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Articles

Podand-Mediated Transport of Ag^+ in a Bulk Liquid Membrane System

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The Podand I (Figure 1) has been studied as cation carrier in a bulk liquid membrane system. Ag^+ and some other transition metal ions (M^{2+} = Cu, Ni, Co, Zn, and Cd) have been transported using the podand as carrier in a bulk liquid membrane system. Studies on the transport of equimolar mixtures of two or three competing components have also been carried out with the same system. Ag^+ exhibited a higher transport rate than the other M^{2+} in the competitive experiments. Ligand structure and the equilibrium constant for complex formation are important parameters in the transport of the metal ions.

Introduction

It is known that metal ions can be transported across a liquid membrane.[1] With an ever-increasing awareness of our energy demand, energy efficient membrane technology is considered to be a valuable approach in the separation process. The effectiveness of separation by a membrane is determined by the flux of cations through the liquid membrane. Polymeric membranes have the disadvantages of usually low fluxes in the condensed phase and poor selectivity. Liquid membranes usually produce higher fluxes and selectivities.[2,3]

In our previous papers,[4~6] we examined the influence of structural variation within a series of macrocyclic ligand carriers upon the selectivity and efficiency of the transport of cations across the bulk liquid membrane, the emulsion membrane, and the supported liquid membrane.

Silver is an element of important commercial value. It is valuable because of its resistance to corrosion and its usefulness in alloys and jewelry. Improved procedures for extracting it from its ores and for recovering it from waste water would be valuable.

Recently, we reported that sulfur-containing podands exhibited high selectivity for Ag^+.[7,8]

A high degree of cation selectivity makes podand I[9] a desirable membrane carrier. We showed that this selectivity was also present in the membrane transport system. For example, high transport selectivity was observed for Ag^+ over many cations using podand. We determined ΔH, ΔS, and Log K for the 1 : 1 interaction of podand I with Ag^+, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+} by titration calorimetry.

Experiment

Experiments of liquid membrane transport were conducted as previously reported using a bulk liquid membrane apparatus (Figure 2) based on the concept of the Schulman Bridge.[10]

Two water phases were separated by a chloroform phase which constituted the membrane. The organic membranes consisted of 3 mL of a 1.0 mM solution of podand I in chloroform placed in the bottom of a glass vial (i.d. 18 mm). The phases were stirred using small teflon magnetic stirring bars placed in the chloroform layers and driven at 120 rpm by Hurst synchronous motors for 24 hours. The two water phases were placed on top of the chloroform and were separated by a glass tube which extended down into the chloroform layer.

One of the two water phases consisted of 0.8 mL of an aqueous metal nitrate solution (source phase), and the other consisted of 5.0 mL of deionized water (receiving phase). The solution of the single source phase was 0.1 M $M(NO_3)_n$, and the binary source phase of the competitive membrane transport was 0.1 M $AgNO_3$/0.1 M $M(NO_3)_n$. Each experiment was repeated three times in a room thermostated to 25± 1 ℃. After 24 hours, 3 mL of the samples from the receiving phases were removed and analyzed for the metal ions of interest using a Perkin Elmer Model 2380 atomic absorption spectrophotometer.

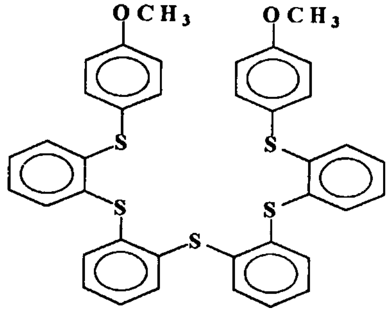

Figure 1. Polyarylthioether (Podand I).

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The measured transport data values were the average of three separate determinations. The standard deviations were less than ± 10%. Blank tests of transport (no podand I present) were performed for each metal source phase solution to determine membrane leakage. However, metal ions were not detected in each receiving phase.

The calorimetric determinations were carried out using a TRONAC model 1250 isoperibol titration calorimeter equipped with a 25 mL glass Dewar flask as the titration vessel and a 10 mL-precision constant-rate burette for titrant delivery. The thermostat was maintained at 25±0.02 ℃ with a TRONAC model 40 precision temperature controller.

Procedures, calibrations, and data analyses including determinations of the stability constant, ΔH, and ΔS values by nonlinear regression methods were adapted from earlier recommmendations.[11]

The ligand solution (4 mM of the podand I, 20 mL) was titrated with 40 mM $M(NO_3)_n$ in 50% THF-methanol solution. The heat of dilution of the metal nitrate (40 mM) was measured in separate experiments by titrating the metal nitrate into 50% THF-methanol solution. The heat of dilution of the podand I was measured by titrating the 50% THF-methanol solution into 4 mM of the podand I solution.

Stability constant, enthalpy changes, and entropy changes were simultaneously obtained using the least square program **FS101E** and **FS101ET (TRONAC, INC. 1804 South Columbia Lane, Orem, Utah 84058).**

The chemicals used and their sources are CH_3OH (Merck, G.R.); $CHCl_3$ (Showa Chem. Co., G.R.); $AgNO_3$ (Hayashi, G.R.); $Cu(NO_3)_2 \cdot 3H_2O$ (Ishisu Pharm. Co., E.P.); $Co(NO_3)_2 \cdot 6H_2O$ (Hayashi Pure Chem. Co., G.R.); $Zn(NO_3)_2 \cdot 6H_2O$ (Hayashi Pure Chem. Co., E.P.); $Cd(NO_3)_2 \cdot 4H_2O$ (Junsei Chem. Co., E.P.); $Mn(NO_3)_2 \cdot 6H_2O$ (Merck, G.R.); and $Ni(NO_3)_2 \cdot 6H_2O$ (Hayashi Chem. Co., G.R.). Deionized water was prepared by passing distilled water through OM-S cartridges.

The synthesis of the podand I has been reported.[9]

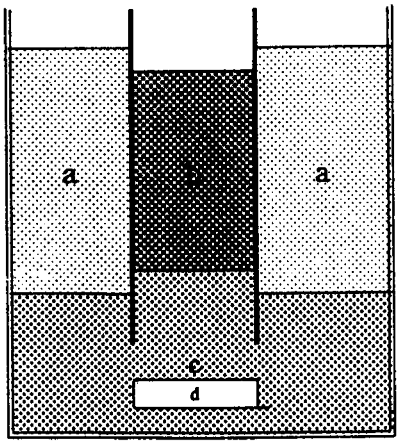

Figure 2. Bulk liquid membrane system: (a) aqueous receiving phase; (b) aqueous source phase; (c) organic membrane phase +carrier; and (d) magnetic stirring bar.

Results and Discussion

The thermodynamic parameters of podand I with Ag^+ and transition metal ions were determined by titration calorimetry. The numerical values of ΔH are listed in Table 1. According to Table 1, the complexation of Ag^+ with podand I is exothermic, and the $T\Delta S$ value is negative. These factors indicate that the interaction of the podand with Ag^+ is enthalpy driven.

Because no significant heat was produced for the podand I with Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+}, the binding strengths of these cations were expected to be very weak.[12] However, Ag^+ exhibited a remarkably large negative enthalpy value, which indicated a strong complexation for the podand I with Ag^+.

Recombination of the podand I with Ag^+, which is a soft acid, to form a complex of a covalent nature is preferentially enthalpy driven. This result reflects the increased covalent character in the complex between the soft acid Ag^+ and the soft base of the ligand containing sulfur atoms.[13]

The results of the membrane transport study are given in Tables 2, 3, and 4. The highly selective transport of Ag^+ was commonly observed, in mixtures of single, binary, and ternary competitive cations.

When neutral podands are used to transport cations, the stability constant can play a significant role in determining both the rates and selectivities of the transport.[14]

The stability constant, log K, for Ag^+ complexation with podand I is 3.43. The flux value of Ag^+ is largest among the metal ions examined. This seems to be due to the highest stability constant of Ag^+.

Table 1. Thermodynamic Parameter for Complexation of Metal Ions by Podand I

Metal ion	ΔH, kcal/mol	$T\Delta S$, kcal/mol	log K
Cu^{2+}	−0.62	*a*	*a*
Ni^{2+}	−0.10	*a*	*a*
Co^{2+}	−0.17	*a*	*a*
Zn^{2+}	−0.05	*a*	*a*
Cd^{2+}	−0.21	*a*	*a*
Ag^+	−10.26	−5.58	3.43

Titrate: 0.004 M podand in 50% THF-methanol. Titrant: 0.04 M Metal ions in 50% THF-methanol. [a] Temperature change was too small for calculation.

Table 2. Transport of Ag^+ and M^{n+} by Bulk Liquid Membrane[b] Containing Podand I as Carrier

Metal ion	Ag^+	Cu^{2+}	Mn^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Cr^{3+}	Fe^{3+}
Transport rate ($\times 10^{-8}$ mol·s^{-1}·m^{-2})	389.6	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*

[a] No transport. [b] Transport condition: source phase (aqueous solution of metal nitrate, 0.8 mL) $[M^{n+}(NO_3)_n]=0.1$ M; membrane phase ($CHCl_3$, 3 mL), [carrier]=1.0 mM; receiving phase (deionized water, 5.0 mL).

Table 3. Competitive Transport of Ag^+ and M^{n+} Simultaneously by Bulk Liquid Membrane[b] Containing Podand as Carrier

Competitive metal	Transport rate ($\times 10^{-8}$ $mol\cdot s^{-1}\cdot m^{-2}$)
Ag^+/Cu^{2+}	614.9/0.3
Ag^+/Mn^{2+}	518.6/*a*
Ag^+/Ni^{2+}	633.7/*a*
Ag^+/Co^{2+}	682.2/*a*
Ag^+/Zn^{2+}	578.9/0.8
Ag^+/Pb^{2+}	672.5/0.2
Ag^+/Cd^{2+}	650.4/*a*
Ag^+/Cr^{3+}	630.4/*a*
Ag^+/Fe^{3+}	571.1/*a*

[a] No transport. [b] Transport condition: source phase (aqueous solution of metal nitrate+$AgNO_3$, 0.8 mL) [$M^{n+}(NO_3)_n$] 0.1 M+$AgNO_3$ 0.1 M; membrane phase ($CHCl_3$, 3 mL), [carrier]=1.0 mM; receiving phase (deionized water, 5.0 mL).

Table 4. Competitive Transport of Ag^+ and M^{n+} Simultaneously by Bulk Liquid Membrane[b] Containing Podand as Carrier

Competitive metal	Transport rate ($\times 10^{-8}$ $mol\cdot s^{-1}\cdot m^{-2}$)
$Ag^+/Cu^{2+}/Cd^{2+}$	685.7/0.4/*a*
$Ag^+/Mn^{2+}/Zn^{2+}$	727.3/*a*/*a*
$Ag^+/Ni^{2+}/Co^{2+}$	693.5/*a*/*a*
$Ag^+/Pb^{2+}/Fe^{3+}$	702.4/*a*/*a*

[a] No transport. [b] Transport condition: source phase (aqueous solution of metal nitrate+$AgNO_3$, 0.8 mL) [$M^{n+}(NO_3)_n$] 0.1 M+$AgNO_3$ 0.1 M; membrane phase ($CHCl_3$, 3 mL), [carrier]=1.0 mM; receiving phase (deionized water, 5.0 mL).

Another reason is the anion effect. Two NO_3^- anions must accompany one transition metal ion (Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+}) in transport, whereas only one NO_3^- anion per Ag^+ cation is necessary for Ag^+ transport. The number of anion per cation which must be dehydrated for the transport to occur significantly affects the distribution coefficient of the transported amount. The flux values of the divalent transition metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+}) are shown in Table 2. The transport of these transition metal ions did not occur. The binding strengths of these metal ions may be very weak because no significant heat was produced for the podand I with the metal ions. To test the selectivity of the present system, the investigations of transports with binary and ternary metal ions were carried out by placing equimolar amounts of Ag^+ and the transition metal ions in the source phase. The competitive transport experiments for binary and ternary system containing Ag^+ and other cations showed that Ag^+ was selectively transported over the other cation (Tables 3 and 4) in the presence of podand I.

We have found that podand I is an excellent carrier for the selective transport of Ag^+ in the presence of other cations. Specific Ag^+ transport through bulk liquid membrane is observed with podand I which should be relevant to silver recovery. The highest degree of transport selectivity for Ag^+ by the podand I in this bulk liquid membrane system may be applicable to the recovery of Ag^+ from solution containing several heavy metal ions, especially in the care of waste water.

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