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PROTON DRIVEN ACTIVE TRANSPORT OF ALKALI METAL CATIONS BY USING ALKYL MONOAZA CROWN ETHER DERIVATIVES

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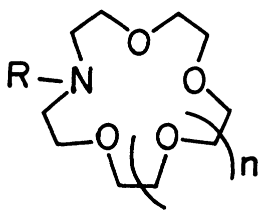
Octyl monoaza 18-crown-6 and the corresponding nitrogen lariat ethers were discolsed to be good carriers for the active transport of alkali metal cations. The transport ability is well corresponding to the complexing ability and the transport system has a characteristic of using the large change in the complexing ability between the acidic and alkaline phases.

Recently, a variety of noncyclic and cyclic synthetic multidentates have been developed as the simple model for natural ionophores and have contributed to the clarification of the host-guest interaction.[1)] As for the transport of alkali metal cations, complexing ability and lipophilicity of ion carriers had been pointed out to be important factors determining transport property.[1,2)] Therefore, a reversible change in complexing ability of the carrier between two interfaces should result in forming an active transport system. In this paper, we describe a simple active transport system using lipophilic aza crown ethers developed on the basis of the standpoint mentioned above.

The preparation and the properties of all synthetic ionophores(1-4) had already been reported in a separate paper.[3)]



1～4

R	n = 1	n = 2
C_8H_{17}	1a	1b
$C_8H_{17}O$	2a	2b
$C_8H_{17}O$ O	3a	3b
$C_8H_{17}O$ O O	4a	4b

Transport experiments were carried out using a U-type cell at 25°C according to the conditions as shown in Fig. 1 and the results are summarized in the Table.

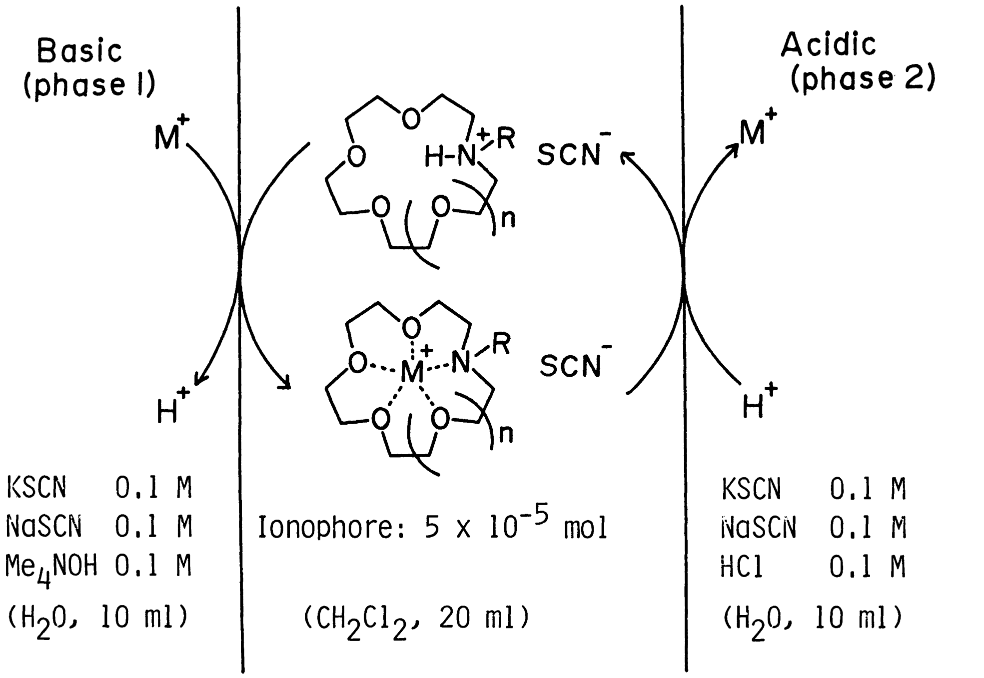


Fig. 1 Transport Process Using Lipophilic Monoaza Crown Ethers

A series of lipophilic monoaza crown ethers were found to possess a much higher active transport ability in comparison with dibenzo-18-crown-6, which is well known to be a good ionophore in the passive transport.[4)] The remarkable difference in the active transport ability between these two types of ionophores would be ascribed to the presence or the absence of nitrogen atom.

Table Competitive Transport of Potassium and Sodium Cations

		Ionophores							
		15-crown-5				18-crown-6			
		1a	2a	3a	4a	1b	2b	3b	4b
Transported Cations (%)[a]	K^+	6	8	18	22	26	56	57	61
	Na^+	4	12	13	15	5	11	12	14

a) atomic absorption analysis, after 48 h.

Monoaza crown ether has a relatively high complexing ability under basic conditions, but under acidic conditions, in which the nitrogen atom is protonated to form the ammonium ion, its complexing ability is remarkably reduced. In addition, the tertiary ammonium thiocyanate complex thus formed in the acidic phase should be lipophilic enough to be sent back to the basic phase through the membrane. Consequently, the large change in the complexing ability between two interfaces and the sufficient lipophilicity of the carrier are considered to be important factors dominating this active transport system.

Octyl monoaza-18-crown-6(1b) transported alkali metal cations effectively and rather selectively compared with the corresponding 15-crown-5(1a) as shown in the Table. Monoaza crown ethers having an electron-donating sidearm (nitrogen lariat ethers) had recently been disclosed to possess a higher complexing ability than the corresponding alkyl monoaza crown ethers having no electron-donating sidearm.[5,6] Izatt *et al.*[2] recently reported that the maximum observed transport occurred for carriers having log Ks values(methanol) from 5.5 to 6.0 for K^+. The log Ks values[7] of lipophilic nitrogen lariat ethers with monoaza-18-crown-6 ring(2b, 3b, 4b) are just within the above range and seem favorable for transport of K^+ in comparison with the corresponding aza crown ether(1b) having a relatively lower value and the cryptands having too high values (for example, the log Ks of [2,2,2]cryptand in methanol: 9.85[2,8]). Although the K^+/Na^+ selectivity was easily achieved in the case of 18-crown-6 series, the Na^+/K^+ selective transport was found to be rather difficult. However, a subtle Na^+/K^+ selectivity obtained by using 2a may give an important suggestion in designing the molecular structures of such ionophores.[9]

In conclusion, it is interesting that the active transport of alkali metal cations can be easily carried out by using such a simple aza crown ether. The clarification of the detailed transport mechanism is in progress.

References

1) Recent reports concerning ion carriers: H.Kuboniwa, K.Yamaguchi, A.Hirao, S.Nakahama, and N.Yamazaki, Chem.Lett., 1982, 1937; K.Hiratani, *ibid.*, 1982, 1021; H.Tsukube, Bull.Chem.Soc.Jpn., 55, 3882(1982); S.Shinkai, H.Kinda, T.Sone, and O.Manabe, J.Chem.Soc., Chem.Commun., 1982, 125; T.M.Fyles, Y.A.M.-Dimer, C.A.McGavin, and D.M.Whitfield, Can.J.Chem., 60, 2259(1982); W.A.Charewitz, G.S.Heo, and R.A.Bartsch, Anal.Chem., 54, 2094(1982).

2) J.D.Lamb, J.J.Christensen, J.L.Oscarson, B.L.Nielsen, B.W.Asay, and R.M.Izatt, J.Am.Chem.Soc., 102, 6820(1980).

3) A.Masuyama, P.-L.Kuo, I.Ikeda, and M.Okahara, Nippon Kagaku Kaishi, 1983, 249.

4) Y.Kobuke, K.Hanji, K.Horiguchi, M.Asada, Y.Nakayama, and J.Furukawa, J.Am.Chem.Soc., 98, 7414(1976).

5) R.A.Schultz, D.M.Dishong, and G.W.Gokel, Tetrahedron Lett., 1981, 2623; J.Am.Chem.Soc., 104, 625(1982); R.A.Schultz, E.Schlegel, D.M.Dishong, and G.W.Gokel, J.Chem.Soc., Chem.Commun., 1982, 242.

6) A.Masuyama, Y.Nakatsuji, I.Ikeda, and M.Okahara, Tetrahedron Lett., 1981, 4665.

7) Cited from ref.3. log Ks(methanol, 25°C) for K^+ and Na^+: 1a, 2.82 and 3.08; 2a, 3.58 and 3.83; 3a, 4.57 and 4.26; 4a, 4.74 and 4.36; 1b, 4.87 and 3.59; 2b, 5.73 and 4.21; 3b, 5.74 and 4.27; 4b, 5.75 and 4.33.

8) M.Kirch and J-M.Lehn, Angew.Chem.Int.Ed.Engl., 14, 555(1975).

9) The excellent Na^+/K^+ selectivity(about 20 times) based on the potentiometric titration had recently been observed in certain lariat ethers having a quinoline-type sidearm. Y.Nakatsuji, T.Nakamura, and M.Okahara, Chem.Lett., 1982, 1207.

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