TRANSITION METAL INDUCED SELECTIVE ALKALINE METAL ION TRANSPORT BY A SYNTHETIC IONOPHORE WITH DOUBLE RECOGNITION SITES FOR METALS

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Abstract: A new series of linear ionophores $\underline{1}$ with double recognition sites for metals was prepared. Selectivity of ion transport for alkaline metal was enhanced in the presence of transition metal.

Recently, intensive attention has been focused on ion transport across an artificial membrane containing functionalized synthetic ionophores, such as crown ethers and cryptands, to control the rate and selectivity of the transport utilizing pH gradient,¹ photochemical energy,² and redox system.³ Transition metal is also chosen to change the affinity of an ionophore to alkaline metal ion by the use of a cyclic ionophore. For example, the tungsten complex of a crown ether containing bipyridyl moiety has a reversed preference of ion transport, as compared to the uncomplexed host itself.⁴

We report here synthesis of a new type of linear ionophores $\underline{1}$ with double recognition sites for different metal ions, and its transport selectivity enhanced by a transition metal through CH_2Cl_2 as a bulk liquid membrane. The two kinds of binding site of the ionophore employed are both polyether and bipyridyl groups which recognize alkaline and transition metal ions, respectively. If it is supposed that 1:1 complex between $\underline{1}$ and transition metal is generated initially by using two bipyridyl groups located at the both ends of polyether chain to result in the formation of a cyclic pseudo crown ether, it will capture the suitable alkaline metal more selectively than the originally uncomplexed linear compound.

The ionophores were prepared according to the procedures shown in Scheme 1. Methyl or dimethyl bipyridines($\underline{2a}$, 5 $\underline{2b}^6$) were monobrominated⁷ by using N-bromosuccinimide(NBS) and azobisisobutylonitrile(AIBN) as an initiator in benzene under reflux for 12 h in 30-40% yields. Then the monobromobipyridines were treated with ethylene glycol oligomers and KOH in dry dioxane under reflux

Scheme



for 12 h to give ionophores 1 in 50-60% yields. $^{1}\mathrm{H}$ NMR spectra of $\underline{1}$ show characteristic absorptions due to the bipyridyl groups at the aromatic region, ca. 7.2 - 8.7 ppm and the polyether moiety at ca. 3.6 ppm. The structure is also supported by IR, UV-VIS spectra, or elemental analyses.⁸ As shown in Fig. 1, the addition of transition $metal(Ni^{2+}, Cu^{+})$ to the ionophore solution causes bathochromic shift(in <u>la</u>, n=3, λ max = 286 nm, ϵ = 2.8x10⁴ ---- > 308 nm, ϵ = 2.6x10⁴) and/or appearance of a new absorption(in <u>lb</u>, n=3, λ_{max} = 476 nm, ϵ = 1.4x10⁴) in UV-VIS spectrum, which clearly indicates the formation of a complex between transition metal and the bipyridyl groups of the ionophores.^{6,9} An apparatus illustrated in Fig. 2 was used for the alkaline metal ion transport across CH_2Cl_2 containing the ionophore(5.7x10⁻⁵ M) at 25°C. The ionophore 1¹⁰ itself was found to transport alkaline metal ion without transition metal, but the transport selectivity was not so large. For example, K^+ is transported 2.5 times as much as Na^+ in <u>1b</u>; both n=3 and n=4(Fig. 3). Prior to examination of the effect of transition metal on the transport experiment, the metal concentration(Cu⁺) both in the source phase(aq. I) and in the receiving phase(aq. II) was adjusted to be the same(1.2×10^{-4} M) at the initial stage. The



Fig.l Absorption Spectra of Ionophores and Their Metal Complexes

Fig.2 Apparatus for Metal Ion Transport throught Liquid Membrane



transport selectivity between K^+ and Na^+ by using <u>1b</u> is enhanced in the presence of transition metal such as Cu^+ , i.e., the ratio of the amount of transported ions between K^+ and Na^+ is ca. 10 after 100 h in n=4. On the other hand in n=3, a detectable enhancement of selectivity was not observed(Fig. 4). This result presumably arises from an initial formation of a cyclic structure(pseudo crown ether) in the complexation between Cu^+ and the ionophore. Formation of

pseudo crown structure should provide a cavity with a different size in the polyether moiety which can take up selectively an alkaline metal ion. Because cyclic ether, 18-crown-6, has a larger binding selectivity for alkaline metal ions($\log K_{\rm K} + / K_{\rm Na} + = 1.78$) than the corresponding linear compound, pentaglyme($\log K_{\rm K} + / K_{\rm Na} + = 0.68$).¹¹ Probably the reason why n=4 in <u>lb</u> has larger enhancement of the selectivity than n=3 in <u>lb</u> is that in n=4 the crown ether has more suitably sized cavity for K⁺ than n=3. Hereby the probable mechanism for the transport by <u>l</u> is shown schematically in Fig. 5. In the present experiment, the rates of the transport for Na⁺ and K⁺ are smaller in the presence of a transition metal than in the absence. The deceleration is probably explained in



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Fig.5
Ion Transport by 1
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terms of the Coulombic repulsion between Cu^+ and the alkaline metal ions bound in the same ionophore, because the CPK model¹² predicts that the pseudo crown moiety locates very close to the Cu⁺ binding sites.

The present study demonstrates that the selectivity of ion transport is enhanced by using $Cu^+-\underline{1}$ complex and that rate control of the transport is also performed. These results promise the synthesis of a more sophisticated allosteric ionophore and a receptor molecule controlled by transition metals.

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