

Studies on the Macrocyclic Mediated Transport in a Bulk Liquid Membrane System of Transition Metal Ions

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Macrocyclic ligands have been studied as cation carriers in a bulk liquid membrane system. Cu^{2+} has been transported using nitrogen substituted macrocycles as carriers and several transition metal ions ($\text{M}^{n+} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} and Ag^{+}) have been transported using DBN_3O_2 , DBN_2O_2 , $\text{Me}_6\text{N}_4\text{14C4}$ and DA18C6 as carriers in a bulk liquid membrane system. Competitive Cu^{2+} - M^{2+} transport studies have also been carried out for the same system. In single cation transport experiments, the best macrocyclic ligand for transport is a ligand that gives a moderately stable rather than very stable complex in the extraction. However, when both cations are present in the source phase, the cation which forms the most stable complex with carrier is favored in transport over other cations. Generally, the nitrogen substituted macrocycles transport Cu^{2+} selectively over M^{n+} . Ligand structure, equilibrium constant (or stability constant) for complex formation, source phase pH and carrier concentration are also important parameters in transport experiments.

Introduction

Interest in the development of techniques for the separation of ions and molecules has increased in recent years. It is well known that ions can be transported across polymeric and liquid type membranes. 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 and by the selectivity of the membrane. Polymeric membranes have the disadvantages of usually low fluxes in the condensed phase and poor selectivities. Liquid membranes usually produce higher fluxes and selectivities.^{1,2}

Active research is recently in progress on the use of macrocyclic compounds as carriers in liquid membrane systems, in view of their capability of highly selective transport of metal ions, particularly of alkaline earth metal ions.^{3,4,5} In most of the previous works, the ion transport mediated by neutral macrocyclic carriers was evaluated in terms of the overall rate of cation transport through liquid membranes. The ion transport, being actually the salt transport when a neutral carrier is employed, consists of four major steps:⁶ first, the mobile carrier reacts rapidly at or near the membrane interface with a cation. Almost simultaneously, this carrier-cation complex reacts with an anion to form an ion pair. The second step in this mechanism occurs when this carrier-ion pair diffuses slowly across the membrane. Third, both cation and anion leave the carrier at the membrane interface on the right. This rapid reaction is reversed because of the electrolyte concentration on the left. Finally, the uncomplexed carrier slowly diffuses back across the membrane (Figure 3).

A characteristic of macrocyclic ligands which make them desirable membrane carriers is their high degree of cation

selectivity. We have shown that this selectivity is also present in membrane transport systems. For example, high transport selectivity has been observed for Pb^{2+} over many cations by using substituted crown ether.⁷ It is of interest, therefore, to examine the relationship between transport selectivities and the rates of individual cation transport through liquid membranes containing macrocyclic carriers. We have studied this relationship using several macrocyclic ligand carriers with Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Pb^{2+} , and Ag^{+} .

Experimental

Liquid membrane transport experiments were conducted as reported earlier by using a bulk liquid membrane apparatus (Figure 1) based on the concept of the Schulman bridge.⁸ Two separate water phases (one containing the salt to be transported) were separated by a dichloromethane phase which constituted the membrane. The membranes consisted of 3.0 ml of a 1.0 mM solution of the macrocyclic carrier in dichloromethane placed in the bottom of a glass vial (i.d. = 18 mm). The membrane was stirred at 25 °C for 24 hr by a 13 mm teflon-coated magnetic stirrer driven by a Hurst Synchronous motor. The two water phases were placed on top of the dichloromethane and were separated by a length of glass tube which extended down into the dichloromethane layer. The two water phases consisted of one 0.8 ml quantity of an aqueous cation solution (source phase) and the other 5.0 ml of distilled, deionized water (receiving phase). The solution of single salt source phase were 0.1 M of $\text{M}(\text{NO}_3)_2$. The solution of binary salt source phase were 0.1 M $\text{Cu}(\text{NO}_3)_2$ /0.1 M of $\text{M}(\text{NO}_3)_n$.

Each experiment was repeated three times in a room thermostated to 25 ± 1 °C. 3 ml of the receiving phase was withdrawn by a syringe at the end of 24 hr and the number of

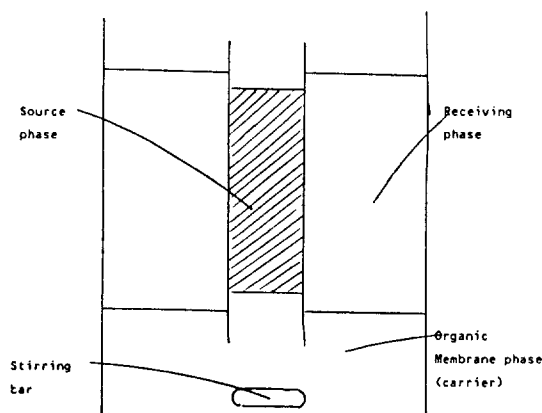


Figure 1. Bulk liquid membrane system.

Table 1. Moles Transported of In Bulk Liquid Membrane System

Source Phase	moles transported $\times 10^8$					
M^{n+}	B15C5	DB18C6	DBN ₃ O ₂	DBN ₂ O ₂	Me ₆ N ₄ 14C4	DA18C6
Co(II)	0 ^a	0	24.6	1.06	0	0
Ni(II)	0	0	1.1	0	0	0
Cu(II)	0	0	33.7	4.44	17.85	0.12
Zn(II)	0.18	0	58.7	11.20	7.45	0.04
Cd(II)	0	0	64.7	11.20	15.98	25.0
Pb(II)	0.72	16.2	34.3	8.96	0	18.5
Ag(I)		3.8	139.0	40.90	40.95	

^aUnit. moles transported/sec. m^2 (J_M).Table 2. Log K values for M^{n+} Cation in 95% Methanol at 25°C

Metal	B15C5	DB18C6 ^a	DBN ₃ O ₂	DBN ₂ O ₂	DA18C6 ^a
Co(II)			7.7	3.4	3.25
Ni(II)			9.9	3.7	3.43
Cu(II)			14.0	8.2	7.59
Zn(II)			7.5	3.0	4.31
Cd(II)			8.7 ^b		5.25
Pb(II)	2.04	1.89	8.1 ^b		6.90
Ag(I)		1.41	8.7 ^b		7.90

^aLog K for the 1:1 interaction of ligand with metal(n) in H₂O at 25°C. ^bL. F. Lindoy's unpublished data.

moles of cation was determined by atomic absorption spectrophotometer (Perkin Elmer Model 2380). The measured flux values (J_M = moles transported/sec. m^2) were multiplied by 10^8 to obtain the J_M value in Table 1 and 2. Each J_M value is the average of three separated determinations. The standard deviations are less than $\pm 15\%$. The J_M values given are valid for the CH₂Cl₂-source phase boundary. Blank experiments (no macrocyclic carrier present) were performed for each source salt solution to determine membrane leakage. No transport was detected for any of the M^{n+} studied under any of the source and receiving phase conditions when macrocyclic carriers were absent from the membrane phase.

The metal solutions were prepared in deionized, distilled

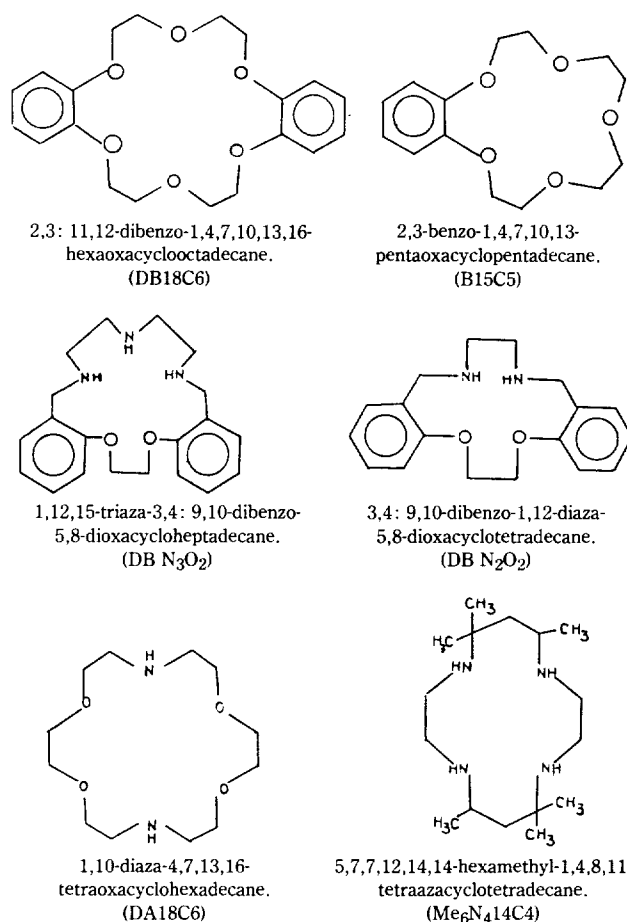


Figure 2. Structures and abbreviations for carrier molecules.

water from the highest grade materials available from the indicated suppliers. The chemicals used and their sources are: Cu(NO₃)₂, Zn(NO₃)₂ (Kanto, G.R); Co(NO₃)₂, Cd(NO₃)₂, Pb(NO₃)₂, Mn(NO₃)₂ (Junsei, E.P); Ni(NO₃)₂ (Hayashi, E.P); AgNO₃ (Hayashi, G.R); B15C5, DB18C6 (Parish) DA18C6, Me₆N₄14C4 (Merch); DBN₃O₂, DBN₂O₂ (Synthesized by our research team, Fig. 2); CH₂Cl₂ (Fluka).

Results and Discussion

Single salt systems. It was found that transition metal ions are transported very little from solutions when a crown ether having all oxygen donor atoms is used as a carrier. Crown ethers having mixed donor atoms of oxygen and nitrogen are found to be much more efficient as transition metal ion carriers. Results from the present study for the transport of Cu(NO₃)₂ using various macrocycle carriers are given in Table 1. Very little Cu²⁺ transport occurs when DB18C6 is used. This is to be expected because of the weak interaction between Cu²⁺ and DB18C6. Successive substitution of two and three oxygen donor atoms of crown ether with nitrogen results in the successive increase in Cu²⁺ fluxes as shown in Table 1 obtained using DBN₂O₂ and DBN₃O₂. We found that the Cu²⁺ transport rate increased across a dichloromethane membrane as the concentration of the DBN₃O₂ and DBN₂O₂ increased (Figure 5). The log K value for Cu²⁺-DBN₃O₂ interaction is several log K units higher than the log K value for Cu²⁺-DB18C6 interaction. The lower fluxes of transition

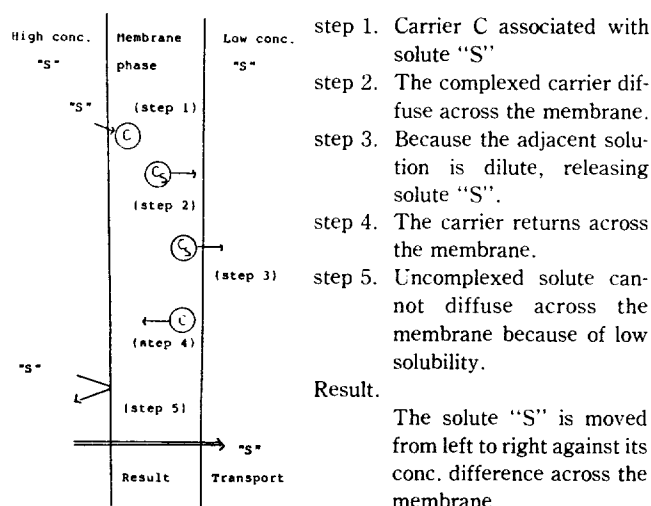


Figure 3. The basic mechanism for liquid membrane separation.

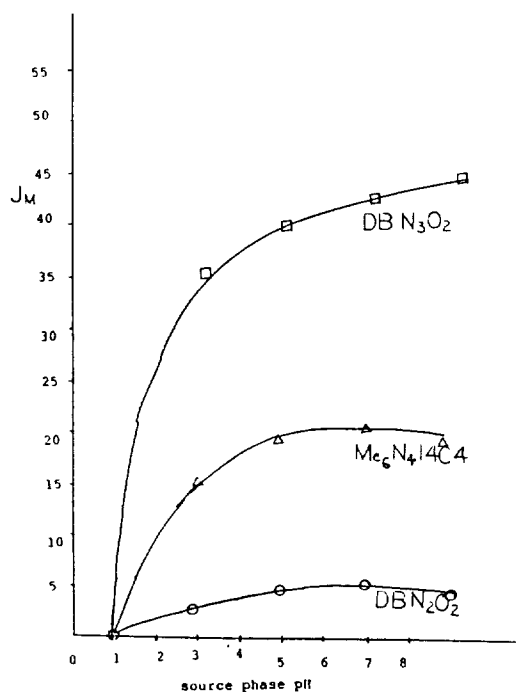


Figure 4. Plot of flux value of Cu^{2+} vs. source phase pH.

metal ions with DA18C6 relative to the other DBN_3O_2 macrocycles may be due to greater macrocycle partitioning and loss of DA18C6 to the aqueous phases because of greater solubility. The stability constants ($\log K$) for M^{n+} -macrocylic ligand interactions are listed in Table 2.^{10,12}

On comparison of the relative transport rates observed for the expected transport rates as predicted from the parameters in Table 2, only the low transport of Ni^{2+} would not be expected. A large fraction of the Ni^{2+} is present in the source phase. Since the interaction of Ni^{2+} with DBN_3O_2 in CH_3OH is similar to that of Zn^{2+} , significant transport was expected in the case of Ni^{2+} . The possible reason for this discrepancy¹³ is that Ni^{2+} is more strongly hydrated than Zn^{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 the membrane at a faster rate than Ni^{2+} , all other factors being equal. The other metal ions, which are transported rapidly

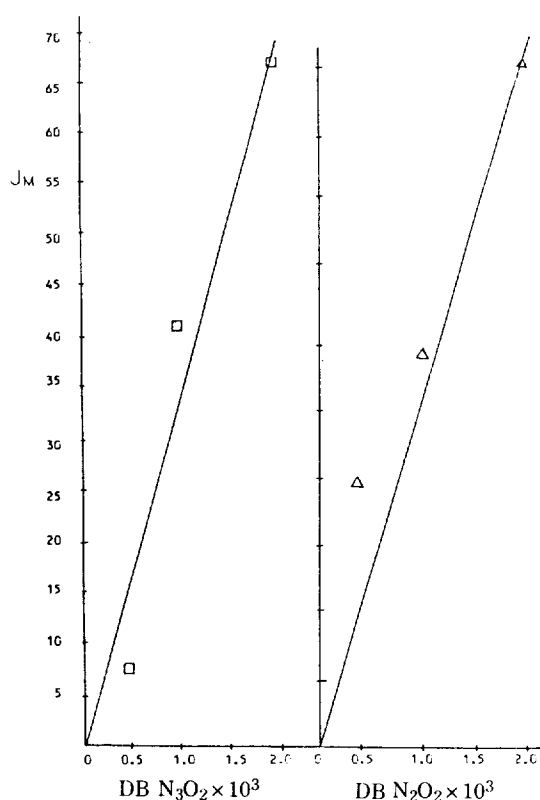


Figure 5. Effect of carrier concentration on Cu^{2+} transport in bulk liquid membrane system.

dly in any of the membrane experiments performed (Cd^{2+} , Co^{2+} , Cu^{2+} , Pb^{2+} and Ag^+) are very weakly hydrated in comparison to Ni^{2+} .

In the case of Ag^+ , very fast Ag^+ transport occurs when DBN_3O_2 and DBN_2O_2 are used as carriers. Because two NO_3^- anion must accompany one transition metal ion (Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Cd^{2+}) in transport while only one NO_3^- anion per Ag^+ cation is necessary for Ag^+ transport. The number of anions per cation which must be dehydrated for transport to occur significantly affects the distribution coefficient of the transported moiety. Transported amount for Cu^{2+} has been found to be affected by the pH of the source phase. The effect of the acidity of the aqueous source solution is shown in Figure 4. In particular, when the pH of the solution is increased, the transported yield steeply increases until it reaches a constant value. This qualitatively indicates that both H^+ and Cu^{2+} compete for nitrogen donor atom of macrocyclic ligand.^{14,15} When DBN_3O_2 is protonated, it can not bind the transition metal ions. When source phase pH is very low (pH = 1), the donor atoms of macrocyclic carrier are all protonated. When source phase pH is too high (pH = 9), copper hydroxide precipitation occurs. Therefore the amount of Cu^{2+} transported decreased.

Binary salt systems. In order to test selectivity of the systems under investigation studies of binary transport of metal ions were carried out by placing equimolar amounts of Cu^{2+} and transition metal ions in the source phase. In Table 3 are listed competitive transport experimental data for binary systems containing Cu^{2+} and one other cation. A striking feature of the data in Table 3 is almost universal as transport selectivity is demonstrated by the macrocyclic ligands for Cu^{2+} over the other cations. This indicates that

Table 3. Moles of Cu(II) and M(II) Transported Simultaneously in Bulk Liquid Membrane System

Source Phase ^a	moles transported $\times 10^8$				
Cu(II)/M(II)	DB18C6	DBN ₃ O ₂	DBN ₂ O ₂	Me ₆ N ₄ 14C4	DA18C6
Cu/Mn	.	38.9 ^b /0	4.46/0	10.0/0	0.12/0
Cu/Co	.	38.7 /0	4.56/0	10.4/0	0.13/0
Cu/Ni	.	37.8 /0	4.56/0	9.8/0	0.21/0
Cu/Zn	.	36.9 /0.1	3.73/0.2	13.4/0.03	0.21/0
Cu/Cd	.	38.3/0.2	3.76/0.1	8.5/0	0.13/0.06
Cu/Pb	.	37.4/0.4	5.05/0.6	10.9/0	0.17/6.7

^aSource phase is 0.1 M Cu(NO₃)₂ 3H₂O plus 0.1 M M(NO₃)₂ nH₂O in water. ^bUnit: moles transported/sec·m²·(J_M).

DBN₃O₂ is an excellent carrier for the selective transport of Cu²⁺ in the presence of one other cation. The large transport selectivity for Cu²⁺, which allowed only minimal flux of any other cation, unexpected in light of previous transport experimental results involving single cation source phases, wherein Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ were transported at significant rates by DBN₃O₂. For example, in single cation source phase experiments Cu²⁺ was transported at 33.7×10^{-8} mol/sec·m² and Cd²⁺ at 64.7×10^{-8} mol/sec·m² by DBN₃O₂. However, when the two metal ions are present in the source phase, the mole ratio of Cu²⁺/Cd²⁺ transported is 38.3/0.2 (Table 3). This result is likely due to the relative stability of the complex of Cu²⁺ (log K, 14.0) and Cd²⁺ (log K, 8.7) with DBN₃O₂. Because stability constant of the DBN₃O₂ with Cu²⁺ in binary cation system is sufficiently large, release of other cation into receiving phase is inhibited. The high degree of transport selectivity for Cu²⁺ by the DBN₃O₂ carriers studied has significant implications. Incorporation of DBN₃O₂ which are selective for Cu²⁺ into liquid membranes may be used to remove Cu²⁺ from environmental system. In a broader sense, these experiments demonstrate the poten-

tial application to selective removal, concentration, purification of Cu²⁺ or other metallic elements from mixture.

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Synthesis of Acyclic Nucleosides of 2-Thio-Pyrimidines and -Purines Using a New Coupling Agent of Lithium Bromide

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Acyclic nucleosides, 1-[[1,3-bis(benzyloxy)-2-propoxy]methyl]-2-thiopyrimidine, 9-[[1,3-bis(benzyloxy)-2-propoxy]methyl]-6-amino-2-thiopurine, 1-(2-acetoxyethoxymethyl)-2-thiopyrimidine, and 9-[[1,3-bis(benzyloxy)-2-propoxy]methyl]-6-amino-2-thiopurine have been synthesized by coupling pyrimidine and purine bases with acyclic acetates using a new coupling reagent of lithium bromide in the presence of trifluoro acetic acid in acetonitrile.

Introduction

Intensive study has been recently directed toward the synthesis of acyclic nucleosides including analogues of acyclovir since acyclic nucleosides such as 9-(1,3-dihydroxy-2-

propoxy)methyl guanine,^{1,2} and 9-(2-hydroxyethoxy methyl) guanine³ of acyclic analogues of guanosine have been found to be a potent and selective antihyperpetic agent together with less toxicity in side effects in comparison with those from guanosine derivatives and 2'-deoxy guanosine. Among the