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Spectroscopic Behavior of the Alkali Salts of Noncyclic Polyethers: Evidence for Interaction between the End Groups[1)]

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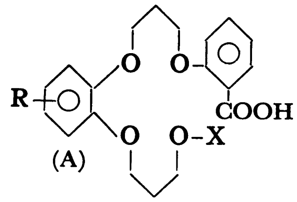
The electronic and fluorescence spectra of the alkali salts of noncyclic polyethers exhibiting selective transport for the lithium ion were investigated. In the electronic spectra hypochromicity in CH_2Cl_2 dependent on the kind of alkali metal ions was observed, and the magnitude of the hypochromic effect decreased in the following order: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. Using the polar solvents, EtOH and MeCN, instead of nonpolar CH_2Cl_2, the hypochromicity is small. Also, in the fluorescence spectra, the quenching phenomenon dependent on the kind of alkali metal ions appeared in the same sequence as the hypochromicity in the electronic spectra. It is suggested that these results, together with our previous results, support a stacking structure between the terminal aromatic rings of the lithium salt in a nonpolar solvent, which has been proposed from the inspection of the CPK model building.

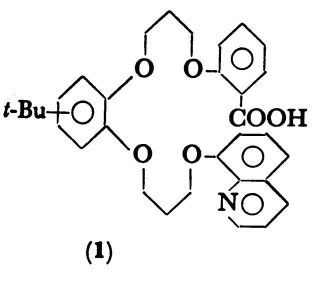
We recently reported that a group of noncyclic polyethers, which have essentially the following framework (A), exhibit Li^+-selective transport through liquid membranes by functioning as a cation carrier.[2)]



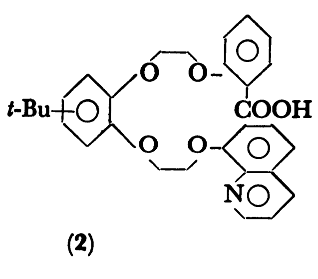
X=aromatic group

When inspecting the CPK model building, it has been presumed that these compounds can form a pseudocyclic structure, the cavity of which has a diameter of 1.4—1.6 Å. Furthermore the terminal groups (X= aromatic group) are presumed to overlap one another face-to-face to form a stacking structure, when hetero atoms are spatially directed to the inside. We concluded, therefore, that the lithium ion best fits the size of the cavity formed and can be transported by the (A)-type compound with high selectivity.

Here, the author attempts to verify this presumption by spectrophotometric methods. For this purpose, 1-[3-(*o*-carboxyphenoxy)propoxy]-2-[3-(8-quinolyloxy)propoxy]-4(or 5)-*t*-butylbenzene (**1**) (X=8-quinolyl, R=*t*-butyl in (A)) was used as a polyether carrier. This compound was chosen because the 8-quinolyl group has a strong absorbance maximum and strong fluorescence. The spectroscopic behavior of a 8-quinolyl terminal group may be able to give some information about the interaction between the polyether and the alkali metal ion as a counter cation of the carboxylate ion. For comparison, polyether **2** containing two oxyethylene chains was used as a **1**-analog.



(1)



(2)

There are many reports that the stacking structure between inter- or intramolecular aromatic rings can be recognized by the electronic and NMR spectra. For example, it has been reported that the stacking between nucleic acid bases could be elucidated by the magnitude of their hypochromic effect on the absorbance of the aromatic rings, which increases with increasing stacking between them.[3)] In addition, the extent of the stacking between them can also be recognized by the chemical shifts of the protons on the aromatic rings in the NMR spectra.[3,4)] As previously-reported, we observed the upfield shift of the 2-position proton on the quinolyl group of **1** in the case of the lithium salt compared with other alkali salts of **1**.[2a)]

Results and Discussion

Electronic Spectra of the Salts of the Polyethers. The author first investigated 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. Figure 1 shows the results for the electronic spectra of the salts of **1** in CH_2Cl_2.[5)] The spectrum of each salt of **1** has one peak (*ca.* 280 nm) and one shoulder (303 nm). The shoulder at 303 nm was confirmed to be due to the absorbance of the quinolyl group because the position of the absorbance and the absorptivity of 8-(3-chloropropoxy)quinoline (λ_{max} 303 nm(CH_2Cl_2), ε 3.50×10^3) are almost in accord with those of the salts of **1**. The absorbance at *ca.* 280 nm for each salt of **1** is attributed to the other aromatic groups. The absorptivity appreciably changes in the electronic spectra with the kind of the alkali metal ion, whereas the positions of both absorbances change little in the range of 278 to 280 nm.

In Fig. 1, the absorptivity in CH_2Cl_2 increases with the increase of the size of the ionic diameter as follows: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Apparently, the absorptivity of one terminal substituent (quinolyl group) is influenced by the kind of counter cation of the carboxylate ion of the other terminal substituent (*o*-carboxyphenyl group). Based on CPK model building, the linear distance between two terminal groups is at

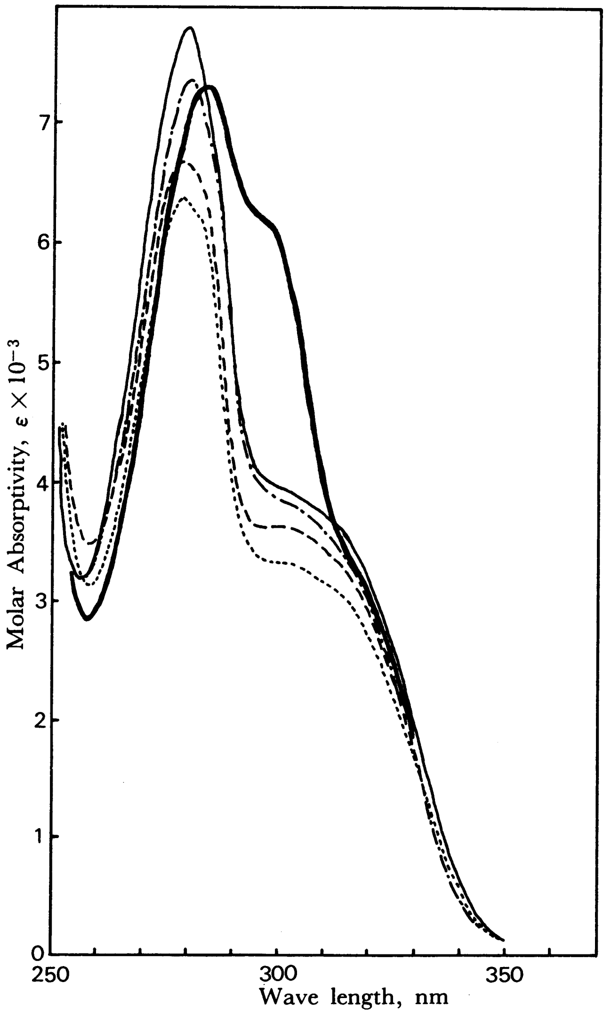


Fig. 1. Electronic absorption spectra of **1** and its alkali salts in methylene dichloride; concentration: 5.66 μmol/50 ml.[6] **1**: ——, Li^+ salt: ------, Na^+ salt: ----, K^+ salt: —·—·—, Cs^+ salt: ——

least 12 Å, when the molecule is linearly extended. The hypochromic effect (H, %) based on the absorptivity of the Cs^+-salt has been defined[3c)] by the following equation:

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

ε: molar absorptivity

M^+: alkali metal ions

Table 1. Hypochromic effect (H, %)

Cation Ionic radius, Å	Li 0.66	Na 0.95	K 1.33	Pb 1.48	Cs[a)] 1.69
(1)	15.6	6.5	4.3	2.2	0
(2)	6.7	4.9	6.4	6.4	0

a) Molar absorptivity of the Cs^+-salt at 303 nm: (**1**) $\varepsilon_{Cs^+}=3.98\times10^3$, (2) $\varepsilon_{Cs^+}=3.89\times10^3$.

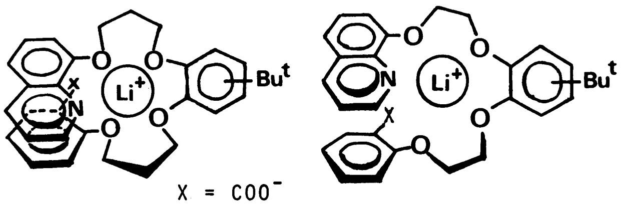


Fig. 2. Molecular structures of the lithium salt of the polyethers, **1** and **2**, on the basis of the CPK model building; a: Li^+ salt of **1**, b: Li^+ salt of **2**.

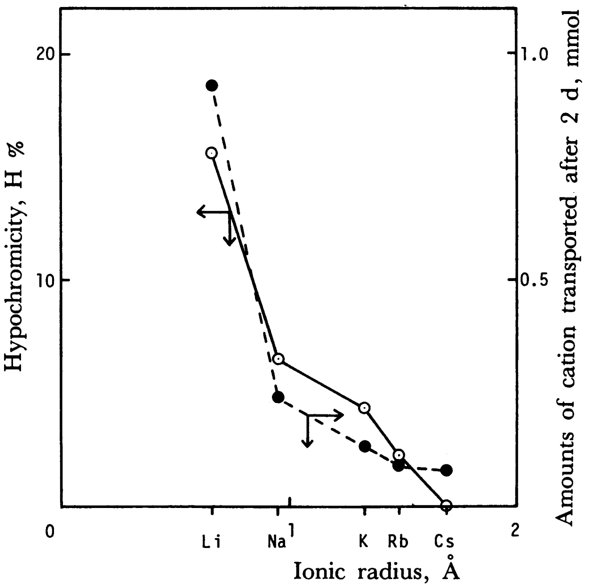


Fig. 3. Influence of the ionic radius of the alkali metal ions on the hypochromicity and the amounts of the cation transported.

Table 1 shows the hypochromic effect (H, %) at 303 nm calculated from this equation (1), which is based on the absorption maximum (shoulder) of the quinolyl group in the salts of **1**. The absorption spectra of the alkali salts of **2** were also measured under the same conditions, and the hypochromic effect at the absorption maximum (shoulder, 303 nm) are also shown in Table 1. In the case of the salts of **2**, it was observed that there is little difference in their hypochromic values. That is, their hypochromic effect is hardly dependent on the kind of alkali metal ion. The results in Table 1 may be closely associated with the following consideration based on CPK model building as previously-reported: i) when polyether **1** can form pseudocyclic structure, the lithium ion best fits the size of the cavity formed, 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 (Fig. 2-a), and ii) the terminal aromatic rings of **2**, on the contrary, can not overlap one another structurally, *i.e.*, on account of the bond angle, size of the terminal groups, *etc.*, as is shown in Fig. 2-b. Furthermore it is noted that the results of the selectivity for alkali metal ions in the transport experiment through a chloroform membrane by these polyethers are consistent with the spectroscopic behavior. The relationship between the hypochromicity and the amounts of cation transported[7)] dependent on the kind of alkali metal ions is shown in Fig. 3.

Thus, the maximum hypochromic effect of the lithium salt of **1** in the electronic spectra is presumed to

TABLE 2. SOLVENT EFFECT IN THE ELECTRONIC SPECTRA OF THE SALTS OF (**1**) ON THE MOLAR ABSORPTIVITY

	CH_2Cl_2		MeCN		EtOH	
	λ_{max}	$\varepsilon\times10^{-3}$	λ_{max}	$\varepsilon\times10^{-3}$	λ_{max}	$\varepsilon\times10^{-3}$
free	284	7.43	284	7.07	282	6.80
	303	5.66	303	5.30	303	5.39
Li^+	279	6.53	278	6.49	280	6.85
	303	3.36	303	3.31	303	3.36
K^+	280	7.48	280	7.07	280	6.63
	303	3.81	303	3.45	303	3.18

reflect the stacking structure of the polyether carrier in the nonpolar solvents such as $CHCl_3$ and CH_2Cl_2. The solvent effects of the alkali salts of **1** on the hypochromic effect in the electronic spectra has been investigated: polar protic EtOH and polar aprotic MeCN used as solvents, and the results are shown in Table 2. Using EtOH, no change of absorptivity due to the kind of the alkali metal ions could be observed. For MeCN, the hypochromic effect by the kind of the alkali metal ions is not as large as in the case of a nonpolar aprotic solvent, CH_2Cl_2. From these results, it is considered that it is not necessary for the noncyclic polyether compound in such a polar solvent to form a pseudocyclic structure in order to wrap around the polar moiety (the alkali ion of the carboxylate), because the salts in a polar solvent could be solvated by the solvent and be solved in it.

The Fluorescence Spectra of the Alkali Salts of the Polyether 1. The fluorescence spectra of the alkali salts of **1** were measured in order to investigate further the interaction between the end groups of the salts of **1** in a nonpolar solvent.[8] The results are shown in Fig. 4. The fluorescence band, which appears on exposure to ultraviolet light by xenon lamp at 321 nm in CH_2Cl_2, is based on the quinolyl group. The relative intensity of the fluorescence maximum apparently decreases with the decrease of the ionic diameter of the alkali metal ion, although the maximum wave length of the fluorescence changes in the range of 386 to 391 nm is dependent on the kind of alkali metal ion.

The dependence of the quenching phenomenon on the kind of alkali metal ion is consistent with the hypochromicity in the electronic spectra, which suggests some interaction between the terminal aromatic groups. As reported recently,[2a] it has been presumed that in the NMR spectra the upfield shift of the proton at the 2-position of the quinolyl group in the case of the Li^+-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 in accord with the behavior both in the electronic and fluorescence spectra.

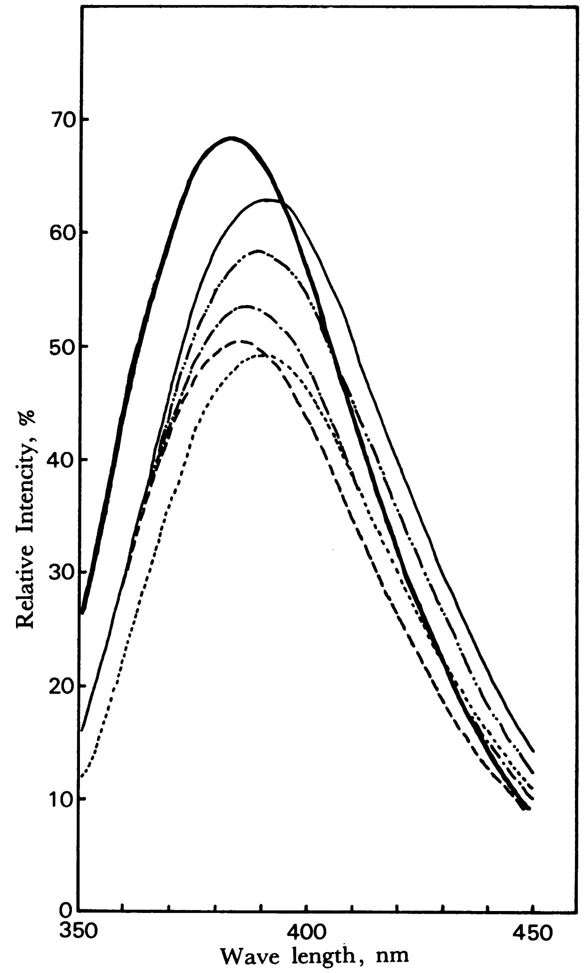


Fig. 4. Fluorescence spectra of the alkali metal salts of **1**; concentration: 5.66 μmol/50 ml of CH_2Cl_2, excitation at 321 nm. **1**: ——, Li^+ salt: ------, Na^+ salt: ----, K^+ salt: —-—-—, Rb^+ salt: —--—--—, Cs^+ salt: ——

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 polyether carriers through a chloroform liquid membrane. In conclusion, the mechanism of cation transport, which we have proposed,[2a] is supported spectrophotometrically: their cation selective transport might occur when the cation can become well incorporated into the pseudocavity of the polyethers formed and then they form the stacking structure between two terminal aromatic groups.

Experimental

Materials. 1-[3-(*o*-Carboxyphenoxy)propoxy]-2-[3-(8-quinolyloxy)propoxy]-4(or 5)-*t*-butylbenzene (**1**) and 1-[2-(*o*-carboxyphenoxy)ethoxy]-2-[2-(8-quinolyloxy)ethoxy]-4-(or 5)-*t*-butylbenzene (**2**) were obtained by the procedure reported previously.[2a] All solvents used were extra-pure grade reagents of Wako Pure Chemical Industries, LTD., which were tested for impurities spectrophotometrically before use. Sodium and potassium hydroxides were analytical grade reagents. Lithium, rubidium, and caesium hydroxides were reagent-grade.

General Spectrophotometric Measurement. Absorption spectra were measured on a Hitachi 330 spectrophotometer in the ultraviolet region. Fluorescence spectra were recorded on a Hitachi 204 fluorescence spectrophotometer.

Exactly, 3.0 mg of the polyether prepared was weighed into a 50 ml-measuring flask. About 5 ml of dichloromethane and 0.1 ml of aqueous solution containing 1.0 M (1 M=1 mol dm^{-3}) alkali metal ion were added. The flask was vigorously shaken for several hours and then the measuring flask filled with dichloromethane to the 50 ml mark. Both the electronic and fluorescence spectra of this solution were measured at room temperature. The alkali metal ions used were Li^+, Na^+, K^+, Rb^+, and Cs^+. In the case of the other solvents, the same procedure was followed. The molar absorptivity for each cation is shown in Fig. 1 and Table 2 for the electronic spectra. For the fluorescence spectra, the relative intensity for each cation is shown in Fig. 4.

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5) Dichloromethane was used as a solvent for the spectroscopic measurement; its properties resemble those of chloroform used as a liquid membrane in the cation transport,[2] and it is more stable in the basic media than is chloroform.

6) The spectrum of the Rb^+ salt is not depicted because the curve is located in the narrow region between the curves of the Cs^+ and K^+ salts (*cf.* Table 1).

7) The results were obtained in the cation transport by **1** for five alkali metal ion species existing together in the source phase (see Ref. 2a).

8) It is difficult to conclude that the fluorescence quenching phenomenon necessarily reflects the formation of the stacking structure of **1**, because many other reasons for the phenomenon can also be considered. However, the results of the fluorescence is interestingly parallel with thóse of the electronic spectra.