THE STRUCTURES OF NONCYCLIC POLYETHER CARRIERS EXHIBITING LITHIUM ION-SELECTIVE TRANSPORT

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ABSTRACT. Several noncyclic polyether compounds containing oxytrimethylene groups and o-carboxyphenyl terminal group were synthesized. It has been found that they can transport lithium ion selectively in the competitive alkali metal ion transport through liquid membranes. The results of the spectroscopic study, together with inspection on the basis of the CPK model building suggest that these polyethers can form a pseudocavity, in which lithium ion best fits, and then the terminal aromatic rings overlap one another face-to-face to form a stacking structure. By using newly synthesized polyethers, which were designed on the basis of the conformational information, the significant contribution of the structures of these polyethers could be verified.

INTRODUCTION

The lithium ion has the smallest ionic radius among the alkali metal ions, but it has the largest hydrated one and the strongest hydration energy among them (1). Therefore, it is not easy to design a molecule with lithium ion-selectivity, and there has been few reports about available compounds which exhibit lithium ion-selective transport through liquid membranes or which extract the lithium ion from aqueous solution into organic solvent, compared with the case of other alkali metal ions. In addition, lithium compounds are widely used in various fields at present, and there is a possibility that large amounts of lithium are required for the production of tritium in the future, which is used as a reactant in the nuclear fusion reaction. Thus, the synthesis of the lithium ion-selective compounds is a very attractive target.
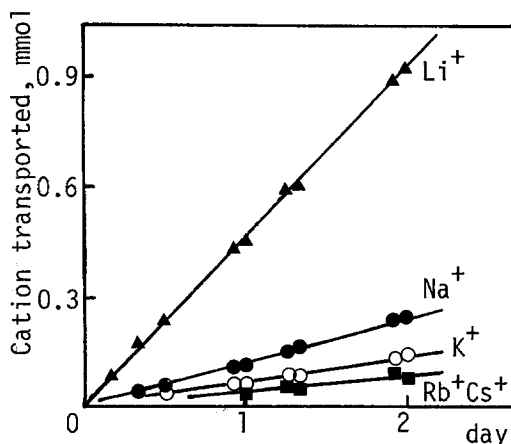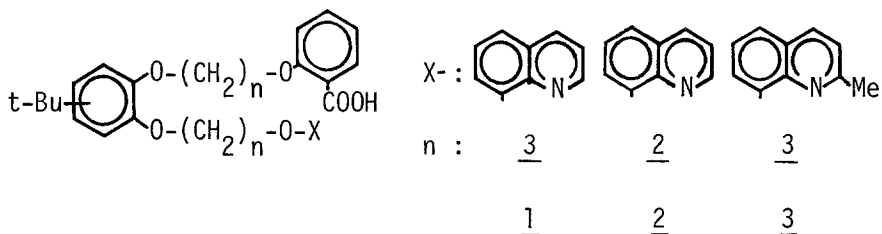So far several polyether family compounds exhibiting lithium ion-selectivity have been reported, e.g., 12-crown-4, 14-crown-4, macrocyclic compounds having tetrahydrofuran as a chain component, cryptand [211], spherand, noncyclic diamide, and so on (2). However these are not always suitable to transport lithium ion selectively through liquid membranes. That is, these are useful as extracting agents or chemical devices for ion selective electrode (3), but are not available and

effective as carriers for the lithium ion-selective separation and
concentration (4).

    We have studied   the synthesis of noncyclic polyether compounds
and their cation transport behaviors (5). Recently, we found that the
noncyclic polyether compounds containing oxytrimethylene chain units,
e.g., 1, could transport lithium ion selectively as is shown in Fig. 1
and against its concentration gradient (5b, 5e).

    Polyethers with a variety of substituents as one end group were
prepared. Also, polyethers with   different alkylene chain-length
were prepared in order to investigate the relationship between the
structures and their transport ability.   The results show
that the polyether compounds should have oxytrimethylene chain
units and aromatic substituents as an end group in order to exhibit
excellently selective and effective transport in this series (5e).

Fig. 1. Plots of cation transported vs. the running time.

On the other hand, it has been considered that the cation transport by the polyether carriers through liquid membranes can proceed most effectively and selectively when the structure of the polyethers can satisfy each process as follows: i) selective uptake of cation at the boundary between phases (a) and (b), ii) solubility into the liquid membrane phase (b) and mobility through it, and iii) smooth and rapid release of cations at the boundary between phases (b) and (c)(Scheme 1).

In this paper   willbe described   the attempt to clarify the relationship between the structure of the polyethers and the ability of the lithium ion-selective transport, on the basis of   spectroscopic methods and   inspection on the basis of   CPK model building. Furthermore, new noncyclic polyether compounds are synthesized on the basis of the information obtained.

(a)	(b)	(c)
Source phase	Organic phase	Receiving phase

$$M^+ \rightarrow C \leftrightarrow M^+$$

$$H^+ \leftarrow C'-M^+ \rightarrow H^+$$

Selective uptake	Solubility Mobility	Release

Scheme 1. Carrier-mediated transport of cations through liquid membranes. M^+ : cation, C : carrier, $C'-M^+$: complex.

MATERIALS AND METHODS

1. Materials

Noncyclic polyether compounds, 1, 2, and 3, were prepared as previously-reported (5e) and used in this study after purification by column chromatography.

Polyethers which contain phenyl, o-ethoxyphenyl, and o-[3-(1-naphthyloxy)propoxy]phenyl end groups, respectively, were prepared as is shown in Scheme 2 and also purified by column chromatography. These were identified by   elemental analysis and   NMR and IR spectroscopic methods.

2. Cation Transport

A U-type glass tube as previously-reported was used for investigating the competitive transport of the alkali metal ions (5c). The tube was placed in a water bath whose temperature was kept at 25 °C. Each phase was agitated at 200/min mechanically.

The transport of alkali metal ions was initiated by the addition of the aqueous solutions. At each time point, 50 μl of the solution was withdrawn from each aqueous phase, and the concentration of the cation was adjusted by using a measuring flask and determined by means of a Shimadzu AA-646 atomic absorption spectrometer. The transport of cations in the blank systems was negligible. The detailed conditions are shown in the tables.

3. Spectrophotometric Measurement

Absorption spectra were measured on a Hitachi 330 spectrophotometer in ultraviolet region. Fluorescence spectra were recorded on a Hitachi 204 fluorescence spectrophotometer. Dichloromethane, ethanol, and aceto-nitrile were used as solvents and the spectra were measured at room temperature.

RESULTS AND DISCUSSION

1. Inspection based on   CPK model building

From a series of studies   the structural significance of the oxytri-methylene chain units in polyether 1 is noted for the appearence of a high selectivity for the lithium ion (5e). In fact, the lithium ion-selectivity in the case of polyether 2, which contains two oxyethylene chain units decreased distinctly compared with the case of 1. In addi-tion, it has been found that the selectivity and efficiency appreciably depends on the kind of the terminal group, X.
    It is necessary that not only free noncyclic polyether compounds but also their alkali salts can   be dissolved into hydrophobic organic solvents in order to functionalize as a cation carrier (see Scheme 1). Therefore, it should be considered that the conformation of the polyethers changes to spatially direct polar parts to the inside when they form the salts with the alkali metal ions.
    When inspecting the CPK model building of 1 (X = 8-quinolyl), we noticed that polyether 1 can form a pseudocyclic structure as is shown in Fig. 2-a, the cavity of which has a diameter of 1.4 - 1.6 Å, and then the terminal aromatic rings overlap one another face-to-face to form a stacking structure, when both ether-oxygen and nitrogen atoms are spa-tially directed to the inside. This indicates that the lithium ion (ionic diameter, 1.32 Å) best fits in the cavity formed among the alkali metal ions. On the other hand, polyether 2 can not form a stacking structure between terminal aromatic rings, even if the hetero atoms are spatially directed to the inside as well as in the case of 1, as is shown in Fig. 2-b. Additionally, it is confirmed in the CPK model building that 2 forms a greater pseudocavity than 1.
    Thus, polyether 1 is presumed to result in forming the pseudocavity in which the lithium ion best fits, because the hydrophobic external wall is tightly formed by the stacking structure between the terminal aromatic rings. This speculation is consistent with that polyether 3 containing 2-methylquinolyl group in place of quinolyl as in 1 exhibits

a lithium ion-selectivity superior to 1. That is, the methyl moiety newly introduced plays a role of a part of the external hydrophobic wall to fill a space(Fig. 2-c).
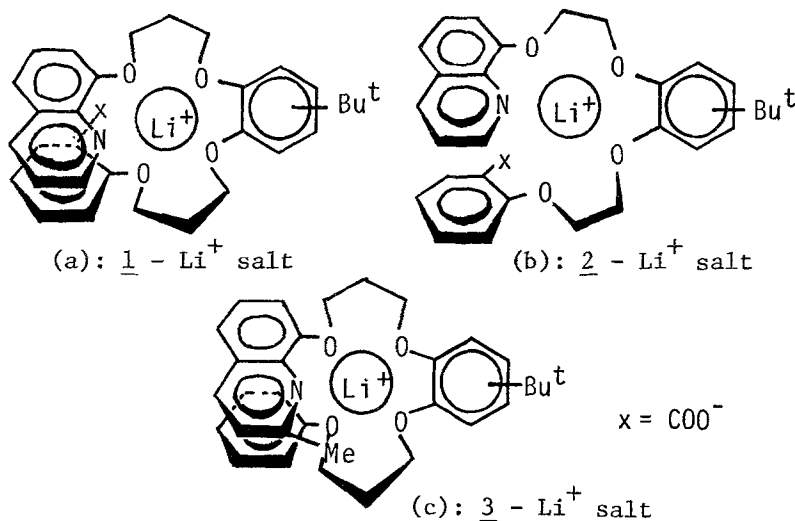

(a): 1 - Li$^+$ salt   (b): 2 - Li$^+$ salt

(c): 3 - Li$^+$ salt   x = COO$^-$

Fig. 2. Postulated structures of the lithium salts in CHCl$_3$ on the basis of the CPK model building.

2. Spectroscopic Behavior of the Alkali Salts of the Polyethers

In order to confirm the stacking structure between the terminal aromatic rings of the lithium salt of 1, the spectroscopic behavior of the alkali salts of the polyethers have been investigated.

So far, there are many reports that the stacking structure between inter- or intramolecular aromatic rings can be differentiated by electronic and NMR spectra. For example, it has been reported that the stacking between nucleic acid bases could be differentiated by the magnitude of their hypochromic effect of the absorbance based on the aromatic rings, which increases with increasing the extent of the stacking between them (6). In addition, the extent of the stacking can also be observed by the chemical shifts of the protons on the aromatic rings in the NMR spectra (6, 7).

Firstly, the effect of the kind of alkali metal ions as a counter cation of the carboxylate ion of 1 and 2 on the absorptivity of their alkali salts was investigated. With the kind of the alkali metal ions, their absorptivity appreciably changes in the electronic spectra (8). The absorptivity in dichloromethane increases with the increase of the ionic size as follows: Li < Na < K < Rb < Cs. Apparently, the absorptivity of one terminal substituent(quinolyl group) is influenced by the kind of the counter cation of the carboxylate ion of the other terminal one(o-carboxyphenyl group). Table 1 shows the hypochromic effect(H, %) at 303 nm, which is based on the absorption maximum (shoulder) of the quinolyl group. In the case of the salts of 2, it was observed that there is little difference between the values of their

hypochromic effect. The results in Table 1 may be closely associated
with the consideration on the basis of the CPK model building as
described-above(Fig. 2-a, 2-b). It is noted that the results of the
selectivity for the alakli metal ions in the transport study through
a chloroform liquid membrane by these polyether carriers are consistent
with those of the spectroscopic behaviors as is shown in Fig. 3. Also,
the solvent effect was investigated. In a polar solvent(ethanol or
acetonitrile), the hypochromic effect was hardly dependent on the kind
of the alkali metal ions. It means that it is not necessary for the
noncyclic polyether compounds in a polar solvent to form a pseudocyclic
structure in order to wrap around the polar parts because the salts in
a polar solvent could be solvated by the solvent and be solved in it.

Table 1. Hypochromic effect (H, %).[*]

Cation	Li	Na	K	Rb	Cs
Ionic radius,Å	0.66	0.95	1.33	1.48	1.69
1	15.6	6.5	4.3	2.2	0
2	6.7	4.9	6.4	6.4	0

* The values were calculated from ε for each cation
  at 303 nm using the equation below.

$$H\ (\%) = (1 - \frac{\varepsilon_{M^+}}{\varepsilon_{Cs^+}})\ \times\ 100$$

$\underline{1} : \varepsilon_{Cs^+} = 3.98 \times 10^3$

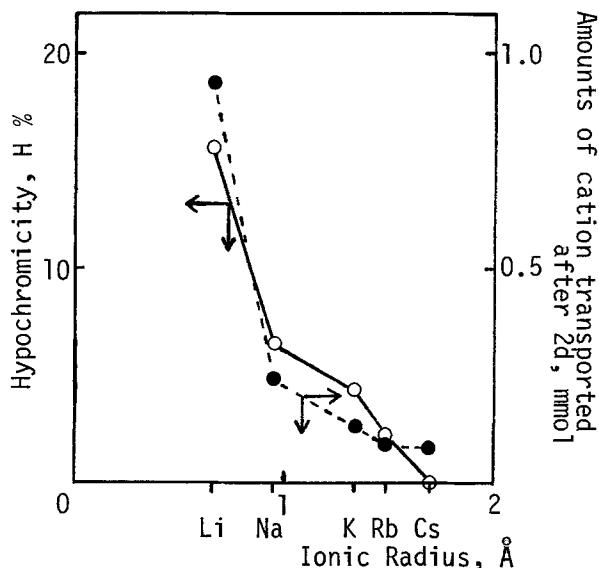$\underline{2} : \varepsilon_{Cs^+} = 3.89 \times 10^3$

Fig. 3. Plots of hypochromicity and amounts of cation
transported vs. the ionic radius of the alkali metal ions.

The fluorescence spectra of the alkali salts of 1 were measured in order to further investigate the interaction between   both end groups of the salts of 1 in a nonpolar solvent. The relative intensity of the fluorescence maximum apparently decreased with the decrease in the ionic size of the alkali metal ions. The quenching phenomenon dependent on the kind of the alkali metal ions is consistent with the hypochromicity in the electronic spectra, which is suggested to reflect the interaction between   both terminal aromatic rings.

As reported recently (5e), it has been presumed that in the NMR spectra the shift to   upfield of the proton at the 2-position of the quinolyl group in the case of the lithium salt of 1 is to be attributed to the shielding effect(ring-current effect) of the aromatic rings on account of the stacking structure between them. This phenomenon is also consistent with the behavior both in the electronic and fluorescence spectra.

Thus, the results, which have been obtained here concerning   the spectroscopic behavior of the alkali metal salts of the polyethers, reflect those of the cation-selective transport by the nocyclic poly-ether carriers through a chloroform liquid membrane, and the mechanism for the appearence of the cation-selective transport, which we have proposed, could be supported spectrophotometrically.

3. Synthesis of New Noncyclic Polyethers and Their Transport Behavior

On the basis of the consideration mentioned-above, some noncyclic poly-ether compounds were newly prepared and their ability   in cation transport was examined by using them as a carrier. It is expected that polyether 7 exhibits the most excellent ability of   selective trans-port among them because polyether 7 has been designed to form a sp-herical conformation with a thick hydrophobic external wall and deep pseudocavity according to the hypothesis proposed. Polyether, 4 - 7, were prepared by the procedure as depicted in Scheme 2.
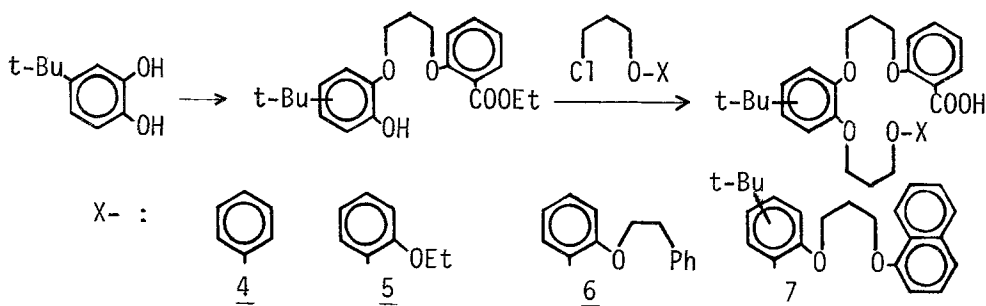
Scheme 2. Synthetic procedure of polyether carriers

Table 2 shows the results of the competitive transport of alkali metal ions through a chloroform liquid membrane. Apparently, the selectivity of these carriers for the lithium ion increases as follows: 4 < 5 < 6 < 7. The kind of one terminal substituent, X, depends significantly on the selectivity of the noncyclic polyether carriers.

Table 2. Cation transport through liquid membranes.

Carrier	Transport rate(μmol/h)			Selectivity	
	Li	Na	K	Li/Na	Li/K
4	19.1	6.9	5.0	2.9	3.8
5	19.1	5.3	4.1	3.6	4.7
6	21.8	5.0	4.5	4.4	4.9
7	18.2	3.8	3.2	4.8	5.8

Initial transport conditions(25 °C):

(Source phase)	(Chloroform membrane)	(Receiving phase)
0.1 M LiOH		
0.1 M NaOH	Polyether	0.05 M H_2SO_4
0.1 M KOH	1.5×10^{-4} mol	
0.1 M H_2SO_4		15 ml
115 ml	$CHCl_3$ 30 ml	

When inspecting the CPK model building of the lithium salt of polyether 7 on the basis of the hypothesis, it can result in the spherical conformation shown in Fig. 4. It is not inevitable that polyether 7, which has a larger chain structure than the other polyethers, should show excellent lithium ion-selectivity, unless we build up the spherical conformation. Thus, the polyether, which has oxytrimethylene and o-phenylene groups alternately, can form a spherical conformation and then the size of its pseudocavity is around 1.5 Å and the lithium ion best fits into it. As is shown in Fig. 4, when forming such a conformation, the hydrophobic external wall and the stacking structure between aromatic rings can be formed. It is therefore presumed that the polyether carrier, which forms the salts with alkali metal ions, favorably lithium ion, can be solubilized into a nonpolar organic solvent and diffused across it.
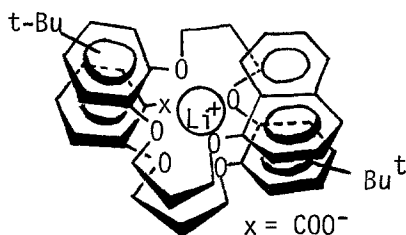

Fig. 4. Spherical structure of 7 – Li$^+$ salt on the basis of the CPK model building

Polyethers, 5 and 6, containing X = o-ethoxyphenyl and o-(2-phenylethoxy)phenyl groups, respectively, can also exhibit   lithium ion-selectivity superior to polyether 4 (X = phenyl). It is suggested that these substituents as well as o-[3-(1-naphthyloxy)propoxy]phenyl group in 7 and 2-methylquinolyl group in 3 play a role of a part of the hydrophobic external wall.

In conclusion, these noncyclic polyether compounds result   in the drastic change of their conformation by the uptake of cation(Scheme 3), that is, the formation of the hydrophobic wall, pseudocavity, and the stacking between aromatic rings, then the salt of the polyether carriers can be solubilized in   organic solvent and diffused easily across a chloroform liquid membrane. Then, at the   other boundary the smooth release of cation which is driven by proton potential occurs.
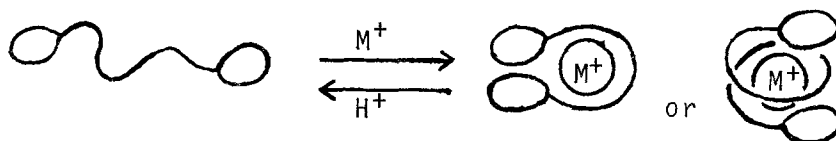
Scheme 3. Conformational change of noncyclic polyethers induced by the uptake of cation.

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