

Reaction 4 is energetically favorable *via* an exothermicity of 26.7 kcal. Scheme 7 could explain the formation of VII.

If one of electrons in the C-C π bond in 2-propenol is excited by an UV photon, the bond could easily interact with the silicon center through a 6-membered transition state as shown in Scheme 7. Note that in case of R = -SiHMe(SiMe₃), Scheme 7 indicates that product VII is formed *via* the coupling of a primary product of V.

Finally one can say that a primary product, compound V is quite unstable under this photolytic condition such that V can easily undergo at least three types of reactions as mentioned earlier. As indicated in the experimental section product, V is not observed even in the 10 hr reaction time, indicating that V is easily dissociated or undergoes the intermolecular reactions shortly after its formation.

Acknowledgment. The present studies were supported (in part) by the Basic Science Research Institute Program, Ministry of Education, 1994 Project No. BSRI-94-3432. BHB is grateful to Center for Molecular Science for partial financial support.

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12. Since one molecule of VI contains two subunits of silylene II, the yield of VI reported here is corrected to be twice larger than the measured yield based on the amount of the unrecovered starting material.
13. The siloxane product has also been observed in the photolysis of I in the presence of ethanol. But the photolysis result is not presented here since the reaction pattern is the same as found in the photolysis experiment employing methanol. But the experimental result can be found in: Hong, S. K. *Generation and Reactivities of Silylenes and Silyl Radicals*; M. S. dissertation, Chungnam National University, Taejeon, Apr 1993.

Studies on the Macrocycle-mediated Transport of Divalent Metal Ions in a Supported Liquid Membrane System

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Received August 17, 1994

Macrocyclic ligands have been studied as cation carriers in a supported liquid membrane system. Cd²⁺ has been transported using nitrogen substituted macrocycles as carriers and several divalent metal ions (M²⁺ = Zn, Co, Ni, Cu, Pb, Mg, Ca, and Sr) have been transported using DBN₃O₂, DBN₂O₂ and PolyNtnoen as carriers in a supported liquid membrane system. Competitive Cd²⁺-M²⁺ transport studies have also been carried out with the same system. Ligand structure, stability constant, membrane solvent and carrier concentration are also important parameters in the transport of metal ions.

Introduction

It is well known that ions can be transported across liquid membrane.¹ With an ever increasing awareness of our energy demands, energy efficient membrane technology is proving to be a valuable approach in separation processes. The effectiveness of a membrane separation study is determined by the flux of species through the membrane.

Liquid membranes usually produce higher fluxes.² There are three types of membranes which are generally employed:

bulk liquid membrane,³ emulsion liquid membrane,⁴ and polymer supported liquid membrane.⁵ In our previous papers^{3,4} we examined the influence of the structural variation within a series of crown ether carriers upon the selectivity and efficiency of the transport of metal ions across the bulk liquid membrane and the emulsion membrane.

Many transport systems for metal ions through a supported liquid membrane (SLM) containing a chelating agent as a carrier have recently been studied.⁶ A solid supported liquid membrane, consisting of a microporous polypropylene

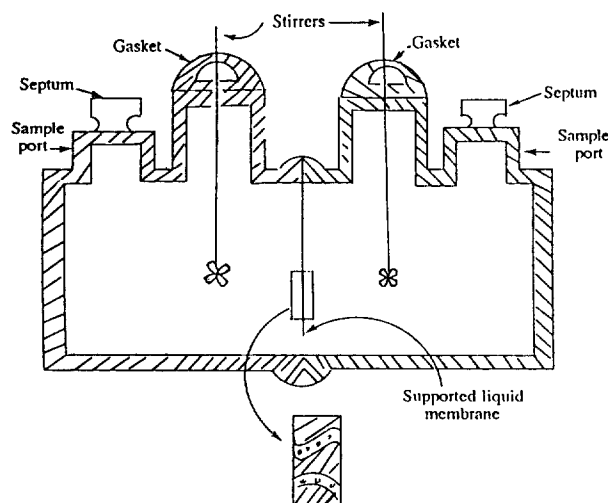


Figure 1. Supported liquid membrane system.

film absorbing an organic solution of chelating agent, separating an aqueous feed compartment containing Cu^{2+} ion and aqueous strip compartment, and initially containing no copper ions, was studied.⁷ The main advantage of the supported liquid membrane over the traditional separation technologies is the low inventory of the organic phase used, hence only small amount of extractant are needed, and very selective and expensive extractants can be used. Other advantages are low capital and operating costs, low energy consumption, the mass transfer in one step, the possibility of achieving high separation factors, and the possibility of concentrating the recovered species during separation.

In the present work we have studied the influence of the membrane solvent on divalent metallic ions transport through the SLM from a given concentrated metallic ion to demineralized water, using crown ether as the membrane carrier and Celgard 2400 as the solid support.

We have shown that the selectivity is also present in the supported liquid membrane transport system. For example, high transport selectivity has been observed for Cd^{2+} over many cations by using the macrocyclic ligand. It is of interest to examine the rates of individual cation transport through the SLM containing the macrocyclic carrier. We have studied the relationship using several macrocyclic ligand carriers with Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Sr^{2+} , Mg^{2+} , and Pb^{2+} .

Experimental

The supported liquid membrane (SLM) cell used is schematically shown in Figure 1, where the flat surface of the each joint was ground smooth to provide a tight liquid seal without use of a gasket. The volume of the each compartment was 200 mL and the surface area of the membrane support was 19.63 cm^2 . The aqueous source and receiving phase compartments were stirred at the same rate of 600 rpm by Hurst Synchronous motors using inserted glass propeller stirring rods which were gasketed to prevent evaporation loss from the cells and the separate sampling ports were covered by septum caps. The SLM was prepared by soaking a sheet of Celgard 2400 film (porous polypropylene) in the organic solvent. A microporous polypropylene membrane,

Celgard 2400 (Celanese Separation Products) with a pore size of $0.04\text{--}0.4 \mu\text{m}$, a thickness of $25 \mu\text{m}$, and a porosity of 45% was used as a supporting medium to hold dichlorobenzene solution containing PolyNtneon. The SLM containing the macrocyclic ligand was placed between cylindrical glass cells of 200 mL each. The two water phases are consisted of one 200 mL quantity of an aqueous metallic ion solution (source phase) and the other 200 mL of distilled and deionized water (receiving phase). The membranes contain a $2 \times 10^{-3} \text{ M}$ solution of the macrocyclic ligand in organic solvent. The solution of the single salt source phase was 0.1 M of $\text{M}(\text{NO}_3)_2$. The solution of binary salt source phase was 0.1 M $\text{Cd}(\text{NO}_3)_2/0.1 \text{ M}$ of $\text{M}(\text{NO}_3)_2$.

Each experiment was repeated three times in a chamber thermostated to $25 \pm 1 \text{ }^\circ\text{C}$. 5.0 mL of the receiving phase was withdrawn by the syringe for the analysis. Several cations initially present in the aqueous feed solution were measured in the aqueous stripping solution at the end of the experiment by atomic absorption spectrophotometer (Perkin Elmer, model 2380).

The measured flux values ($J_m = \text{mole transport}/\text{sec} \cdot \text{m}^2$) were multiplied by 10^7 to obtain the J_m value in the Table 4. The standard deviations are less than $\pm 10\%$. Blank tests (no macrocyclic carrier present) were performed for each source salt solution to determine the membrane leakage. No transport was detected for any of the M^{2+} studied under the conditions of all sources and receiving phase when macrocyclic carrier was absent from the membrane phase. The metal solutions were prepared in deionized water from the highest grade materials available from the indicated suppliers. The chemical used their source are $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, (Kanto, E. P.); $\text{Co}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, (Junsei, E. P.); $\text{Ni}(\text{NO}_3)_2$ (Hayashi, G. R.); DBN_3O_2 , DBN_2O_2 , PolyNtneon (synthesized by our research team, Figure 2).⁹

Results and Discussion

Selection of Solvent and Ligand. The SLM is consisted of an organic carrier solution immobilized in a thin microporous film separating the two aqueous phases. The organic solvent which should be immiscible with water, non-volatile, and inert to the support must have a suitable polarity related to an optimal value of the association constant of the complex.

In the present work, we have examined the influence of the membrane solvent. Dichloromethane, 1,2 dichlorobenzene, 1-phenyl hexane, and *o*-nitrophenylbutyl ether were evaluated as the solvent for the SLM. Dichloromethane has been used successfully as a solvent in the bulk liquid membrane system.

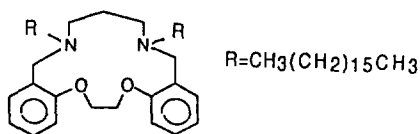
Dichloromethane has the advantage to a large number of macrocyclic carriers, but it is insufficient as the solvent for the SLM because of its high volatility and water solubility. The solubility of PolyNtneon in *o*-nitrophenylbutyl ether is not good. As shown in the Table 1, 1,2-dichlorobenzene is the best solvent for copper ion transport through the SLM. 1,2-Dichlorobenzene has the advantage of low volatility and immiscible with water.

We have used DBN_2O_2 , DBN_3O_2 and PolyNtneon (Figure 2) as the carrier. When DBN_2O_2 and DBN_3O_2 were employed as the carrier, the transport of copper ion did not occur.

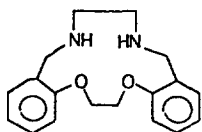
Table 1. The relations between ligand and solvent

Solvent	Ligand		
	DBN ₂ O ₂	DBN ₃ O ₂	PolyNtnoen
1,2-Dichlorobenzene	0	0	64.3 ^a
1-Phenyl hexane	0	0	0
Dichloromethane	0	0	0
O-Nitro phenyl-butyl ether	0	0	insoluble

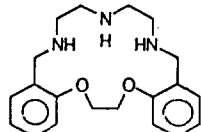
^a Flux of Cu²⁺, unit are moles/s·m²×10⁷.



N,N-dihexadexyl - 1,12-diaza-3,4;9,10-dibenzo-5,8-dioxo-cyclopentadecane (PolyNtnoen)



3,4;9,10-dibenzo-1,12-diaza-5,8-dioxacyclotetradecane (DBN₂O₂)



3,4;9,10-Dibenzo-1,12,15-triaza-5,8-dioxacyclohepta decane (DBN₃O₂)

Figure 2. Macrocyclic ligands used in this study.

On the other hand, it was found that high transport of copper ion was obtained by the use of the SLM containing PolyNtnoen. The lipophilic group (R=CH₃(CH₂)₁₅CH₃) is attached to the arm of the PolyNtnoen but it is not attached to the arm of DBN₂O₂ and DBN₃O₂. Also, it should be pointed out that DBN₂O₂ and DBN₃O₂ are unstable in the SLM system while the PolyNtnoen is stable. Therefore, the PolyNtnoen containing the SLM is very hydrophobic, which facilitates the transport of copper ion. As seen the Table 2, transport of metallic ion was not observed in the case the SLM when no PolyNtnoen was used.

Single salt system. The dependence of the transport of copper ion on the PolyNtnoen concentration was examined. The experimental conditions were as follow: the concentrations of the ligand were varied from 0.0005 to 0.004 M and 0.1 M Cu(NO₃)₂ was used.

Table 3 illustrates the amounts of the transport of the copper ion as a function of the PolyNtnoen concentration. In the range of the concentrations of carrier, the transport of the copper ion was increased in proportion to the concentration of PolyNtnoen concentration in the SLM. The flux values of the transport of transition metal ions are summarized in the Table 4.

The magnitude of the transport of the metallic ions by the SLM using PolyNtnoen as the carrier were in the order of Cd²⁺>Pb²⁺>Sr²⁺>Cu²⁺>Co²⁺>Ca²⁺>Zn²⁺>Ni²⁺>Mg²⁺. When neutral macrocycles are used to transport cations, the stability constant can play a large role in determining both

Table 2. Flux values of metal ions in a supported liquid membrane without carrier

Hour	Metal ion		
	Cu ²⁺	Ca ²⁺	Cd ²⁺
5	0	0	0
9	0	0	0
24	0.7 ^a	0.1 ^a	0.1 ^a

^a Flux units are moles/m²·s×10⁷. Blank test.

Table 3. Single flux^a of copper ion in a supported liquid membrane as a function of the carrier concentration

Hour	PolyNtnoen			
	0.0005 M	0.001 M	0.002 M	0.004 M
5	0.1	0.5	2.6	51.8
9	0.9	8.3	13.7	197.5
24	4.4	46.3	64.2	453.7

^a Flux units are moles/m²·s×10⁷

Table 4. Single flux^a of several metal ions in a supported liquid membrane^b containing 0.002 M PolyNtnoen in the membrane phase

Hour	Metal ions					
	Cu ²⁺	Zn ²⁺	Cd ²⁺	Ni ²⁺	Co ²⁺	Pb ²⁺
5	2.6	1.6	8.3	2.1	1.4	6.2
9	13.7	9.4	28.2	8.6	10.5	29.9
24	64.3	40.0	134.2	30.6	49.8	114.0

^a Flux units are moles/m²·s×10⁷. ^b Phase composition: source phase, 0.1 M M(NO₃)₂; membrane phase, Celgard 2400 film saturated with dichlorobenzene 0.002 M in the PolyNtnoen; receiving phase, diionizable water.

Table 5. Single flux of alkaline-earth metal ions in a supported liquid membrane containing 0.002 M PolyNtnoen in the membrane phase

Hour	Metal ion		
	Sr ²⁺	Ca ²⁺	Mg ²⁺
5	4.3	3.4	2.5
9	16.9	9.3	15.0
24	72.8	41.6	27.6

Flux units are moles/m²·s×10⁷. Phase composition; source phase, 0.1 M M(NO₃)₂; membrane phase, Celgard 2400 film saturated with dichlorobenzene 0.02 M in the PolyNtnoen; receiving phase, diionizable water.

transport rates and selectivities. The above results are hard to explain because the stability constants of PolyNtnoen with metallic ions have not been reported. However, the stability constants (log *K*) of Ntnoen (cavity size 4.20 angstrom) with the transition metals were investigated.⁸ The log values of the stability constants are Cu²⁺ (7.2), Ni²⁺ (5.4), Zn²⁺ (4.7),

Table 6. Competitive flux of several metal ions vs Cd^{2+} in a support liquid membrane containing 0.002 M PolyNtnoen in the membrane phase

Hour	Metal ion $\text{Cd}^{2+}/\text{Zn}^{2+}$	$\text{Cd}^{2+}/\text{Cu}^{2+}$	$\text{Cd}^{2+}/\text{Co}^{2+}$	$\text{Cd}^{2+}/\text{Ni}^{2+}$	$\text{Cd}^{2+}/\text{Sr}^{2+}$	$\text{Cd}^{2+}/\text{Pb}^{2+}$	$\text{Cd}^{2+}/\text{Mg}^{2+}$
5	1.6/1.8	5.3/5.4	1.2/1.3	2.6/0.4	4.1/4.6	10.1/8.0	3.9/3.6
9	10.0/9.8	31.4/36.3	13.6/7.8	9.8/1.6	21.6/23.2	41.2/54.6	13.9/15.4
24	39.7/35.6	135.3/125.7	30.1/33.4	36.7/3.5	78.3/84.5	180.5/188.1	55.2/54.1

Flux units are moles/m²·s×10⁷. Phase composition; 0.1 M $\text{Cd}(\text{NO}_3)_2$ /each of $\text{M}(\text{NO}_3)_2$; membrane phase, Celgard 2400 film saturated with dichlorobenzene 0.002 M PolyNtnoen; receiving phase, diionizable water.

and Co^{2+} (4.1). PolyNtnoen seemed to be similar to Ntnoen without the attachment of the alkyl group. Therefore, the trend of the variation of the stability constants of PolyNtnoen with the transition metal ions would be similar to that of Ntnoen. The flux value of Cu^{2+} ion is larger among the ions examined. This seems to be due to the highest stability constant of the ion. While the stability constant of Ni^{2+} is higher than those of Co^{2+} and Zn^{2+} , the flux value of Ni^{2+} appeared to be the smallest value. The possible reason for this discrepancy is that Ni^{2+} is more strongly hydrated than Zn^{2+} and Co^{2+} . Stronger solvation of Ni^{2+} in the aqueous source phase compared to that of Zn^{2+} would cause Zn^{2+} to be extracted into membrane faster than Ni^{2+} . The other metal ions, which are transported rapidly in any of the membrane experiments performed (Cd^{2+} , Cu^{2+} , and Pb^{2+}) are weakly hydrated in comparison to Ni^{2+} . There are two cases in which low flux value were appeared in general. One is the case low stability constant, and the other is the case of which the metallic ion hard to transfer from the membrane to the receiving phase because of strong bonding between the metallic ion and the ligand.

Although we do not have the stability constant of Cd^{2+} which showed the largest flux value in our experiment, we may be able to predict an adequate stability constant for the transport of Cd^{2+} . The flux values of alkaline earth metal ions are shown in the Table 5. The transport of Sr^{2+} was much higher than those of Mg^{2+} and Ca^{2+} ions. Ionic diameters of the alkaline earth metal ions are Sr^{2+} (1.27 Å), Ca^{2+} (1.06 Å) and Mg^{2+} (0.78 Å). The cavity diameter of PolyNtnoen is 1.35 Å. We found that the strontium ion transport through the SLM was very high. The fit of Sr^{2+} into PolyNtnoen is quite good and the highest transport of Sr^{2+} ion among these cations is not surprising.

Binary salt system. In order to test the selectivity of the systems under investigation studies of the binary transport of metal ions were carried out by placing equimolar amounts of Cd^{2+} and other metal ions in the source phase. Competitive transport data are given in the Table 6 for two component mixtures of the metal ions. We used PolyNtnoen as carrier in this study. The single species results were in

the order of $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+}$. Surprisingly different results were obtained from the competitive transport experiments (Table 6). These results underscore the dangers of extrapolating anticipated competitive transport behavior from single species measurements. There were no significant differences in the transport of Cd^{2+} , Zn^{2+} , Cu^{2+} , Co^{2+} , Sr^{2+} , Pb^{2+} and Mg^{2+} (see Table 6) through the SLM.

Cadmium ion selectivities for the transport of the above metallic ions by the SLM containing PolyNtnoen as a carrier were very poor, but high Cd^{2+} transport selectivity was observed for cadmium ion the competitive transport of Ni^{2+} . The higher degree of transport selectivity for Cd^{2+} by PolyNtnoen carrier in the supported liquid membrane system employed may be applicable to Cd^{2+} from the solution containing nickel ion.

Acknowledgment. This work was supported by a grant from the Basic Science Research Program, Ministry of Education (RSRI-93-302) and by Korea Science and Engineering Foundation (94-1400-10-01-3).

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