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SELECTIVE ALKALI METAL ION TRANSPORT WITH SYNTHETIC IONOPHORES

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It has been reported that potassium and sodium ions were preferentially transported through a lipid membrane with antibiotic nigericin and monensin which contained high proportions of ethereal oxygens distributed periodically along the hydrophobic backbone composed of 2,5-tetrahydrofuranyl units. Both nigericin and monensin, which are called carboxylic ionophores, are linear polyethers ranging in molecular weights from 600 to 700 with a hydroxy group and a carboxy group at each end and are capable of forming macrocyclic rings with alkali metal ions by end-to-end hydrogen bonds. The important features of the natural polyethers as an ion carrier are as follows: the cooperative solvation of an alkali metal ion with ethereal oxygens was caused by cyclization of the polyether chain around a cation to form a lipid-soluble complex which carries an alkali metal ion through a lipid membrane and the selective complexation occurred by fit of the diameter of an alkali metal ion to the inner diameter of the macroring.

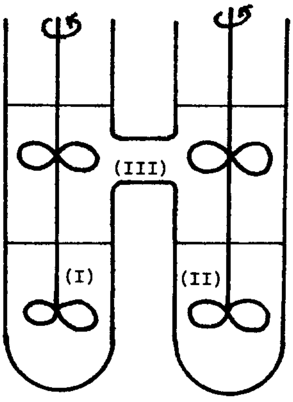
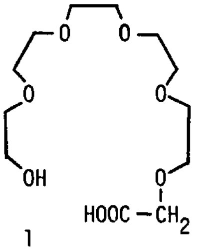


Figure 1. H-type cell for ion transportation: (I), 10 ml of 0.05N aqueous HCl solution; (II), 10 ml of 0.05N aqueous MOH solution (M, alkali metal); (III) 1-Hexanol membrane (20 ml) including 2 x 10^{-5} mole of synthetic ionophores.

In this study, α-carboxy,ω-hydroxy polyethers containing ethylene and 1,2-phenylene units (**1**~**4**) were synthesized as the model compounds for the carboxylic ionophores and examined their abilities of selective ion transportation.



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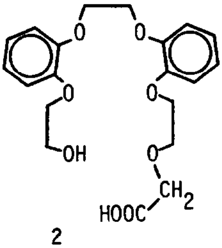

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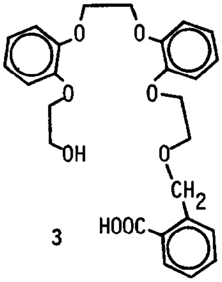

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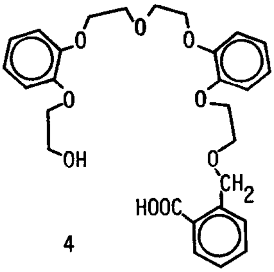

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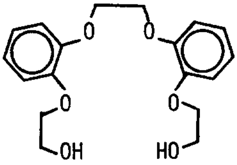

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Transportation of alkali metal ion was carried out in a H-type cell with stirring at room temperature (Fig. 1). The amounts of the transported alkali metal ions from the aqueous solution of alkali metal hydroxide, (II), to the aqueous solution of HCl, (I), through a liquid membrane of 1-hexanol containing synthetic ionophores, (III), were measured by flame analyses.

In the experimental results shown in Figure 2~4, potassium ion was preferentially transported by the synthetic ionophore, **2**, and rubidium ion by **3** and **4**. The radii of the alkali metal ions, which were favorable for transportation, correspond to the hole sizes of the synthetic ionophores, which were estimated by assuming the ring closure by the end-to-end hydrogen bonding. The cyclic structure of the complex formed with the synthetic ionophore, **2**, and an alkali metal ion was proposed as illustrated in Figure 5. The cyclic conformations of the synthetic ionophores, **2**, **3**, and **4**, with sodium, potassium, and rubidium ions were supported by the characteristic absorption maxima splitted at 275 and 280 nm in the UV spectra of the carboxylates as was observed in the case of crown ether complex with alkali metal salts[2]. Lithium ion was also carried to some extent by **3** and **4**, although the ionic diameter is much smaller than the inner diameters of **3** and **4** (Fig. 3 and 4), which was unable to be interpreted by the fit of sizes between the cavity of the macroring and lithium ion. Large solubility of the lithium carboxylates in 1-hexanol might effect the transportation.

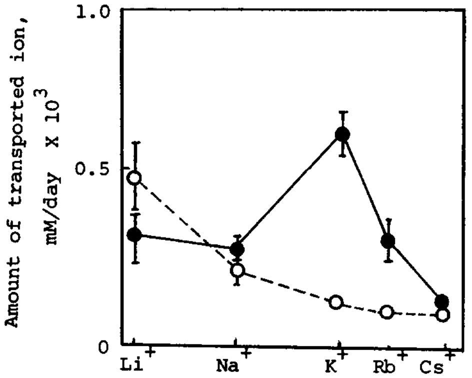

Fig. 2. Amount of alkali metal ions transported by 2; The broken line shows the results of the control experiments.

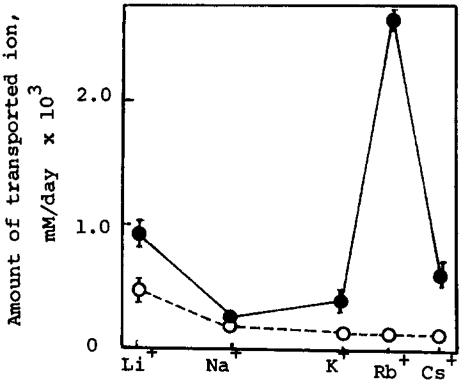

Fig. 3. Amount of alkali metal ions transported by 3; The broken line shows the results of the control experiments.

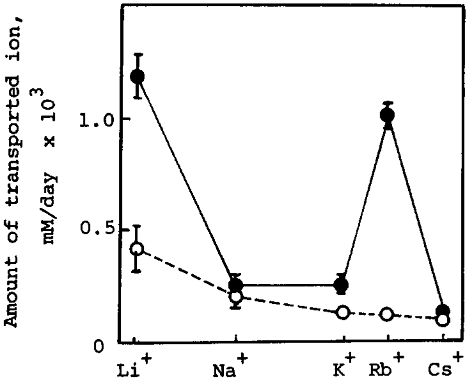

Fig. 4. Amount of alkali metal ions transported by 4; The broken line shows the results of the control experiments.

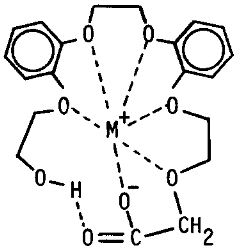

Fig. 5. The posturated structure of the complex between the synthetic ionophore, 2, and an alkali metal ion.

As compared with the synthetic ionophore with two benzo radicals, 2, the alkyl polyether with the same number of ethereal oxygens, 1, shows little transport activity for any alkali metal ions. The results are explained as follows: the substitution of ethylenic hydrogens for benzo groups increased the stability of the cyclic conformation and the solubility of the salts in 1-hexanol, and consequently suppressed the solubility in an aqueous layer leading to the high ability of ion transportation. α,ω-Dihydroxy polyether, 5, which does not contain a carboxy group and has an analogous structure with that of 2, could not transport any alkali metal ions. This indicates that carboxy group is essential for the ion transport.

Another interesting property of carboxylic ionophores is the active ion transport against the alkali metal ion concentration gradient. Unfortunately, the active ion transport was not clearly observed with the synthetic ionophores in this study, because the amount of the ion transported was not so large. It will be possible to increase the rate of transport by devising the structure and material of the membrane and seeking for other α-carboxy,ω-hydroxy polyethers, which have more hydrophobic backbone and form stable macrocyclic complexes with alkali metal ions.

References

1. B. C. Pressman, " Inorganic Biochemistry ", vol. 1, Chapter 6, p203, G. L. Eichhorn, Ed., Elsevier Science Publishing Co., Amsterdam, London, New York, 1973.
E. M. Choy, D. F. Evans, and E. L. Cussler, J. Amer. Chem. Soc., 96, 7085 (1974).
2. C. J. Pedersen, Federation Proc.,27, 1305 (1968).