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A NONCYCLIC NEUTRAL CARRIER EXHIBITING EXCELLENTLY Li^+-SELECTIVE TRANSPORT1)

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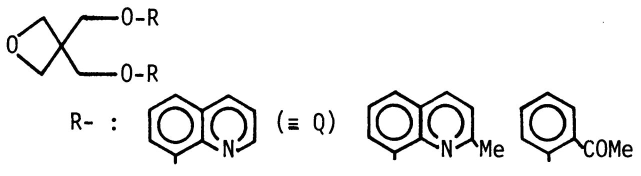
3,3-Bis(8-quinolyloxymethyl)oxetane, which has been newly synthesized as a carrier in the cation transport through liquid membranes, exhibits extremely high Li^+-selectivity. From the investigation of structural effect, introduction of 8-quinolyl terminal group, oxetane ring, and trimethylene chain to the structure of carrier is suggested to be important for excellent Li^+-selectivity.

Various types of podands, chorands, cryptands, and so on, have been investigated as host molecules, which have the capability to selectively extract guest ions from aqueous solution into a hydrophobic membrane phase and to transport ions across such a membrane by carrier translocation.2) In general, podands(noncyclic polyethers) have considerably small extractability, selectivity, and ability of transport for ions relative to other ligating systems.3) Therefore, introduction of ionizable moieties such as COOH and OH or various functional groups to podands has been undertaken to improve their functions.4 - 7) As a result, carriers exhibiting actively and efficiently ion-selective transport through liquid membranes have been reported.5,6) On the other hand, noncyclic neutral polyether diamides have been confirmed to be greatly available as carriers for ion-selective liquid membrane electrodes by Simon et al.8) Through these studies, increasing attention has been focused to the noncyclic host compounds for cations. In this paper, we wish to report on the neutral polyether carrier, which has been newly synthesized, can exhibit highly Li^+-selective transport but small transport-efficiency compared with previously-reported noncyclic polyethers.5)

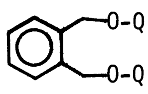
Compounds, 1 - 3, were obtained from the reaction of 3,3-bis(chloromethyl)-oxetane9) with 8-quinolinol, 2-methyl-8-quinolinol, or 2-acetylphenol, respectively, under the presence of base in DMF or DMSO. Compounds, 4 - 6, were obtained from the reaction of the corresponding dihalides with 8-quinolinol in a similar manner. These compounds were purified by column chromatography(alumina - chloroform) followed by recrystallization from cyclohexane.10)



1 2 3

$Q-(CH_2)_n-Q$ 4 : n = 3

5 : n = 4



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Transport of alkali and alkaline earth metal ions by these carriers was carried out in the liquid membrane system containing plural cation species in the source phase under the initial transport conditions shown in Tables 1 and 2 using a previously-reported U-type glass tube at 25 ± 0.2 °C.[11)] The each solution was stirred at 200 r.p.m. mechanically. The amounts of metal ions transported were determined by atomic absorption analysis.

Figure 1 shows the plots of amounts of cation transported by 1 vs. the running time. The amounts of the cation transported increased linearly with the running time even after 6 days. The results after 2 days are summarized in Table 1. Cation-transport hardly occurred without carrier. Carriers, 1 and 4, can transport a large amount of Li$^+$ with excellent selectivity compared with other carriers. Apparently, 3 can not transport any cation, that is, 3 does not function as a carrier. Interestingly, both transport ability and selectivity of 2, of which 2-methyl-8-quinolyl terminal groups are substituted for 8-quinolyl ones of 1, extremely decrease compared with those of 1. The selectivity for Li$^+$ by 1, to which oxetane ring are introduced, are appreciably improved compared with that by 4. The influence of the chain length were also investigated; carriers, 1 and 4, in which three carbon atoms lie between terminal aromatic groups, apparently exhibit excellent both Li$^+$-selectivity and efficiency compared with 5 and 6, in which four carbon atoms lie between them. Under the same conditions, one of the well-known cyclic polyethers, dicyclohexyl-18-crown-6 (7) transports K$^+$ selectively. However, K$^+$-selectivity of cyclic carrier 7 is inferior to Li$^+$-selectivity of noncyclic 1, while 7 can transport cations more efficiently than 1.

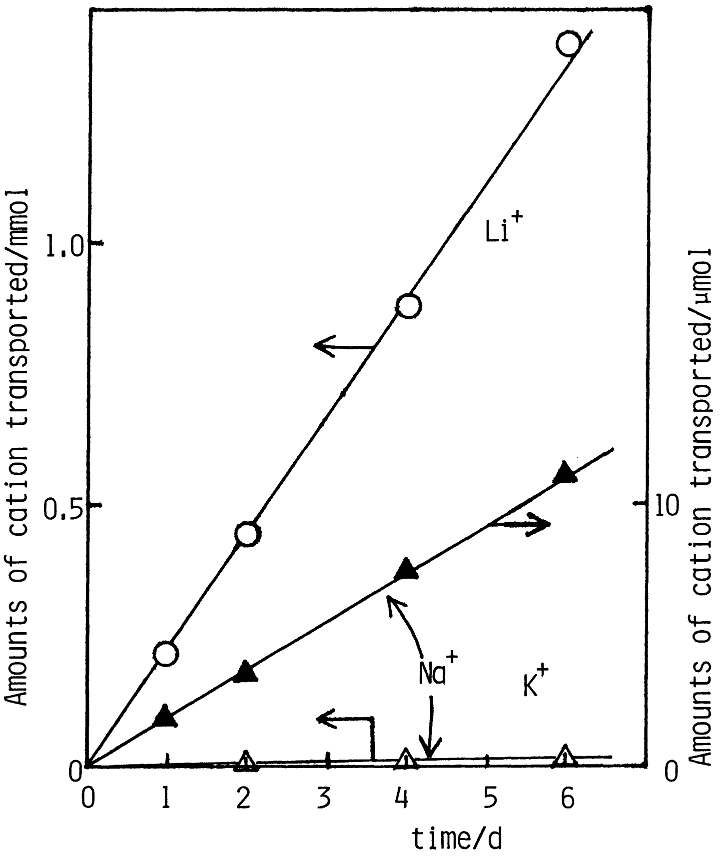

Fig. 1. Plots of amounts of cation transported by 1 vs. the running time; initial transport conditions: see Table 1.
○ : Li$^+$, △,▲: Na$^+$

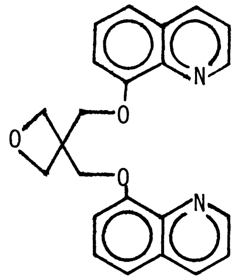

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Table 1. Cation Transport through Liquid Membranes by Synthetic Carriers

Carrier	Cation transported after 2 days(μmol)[a) Li]	Na	K	Selectivity Li/Na	Li/K
1	440	4.0	1.1	110	400
2	23	5.3	1.1	4.3	21
3	0	≈2	≈1	-	-
4	880	26	2.2	34	400
5	31	5.1	1.5	6	21
6	17	12	4.0	1.4	4.3
7	89	400	10300	(K/Li= 116	K/Na= 26)
No carrier	0	≈2	≈1	-	-

Initial transport conditions(25 °C):

(Source phase)	(Chloroform membrane)	(Receiving phase)
1 M LiCl 1 M NaSCN 1 M KSCN 15 ml	1.5 x 10^{-4} mol of carrier in 30 ml of $CHCl_3$	H_2O 15 ml

Table 2. Cation Transport through Liquid Membranes by 1

	Cation transported after 2 days(μmol)[a)] Li	Mg	Ca	Ba
Without LiCl	-	0.4	0	0
+ 0.5 M LiCl	120	0.2	0	0

a) Reproducibility, ± 10 % or better.

Initial transport conditions(25 °C):

(Source phase)	(Chloroform membrane)	(Receiving phase)
0.5 M $MgCl_2$ 0.5 M $Ca(SCN)_2$ 0.5 M $BaCl_2$ (+ 0.5 M LiCl) 15 ml	1.5 x 10^{-4} mol of 1 in 30 ml of $CHCl_3$	H_2O 15 ml

Next, Table 2 shows the results of the transport for alkaline earth metal ions by 1. The transport for divalent cations hardly occurred in the case of the absence of LiCl in the source phase, while Li^+ was selectively transported among these cations when LiCl was added to the source phase. The ratio of Li^+ toward Mg^{++} transported reached 600. Thus, 1 exhibits excellent Li^+-selectivity among alkali and alkaline earth metal ions.

It should be noted that 2 decreased largely its Li^+-selectivity and ability of cation-transport compared with 1. When inspecting the CPK model of these carriers, it is noticed that steric hindrance between the two methyl groups at the 2-position of quinolyl group of 2 may contribute to weekening the formation of Li^+-complex. That is, 2 is presumably difficult to form a pseudocavity to fit the size of Li^+, and therefore, the ion complex may hardly dissolve into the organic layer. In the ^{1}H-NMR spectrum of 1 and 1 with alkali salts in CD_3CN, the largest downfield shifts (Δδ) of the protons of both $C\underline{H}_2$-O-quinolyl and 8-quinolyl groups, of which adjacent hetero atoms may take part in coordination to cation, have been observed in the case of Li^+ salts (O-$C\underline{H}_2$-quinolyl, Δδ 0.22 ppm). On the other hand, the downfield shifts are small in the case of Na^+ salts (O-$C\underline{H}_2$-quinolyl, Δδ 0.08 ppm), and the spectrum of 1 with K^+ salts is almost the same as 1 itself. It means that the interaction between 1 and K^+ salts can not be detected. These results can suggest the preferable uptake of Li^+ inside the pseudocavity formed by 1.

In conclusion, we could synthesize a novel neutral polyether compound exhibiting highly Li$^+$-selective transport, which has a relatively simple and symmetrical structure. The Li$^+$/Na$^+$ ratio of 110 observed with 1 are the highest yet achieved in competitive alkali metal ion-transportations with not only noncyclic[12] but also cyclic carriers.[13] From the structural investigation, some informations for designing neutral carriers have been obtained. Unfortunately, such neutral carriers, even 1 and 4, have relatively small ability of cation-transport and thus are not always adequate for the purpose of effective cation-separation. Further effort should be done for the modification of the structure of 1. Anyway, the excellent Li$^+$-selectivity of 1 in cation transport should have wide applicability.

References

1) Part XII on "Synthesis and Properties of Noncyclic Polyether Compounds." Part XI: K. Hiratani, H. Sugihara, and K. Taguchi, J. Inclusion Phenomena, 2, 161(1984).

2) Top. Current Chem., "Host Guest Complex Chemistry, I, II, and III," ed by F. Vögtle, Springer-Verlag, Berlin(1981(I), 1982(II), and 1984(III)).

3) E. Weber and F. Vögtle, Top. Current Chem., "Host Guest Complex Chemistry I," 98, 3 - 41(1981).

4) F. Vögtle and E. Weber, Angew. Chem., Int. Ed. Engl., 18, 753(1979).

5) H. Kuboniwa, K. Yamaguchi, A. Hirao, S. Nakahama, and N. Yamazaki, Chem. Lett., 1982, 1938.

6) K. Hiratani, Chem. Lett., 1982, 1021; K. Hiratani, K. Taguchi, H. Sugihara, and K. Iio, Bull. Chem. Soc. Jpn., 57, 1976(1984).

7) W. Wierenga, B.R. Evans, and J.A. Woltersom, J. Am. Chem. Soc., 101, 1334(1979).

8) D. Amman, W.E. Morf, P. Anker, P.C. Meier, E. Pretsch, and W. Simon, Ion-Selective Electrode Rev., 5, 3(1983).

9) T.W. Campbell, J. Org. Chem., 22, 1029(1957).

10) 1: mp 135-136 °C, ^{1}H NMR(δ, CDCl$_3$) 4.91(4H,s,C-CH$_2$-O), 5.05(4H,s,oxetane-CH$_2$), 7.35-7.73(8H,m,aromatic-H), 8.31(2H,m,4C-H of quinoline), 9.13(2H,m,2C-H of quinoline); 2: mp 73-75 °C, ^{1}H NMR(δ, CDCl$_3$) 2.80(6H,s,CH$_3$), 4.93(4H,s,C-CH$_2$-O), 5.07(4H,s,oxetane-CH$_2$), 7.45(2H,d,aromatic-H), 7.51(6H,s,aromatic-H), 8.19(2H,d, aromatic-H); 3: mp 123-124 °C, ^{1}H NMR(δ, CDCl$_3$) 2.65(6H,s,COCH$_3$), 4.58(4H,s,C-CH$_2$-O), 4.87(4H,s,oxetane-CH$_2$), 7.06-8.06(8H,m,aromatic-H); 4: mp 124-125 °C, ^{1}H NMR(δ, CDCl$_3$) 2.77(2H,t,OCH$_2$C$\underline{\text{H}}_2$CH$_2$O), 4.67(4H,t,OC$\underline{\text{H}}_2$CH$_2$C$\underline{\text{H}}_2$O), 7.18-7.76(8H,m, aromatic-H), 8.28(2H,m,4C-H of quinoline), 9.17(2H,m,2C-H of quinoline); 5: mp 132-133 °C, ^{1}H NMR(δ, CDCl$_3$) 2.32(4H,m,OCH$_2$C$\underline{\text{H}}_2$C$\underline{\text{H}}_2$CH$_2$O), 4.43(4H,t,OC$\underline{\text{H}}_2$CH$_2$CH$_2$C$\underline{\text{H}}_2$O), 7.06-7.70(8H,m,aromatic-H), 8.20(2H,m,4C-H of quinoline), 9.17(2H,m,2C-H of quinoline); 6: mp 146-147 °C, ^{1}H NMR(δ, CDCl$_3$) 5.77(4H,s,CH$_2$), 7.20-7.94(12H,m, aromatic-H), 8.27(2H,m,4C-H of quinoline), 9.17(2H,m,2C-H of quinoline).

11) K. Hiratani, I. Nozawa, T. Nakagawa, and S. Yamada, J. Membr. Sci., 12, 207(1982).

12) A. Shanzer, D. Samuel, and R. Korenstein, J. Am. Chem. Soc., 105, 3815(1983).

13) K. Kimura, H. Sakamoto, S. Kitazawa, and T. Shono, J. Chem. Soc., Chem. Commun., 1985, 669; R.A. Bartsch, B.P. Czech, S.I. Kang, L.E. Stewart, W. Walkowiak, W.A. Charewicz, G.S. Heo, and B. Son, J. Am. Chem. Soc., 107, 4997(1985).

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