Conductometric Behavior of Univalent Cation-Podand Complexes in Methanol

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The stability constants, log K of the 1 : 1 complexation for IA ions, Ag⁺, and Tl⁺ with a series of podands having different aromatic end-groups (I-IV) have been determined conductometrically in methanol at 25.0 ℃. Exceptionally the equivalent conductivity, λ_{eq} of Li⁺ and Na⁺ were increased by the addition of I, because the complexed ions are less mobile than solvated ions. The order of log K values for I was Ag⁺≫Tl⁺>K⁺>Na⁺>Rb⁺>Cs⁺>Li⁺. The log K sequence of the podands for the certain cations was I>II>III≧IV. And every podands except IV showed the maximum selectivity for Ag⁺ among the cations. These results were discussed in terms of the aromatic end-group effects, such as heterodonor atoms or conformational changes by π-π stacking interactions. The detailed conformations of π-π stacking were also discussed by the observations of upfield shifts of some aromatic protons upon complexation from ¹H NMR spectra.

Introduction

Acyclic ionophore antibiotics[1] including monesin, nigericine and grisorixin wrap themselves around the cation in a manner very similar to the cyclic species. The acyclic oligoethers, called podands, can be obtained simply and cheaply: there is no need for high-dilution or template effects in preparation[2,3]. Podands with aromatic end-groups wrap themselves around the cations such as Na⁺ and Rb⁺ in a helical manner to make pseudo-cycle both in solid and solution states[4,5]. Crown ethers[6] require the lower energy for conformational adaptation because of preorganized conformation for complexation but in the case of podands the larger energy[7,8] is required due to its own flexibility. Thus, the log K values of complexes of podands versus crown ethers are reduced, in spite of favorable configuration.

Vögtle *et al.*[2,3] have synthesized some open-chain hosts containing nitrogen donors in aromatic end-groups, and investigated the structure of complexes by X-ray in solid states. Owing to the higher cation selectivities, a numerous thermodynamic data on complexation of crown ethers[6] are available while the thermodynamic[7,8] and structural[4,9] studies for the complexation of the podands in solution have not been examined intensively.

Log K of uncharged host with univalent cation complexes can be determined by various methods, such as calorimetry[7,10], potentiometry[11], spectrophotometry[5], NMR[1,2] and so on. Most of these techniques have some problems, *i.e.*, measurements in nonideal solutions and association between cation and anion, and it is difficult to determine accurate log K of complexes under these conditions. But by conductometry, log K can be measured with high precision especially, for the weak or medium strength of the interactions[13] (2<log K<6) at extremely low concentration in solution where interactions between cations and anions are known to be very small. In fact, a lot of log K values for the podand complexation with univalent cations are expected within this region[14].

More recently, Takeda[14] well reviewed the conductometric behaviors of cation-macrocycle complexes in solutions. The conductance studies on the interacions of cation with high
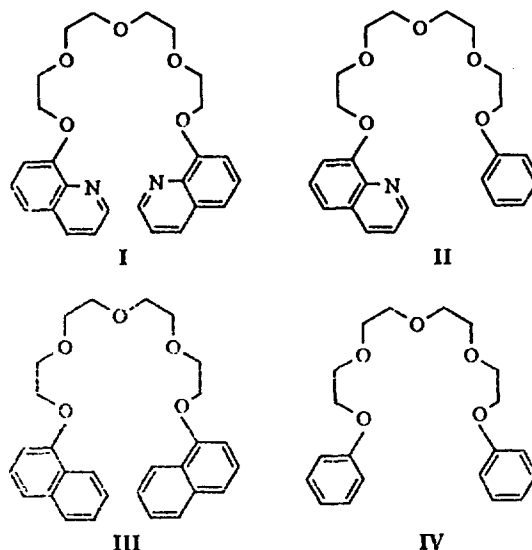

Figure 1. The podands used in this work.

molecular polyoxyethylene glycol mono- or dialkyl ethers were performed in the qualitative or semi-quantitative manners by some workers[15]. But the quantitative study on the characteristics for the interaction of monomeric podands with cation conductometrically has not been widely reported[16].
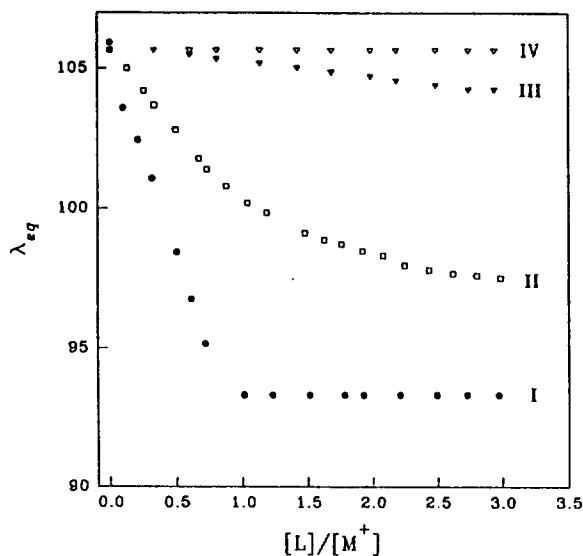
In this work, we have studied the behavior of some univalent ions in the presence of podands having different aromatic end-groups in methanol systems, and determined the log K for the complexations conductometrically. The detailed conformational changes of ionophores can be understood by the chemical shift changes of ionophore on complexation[17]. Therefore, ¹H NMR experiment has been also performed to evaluate the conformation of podand-M⁺ complexes in solution.

Experimental

Materials. All of the podands in Figure 1 were synthesi-

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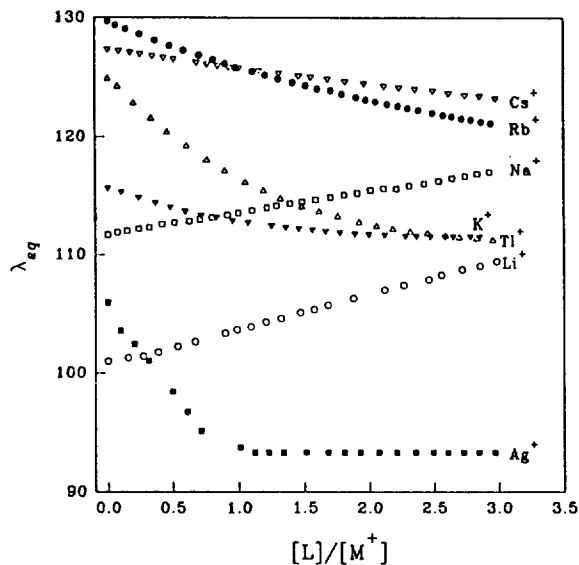
Figure 2. λ_{eq} versus $[L]_t/[M]_t$ curves for 1-univalent cation perchlorate systems in methanol at 25.0 $^\circ$C.

Figure 3. λ_{eq} versus $[L]_t/[M]_t$ curves for podand-Ag^+ systems in methanol at 25.0 $^\circ$C.

zed on the basis of Williamson ether method[2]. They were prepared by the reaction of corresponding dichlorides with aromatic alcohol in the presence of KOH in ethanol and the detailed procedures were reported in the literature[5,18]. Pure products were obtained by chromatography on silica-gel with *n*-hexane/ethylacetate.

Lithium, sodium, potassium, silver and thallium perchlorates were obtained commercially as maximum purity. Cesium and rubidium perchlorates were prepared by adding an equimolar perchloric acid to aqueous solution of cesium chloride or rubidium bromide, respectively. All of perchlorates were recrystallized from water three times and dried at 80 $^\circ$C under reduced pressure before use. Methanol was purified by reflux with magnesium and iodine[19].

Apparatus and Procedures. The conductivity measurements were made on a Solea Tacussel conductivity meter, Model CD810. The conductivity cell was used with cell constant of 0.7755 cm^{-1}, calibrated with standard KCl solutions.

Our method is a slight variation of procedures described by Takeda *et al.*[20] The accurate concentration of perchlorate solution (0.49-0.51 mM, 40.0 mL) was in water-jacketed glass vessel thermostated (25.00±0.02 $^\circ$C). The stock solution of podand was prepared by dissolving an accurately weighted amount of ligand (0.9-1.1 mM) in perchlorate solution which had same composition as the titrant. This is an elegant way to avoid any dilution effect of the salt solution. Then a step-by-step increase in the podand concentration was effected by a titration until the conductivity of the solution scarcely changes. In many cases, the total concentration of the podand was from 3 to 5 times as large as that of the perchlorate.

The conductivities of the solution in the vessel were measured after each increased in podand concentration, and the data was collected, transformed and analyzed automatically by ADC embedded in IBM-PC[21]. The log K values were calculated simultaneously by non-linear regression program, KINFIT4[22] with high accuracy.

All ^{1}H NMR spectra were recorded at 200 MHz on a Varian Gemini 200 spectometer using TMS in CDCl$_3$. Chemical

shifts of each protons on aromatic moiety of podands as well as ether chain upon the addition of equimolar amount of AgClO$_4$ were determined by a frequency counter in Herz scale.

Results and Discussion

The changes of λ_{eq} *vs.* $[L]_t/[M]_t$ were monitored, while adding podand I to the solution of constant concentration of univalent cations by mole ratio about 3. The results are ploted in Figure 2. Figure 3 represents the changes of λ_{eq} for Ag^+ by the additions of podands in Figure 1. $[L]_t$ and $[M]_t$ are the total concentration of each podand and univalent cation, respectively.

λ_{eq} **change by complexation.** The λ_{eq} by the additions of neutral species to the constant concentration of electrolyte solutions can be explained by the results of the viscosity changes, ion-pairing or complexations[20]. In this study, the concentration of cation perchlorates or added podands were kept very low, the influences of viscosity and ion-pairing on the change of λ_{eq} could be negligible[20]. Therefore, the λ_{eq} change was mainly due to the complexation between the cation and podand.

Figure 2 shows the decrease of λ_{eq} with the increase in the mole ratio except for the Li^+ and Na^+-I systems. In general, the complexed ion has lower mobility than does solvated one. So the decrease of λ_{eq} induced by the addition of podands is more typical behaviors on complexation[23].

The similar conductance behaviors for Li^+ and Na^+ with some crown ethers in polar mediums were reported by us[24] and other workers[23] previously. But this is the first case for the acyclic host. In our opinion, the increase of λ_{eq} for Li^+ and Na^+ may be due to the reaction process from the well-solvated ion with higher charge density through the desolvation to the weak and smaller complexed ion formation with I.

**Determination of log K.** In the cases of Ag^+- and Tl^+-I systems, the slopes of each curve change sharply at

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Table 1. Log K of Complexation for Univalent Cations with Podands in Methanol at 25.0 ℃

Podands	Cations						
	Li+	Na+	K+	Rb+	Cs+	Ag+	Tl+
I	1.99	3.01(3.2)[a]	3.45(3.5)[a]	2.73(3.0)[a]	2.18	7.68[b]	3.81
II	c	1.89	2.44	1.58	1.99	4.07	2.18
III	c	c	c	c	c	1.98	c
IV	c	c	c	c	c	c	c

[a] spectrophotometry, from and ref. 5. [b] potentiometry using Ag+-ISE, from ref. 18. [c] no conductivity change during titration, not suitable to calculate log K.

the point when $[L]_t/[M^+]_t = 1$, indicating that I forms a stable 1 : 1 complex with Ag+ or Tl+ in methanol. For IA ion systems, no such clear breaking point was observed. Three factors play an important role in causing the clear breaking point[14]. (1) ligand forms a stable complex with a cation (log $K > 4.2$). (2) The difference in mobility between the complex and the free cation is large. (3) No complex other than 1 : 1 ionophore-cation is formed. From the other techniques, such as NMR titration[9] or potentiometry[8], IA ions form 1 : 1 complexes with the podands but the lower log K values are expected[14].

When the podands form 1 : 1 complexes with the cations under these experimental conditions, the equilibrium equation is given as

$$\begin{array}{cccc} M^+ & + & L & \rightleftarrows & ML^+ \quad\quad (1) \\ \alpha[M]_t & & [L]_t - (1-\alpha)[M]_t & & (1-\alpha)[M]_t \end{array}$$
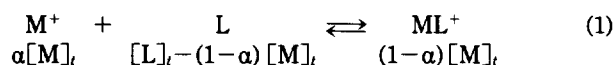
where M^+, L and α are the univalent cation, the podand and the fraction of free ion respectively. The stability constant, K is defined by

$$K = \frac{[ML^+]}{[M^+][L]} = \frac{(1-\alpha)}{\alpha[L]} \quad\quad (2)$$

The equivalent conductivity of complex solution, λ_{eq} can be written by Eq. (3).

$$\lambda_{eq} = \alpha \lambda_{MX} + (1-\alpha)\lambda_{MLX} \quad\quad (3)$$

Eq. (2) can be transformed via Eq. (3) into

$$K = \frac{\lambda_{MX} - \lambda_{eq}}{(\lambda_{eq} - \lambda_{MLX})[L]} \qu\quad (4)$$

where $[L] = [L]_t - [M^+]_t (\lambda_{MLX} - \lambda_{eq})/(\lambda_{MX} - \lambda_{MLX})$

The λ_{MLX} value was estimated from the λ_{eq} values at the points of large $[L]_t/[M^+]_t$. The K values in Eq. (4) were calculated from λ_{MLX} values by non-linear regression analysis[22]. The log K values for the complexation of M-podands are listed in Table 1.

End-group effect on log K. According to Table 1, the stability sequence of the podands for each cations is I>II>III≥IV. As the quinoline end-groups having nitrogen donor atom in I was substituted for nonactive aromatic residues such as phenyl or naphthyl, the log K values decreased remarkably. The larger stability of I or II for the cations is due to the nitrogen donor in quinoline as the strongest donor atom and formation of the pseudo-cycle conformation by π-π stacking interaction[5,9].

Since no significant amount of λ_{eq} changed for the cations with III and IV, the binding strength of these cations except
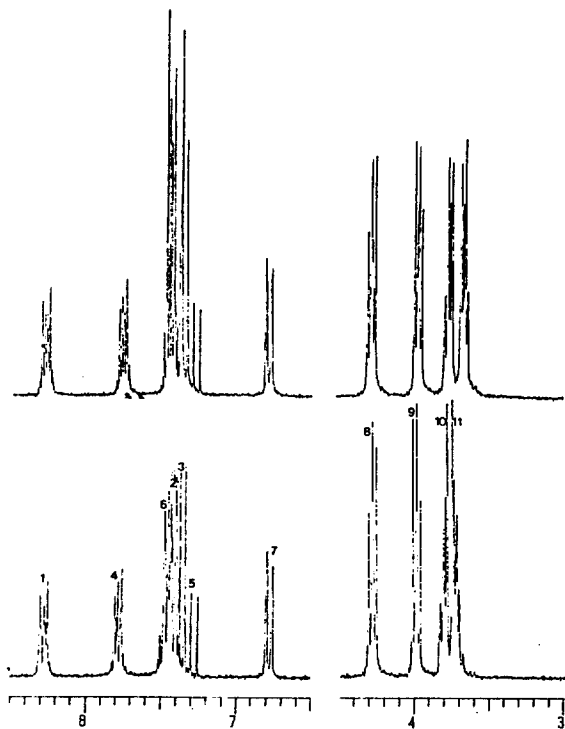
Ag+ was expected to be very weak. In general, the open-chain oxygen ligand, glyme/podand, suffers substantial conformational change to wrap around a cation in a pseudo-circular or helical arrangement of donor atoms. The enthalpic gain arising from the electrostatic cation-donor interaction is almost completely offset by the entropic loss due to the resulting conformational fixation. Therefore, little net gain is obtained in the free energy. In this work, the results for III and IV in Table 1 well conformed this illustrations even though IA ions (hard acids) prefer to interact with oxygen (hard base)[25]. Otherwise, the results that II showed the intermediate values in log K between I and IV reflect the participation of the nitrogens into the certain cation bindings effectively.

Ag+-podand complexations. The log K values for the complexation of Ag+ with each podands are much higher than those for the other cations. The log K sequences of I with the cations, for example, are Ag+≫Tl+>K+>Na+>Rb+>Cs+>Li+. This is not surprising because cation-dipole interactions are mainly responsible for the interactions between ligands and cations. Ag+ can act as not only a strong acid for nitrogen but also the electrostatic ion for oxygen. The experimentally estimated bond energy for O-Ag+ are known as 6 kJ mol⁻¹ in methanol[7]. Especially by the existance of each nitrogen, the difference in log K is about 3 or 4 order of magnitude. This result may be due to the favorable enthalpy changes, because the order of $-\Delta H$ values for the interaction with Ag+ are known as N>S>O[6]. Otherwise, for Group IA ions, the log K sequences of I are similar to those of 18-crown-6. But the binding selectivity of I (K+/Na+ =2.8) is quite lower than those of 18-crown-6 (K+/Na+ =209)[6]. This indicates that ion-cavity size concept is less important to determine the log K for the semi-rigid or flexible hosts, such as podands.
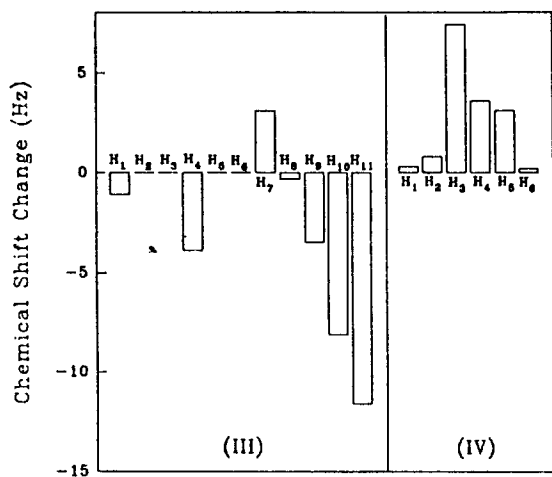
The more interesting result is the comparison of III with IV in log K values for Ag+. Figure 3 shows the changes of λ_{eq} vs. $[L]_t/[M^+]_t$ for complexations of Ag+ with I-IV. Comparing the changes of λ_{eq} for Ag+ by the additions of III and IV, the podand having naphthyl end-groups, III showed larger decrease owing to the higher stabilities than phenyl analogue, IV.

Since the naphthyl group has a larger π-area than does the phenyl group, the extent of the π-π overlap could be greater or easier[26]. However, for the detailed discussion NMR study is required[17].

π-π Stacking by ¹H NMR. To understand the conformation of naphthyl and phenyl ionophore on complexation and to relate these conformations to the complexing abilities
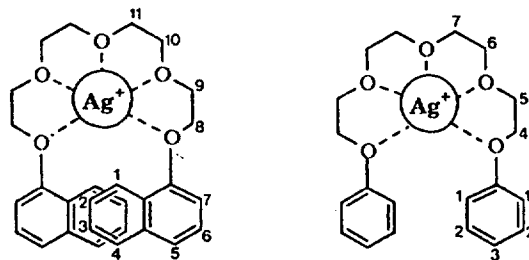
Figure 4. ¹H NMR spectra (200 MHz) of III (below) and III-Ag⁺ complex (above) in CDCl₃.

Figure 6. Proposed structures of Ag⁺-III (left) and Ag⁺-IV (right) complexes in solution.

move downfield[27]. But by contrast, the π-π stacking produces the upfield shifts of some protons in aromatic moieties[26]. In Figure 5, the every protons of IV both in phenyl and ether chain shifted downfield. This result suggests not the π-π stacking but the weak interaction between Ag⁺ and oxygens (Figure 6, right).

But in the case of III, it is quite complicate. So to speak, the upfield shift of H_1 and H_4 in naphthyl groups are caused by partial overlap between of them since the protons exist in the shielding or anisotropic region[26] of each naphthyl end-groups. Therefore, we suggest that the upfield shift of aromatic protons in III is ascribed to partial π-π stacking between aromatic end-groups having lager π-area, such as the case of I with Na⁺ reported in our previous work[9] (Figure 6, right).

In Figure 5, however, the fairly large upfield shifts of ether protons (H_{8-11}) in III still remain in question. Vögtle et al.[28] also reported that upfield shift of aliphatic protons having sufficiently long chain (six CH_2CH_2O unit) induced by IIA ions without detailed comment.

Figure 5. Changes in proton chemical shifts (Δδ in Herz) of III and IV between before and after complexations with Ag⁺ in CDCl₃. $\Delta\delta = \delta_{complex} - \delta_{ligand}$. Assignment of each protons were shown in Figure 4.

monitored by conductivity, we measured changes in the chemical shifts of the protons of III and IV upon the addition of equimolar amounts of Ag⁺. The NMR spectra of III and III+Ag⁺ are shown in Figure 4. The interpretation of each protons in both cases was possible[17]. The chemical shifts changes in Herz scale for III and IV upon the equimolar addition of Ag⁺ are shown in Figure 5. The bars toward negative direction mean the upfield shift by complexation.

When a donor atom participates in coordination with metal ions, the chemical shifts of neighbouring protons tend to

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Characteristics of Products in the Reaction 40 MeV/nucleon ^{14}N+Ag

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Cross sections and recoil properties have been measured for the fragments produced in the interaction of silver with 40 MeV/nucleon ^{14}N ions using off-line γ-ray spectroscopy. The data were used to obtain the isobaric-yield distribution, the mass yield distribution, and the fractional momentum transfer. The values of forward-to-backward ratios were measured to be very large, indicating that substantial momentum transfer occurs at this energy regime. The results are compared with other studies of the interaction of silver with intermediate-energy heavy ions.

Introduction

Nuclear reactions in intermediate-energy regime have attracted considerable interest in recent years because of the change in the reaction dynamics. In low-energy regime(<10 MeV/nucleon) nuclear reactions are dominated by mean-field dynamics, characterized by complete fusion. On the other hand, nuclear reactions in high-energy regime(>100 MeV/nucleon) involve the dynamics of nucleon-nucleon interactions, signified by fragmentation. The intermediate-energy reactions must therefore experience the onset of high-energy reaction processes.

Several intermediate-energy heavy ion reactions have been studied. Lund *et al.*[1-3] found that the high-energy dynamics are operative in the interaction of silver with 86 MeV/nucleon ^{12}C ions. Multiple dissociation of heavy ion projectiles has been observed at 32.5 MeV/nucleon.[4] In the O-induced reactions on Al, Ni, and Au targets, breakup of the projectile was reported by Badalà *et al.*[5]

In this work, the results for the study on the interaction of silver with 40 MeV/nucleon ^{14}N ions are presented. The cross sections and recoil properties of the reaction products were obtained utilizing recoil-ranges techniques, as mentioned in our previous works.[6-8] The isobaric-yield distribution, the mass yield distribution, and the fractional momentum transfer are deduced from the data.

Experimental

The experiment was performed at the K500 cyclotron of the National Superconducting Cyclotron Laboratory(NSCL) at Michigan State University. The target stack consisted of silver foil, 30.0 mg/cm^2 thick, surrounded by 10.1 mg/cm^2 thick Mylar foils. The stack was surrounded by two additional Mylar foils, which served to guard the other foils from possible external sources of radioactive products.

The target stack was mounted on an aluminum foil holder, located in an evacuated chamber and irradiated with 40