rather crucial to attain such a high sodium-selectivity in the cation transport using the bis(monoazacrown ether) membrane. In the opposite sense, the transport selectivity can be easily regulated by varying the pH condition. In this point of view, the bis(monoazacrown ether)s are distinct from the previous bis(crown ether)s containing only oxygen atoms as the ring heteroatoms.

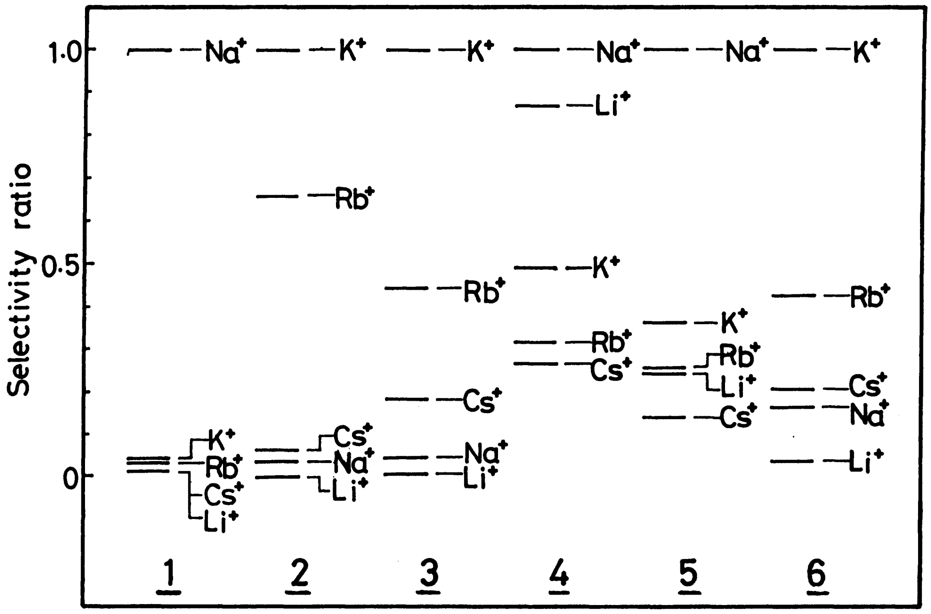


Fig. 1. Selectivity ratios of metal ions over most favorably transferred one in cation transport through membranes of bis(monoazacrown ether)s and their monocyclic analogs 1 through 6.
source phase: alkali metal chlorides of 1 x 10^{-2} M each and picric acid of 5 x 10^{-3} M in ethanolamine - HCl buffer (pH 10), 20 ml. receiving phase: the same as the source phase without any metal salt. The metal ion concentrations in the both aqueous phases were determined by flame photometry. (1 M = 1 mol dm^{-3})

Table 1. Effect of pH in aqueous phases upon selectivity ratio (M$^+$/Na$^+$) in cation transport through 1 membrane.

pH	Selectivity ratio				
	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
10.0	0.01	1	0.05	0.03	0.01
9.0	0.09	1	0.18	0.11	0.02
8.0	0.34	1	0.71	0.79	0.60
7.0	0.41	1	0.94	1.05	0.68
5.0	0.97	1	1.78	1.90	1.90

Application of the lipophilic bis(monoazacrown ether)s to proton-driven cation transport systems, which permit proton to pump other cations against their concentration gradients, is also feasible. In preliminary experiments for the proton-driven transport of alkali metal ions through the 1 membrane, excellent sodium-selectivities were again attained.

References

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8) A film disk of 3 cm diameter was impregnated with several drops of a 4×10^{-2} M ionophore NPOE solution. The external solution of the membrane was carefully wiped off with filter papers. The membrane was then fixed tightly to the glass cell using silicon rubber and clips. The exposed membrane area was about 1 cm^2.

9) The aqueous phase was adjusted to an appropriate pH by using buffers, which are tris(hydroxymethyl)aminomethane - HCl systems for pH 8 and 9, a 3-(N-morpholino)-propanesulfonic acid - tetramethylammonium hydroxide system for pH 7, and a 2-(N-morpholino)ethanesulfonic acid - tetramethylammonium hydroxide system for pH 5.

10) The transport rate for the blank membrane, although quite low compared to the ionophore-mediated transport, follows the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

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