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Highly Ag^+-selective podands: thermodynamics of complexation and membrane transport[☆]

Shim Sung Lee[a,*], Jong Hwa Jung[a], Sang Hyeok Yu[b], Moon Hwan Cho[b]

[a] *Department of Chemistry, Gyeongsang National University, Chinju 660-701, South Korea*
[b] *Department of Chemistry, Kangweon National University, Chuncheon 200-701, South Korea*

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Abstract

ΔH values for the 1:1 interaction of some sulfur-containing podands with Ag^+, K^+, Cu^{2+}, Cd^{2+} and Pb^{2+} have been measured by calorimetry in methanol. For the Ag^+ complexation, $\log K$ values were determined by potentiometry using an Ag^+-ISE and, in this case, $T\Delta S$ could be obtained. The complexations were enthalpy driven and Ag^+ exhibited remarkably higher complexation selectivity due to the increase of covalent binding between soft acid and soft base. The reaction enthalpy and entropy are discussed in terms of donor atom, end group and donor site effects, respectively. In the membrane transport study, efficient and highly selective Ag^+ transfer was observed both in single and competitive cation experiments.

Keywords: Complexation; Membrane transport; Podand; Silver ion; Thermodynamic parameters

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1. Introduction

Syntheses of the podands, oligoethylene glycol derivatives with aromatic end groups at both ends, are easily performed because the expensive and time-consuming step is omitted [1]. Some podands with a quinoline end group wrap themselves around cations such as Na^+ or Rb^+ in a helical manner to make a pseudo-cavity in both solid [2] and solution [3] states. Generally, the selectivity of podands for cation complexations are lower than that of crown ethers [4]. However, according to our previous work

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[*] Corresponding author.

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[5], Ag^+ is expected to show the highest selectivity among univalent cations to some sulfur-containing podands. There have been few reports on the thermodynamics of interactions between O/S donor podands and cations [3].

In this study, we have synthesized a series of sulfur-containing podands to elucidate the extent to which the individual building blocks control the selectivity of complex formation with cations. Their basic molecular framework was altered by variation of the donor atom, the donor site, or by insertion of a spacing group into the middle of the ether chain and aromatic end groups (Fig. 1). The enthalpic changes of complexation with Ag^+, K^+, Cu^{2+}, Cd^{2+} and Pb^{2+} were determined by calorimetric titration. The log K values with Ag^+ were determined by potentiometric titration.

In addition, membrane transport experiments were performed to examine the transport selectivity for Ag^+ over other cations by using the podands as carriers.

2. Experimental

2.1. Materials

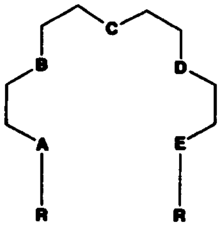
The salt used, metal nitrates (Merck), were anhydrous and of the highest purity. The methanol (Aldrich) used in all of our measurements was distilled over calcium hydride.

Podands, 1, 3, 7 and 8

These were prepared according to the methods reported in the literature [3–6]. The other podands were synthesized by reaction of the corresponding chlorides with aromatic alcohol in the presence of KOH in ethanol.

Podands 2

Thiophenol (60 mmol) and KOH (60 mmol) were dissolved in boiling ethanol (150 ml). Under reflux conditions, 1-phenoxy-11-chloro-3,6,9-trioxatridecan (45 mmol) in ethanol (50 ml) was added dropwise. The mixture was refluxed for 21 h. After cooling to



Podand	R	Donor atoms in ether chain				
		A	B	C	D	E
1	Phenyl	O	O	O	O	O
2	Phenyl	S	O	O	O	O
3	Phenyl	S	O	O	O	S
4	Phenyl	O	S	O	S	O
5	Benzyl	S	O	O	O	S
6	Benzyl	O	S	O	S	O
7	Phenyl	O	S	S	S	O
8	Phenyl	S	S	O	S	S

Fig. 1. Podands used in this work.

room temperature, the mixture was filtered and evaporated. The residue was dissolved in chloroform. To separate unreacted thiophenol, the mixture was extracted several times with dilute NaOH. The organic layer was dried over $MgSO_4$, concentrated and purified by column chromatography over silica gel (eluent, *n*-hexane: ethylacetate 4:1 v/v; R_f value, 0.31; yield, 60%, ^1H NMR ($CDCl_3$), 3.0–4.0 (m, 16H $-OCH_2$), 7.5–8.0 (m, 10H aromatic); IR (KBr), 3150 (aromatic C–H, m), 2920, 2870 (aliphatic C–H, m), 1590 (aromatic C=C, s), 1137 (alkyl, C–S, w), 740 (allyl C–S, s) cm^{-1}).

Podand 4

Di(2-mercaptoethyl)ether (50 mmol) and KOH (100 mmol) in ethanol (50 ml) were dissolved in boiling ethanol (150 ml). Under reflux conditions, (2-chloroethoxy)benzene (90 mmol) was added dropwise. The mixture was refluxed for 5 h. The synthetic procedure was almost the same as that used for podand **2** (eluent, chloroform: *n*-hexane 4:1, v/v; R_f value, 0.30; yield 70%; ^1H NMR ($CDCl_3$); 2.7–2.9 (m, 8H $-SCH_2$), 3.6–3.7 (m, 8H $-OCH_2$), 7.3–7.45 (m, 10H aromatic); IR (KBr), 3045 (aromatic C–H, m), 2900 (aliphatic C–H, m), 1580, 1500 (aromatic C=C, s), 1100 (alkyl C–S, w), 740 (allyl C–S, s) cm^{-1}).

Podand 5

Benzylmercaptane (120 mmol) and KOH (120 mmol) were dissolved in boiling ethanol (150 ml). Under reflux conditions, 1-phenoxy-11-chloro-3,6,9-trioxatridecan (45 mmol) in ethanol (50 ml) was added dropwise. The mixture was refluxed for 5 h. The synthetic procedure was almost the same as that used for podand **2** (eluent, *n*-hexane: ethylacetate 4:1, v/v; R_f value, 0.30; yield 60%; ^1H NMR ($CDCl_3$), 2.4–2.8 (t, 4H, $-SCH_2$), 4.0–3.4 (m, 16H, CH_2OCH_2), 7.2–7.5 (m, 10H aromatic); IR (KBr), 3050 (aromatic –CH, m), 2930, 2870 (aliphatic –CH, s), 1580 (aromatic C=C, s), 1120 (alkyl C–O, s), 740 (allyl C–S, s) cm^{-1}).

Podand 6

Di(2-mercaptoethyl)ether (50 mmol) and KOH (100 mmol) in ethanol (50 ml) were dissolved in boiling ethanol (150 ml). Under reflux conditions, (2-chloroethoxymethyl)-benzene (110 mmol) was added dropwise. The mixture was refluxed for 3 h. The synthetic procedure was almost the same as that used for podand **2** (eluent, chloroform: *n*-hexane 4:1, v/v; R_f value, 0.25; yiled 70%, ^1H NMR ($CDCl_3$), 2.7–2.9 (m, 8H $-SCH_2$), 3.6–3.7 (m, 8H $-OCH_2$), 4.55 (s, 4H $-OCH_2$), 7.3–7.45 (m, 10H aromatic); IR (KBr), 3030 (aromatic C–H, m), 2910 (aliphatic C–H,m), 1570 (aromatic C=C, s), 1100 (alkyl C–S, w), 740 (allyl C–S, s) cm^{-1}).

2.2. Procedure

Log K values of Ag^+ complexes with the podands were determined by potentiometric titration using an Ag^+-ISE (Orion 94-16) in methanol at 25.0°C. The experimental technique has already been described [3, 5, 7].

Determinations of reaction enthalpies were performed using a Tronac Model 1250 isoperibol calorimeter described previously [8, 9]. Typically, a run consisted of three sections: the initial heat capacity calibration, titration (at 25.00 ± 0.01°C), and the final heat capacity calibration. The experimental procedure consisted of titrating in methanolic solution of 3 mM podand with 30 mM metal nitrate. Heats of dilution were determined by titrating the methanolic solution of the metal nitrate in the absence of the podand.

Membrane transport experiments were carried out using a bulk liquid membrane cell based on the concept of the Schulman bridge at 25°C. The details of the transport conditions are summarized in the footnotes of Table 2 (below). The receiving phase was sampled after 24 h and analyzed for cation concentration using a Perkin-Elmer 2380 atomic absorption spectrophotometer.

3. Results and discussion

The complexation enthalpies of the podands **1**–**8** with the cations were determined by a precise calorimetric titration technique. The numerical values of ΔH are listed in Table 1. In determining the $\log K$ values of Ag^+ complexes with the podands, the

Table 1
ΔH (kJ mol^{-1}), $\log K$, and $T\Delta S$ (kJ mol^{-1}) for the 1:1 interactions of several cations with podands in methanol at 25.0°C

Podand	Parameter	Ag^+	K^+	Cu^{2+}	Cd^{2+}	Pb^{2+}
1	ΔH	−0.50	−1.42	ND	ND	−6.02
	$\log K$	<2				
	$T\Delta S$					
2	ΔH	−38.20	−0.17	ND	ND	ND
	$\log K$	3.88				
	$T\Delta S$	−16.07				
3	ΔH	−49.54	−0.59	ND	ND	ND
	$\log K$	5.50				
	$T\Delta S$	−18.16				
4	ΔH	−68.02	−0.12	ND	ND	ND
	$\log K$	6.29				
	$T\Delta S$	−32.13				
5	ΔH	−57.70	−0.38	ND	ND	ND
	$\log K$	7.37				
	$T\Delta S$	−15.65				
6	ΔH	−69.07	−0.16	ND	ND	ND
	$\log K$	7.27				
	$T\Delta S$	−27.59				
7	ΔH	−91.75	−1.74	−17.57	ND	ND
	$\log K$	7.65				
	$T\Delta S$	−48.11				
8	ΔH	−74.52	−3.35	−7.32	−9.33	−6.23
	$\log K$	9.15				
	$T\Delta S$	−22.28				

Key: ND means not determined.

potentiometric titrations were very successful because the Ag^+-ISE responded in a nearly Nernstian manner in methanol [3, 5]. Furthermore, this direct method yielded not only reasonably accurate results over quite a wide range of log K, but also sharp equivalent points revealing the 1:1 stoichiometry of the complexes. Some typical titration curves using the Ag^+-ISE in methanol are represented in Fig. 2. And the log K and $T\Delta S$ values for the complexation of Ag^+ with the podands are also listed in Table 1 together with ΔH.

According to Table 1, the complexation of the cations with the podands is exothermic in each case, and $T\Delta S$ values are negative. These facts indicate that the interactions of the podands with the cations are enthalpy driven.

Because no significant heat was produced or expected for K^+, Cu^{2+}, Cd^{2+} and Pb^{2+} with some podands, the binding strengths of these cations were expected to be very weak. Ag^+ exhibited, however, remarkably large $-\Delta H$ values, comparable to those obtained for cyclic ionophores [10].

3.1. Donor atom effect

The Ag^+ complexation data in Table 1 illustrate the effect of substitution of sulfur for oxygen on ΔH values in analogous ether chains. Podand **1** which only contains O donor atoms forms the weakest complex with Ag^+. The ΔH values should reflect more accurately than any other thermodynamic quantity the energy changes involved in making or breaking bonds when substitution of one donor atom for another is made [11]. Therefore, the large $-\Delta H$ values for Ag^+ interactions with podands **2–8** indicate the participation of sulfur in cation binding. These results probably reflect the increased

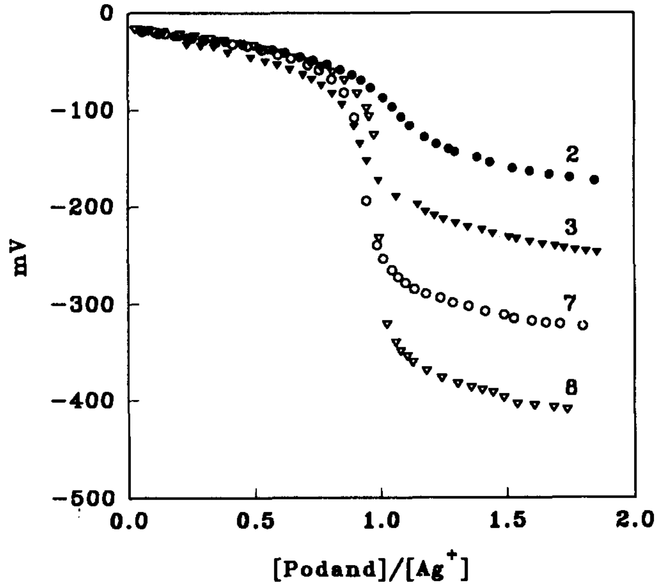


Fig. 2. Potentiometric titrations of Ag^+ with some podands using an Ag^+-ISE in methanol at 25.0°C.

covalent character between soft acid soft base [12] in the Ag^+ complexes of ligands containing S.

For each S substituent, K values increase by about 2 orders of magnitude. As we can see from the data, the large increase in $\log K$ is due to increasingly favorable enthalpy changes.

In general, the open-chain oxygen ligand, glyme/podand, suffers substantial conformational change on wrapping around a cation in a pseudo-circular or helical arrangement of donor atoms [13–16]. 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 contrast, the preorganized crown ether does not have to change its original conformation to a great extent upon complexation [11, 17]. So the complex stability is governed predominantly by the enthalpy change arising mostly from the bond formation.

In this work, relatively large $-T\Delta S$ values were obtained, but entropy changes were insensitive and comparable in magnitude for each number of S substituents. Otherwise, ΔH increases monotonously with the number of substituted S for O. Therefore, the large enthalpic gain alone may well explain the complex stability, while the entropic contribution is less important in determining the complex stability.

3.2. End group effect

Comparing the $\log K$ values of **3** and **5**, the podands with benzyl end-groups, **5** showed much higher stability than the phenyl analogue, **3**. The origin of the drastic enhancement in $\log K$ values is not entropic but results from a positive contribution by the larger $-\Delta H$ value of **5** than **3**. The role of the methylene spacing group, which can be ascribed to the higher flexibility, strongly suggests that these complexes are stabilized not only by a spherical wrapping effect, the same as the glymes, but also by an oriented face-to-face association structure as a part of π–π stacking between aromatic moieties [3–5].

Thermodynamically, π–π stacking has not been related to entropy effects but to enthalpy which can be the important driving force favoring π–π stacking [4, 16]. The net difference in ΔH between complexation of **3** ($-49.54\,\mathrm{kJ\,mol^{-1}}$) or **5** ($-57.70\,\mathrm{kJ\,mol^{-1}}$) with Ag^+ may be due to the formation of π–π stacking. Similar observation by NMR concerning the reactions of other podands which are able to form pseudo-cycles have been reported [1, 5].

But in case of **4** and **6**, the difference in $\log K$ values stems from enthalpy contributions. Since both are long enough to form pseudo-cycles around the cation, enthalpic changes are nearly the same.

3.3. Donor site effect

The variation of S position in O_3S_2-type podands (**3** and **5**, A, E-dithia; **4** and **6**, B, D-dithia) showed the opposite effect on the magnitude of $\log K$ for the podands with phenyl (**3** $\ll$ **4**) and benzyl (**5** $\geqslant$ **6**) end groups. The positions described alphabetically are indicated in Fig. 1.

In our opinion, this opposite donor site effect is evidence for the different conformational changes of podands on complexation. For podands with the same end group, two S atoms in the B and D positions were more favorable in enthalpy but more unfavorable in entropy than in the A and E positions on complexation with Ag^+. The larger $-T\Delta S$ values for B, D-dithia podands, **4** and **6**, could be explained by the higher rigidity increase of the ligands before and after complexation. The enthalpic contributions by variation of donor site on complexation are, however, not so straightforward.

For the complexation of podands with a benzyl end group, however, chelating two S atoms in the A and E positions to Ag^+ is coupled with wrapping effectively in the short range, to give an increment of $\log K$. No further detailed discussion is possible here, but the donor site effect coupled with the introduction of a spacing group could be an important factor in controlling the cation selectivity.

3.4. *Membrane transport*

The thermodynamic properties of the podands are expected to induce the specific transport of Ag^+. Therefore, single and competitive transport of Ag^+ towards any other ions was performed in bulk liquid membrane using some podands as carriers. The transport rates are listed in Tables 2 and 3. Interestingly, in single-ion transport no ions were transported except Ag^+ by both carriers **3** and **7**. According to Table 3, efficient and highly selective Ag^+ transfer is obtained in competitive ion transport experiments. In particular, Ag^+ transport against Cu^{2+} has industrial interest and the result of this work is superior to that previously reported [18].

4. Conclusions

It was possible to control the selectivity of Ag^+ against certain cations by means of the number and position of S atoms and the flexibility of the end groups in the podand structures. Specific Ag^+ transfer through a liquid memabrane was observed; this is

Table 2
Cation transport[a] by bulk liquid membrane containing podands as carrier

Podand	Transport rate/(10^{-8} mol s^{-1} m^2)[b]								
	Ag^+	Li^+	Na^+	K^+	Mn^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}	Zn^{2+}
3	462.7	a	a	a	a	a	a	a	a
7	528.1	a	a	a	a	a	a	a	a

[a] Transport conditions: source phase (aqueous solution of nitrate, 0.8 ml), $[M^{n+}(NO_3)^n] = 0.1$ M; membrane phase (CH_2Cl_2, 3.0 ml), (carrier) = 1.0 mM; i.d. of glass vial = 18 mm, stirred by 13 mm teflon-coated magnetic stirring bar driven by a Hurst Synchronous motor; receiving phase (deionized water, 5.0 ml). [b] The average value of three independent determinations. The experimental values deviate from the reported values by an average of ± 10%.

Key: 'a' indicates no transport.

Table 3
Competitive transport[a] of Ag^+ and M^{n+} simultaneously by bulk liquid membrane containing podands as carrier

Ag^+/M^{n+}	Transport rate/(10^{-8} mol s^{-1} m^2)		
	3	**7**	**8**
Ag^+/Li^+	619.0/a	515.1/a	ND
Ag^+/Na^+	620.6/a	629.8/a	ND
Ag^+/K^+	617.5/a	639.1/a	ND
Ag^+/Cu^{2+}	756.3/a	608.3/a	355.4/a
Ag^+/Zn^{2+}	609.8/4.1	654.5/3.9	413.6/a
Ag^+/Co^{2+}	623.7/a	605.2/a	347.2/a
Ag^+/Ni^{2+}	464.9/a	472.6/a	305.8/a
Ag^+/Mn^{2+}	606.7/a	667.1/a	ND

[a] Transport conditions were identical to those noted in the footnotes of Table 2 except the composition of source phase which was $AgNO_3$ and $M^{n+}(NO_3)_n$ (1.0 mM, respectively).

Key: 'a' indicates no transport and ND means not determined.

relevant to silver recovery. Further investigations on the acyclic ionophore expected higher selectivity for the specific ion are in progress and the results will be reported later.

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