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Separation of the Heavy Metals by macrocycles-mediated Emulsion Liquid Membrane Systems

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Abstract

Result of this study indicate that two criteria must be met in order to have effective macrocycle-mediated transport in these emulsion system. First, one must effective extraction of the post transition metals, Cd^{2+}, Pb^{2+} and Hg^{2+},into toluene membrane. The effectiveness of this extraction is greatest if log K values for the metal-macrocycle interaction is large. Second, the ratio of the log K values for the metal ion-receiving phase to the metal ion-macrocycle interaction must be large enough to ensure quantitative stripping of the metal ion at the toluene phase interface. Control of the first step can be obtained by appropriate selection of macrocycle donor atom, substituents, and cavity radius. The second step can be controlled by selecting the proper complexing agent for inclusion in the receiving phase. The order of the transport, when using the several A^- species such as SCN^-,I^-,Br^- and Cl^- is the order of the changing degree of solvation for A^- and the transport of the metals is also affected by the control of concentration for receiving species because of solubility-differences. In this study, we can seperate each single metal ion from the mixture of Cd^{2+}, Pb^{2+}, and Hg^{2+} ions by using the toluene membranes controlled by optimized conditions. Transport of the single metal is also very good, and alkaline and alkaline earth metals as interferences ions did not affect the seperation of the metals in this macrocycle-liquid membrances but transition metal ions were partially affected as interferences for the post transition metal ions.

Key words : Heavy metals, Macrocycle-emulsion Liquid membrane, Transport, Seperation, Concentration.

1. Introduction

Heavy metal cation like Ti^+, Cd^{2+}, Hg^{2+}, Pb^{2+} are very toxic(Bremer, 1973 ; Catshetal, 1975). The design of highly selective ligands which may remove hamful cations(Williams, 1976) while only minimally affecting the levels of the biologicaly important ones(Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+})(Williams, 1970 ; Martell, 1975) is both fundamental interest providing strategies for selectivity control and potential practical importance for therapeutical decorporation or administration allowing the selective removal of toxic cations from their transport into organisms as well as the control of metal ions in the environment(Hirosh : et al., 1989).

The development of new techniques for metal recovery from waste solutions has received a great deal of attention in recent year. One of the techniques for use in recovering metal cations from solution is the water-oil-water emulsion membrane.

Such membrane systems containing macrocycles of the cyclic polyether type can be designed to facilitate the carrier-mediated selective transport of cations from mixtures of two or more metal ions. The advantages of the emulsion membranes over liquid-liquid extraction in separation systems have been noted(Nakatsuji et al., 1985).

Transport in the emulsion membrane system requires that the cation bind with the macrocycle at the source phase-membrane interface, move across the organic phase due to a concentration gradient, and be released by the macrocycle and complexed by a complexing agent in the receiving phase. Transport is most effective (1) when macrocycle partitioning is favored by the organic phase due to a decidedly higher macrocycle solubility in the organic solvent than in water, and (2) when the macrocycle binds strongly with the cation to be transported, but binds less strongly to the cation than the receiving phase complexing agent does. Hence, the important parameters involved in choosing a macrocycle to transport a particular cation are the relative magnitudes of the log K values of the cation-macrocycle and cation-complexing agent complexes, and the distribution coefficient of the macrocycle beteen the organic solvent and water. In competitive transport experiments involving mixtures of ions, selective cation-macrocycle interaction becomes an important createrion for choosing a macrocycle to achieve transport selectivity.

The effects of the following factors on cation transport in emulsion membranes were studied : receiving phase anion type(Christensen et al., 1983), macrocycle concentration(Christensen, (Izatt et al., 1983, 1982), receiving phase anion concentration(Christensen et al., 1983), source phase cation mixtures(Izatt et al., 1983, 1984) source phase anion concentration, Izatt et al, 1984), and source phase cation type(Izatt et al., 1983, 1984). The transport of heavy metals by emulsion membrane that has not been studied in the other laboratory was studied by using the macrocycles that the log K value of cation-macrocycle are various and that the distribution coefficient various. In the present paper, macrocycles of varying size, substituent groups, donor atoms, and ring number are compared with their ability to transport of

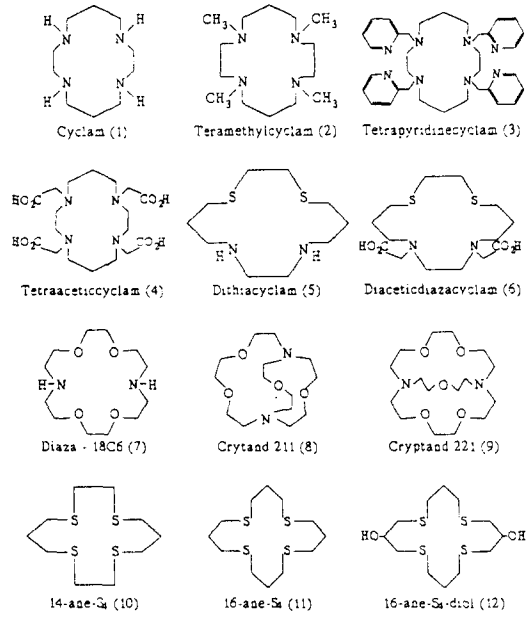

Figure 1. Stuctures of macrocycles

post transition metal ions. All other parameters are held constant. The selection of post transition metal ions was based on the obserd ability of cations to transport well in this emulsion systems.

2. Experimental

Emulsion Liquid Membrane Transport of Cd^{2+}, Pb^{2+} and Hg^{2+} by Macrocycles Materials : The emulsion membrane(Figure 2) was prepared

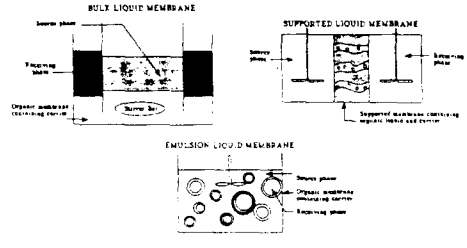

Figure 2. Representation of Bulk, Supported, and Emulsion Liquid Membrane Type.

from an organic membrane phase and from aquous source and receiving phase as described. The organic phases consisted of a 10-2M-macrocycles(Figure 1) solution in toluen (Fisher), which was 3%(V/V) in the nonionic surfactant, sorbitant monooleate. Blank experiments were performed with macrocycles absent from the pure toluene phase. One set of source phases contained either 0.2M Li(SCN), LiCl, LiBr or NaI (Millinckrot). The source phases also contained either 10^{-3} M $Hg(NO_3)$ for competive transport experiments. The lithium and sodium salts were used because it has been shown that macrocycles(Figure 1) form weak complexes with Li^+ and Na^+. Thus, Li^+ and Na^+ in the receiving phase would not compete with the cations of the source phase for the macrocycle carrier in the membrane. For the experimenters to discuss the effects of coextensive ions, the source phase contained 2×10^{-1}M NaSCN along with 10^{-3}M $Cd(NO_3)_2$, $Pb(NO_3)_2$, $Hg(NO_3)_2$ and/or $Cu(NO_3)$, $Zn(NO_3)_2$, $Li(NO_3)_2$, $Na(NO_3)$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Fe(NO_3)_2$, and Li (NO_3)(Fischer, Baker and Sargent-Welch) at a concentration of 10^{-3}M. Experiments were performed with all of the above the source phase both with and without 3.0×10^{-1}M $Na_2S_2O_2$ and $Na_4P_2O_7$ (Fluka) in the receiving phase(Izatt et al., 1986) as need, to balance the ionic strengths of these phases.

Experimental Procedure and Analysis ; The blended emulsion(1.2mℓ) was then place on top of 6mℓ of the aqueous source phase in each of six small bottles with ground glass tops. The bottles had an internal diameter of 24mm and a height of 51mm. The aqueous source phase contained 0.0002 M $Pb(NO_3)_2$, $Cd(NO_3)_2$, or $Hg(N_3)_2$(Aldrich). The emulsion was stirred into the source phase solutions(see Figure 2) with a teflon magnetic stirrer bar at 600 rpm at room temperature(25+0.1℃). The magnetic stirring bars were 22mm long. Stirring was stopped at a different time for each bottle corresponding to 3, 6, 9, 15, 20, and 25 minute intervals. After stirring was stopped, a settling period of 3 minutes was allowed for separation of the emulsion and sorce phases before sampling the source phases. A sample of the source phase solution was taken also, at zero time, before exposure to the emulsion. Metal concentrations analyses were carried out using a Thermo-Janeral Ash-Environ-II type ICP emision spectrophotometer. Each experiment was done at least in triplicate with preparation of fresh emulsions for each determination at the six different time intervals.

The effect on metal ion analysis of small amounts of $Li_4P_2O_7$ from emulsion breakage was determined by adding known amounts of $Li_4P_2O_7$ to a known metal ion solution and analyzing the resulting solution for metal in by ICP emission sprctrophotometry. Each sample taken during the emulsion membrane transport was analyzed for Li^+ as well as metal ion so that the effect of $Li_4P_2O_7$ could be subtracted from the readings in order to determine the true metal ion concentration.

3. Results and Discussion

The effects of source and receiving phases for separation of post metals : The αi values presented in this paper are defined as the fraction of the toal M(m) concentration present as an MAi complex(i. e $\alpha i=[MA_i]\sum_{j=0}^{n}[MA_i]$ where the charges are omitted for simplicity). In table 1, the α_2 value for M(m)(M(m)=Cd(II) Hg(II), and Pb (II)) is given where $A=SCN^-$, I^-, Br^-, or Cl^- and the $[A^-]$ is such that α_2 for Cd(II)-Hg(II) separation is predicted from the values in Table 1. For $A=I^-$ or Br^-, selective transport of Cd (II) over both Hg(II) and Pb(II) should occur, but the rate of Cd(II) transport should decrease compared to the case where A=SCN since α_2 is less when $A=I^-$ or Br^-. When $A^-=Cl^-$, Cd(II)-

Pb(II) separation should be poor and there should be less Cd(II)-Hg(II) separation than in the order A^- cases.

As stated in the introduction, M(m)-nacrocycle and M(m)-receiving phase agent interaction also influence selectivity. The constants for M(m) interaction with macrocycles (carrier) in water and methanol-aceton were given earlier(Jung, 1993) and those for M(m) interaction with $S_2O_3^{2-}$ and $P_2O_4^{4-}$(receiving phase agent) in water are obtaind from references(Izatt. et al., 1987), where M(m)=Cd(II), Pb(II), Hg(II), and Zn(II). we expected that post metal ion-selectivity would be higher than Zn^{2+}-selectivities because the constants for Zn(II)-interaction with macrocyles studied are lower than those of post transition metals.

The results of the transport experiments were given in Figure 3-4 and Table 1-2. when NO_3^- is present in receiving phase, the relative transport rates of the Cd^{2+}, Pb^{2+}, and Hg^{2+} match well the α_2^{0-} based predictions. The effect of NO^{3-} in the receiving phase is minimal since M(II)-NO^{3-} interaction is weak for all three cations(Izatt, 1987). we expected that the selective transport of Cd^{2+} over the Pb^{2+} and Hg^{2+} would be improved if the concentration and varieties of the source

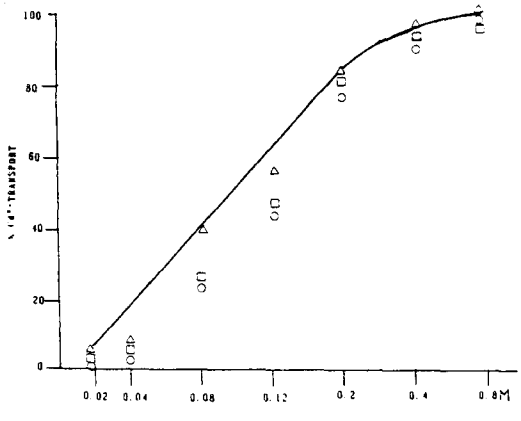

Figure 3. Plot of %-Transport of Cd^{2+} vs. Concentration of SCN-as Source Phase in NO_3^-(○), $S_2O_3^{2-}$(△), and $P_2O_7^{4-}$(□) as Receving Phase after 15 Minutes.

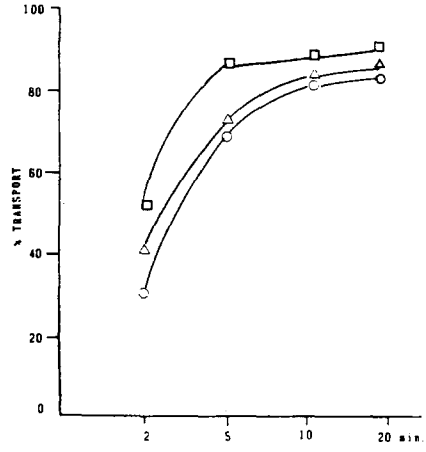

Figure 4. Plot of %-Transport of Cd^{2+}(○) Pb^{2+}(△) and Hg^{2+}(□) vs. Stirring Time in 0.4M SCN^- and 0.56M Cl^- as Source Phase using the 0.02M Macrocycle 4 in Toluen/0.282M NO_3^-, $S_2O_3^{2-}$, and $P_2O_7^{4-}$ Emulsion Membrane, the M(m) are present at 0.001M.

and receiving phase are optimized in emulsion membrane with macrocycles.

Separation of Cd^{2+} over Pb^{2+} and Hg^{2+} ; The selective transports of Cd^{2+} over Pb^{2+} and Hg^{2+} were enhanced under condition of 0.4M-SCN^- and NO_3^- as source and receiving phase, respectively. And the selective transport of the other post transition metal ions could be improved by proper selection of carrier agent. The addition of $S_2O_3^{2-}$ to the receiving phase enhances the transport of all three metals due to the interaction of all three with $S_2O_3^{2-}$ for the macrocycles studied in this section. As predicted, however, the selectivities of Cd^{2+} transport compared to Pb^{2+} trans-

Table 1 Fraction of Cd(II), Pb(II), Hg(II) Present as MA_2 in the Source Phase as a Function of A^-

		$a°_2$		
A^-	$[A^-]M$	Cd^{2+}	Pb^{2+}	Hg^{2+}
SCN^-	0.40	0.47	2×10^{-3}	9×10^{-5}
I^-	0.04	0.26	1.2×10^{-3}	1×10^{-3}
$Br^{0.30-}$	0.30	0.303	0.22	1×10^{-3}
Cl^-	0.56	0.44	0.16	0.02

$a°_2$: The fraction of M(m) presen as MA_2.[The $a°_2$ values were calculated from $\log\beta(_2O)$ values for formation of MAn^{2-n}(Izatt, 1982)]

Table 2 Competive Transport of Cd(II), Pb(II), and Hg(II) with Maximum CdA_2 in the Source Phase and NO_3^-, $S_2O_3^{2-}$, and $P_2O_7^{4-}$ in the Receiving Phase as a Function of A^-

			Percent Transport							
			NO_{3-}			$S_2O_2^{2-}$			$P_2O_7^{4-}$	
A^-	$[A^-]M$	time(min)	Cd^{2+}	Pb^{2+}	Hg^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}	Cd^{2+}	Pb^{2+}
SCN^-	0.4	5	86	8	2	99	64	32	10	86
I^-	0.04	5	89	5	12	98	82	87	12	84
Br	0.3	20	46	16	4	24	39	95	4	90
Cl	0.56	20	28	18	8	18	32	90	19	87

a : percent transport in aquous source phase/0.02M-macrocycle 4 in toluen/0.2840 NO_3^- or $P_2O_7^-$ emulsion membrane, the m(m) are present at 10^{-3}M.
Time : equilibrium time.

port is enhanced. While those of Cd^{2+} transport compared to Hg^{2+} are reduced because the stabilities of Hg^{2+} with macrocycles used as carrier are too high.

From the transport results of Table 2, it can be seen that the time requied to reach equilibrium is longer and the amount of Cd^{2+} transport at equilibrim is smaller when $A^-=Cl^-$ or Br as compared to $A^-=SCN^-$ or I^-. These results can not be explained by the relative magnitude of the Cd^+-α_2^0 value. The results in Table 2 were determined in souce phase with no other M(m) present. Thus the Cd, Pb, and $HgA_2(aq)$($A^-=SCN^-$, I^-, Br^- or Cl^-) concentrations were maximized and the equilibrium of each post metal ions reach after 5 minutes, for Cd^{2+} by using the SCN^- and I^-, after 20 minutes, for Pb^{2+} and Hg^{2+} by using the halogen ions (I^+, Br^+, and Cl^+), by contacting the source phase with the emulsion. The order of the transport, when using the several, A apecies is also the order of the changing degree of solvation for A . The same results are observed for the other sets of emulsion membrane such as DC 18C6-toluene(Izatt, 1987).

Separation of Hg^{2+} over Cd^{2+} and Pb^{2+} ; When $A^-=SCN^-$ and $SCN^-=0.4M$, $Cd(SCN)_2$ and $Pb(SCN)^{3-}$, $Hg(SCN)_4^{2-}$ are the major species present in the source phase. Under these conditions, Cd^{2+} transport in macrocycles-mediated membranes is favored over the Pb^{2+} and Hg^{2+} transport

(Table 2). However, when $[SCN^-]=0.004M$ in a source phase that is 200ppm in post transition metal ions, the major species presented in source phase, in almost quantitative amounts, will be Hg^{2+} and 20 values for Hg^{2+}, Cd^{2+}, and Pb^{2+} are 0.48, 2×10^{-4}, and respectively. Under the condition, we would expect Hg^{2+} to be transport over Pb^{2+} and Cd^{2+} in macrocycles-mediate membrane systems.

With $S_2O_3^{2-}$ in the receiving phase, 63% of the Hg^{2+} was transported in 5 minutes and with NO_3^- in the receiving phase, 63% Hg^{2+} were transported in 5 minutes but 89% of the Hg^{2+} was transported in 10 minutes, which is compared with the data of Table 2. Also, we obtained results like Table 3 with other macrocycles-mediate membranes. The initial slower rate of Hg^{2+} transport with NO_3^- rather than $S_2O_3^{2-}$ in the receiving phase is a consequence of the reduced $Hg(SCN)_2$ concentration gradient in the membrane as the concentration of $Hg(SCN)_2$ builds in the receiving phase. Further more, the Hg^{2+} species is concentrated about 50-fold for NO_3^- and 3-fold for SCN^- in receiving phase. However, after a small amount of Hg^{2+} transport has occurred, $Hg(SCN)_2$ begins to precipitate in receiving phase, if $S_2O_3^{2-}$ is not present(Izatt, 1978). At this point, the maintenance of the SCN^- concentration gradient in the membrane when NO_3^- species is present in the receiving phase is prevented from the precipitation of $Hg(SCN)_2$.

Separation of Pb^{2+} over Cd^{2+} and Hg^{2+} ; The aquouse receiving phase contained $10^{-2}M$ $Li_4P_2O_7$ was prepared form reagent grade sodium pyrophosphate and LiCl by the exchange procedure. The lithium salt was used because it has been shown that macrocycles studied in this section form weak comolexes with Li^+. Thus, Li^+ in the receiving phase would not compete with the other cations of the source phase for the macrocycle carrier in membrane.

The Hg^{2+} was preremoved form mixture because it is highly interacted with macrocycles. When $A^-=SCN^-$, and $[SCN^-]$ is 0.004M in source phase that is 200 ppm in Cd^{2+} and Pb^{2+}, the major species of the Pb^{2+}, $Pb(SCN)^+$, $Pb(SCN)_2$ and $Cd(SCN)_2$ present under this condition.

We expected that Cd^{2+} and Pb^{2+} will be interacted with $P_2O_7^{4-}$ in the receiving phase. However, the stability of Pb^{2+}-$P_2O_7^{4-}$ is higher than that of Cd^{2+}-$P_2O_7^{4-}$(Mcdowell, 1983) and the Log K values for Pb^{2+}-macrocycles(expect for L_7 and L_8) interaction is significantly smaller than those of Pb^{2+}-$P_2O_7^{4-}$ interaction. Thus, the Pb^{2+}, $(PbSCN)^+$ are interacted with $P_2O_7^{4-}$ in receiving phase, and than Pb^{2+} or $Pb(SCN)^+$ is removed in the type of Pb^{2+}-complexes with carriers from Pb-$P_2O_7^{2-}$-ion pairs by contacting emulsion membranes.

With $P_2O_7^{4-}$ in the receiving phase, 68% of the Pb^{2+} was transported in 5 minutes and with NO_3^- and $S_2O_3^{2-}$ in the receiving phase, 2 and 12% of Pb^{2+} was transported in the same time. But 85% of Pb^{2+} was transported in 10 minutes by using the L_4 toluene emulsion membrane(Table 2 and 3) and also we obtained results like Table 2 and 3.

Table 3 Competive Transport[a] of Cd(II), Pb(II) and Hg(II) with 0.004 SCN^- in the Source Phase and with NO_3^-, $S_2O_3^{2-}$ and $P_2O_7^{4-}$ in the Receving Phase as a Function of Time

Equlibrium Time(min)	Percent Transport							
	NO_3^-			$S_2O_3^{2-}$			$P_2O_7^{4-}$	
	Cd^{2+}	Pb^{2+}	Hg^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}	Cd^{2+}	Pb^{2+}
5	84	2	46	4	14	48	10	68
10	9	7	78	6	17	89	12	85
20	16	12	89	12	18	92	18	87

Table 4 The Single Post Metal Ions Concentration and Transport Data of Emulsion Stirring for Different Macrocycles a Function of Time

Macrocycles	Time (min)	Post Metal Concentration(ppm)				Percent Transport		
		Initial	Final					
			Cd^{2+}	Pb^{2+}	Hg^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}
1		220						
	2		132	183	127	40	17	43
	5		78	72	48	65	67	78
	10		47	53	45	79	76	80
	20		45	45	44	80	80	81
2		218						
	2		140	152	125	36	31	43
	5		71	64	41	68	71	81
	10		46	44	38	79	80	83
	20		42	39	35	81	82	84
3		220						
	2		130	134	102	41	39	54
	5		63	58	31	71	81	83
	10		44	42	37	80	81	83
	20		42	40	33	81	82	85
4		223						
	2		103	131	96	54	41	57
	5		61	52	26	73	77	88
	10		40	29	13	82	87	94
	20		35	22	9.0	86	90	96
5		208						
	2		129	181	146	38	13	30
	5		58	78	42	72	62	80
	10		35	56	25	83	68	88
	20		31	54	21	85	74	90
6		216						
	2		143	164	138	34	24	36
	5		89	52	31	59	56	86
	10		62	38	22	72	83	90
	20		60	31	19	73	86	91
7		218						
	2		157	182	156	38	17	28
	5		147	159	72	33	27	67
	20		128	144	56	34	57	74
	20		120	141	54	35	58	75
8		220						
	2		165	173	147	24	22	33
	6		165	173	147	24	22	33
	10		152	138	78	31	37	75
	20		150	132	72	32	40	78
9		216						
	2		134	170	132	38	22	39
	5		114	96	48	47	56	78
	10		92	69	38	59	68	82
	20		89	64	30	59	70	86

Effect of Macrocycle Donor Atoms : Table 4 shows the percentage of post transition metal ion transported versus time for L_1 and L_5. The two macrocycles have the same number of ring atoms as cyclam, but L_5 is different from cyclam(L_1) by having S substituted for the two oxygen atoms. The greater percentage of Hg^{2+} transported(83% in ten minutes) was found with L_5. However, percentage of the other post transition metals transported were reduced as compared with L_1. In Figure 5, the already significant transport of Hg^{2+} in the emulsion membrane with the macrocycle, L_6, is enhanced by the substitution of two sulfur atoms for nitrogen atoms. These results were also concidence with magnitude of stability constants of complexes.

However, the Hg^{2+}-transport in L_5-emulsion membrane was not remarkably increased for L_1 despite the fact that the Log K for Hg^{2+}-L_5 interaction is higher than that for interaction of Hg^{2+} with L_1. The substitution of sulfur donor atom result in reduced water solubility and, apparently, decreases the distribution conficient enough to overcome the Log K disadvantage in transport Hg^{2+} (Friedman et al., 1973). From these Log K values, we note that the nitrogen containing macrocycle(L_1) has for affinity for Pb^{2+} and Cd^{2+} than the oxygen donor atoms(L_7), and sulfer containing macrocycles. While L_5 has more affinity for Hg^{2+} than all nitrogen macrocycles because Hg^{2+} has more soft acidic than Pb^{2+} and Cd^{2+} metal ions.

Effect of Macrocycle Substituents : Table 4 and Figure 5 show the transport of post transition metal ions versus time using L_1, and derivatives of macrocycle(L_2, L_3, L_4, and L_6). In these results, it is seen that the addition of four or two-carboxylate groups enhance post transition metal ions transport greatly. However, addition of four methyl and methylpyridine groups for L_1 were not markably, increased as compared with post transition metal ions transported by L_1. These results can be predicted in magnitude of stability constants for complexes. However, as predicted in effect of macrocycle donor atom, L_3-post transition metal ions transport more readily than L_1 and L_2 despite the fact that the Log K for post transition metal ions-L_3 interaction is higher than that for interaction of the post transition metal ions with L_1 and L_2. It is results that distribution ratio is deceased between water and toluene layer because addition of organic substituent such as methyl phenyl ring , and result in reduced water solubility.

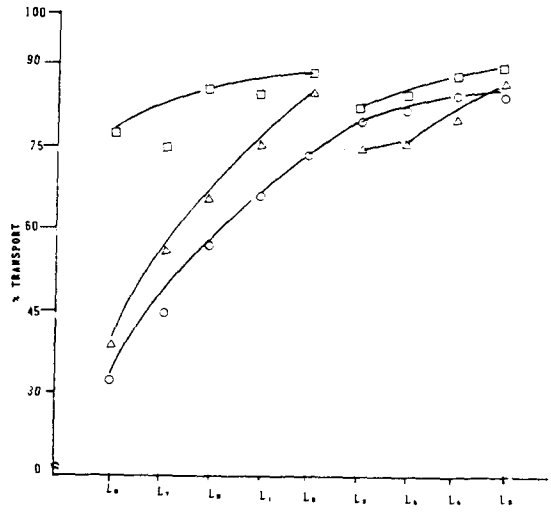

Figure 5. Plot of %-Transport of Cd^{2+}(○), Pb^{2+}(△) and Hg^{2+}(□) vs. Ligand Number in 0.4M SCN^- and 0.004 M SCN^- as Source Phase using the 0.02M Macrocycle in Toluene/0.282M Na_3^-, $S_2O_3^{2-}$, and $P_2O_7^{4-}$ Emulsion Membrane after 15 Minutes.

When macrocycle-cation interaction exceeds in receiving phase anion-cation interaction for two different macrocycles with similar distribution coefficients, in which case will more cation transport occur ? The post transition metal ions transported by cryptand 221(L_9) and 211(L_8) indicates that the macrocycle with the larger log K value

for cation interaction will transport the cation more readily.

Competive transport of post metal ions versus several other ions ; The transport data of binary ions containing the post transition metal ions were given in table 5. The interference ions for the post transition metal ions were partial transition metal. In SCN^--NO_3^- system, transition metal ions were interfered for the Cd^{2+}, but the other ions were not interfered for the Cd^{2+}. The Cu^{2+} of the transition metals were markably interfered for the post transition metals. These results, as predicted in effect of macrocycle substiuent, are dependent on the magnitudes of the stability constants of complexes.

We would not expect only the low transport of Ni^{2+}. A large fraction of the Ni^{2+} is present in the source phase as $Ni(SCN)_2$, since the interaction of the with partial macrocycles in methanol are similar to those of Cd^{2+}, significant transport was expected in case of Ni^{2+}.

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Table 5 The Transports[a] Percent of Binary Ions by Emulsion Liquid Membrane after 15 Minutes

Binary Ion	Source-Recieving Phase System					
	$SCN^- - NO_3^-$		$SCN^- - S_2O_3^{2-}$		$SCN^- - P_2O_7^{4-}$	
	A^{m+}	Cd	A^{m+}	Hg^{2+}	A^{m+}	Pb^{2+}
Cu^{2+}/M^{2+}	32	68	26	74	13	87
Zn^{2+}/M^{2+}	20	80	4	96	2	98
Ni^{2+}/M^{2+}	18	82	3	97	2	98
Na^+/M^{2+}	5	95	2	98	1	99
Li^+/M^{2+}	4	96	3	97	2	98
Mg^{2+}/M^{2+}	4	96	1	99	5	95
Ca^{2+}/M^{2+}	2	98	1	99	6	94
Fe^{2+}/M^{2+}	15	85	4	96	8	92

a : Percent transport in 0.4M SCN^- or 0.004M-SCN^-/0.002M-tetramethylacetic cyclam (Ligand No. 4) in toluene/0.282M- NO_3^- or $P_2O_7^{4-}$ emulsion liquid membrane. M^{2+} were Cd^{2+}, Hg^{2+} and Pb^{2+}, and A^{m+} were Cu^{2+}, Zn^{2+}, Ni^{2+} Na^+, Mg^{2+}, Ca^{2+} and Fe^{2+} as interference ions.
All of the metal ions were 10^{-3}M.

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거대고리 화합물을 매질로한 에멀존 액체막계에 의한 중금속이온의 분리

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「에멀존」계에서 거대고리화합물에 의한 효과적인 수송현상을 두가지 관점에서 논의하였다. 하나는 중금속이온 (Cd^{2+}, Pb^{2+} 및 Hg^{2+})을「토루엔」막으로 추출하는 경우, 만일 금속-거대고리 화합물의 상호작용이 크다면 이 추출효과는 증가한다. 두번째「토루엔」-물 경계면에서, 금속이온을 정량적으로 용리시키기 위해서는 금속이온-Recieving Phase와 금속이온-거대고리화합물 사이의 상호작용에 대한 LogK의 차가 충분히 커야한다.

첫번째는 거대고리 화합물의 주개원자, 치환체, 그리고 공동반경을 고려함으로써 해결된다. 두번째는 Recieving Phase에서 금속이온을 포획할 수 있는 적당한 착화제를 선택함으로서 해결된다. 이 연구의 결과들은 이론과 잘 일치하며, 시료용액의 종류는「에멀존」막에 의한 금속이온의 수송현상에 영향을 준다. SCN^-, I^-, Br^- 및 Cl^- 이온과 같은 A^- 이온을 사용할 경우, 수송순서는 A^- 이온의 용매화순서의 크기에 일치하며, 용해도의 차이때문에 금속이온의 수송능력은 Receiving Phase의 화학종 농도의 크기에 영향을 받는다. 이 연구에서는 적당한 실험조건하에서 조절된「토루엔」막을 사용함으로서 Cd^{2+}, Pb^{2+} 및 Hg^{2+} 이온의 혼합물로부터 각각의 단일이온들을 효과적으로 분리농축할 수 있었다.

그리고 Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, 이온들은 중금속이온들을 분리농축하는데 부분적으로 방해를 하였다. 그러나 알칼리 및 알칼토금속이온은 방해하지 않았다.