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A NEW SYNTHETIC IONOPHORE EXHIBITING SELECTIVE Li^+ TRANSPORT[1)]

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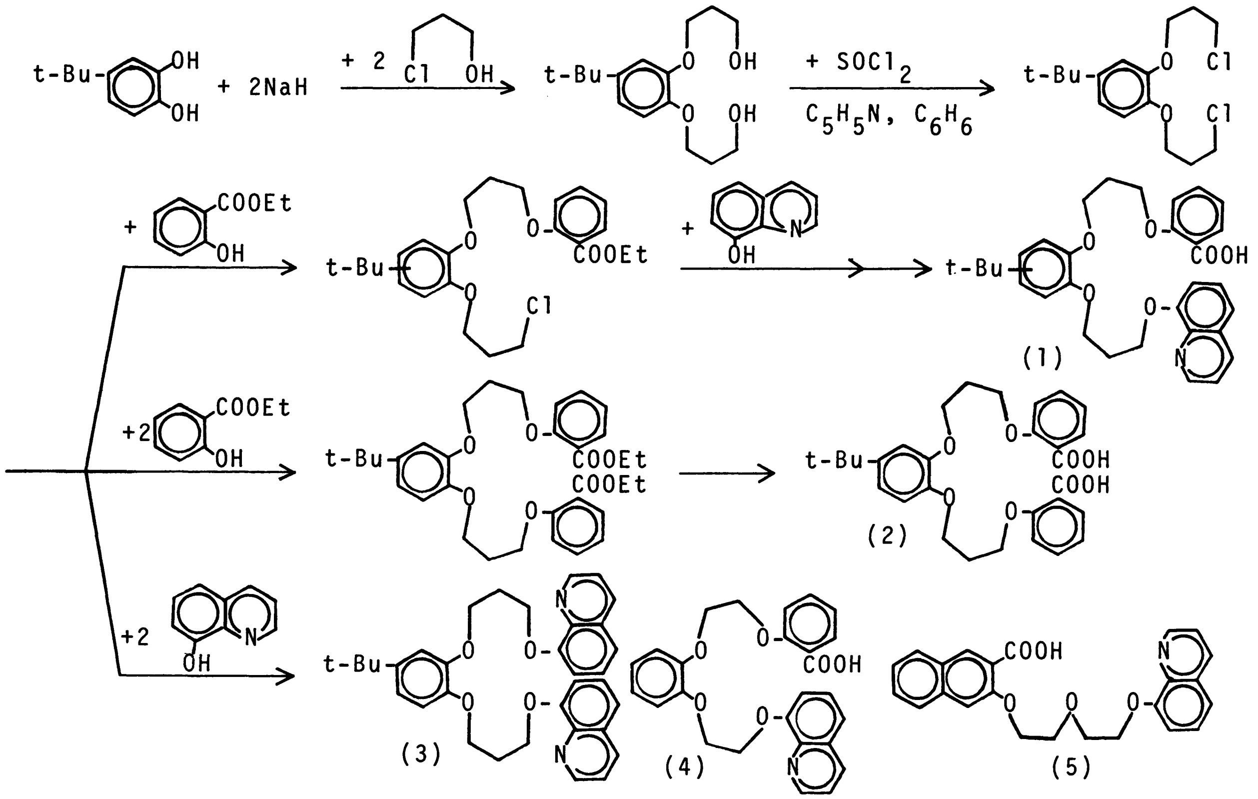
A noncyclic polyether, which contains 1,3-propylene oxide chain unit and both 8-quinolyl and o-carboxylphenyl terminal groups, exhibits highly selective transport of lithium ion for sodium and potassium ion species which are all together in aqueous solutions, against the concentration gradient through chloroform liquid membrane.

Although a number of synthetic noncyclic ionophores have been reported which exhibit the selective and/or active transport of alkali or alkali earth metal ions across liquid membranes,[2)] neither noncyclic nor cyclic ionophore exhibiting selective and efficient transport of lithium ion has been reported.[3)] Additionally, lithium is a useful element, for example, as starting material for the production of tritium.[4)] The author, therefore, belives that the designing and constructing of ionophore with lithium ion-selectivity are of particular interest not only in view of the molecular structure but also for the reason of potential applications to the separation and concentration of ion species.

The author here wishes to report a new noncyclic polyether compound which transports lithium ion selectively through liquid membranes against its concentration gradient. In this study, the noncyclic compounds, (1), (2), and (3), were prepared as a new type of ionophores involving 1,3-propylene oxide chain unit. Also, in a similar manner, the compound (4) containing ethylene oxide chain unit was prepared for the comparison with (1). The compound (5)[5)] was also used in the transport experiment for the comparison. These compounds were identified by the elemental analysis and the NMR, IR, and Mass spectroscopic methods.



Uphill transport of alkali ions by these ionophores was carried out in the liquid membrane system containing lithium, sodium, and potassium ion species in aqueous solutions under the initial transport conditions shown below using a previously-reported U-type glass tube at 25 ± 0.2°C.[5)] The each solution was stirred at 200 r.p.m. mechanically. The amounts of alkali ions transported were determined by atomic absorption analysis. In Figure 1 are shown the changes of amounts of cation transported with time by the ionophores, (1) and (2). In Table 1 are summarized the amounts of ion transported after 2 days and selectivity by these ionophores.

Initial transport conditions:

(Source Phase)	(Chloroform Membrane)	(Receiving Phase)
15 ml of aq. solution containing	Ionophore 1.5×10^{-4} mol in 30 ml of chloroform	15 ml of aq. solution containing
0.1 M LiOH		0.1 M LiOH
0.1 M NaOH		0.1 M NaOH
0.1 M KOH		0.1 M KOH
0.1 M H_2SO_4		0.2 M H_2SO_4

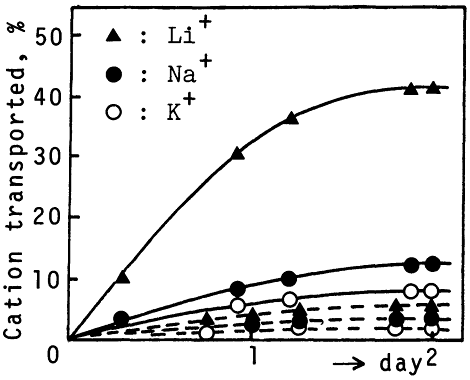


Fig. 1. Ion transport by (1) and (2) for Li$^+$, Na$^+$, and K$^+$ existing together; (1): ——, (2): ----

As shown in Table 1 and Fig. 1, the ionophore (1) can transport lithium ion with the highest selectivity and the largest transport rate among these compounds, while the ionophores, (2), (4), and (5), transport lithium ion less selectively and smaller transport rate under the same conditions than (1). The ionophore (3) without o-carboxylphenyl group cannot transport any alkali ion. The ionophore (4) with ethylene oxide chain unit can transport moderate amount of cations after 2 days, although lithium ion is transported by (4) less selectively than (1). In Table 1, 41% of lithium ion transported from the source phase to the receiving phase after 2 days corresponds to 0.62 mmol of lithium ion. Furthermore, the ratios(Li/Na and Li/K) of the amount transported after 2 days reach 3.4 and 5.1, respectively. Additionally, it is confirmed that the extractability of (1) is in the order $Li^+ > Na^+ > K^+$. These results are consistent with those of the cation transport by (1).

Table 1. Amounts of cation transported by the synthetic ionophores through chloroform liquid membrane after 2 days

Ionophore	Amounts of ion transported, %*				Selectivity	
	Li	Na	K	Total	Li/Na	Li/K
(1)	41	12	8	61	3.4	5.1
(2)	6	3	2	11	2	3
(3)	0	0	0	0	-	-
(4)	20	16	9	45	1.3	2.2
(5)	10	7	6	23	1.4	1.7

* Reproducibility, ± 10%.

When inspecting the CPK model of these ionophores, it is noticed that (1) is able to form pseudocyclic structure with the diameter of pseudocyclic cavity, 1.4 - 1.6 Å, when the two terminal aromatic rings form stacking structure (see Fig. 2), whereas (4) and (5) form pseudocyclic structure with larger size of the cavity than (1) and the terminal aromatic rings can not form stacking structure. It is considered from the CPK model bilding that the steric difference between (1) and other ionophores is reflected by the size of pseudocyclic cavity; that is, the CPK model predicts the size of (1) to be the most suitable for the size of lithium ion among them. The results of cation transport are compatible with that expected on the basis of CPK model building.

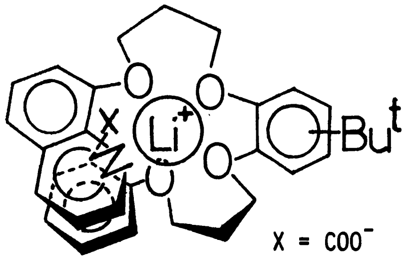


Fig. 1. Pseudocyclic structure of (1)-Li^+ salt on the basis of the CPK model.

In conclusion, these results could give an important suggestion on the designing of the molecule of noncyclic ionophore with ion-selectivity: 1) number of carbon atoms between two oxygen atoms affects greatly the selectivity and the transport rate;$^{6)}$ 2) the ion-selectivity of noncyclic ionophore with the same skelton changes drastically by selection of the two end groups, that is, the introduction of both basic 8-quinolyl and o-carboxyl phenyl terminal groups is much more effective than that of two o-carboxylphenyl groups (ionophore (2)) or two 8-quinolyl groups (ionophore (3)) in the transport of alkali ions.

Further investigation on the relationship between the selectivity and the structure of the synthetic ionophores is now in progress.

References

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