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High Cation Extractabilities of Acyclic Ionophores Having Quinaldate Moieties and Their Conformations in Solution

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New acyclic ionophores with two quinaldate terminal moieties showed efficient extraction abilities toward alkali metal ions; one of them extracted K^+ on about the same level with unsubstituted 18-crown-6. Their conformations in solution were examined by ^1H NMR.

After the discovery of macrocyclic host molecules,1) glyme-type ionophores with acyclic structure have been set on a lower position because of their low complexing abilities. Increasing attention, however, has been recently focused on the studies that treat new types of acyclic host compounds having semi-rigid moieties2) which possess recognition sites not only for ion-dipole interaction but also for aromatic π-stacking or hydrogen bonding interaction. Such a "structural effect" contributes to creating favorable complexing abilities which have hardly been achieved by simple acyclic host compounds.

It is well known that the oligoethylene glycol derivatives with quinolinyloxy moieties show excellent complexing abilities among acyclic ionophores.3) Recently, we found the good relationship between the extractability of acyclic host compounds toward alkali metal cations and the extent of stacking interaction of two quinoline moieties.4)

In this communication, we describe the design of efficient acyclic ionophores having the quinaldate moieties which work both as stacking surfaces and as coordination sites.

We prepared a series of acyclic ionophores with ester groups, **1-4** having di-, tri-, tetra-, pentaethylene glycol moieties from the corresponding oligoethylene glycol dichloride and methyl 8-hydroxyquinaldate5) using K_2CO_3 and tetrabutylammonium chloride (as a phase transfer catalyst) in CH_3CN.6) Their extraction properties toward alkali metal picrates were compared with the homologues without the ester moiety **5**, **6**, 18-crown-6 **7**, or heptaglyme **8**.

Extraction profiles conducted under the conditions using equimolar amounts of the ionophore and alkali metal picrate[7)] are shown in Fig. 1. New ionophores **1-4** showed far better complexing ability than **6** which possesses the best extractability among their series[4)] without the donor group on the 2-position of the quinoline ring. Especially, it is very exciting that **3** showed a high extractability toward K^+ on the same level with 18-crown-6.

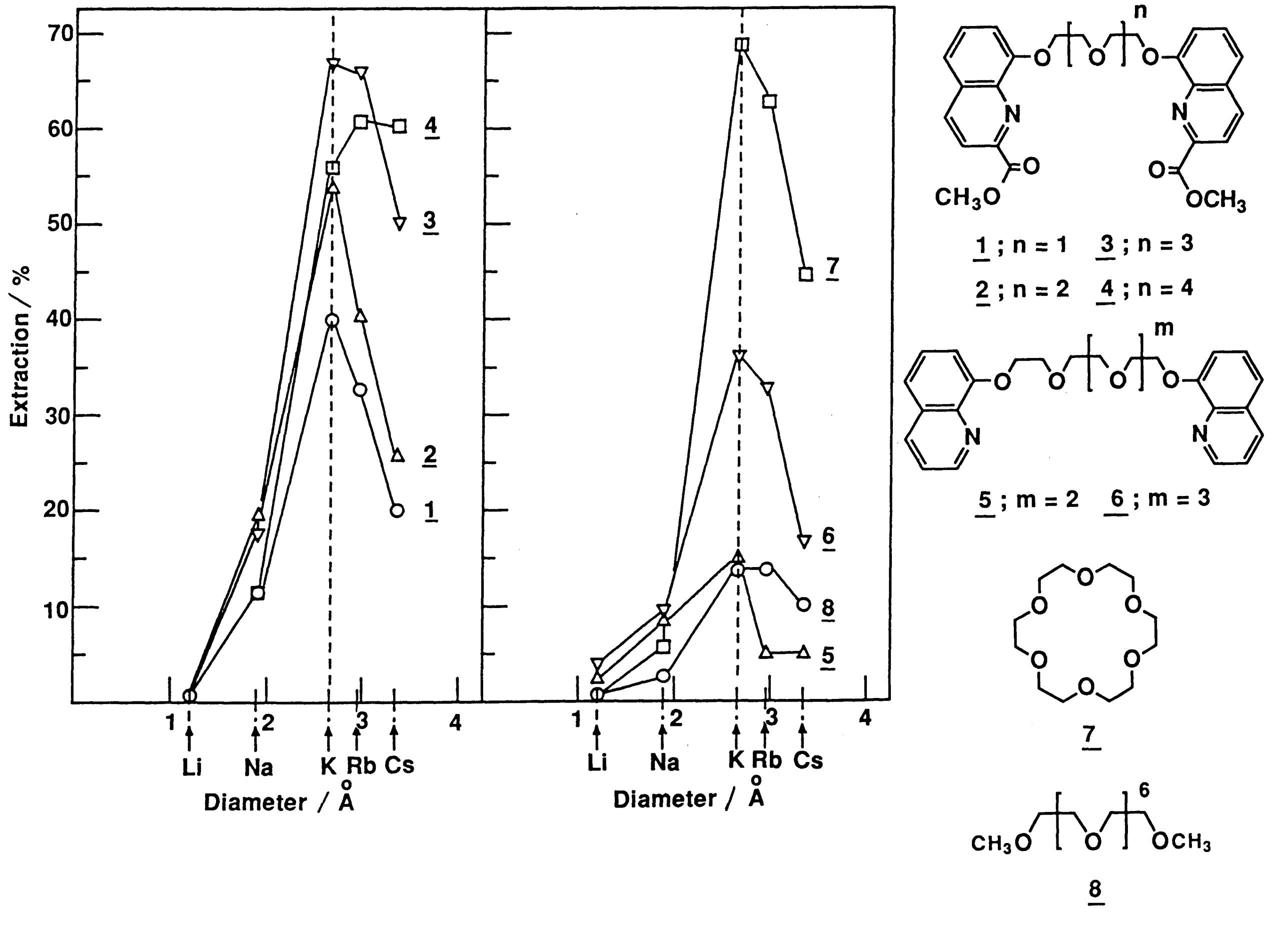

Fig. 1. Solvent extraction of alkali metal picrate by acyclic ionophores: organic phase (CH_2Cl_2, 10 mL) / aqueous phase (10 mL); [MOH] = 50 mM; [Extractant] = [Picric acid] = 0.5 mM; 22 °C; 9 h.

The order of the extraction abilities of three different types of acyclic host compounds having eight donor atoms toward K^+ is **2**>**6**>**8**. This fact suggests that the high extractability of **3** is attained not only by the effect of structural fixation based on the stacking between quinolinyloxy moieties but also by the supplemental coordination of the donor group on the 2-position of the quinolinyl moiety. Focusing on the difference in the length of the oxyethylene chain, maximum extraction efficiency was observed in **3**. The same trend was also found in the case of the corresponding homologues such as **5** and **6**.4) The longest ionophore **4** did not show K^+ selectivity but showed Rb^+ selectivity; the extractability of **4** was slightly lower in comparison with that of **3**.

^{1}H NMR spectra give much information concerning the conformations of the ionophores in solution. In order to evaluate the detailed conformations of the ionophores and to relate these conformations to the complexing abilities determined by the solvent extraction, we measured the changes in the chemical shifts upon the addition of alkali metal thiocyanates with 400 MHz ^{1}H NMR.8) When a donor atom participates in coordination with a metal ion, chemical shifts of neighboring protons generally tend to move downfield. On the contrary, aryl π-stacking produces an upfield shift.2) The changes in the chemical shifts of the three types of ionophores with an equimolar addition of KSCN are shown in Fig. 2.

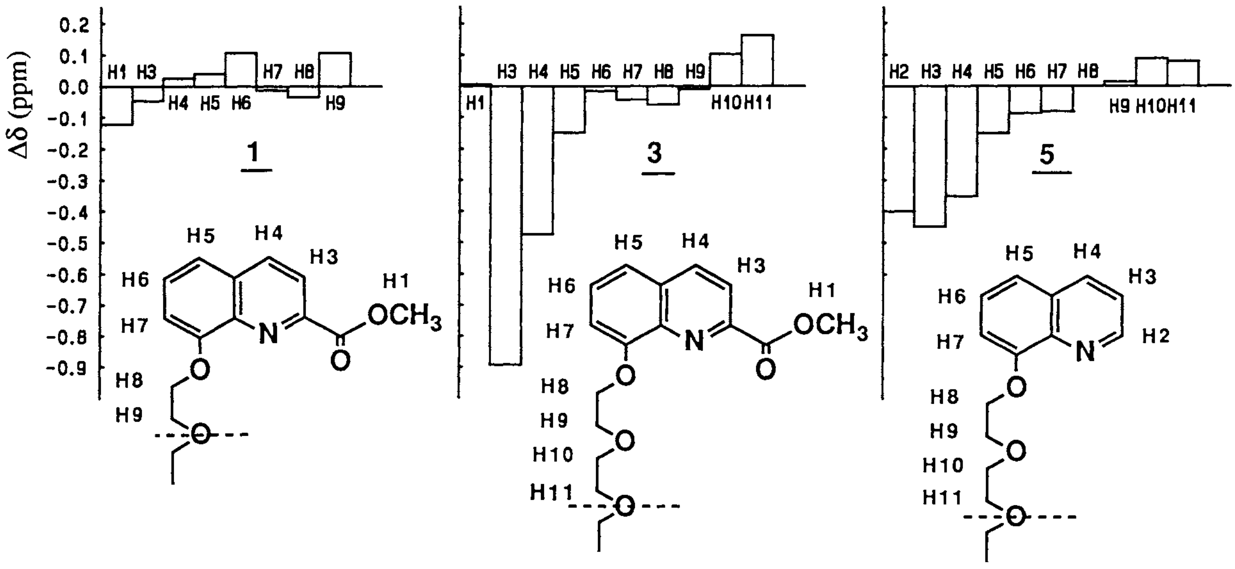

Fig. 2. Changes in chemical shifts of several ionophores with equimolar additions of KSCN: $\Delta\delta = \delta_{\mathrm{KSCN}} - \delta_{\mathrm{None}}$; [Ionophore] = 0.05 M; in $CDCl_3$; 27 °C.

As previously described,4) **5**, which showed the characteristic upfield shift, seemed to form a pseudo-cyclic structure like that of 18-crown-6 based on the partial stacking interaction between the quinoline rings on complexation with K^+. Although **1** scarcely showed any upfield shift on the quinolinyl proton, **3** clearly showed large upfield shifts on H3 and H4 and the tendency of the shifts of **3** was very similar to that of **5**. This finding suggests the conformational resemblance between them. **3** is also considered to form a pseudo-cyclic structure on complexation with K^+. The similarity of the conformation of the two ionophores is reasonable, judging from the equality of the length of the oxyethylene moiety. The donor group at the 2-position of the quinoline ring affords the additional coordination site for complexation with KSCN.[9)]

That is to say, the high extractability of **3** should be explained by considering the effect which consists of the aromatic stacking and the suitable arrangement of the donor atoms.

Further investigation concerning the influence of structure on complexing ability is now in progress.

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8) Chemical shifts were assigned from coupling constants of each proton as referred to the following literature: T. J. Batterham, "NMR spectra of Simple Heterocycles," John Wiley & Sons, New York(1973).

9) The effective coordination of the terminal ester groups of **1-3** toward K^+ was directly observed by ^{13}C NMR and IR spectroscopy. The ^{13}C NMR and IR spectra showed considerable upfield shifts of the C=O carbon (0.2-1.8 ppm) of **1-3** in $CDCl_3$ and the increase of the frequency of C=O stretching vibration band of **2** (10 cm^{-1}) in $CHCl_3$, respectively, upon the addition of an equimolar amount of KSCN. To determine which coordinates with K^+, carbonyl-oxygen or ester-oxygen, NOE experiments were performed by ^1H NMR. We think that the carbonyl-oxygen affords the additional coordination site because **1** showed considerable NOE between H1 and H3 in the presence of KSCN. Further NOE experiments are also now in progress.

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