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Study on Separation of Heavy Metal Ions in A Neutral Macrocycle-Mediated Emulsion Liquid Membrane System

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The preferential transport phenomena of neutral cation-anion moieties in neutral macrocycle-facilitated emulsion liquid membrane were described in this study. Emulsion membrane systems consisting of (1) aqueous source phase containing 0.001 M $M(NO_3)_2$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+}, and Pb^{2+}) (2) a toluene membrane containing 0.01 M ligand (DBN_3O_2, DA18C6, DT18C6, TT18C6, HT18C6) and the surfactant span 80 (sorbitan monooleate) (3% v/v) and (3) an aqueous receiving phase containing $Na_2S_2O_3$ or $NaNO_3$ were studied with respect to the disappearence of transition metal ions from the source phase as a function of time. Cation transports for various two component or three component equimolar mixture of transition metal and Cu^{2+} in a emulsion membrane system incorporating macrocyclic ligand (HT18C6) as carrier were determinded. Cu^{2+} was transported higher rates than the other M^{2+} in the mixture solution. Equilibrium constants for cation-source phase co-anion, cation macrocycle and cation-receiving phase reagent interaction are examined as parameters for the prediction of cation transport selectivities.

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 liquid type 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 and by the selectivity of the membrane. Liquid membranes usually produce higher fluxes and selectivities[2,3]. We examine the influence of structural variation within series of crown ether carriers upon the selectivity and efficiency of metal ions transport across three types of liquid organic membranes. The three membrane types are bulk liquid membrane[4], emulsion membrane[5] and polymer-supported liquid membranes[6]. One of the techniques for use in separation of metal ions from solution is the water-in-oil emulsion into a water source phase. The water-in-oil emulsion is stabilized by a surfactant, such as span 80 (sobitan monooleate). The emulsion membrane systems were first introduced by Li[7] in 1968. They can be made by stirring a water-in-oil emulsion into a water source phase. The water-in-oil emulsion is stabilized by a surfactant. The interfacial area of emulsion membranes per unit volume is large because of the small size of the emulsion globules that are stirred into the source phase. The membrane is also very thin, and both of these features are desirable to enhance the cation flux. The transport process consists of the following sequence of steps[8]: (1) complexing of M^{n+} by carrier to form M^{n+}-carrier: (2) M^{n+}-carrier partitioning with an anion such as A^{n-} into the organic membrane: (3) diffusion of the species $(M^{n+})_n$-carrier-$(A^{n-})_n$ across the membrane: (4) release of M^{n+} and A^{n-} into receiving phase containing a sink anion, which complex with the M^{n+}, diffusion of carrier back across the membrane to the source phase/membrane interface where the cycle is repeated. A characteristic of macrocyclic ligands (Figure 2) which make them desirable membrane carriers is high deg-
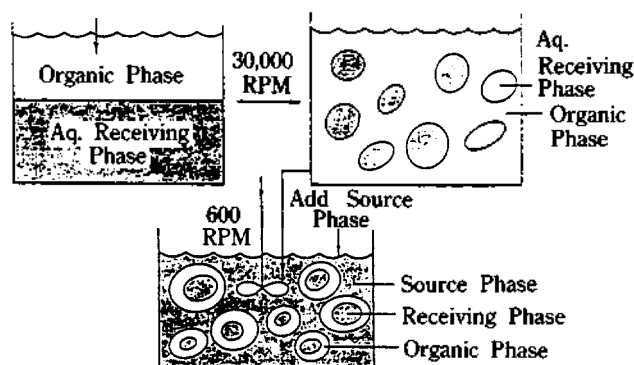

Figure 1. Emulsion liquid membrane system.

ree of cation selectivity. It has shown that this selectivity is also present in membrane transport system. It is of interest, therefore, to examine the relationship between transport seletivities and the rates of individual cation transport through emulsion membranes containing macrocyclic carriers. We have studied this relationship by using several macrocyclic carriers with transition metal ions.

Experimental

The emulsion liquid membrane (Figure 1) was prepared from the organic membrane phase, the aqueous source and receiving phases. The organic phase consisted of toluene in which was dissolved macrocyclic carrier (0.02 M) and 3% v/v of the nonionic surfactant sorbitan monooleate (span 80, Hayashi, E.P). The internal (receiving) aqueous phase contained either $Na_2S_2O_3$ (Hayashi, E.P) or $NaNO_3$ (Junsei, E.P). The external (source) phase contained either LiSCN (Shinyo, E.P) or LiBr (Wako, E.P). These source phases also contained $M(NO_3)_2$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+}, and Pb^{2+}). The source phase or the receiving phase, as needed, contained $LiNO_3$ (Kanto, G.R) at a concentration necessary to equalize the ionic strength of 1.0. The metal solutions were prepared in deionized, distilled water from the highest
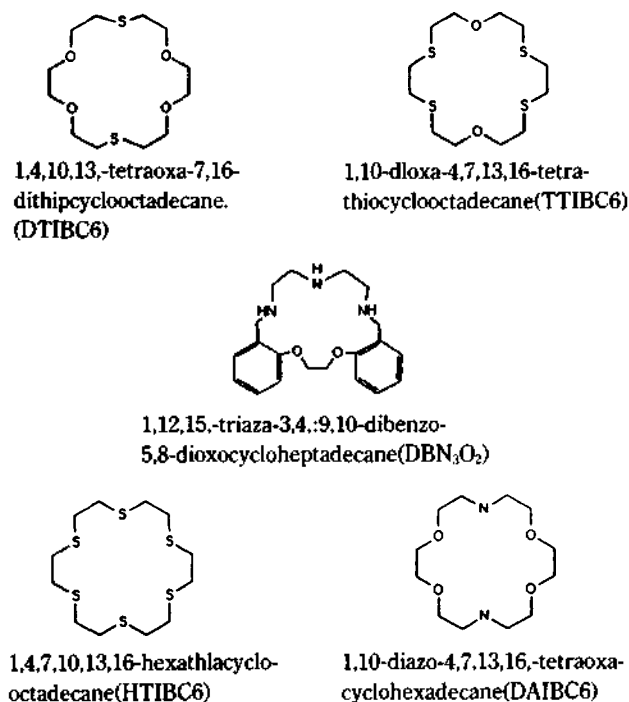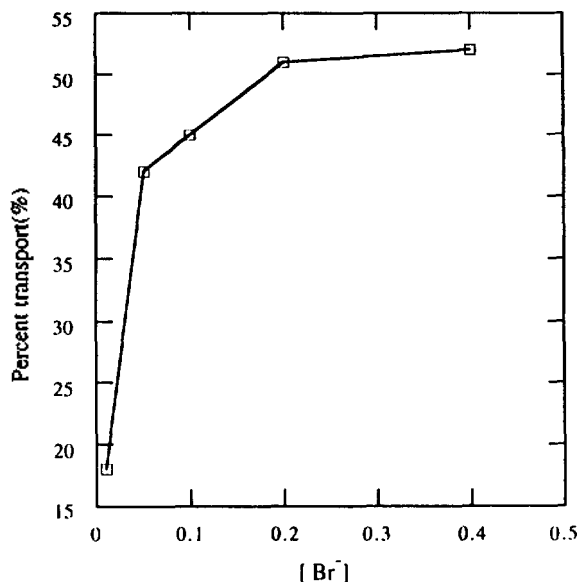
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1,4,10,13,-tetraoxa-7,16-
dithipcyclooctadecane.
(DTIBC6)

1,10-dloxa-4,7,13,16-tetra-
thiocyclooctadecane(TTIBC6)

1,12,15,-triaza-3,4,:9,10-dibenzo-
5,8-dioxocycloheptadecane(DBN$_3$O$_2$)

1,4,7,10,13,16-hexathlacyclo-
octadecane(HTIBC6)

1,10-diazo-4,7,13,16,-tetraoxa-
cyclohexadecane(DAIBC6)

Figure 2. Macrocyclic ligands used in this study.

Table 1. Single Transport of Several M^{2+} in an Emulsion Liquid Membrane Containing 0.4 M SCN$^-$ in Source Phase and S$_2$O$_3^{2-}$ in the Receiving Phase

Soruce Phase	Percent Transport			
M^{2+}	DA18C6	DT18C6	TT18C6	HT18C6
Mn	30.9	17.6	0.0	5.9
Co	27.6	0.0	3.9	0.0
Ni	3.6	0.9	0.0	3.6
Cu	72.1	68.2	73.0	89.1
Zn	31.2	13.3	0.8	2.1
Sr	8.6	0.0	0.0	2.4
Cd	87.0	15.2	0.8	3.9
Pb	96.0	57.7	6.9	9.1

Percent transport in a 0.4 M SCN$^-$/0.01 M ligand in tolune/ 0.282 M S$_2$O$_3^{2-}$ emulsion membrane.

Table 2. Log K Values for M^{2+} Cation in 95% Methanol at 25°C

M^{2+}	DBN$_3$O$_2$	DA18C6^a	DT18C6	TT18C6	HT18C6
Mn		2.5			
Co	7.7	2.5	d		c
Ni	9.9	2.5	d		c
Cu	14.0	6.2	6.1		2.3^b
Zn	7.5	3.2			
Sr		2.6			
Cd	8.7	5.3			
Pb	8.1	6.9	3.1^a		

^{a}Log K for the 1:1 interaction of ligand with M^{2+} in H$_2$O at 25°C. ^{b}Log K for the 1:1 interaction of ligand with M^{2+} in 85% MeOH. ^{c}No complexation in 85% MeOH, ^{d}Too small.

Figure 3. Single transport of Cu^{2+} in emulsion liquid membrane as a function of Br$^-$ concentration in source phase.

Samples of the original source phase solutions were also taken, all samples were analyzed for cation concentration by atomic absorption spectrophotometry (perkin Elmer Model 2830). The experiments were done in triplicate with fresh emulsions prepared each time.

Results and Discussion

grade materials available from the indicated suppliers. The chemicals used and their sources are: Cu(NO$_3$)$_2$, Zn(NO$_3$)$_2$ (Kanto, G.R); Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$, Cd(NO$_3$)$_2$, Pb(NO$_3$)$_2$, Mn(NO$_3$)$_2$ (Junsei, E.P); Ni(NO$_3$)$_2$ (Hayashi, E.P); Toluene (Hayashi, E. P); HT18C6, DT18C6, TT18C6 (Parish); DA18C6 (E. Merch). In each experiment, the emulsion (1.8 m*l*, consisting of the membrane and receiving phases) and source phases (9 m*l*) were stirred together continuously at 25°C and 600 rpm with an inserted glass propeller in a weighing bottle for a period of time. Thirty seconds were allowed for the membrane and the source phase to separate upon cessation of stirring before sampling the source phase.

When neutral macrocyclic ligands are used to mediate metal ion transport, anion must accompany the M-macrocycle complex to maintain the electrical neutrality. The largest metal ion transport rates were found either if anion had a small negative free energy of hydration or if the cation interacted with anion to form ion pair[9]. The percentage of Cd^{2+} transported (shown in parentheses)[10] as a function of [A$^-$] was SCN$^-$(82), I$^-$(77), Br$^-$(22) and Cl$^-$(8). The order of decreasing transport using the several A$^-$ species is also the order of increasing degree of hydration for A$^-$. A study of Cu^{2+} transport with varying [SCN$^-$] could not be carried out since Cu(SCN)$_2$ is insoluble in aqueous solution. Therefore, we studied Cu^{2+} transport with [Br$^-$] instead of [SCN$^-$]. The transport of Cu^{2+} with varying source phase [Br$^-$] in a Br$^-$/toluene/S$_2$O$_3^{2-}$ emulsion membrane is shown

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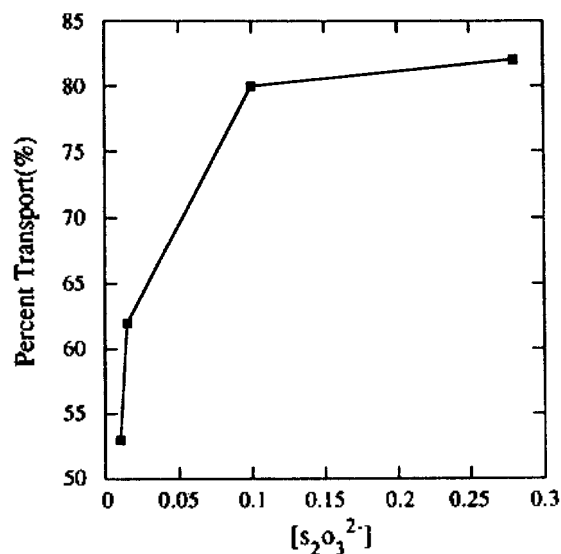
Figure 4. Transport of Cu^{2+} in emulsion liquid membrane as a function of $S_2O_3^{2-}$ concentration in receiving phase by DBN_3O_2.

Table 3. Log K Values for Complexation of M^{2+} and Anion

Cation / Anion	Pb	Cu	Cd	Mn	Ni
$S_2O_3^{2-}$	5.1	12.2	6.4	'	'
NO_3^-	'	'	'	'	'

*Lange's Handbook of Chemistry. ' We have not found these data.

Table 4. Competitive Transport of Several M^{2+} *vs.* HT18C6 in an Emulsion Liquid Membrane

M^{2+}	Percent Transport	M^{2+}	Percent Transport
	Cu^{2+} / M^{2+}		Cu^{2+} / M^{2+}
Mn	21.9 / 5.9	Sr	25.2 / 0.0
Co	15.9 / 0.0	Cd	40.3 / 5.5
Ni	31.9 / 6.3	Pb	11.7 / 4.5
Zn	20.1 / 2.5		

Transport after 5 minutes.

Figure 5. Single transport of several M^{2+} in emulsion liquid membrane as a kind of NO_3^- or $S_2O_3^{2-}$ in the receiving phase by DBN_3O_2.

in Figure 3. The percent transport of Cu^{2+} approaches 20% as [Br^-] becomes small, but that of Cu^{2+} predominates when the concentration of [Br^-] become 0.2 M. Results from the present study for the transports of transition metal ions using various macrocycle carriers are given in Table 1. In the experiment for the transition metal ion transport, metal ion-macrocycle interaction has an influence in the transport rates. Significant transport with DA18C6 was observed for Pb^{2+}, Cd^{2+} and Cu^{2+}. The log K for the Pb^{2+}-DA18C6 interaction is higher than that for the other cation. Therefore, transport of Pb^{2+} is very high. In Table 2, stability constants are given for the interaction of transition metal ions with macrocyclic ligands. The log K for the Cu^{2+}-HT18C6 interaction is several log K unit higher than the log K value for another metal ion-HT18C6 interaction. Therefore, the signifi-

cant transport was observed for Cu^{2+} over all the other metal ions tested.

The percent transport of Cu^{2+} in emulsion liquid membrane as a function of receiving phase anion by DBN_3O_2 are presented in Figure 4. Generally a direct correlation is found between the log K value of the metal ion to anion and the amount of metal ions transported. In order for metal ion transport to occur, the log K value of the metal ion to anion must be larger than that of metal ion with macrocyclic ligand. The transport of the cation from the source phase into the organic phase requires that a stable M^{n+}-macrocycle complex be formed.

However, the stability of this complex must be lower than that of the M^{n+}-anion species in the receiving phase in order for metal ion transport to occur. When NO_3^- is present in receiving phase, the transport of metal ions were low. The effect of NO_3^- in the receiving phase is minimal since M^{2+}-NO_3^- interaction is weak for all cations. In Figure 5, $S_2O_3^{2-}$ in replacement of NO_3^- in the receiving phase enhances the transport of all the cations since M^{2+}-$S_2O_3^{2-}$ interaction is greater than M^{2+}-NO_3^- interaction. In Table 3, further more, the relative amount of enhancement influence the stability constant of M^{2+}-$S_2O_3^{2-}$ interaction. We expect that Cu^{2+}-M^{2+} separation would be enhanced by the presence of $S_2O_3^{2-}$ in the receiving phase, because Cu^{2+}-$S_2O_3^{2-}$ interaction are the largest in this studied system.

Time-dependent studies as a fuction of initial metal salt concentration for Cu^{2+}-M^{n+} mixtures are given in Table 4 and 5. The highest initial transport in each mixture was found with Cu^{2+} which is also the cation which form the more stable complex with HT18C6. In Table 4 and 5, small amount of the Cu^{2+} was transported in 5 minutess and the transport selectivity of Cu^{2+} *vs.* M^{2+} is very poor, but large amount of the Cu^{2+} was transported in 7 minutes and the transport selectivity of Cu^{2+} *vs.* M^{2+} is very high. We know that equilibrium state need 7 minutes in this emulsion membrane system. Competitive transport data are given in Table 5 for two component mixtures of metal ions. We used HT18C

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Table 5. Competitive Transport of Several M^{2+} vs. HT18C6 in an Emulsion Liquid Membrane

M^{2+}	Percent Transport	M^{2+}	Percent Transport
	Cu^{2+} / M^{2+}		Cu^{2+} / M^{2+}
Mn	99.6 / 0.0	Sr	99.6 / 3.8
Co	97.2 / 6.7	Cd	97.2 / 3.4
Ni	91.4 / 0.0	Pb	92.4 / 8.2
Zn	92.4 / 8.2		

Transport after 7 minutes.

Table 6. Competitive Transport of Three Component Mixture in an Emulsion Liquid Membrane

M_1^{2+}	M_2^{2+}	Percent Transport		
		Cu^{2+}	M_1^{2+}	M_2^{2+}
Mn	/ Ni	87.0	/ 1.3	/ 2.2
Co	/ Cd	75.2	/ 0	/ 1.0
Zn	/ Sr	85.6	/ 0	/ 0
Cd	/ Pb	86.0	/ 1.6	/ 1.5

Transport after 7 minutes.

6 as carrier in this study. Significant transport was observed for Cu^{2+} over all the other metal ions tested. Experiments were carried out by placing equimolar amounts of Cu^{2+} ion and transition metal ions in the source phase. In Table 6 are listed experimental data of competitive transport for three component systems containing Cu^{2+} ion and two other metal ions. Binary result can in most case be extended to the ternary system since competition for a single ligand occur in both binary and ternary systems. Cu^{2+} was found the highest transport in each mixture. Log K data indicate that the Cu^{2+}-HT18C6 complex is more stable than those of transition metal cation, which is consistent with high Cu^{2+}

transport and low other metal ion transport in the HT18C6. Cu^{2+} bind the carrier in the membrane and is transported, while little carrier remains available to bind and transport other cations. The selective transport of Cu^{2+} over other cations with HT18C6 is a reflection of the greater affinity of HT18C6 for Cu^{2+} compared to that for the other cation. The highest degree of transport selectivity for Cu^{2+} by HT18 C6 carrier in this emulsion membrane system employed may be applicable to remove Cu^{2+} from the solution containing several heavy metal ions, especially from waste water.

In a sense for commercial or analytical application, the emulsion membrane system can be employed for the separation of Cu^{2+} from several metal-containing species.

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A Sensitivity Analysis for Three-Parameter Ellipsometry

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In the three-parameter ellipsometry (TPE), also known as reflectance-ellipsometry, the ellipsometric measurements, Ψ and Δ, are combined with the reflectometric measurement, R, to determine the optical parameters and the thickness of a light-absorbing thin film. The constant Ψ, Δ, and R surfaces are analyzed graphically to understand the nature of the TPE solutions. A sensitivity analysis is shown to be useful not only for identifying the film properties which affect most the TPE measurements, but also for estimating errors in film properties arising from the uncertainties in measurements.

Introduction

In conventional ellipsometry, the change in the polarization

of the light reflected from surface covered by thin film is measured to determine the optical properties of the film[1,2]. Because of the surface selectivity and the high sensitivity