Emulsion Liquid Membrane Transport of Heavy Metal Ions by Macrocyclic Carriers

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Abstract

New two macrocyclic compounds using as carriers of liquid emulsion menbrame, have been synthesized. These reuslts provide evidence for the usefulness of the theory in designing the systems. The efficiency of selective transport for heavy metal ions have been discussed from the membrane systems that make use of SCN^-, I^-, CN^- and Cl^- ion as co-anions in source phase and make use of $S_2O_3^{2-}$ and $P_2O_7^{4-}$ ion as receiving phase, respectively.

The transport rate of $M(II)$ was highest when a maximum amount of the $M(II)$ in the source phase was present as $Cd(SCN)_2([SCN^-]=0.40M$, $Hg(SCN)_2([SCN^-]=0.40M)$ and $Pb(CN)_2([CN^-]=0.40M)$. The $Cd(II)$ and $Pb(II)$ over each competitive cations were well transprted with $0.3M-S_2O_3^{2-}$ and $0.3M-P_2O_7^{4-}$, respectively in the receiving phase.

Results 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 M^{n+} into the toluene systems. The effectiveness of this extraction is the greatest if logK for M^{n+}-macrocycle interaction is large and if the macrocycle is very insoluble in the aqueous phase. Second, the ratio of the logK values for M^{n+}-receiving phase ($S_2O_3^{2-}$ or $P_2O_7^{4-}$) to M^{n+}-macrocycle (L_1 or L_2) interaction must be large enough to ensure quantitative stripping of $M^{n+}(Cd^{2+}$, Hg^{2+} or $Pb^{2+})$ at the toluene receiving phase interface.

L_1(3.5-benzo-10,13,18,21-tetraoxa-1,7,diazabicyclo(8,5,5) eicosan) forms a stable Cd^{2+} and Pb^{2+} complexes and L_1 is very insoluble in water and its Cd^{2+} and Pb^{2+} complex is considerably less stable than $Cd^{2+}-(S_2O_3)_2^{2-}$ and $Pb^{2+}-P_2O_7^{4-}$ complexes. On the other hand, the stability of the $Hg^{2+}-L_1$ complex exceed that of the $Hg^{2+}-(S_2O_3)_2^{2-}$ and $Hg^{2+}-P_2O_7^{4-}$, and the distribution coefficient of L_2(5,8,15,18,23,26-hexaoxa-1,12- diazabicyclo-(10,8,8) octacosane) is much smaller than that of L_1. Therefore, the partitioning of L_2 is favored by the aqueous receiving phase, and little heavy metal ions transport is seen despite the large logK for $Hg^{2+}-L_1$ and $M^{n+}(Cd^{2+}$, Pb^{2+} and $Hg^{2+})-L_2$ interactions.

Key Words : macrocycles, transport, heavy metal, co-anion, source phase, receiveing, complex separation, interaction, destribution coefficient.

1. Introduction

Membrane systems allow high selectivity as well as energy and material use efficiency to be obtained in separations relative to many other systems. In particular, carrier-mediated transport allows for highly specific molecular recognition reactions to be used on a contineous basis in performing separations(Danesi et. al., 1987, Godard, 1985).

This potential for making efficient and selective separations has led to the study of

several membrane types as well as many carrier molecules.

Emulsion Liquid Membrane systems have been studied, this system is illustrated in Figure 1. This system(Izatt, 1986, 1988) has a very thin membrane and immense surface area resulting in rapid transport. Desired species are also concentrated by a large factor upon transport from the source to the receiving phase. This concentration is due to the large aqueous source phase to receiving phase voulume ratio in these systems. This large ratio results when the organic phase-receiving phase emulsion volume is added to a much larger source phase volume. In the emulsion system, both the membrane solvent and carrier molecule need to be only moderately hydrophobic in order to maintain membrane stability and to retain the carrier molecule in the membrane phase.
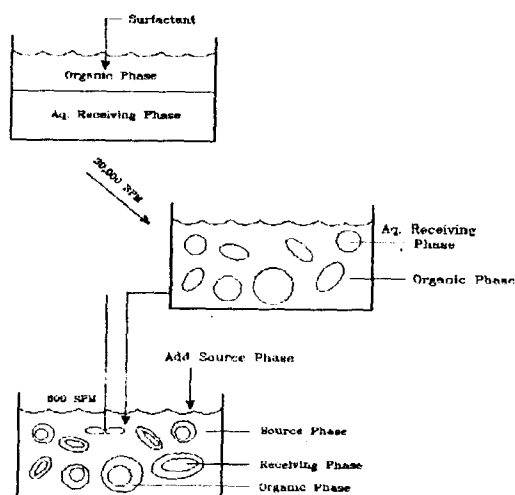

Fig. 1. Formation of an Emulsion Liquid Membrane (ELM)

·The emulsion liquid membrane(ELM) has been particularly effective in macrocycle-

mediated metal cation separation experiments. The ELM is superior to other artificial membranes in that 1) there is a large surface area at both aqueous-oil interface which enhances macrocycle-cation interaction, and the rate of cation transport, 2) the transported cation is concentrated since the volume of the recieving phase is smaller than that of the source phase, and 3) emulsion can be made stable for long time periods(Izatt et. al. 1986). The main disadvantages of the ELM are 1) the need to break down the emulsion after transport has occurred to recover the metal from the receiving phase and to recycle the macrocycles containing organic phase, and 2) the co-transport of H_2O in some case.

Macrocycles are effective carrier molecules in membranes for metal separations since they often selectively interact with particular cations in a family of elements.

Futhermore, lipophilic side chains can often be attached to the macrocycle ring without significantly altering the interactive properties of the macrocycles(Izatt et al., 1985), but enhancing the distribution to the organic phase over the aqueous phase of both the macrocycls and the macrocycle-cation complex (Izatt et al., 1988) Hence, the macrocyce can be retained in the membrane and can effectively extract cations into the membrane.

Behr, Kirch and Lehn (Behr et al., 1985) have shown that macrocycle-medeated cation transport in many membrane systems is limited. The parameters affecting limited transport are the diffusion coefficient and the distribution coefficient of the transported moiety.

Futhermore, the diffusion coefficients of a different cation-macrocycle complex should be similar since their structures are similar, Hence, selective cation transport is basically a function

of the factors affecting the distribution coefficients of the cation complexes involved in transport.

Most of the macrocycle studied have been neutral ligands. When neutral macrocycles are used to mediate cation transport, anion(A^{n-}) must accompany the cation-macrocycle complex to maintain electrical neutrality, Hence, the effect of the solvated A^{n-} on the distribution moiety into the organic membrane from the aqueous source phase is a factor in cation transport.

Metals present in the source phase as complex anions can often be separated in our emulsion membrane systems. Transport of such an anion requires a source phase of the cation to be present that either interacts with the macrocycle (Izatt et. al. 1985) or ion pairs with such an anion to form a moiety that is distributed to the membrane (Izatt et. al, 1990). Transport is enhanced for a particular complex anion that is less hydrated than other complex anions present. Further transport enhancement can be obtained by incorporating in the receiving phase a reagent that interacts with the metal present as part of the complex anion.

Selective transport of a particular cation also requires that the other cations in the source phase either do not interact with A^{n-} or form highly charged anionic complexes with $M^{m+}-A^{n-}$ interaction does not occur, the co-anion must be dissolvated in order for cation transport to take place(Izatt et. al. 1987). In the case where a heghly charged anionic complex is formed, several cation-anion bonds must be broken for cation-macrocycle complexation occur. In either of these case where a thermocynamic barrier to the formation of a neutral macrocycle – cation – anion moiety exist, if macrocycycle cation interaction and

cation-recieving phase complexing agent interaction do not provide sufficient free energy to overcome the free energy barrier, tranport of that cation will be inhibited. Therefore, a knowledge of the equilibrium constants for cation-anion interaction, cation-macrocycle interaction, and cation-received phase comeplexing agent interaction allows one to design cation seletivity into this type of membrane system.

Complete descriptions and evidence for the mechanisms involved in the A^{n-} and M_xA_y separation schemes have been reported (Izatt et. al. 1987) and macrocycles of varying size, substituent groups, donor atoms and ring number were compared for their ability to transport of the post transition metal ions(Oh Jin Jung, 1993). In this present paper, we have synthesized new two macrocyclic compounds having nitrogen bridgeheads (Figure 2) and resonable cavity size more closely matching the post transition metals such as Cd^{2+}, Pb^{2+} and Hg^{2+} ions, and Cd^{2+}, Pb^{2+}, Hg^{2+} and other transition element-transport results using the emulsion membrane containing synthetic macrocyclic compounds are presented.
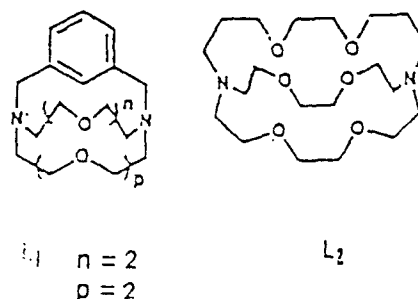

L₁   n = 2   L₂
        p = 2

Fig. 2. Structures of Macrocycles

These results provide evidence for the usefulness of the theory in designing membrane

systems for selective cation transport. The system discussed makes use of SCN^-, I^-, CN^- and Cl^- as a source-phase complexing anion to produce selective transport of Cd^{2+}, Pb^{2+} and Hg^{2+} ions. The effect of ionic strength differences between the aquous source and receiving phase in the emulsion membrane was also examined. Distribution coefficients for the macrocycles between toluene and water were determined and effect of enhancement for the transportation has also been discussed when hydrophobic substituent groups are incorporated on the macrocycle.

2. Experiment

The emulsion system was formulated from the organic membrane phase and the aquoeous receiving and source phase as described previously(Jung, 1993) The organic phase consisted of 0.02M macrocycles (Figure 2), 3.5-benzo-10,13,18,21-tetraoxa-1.7-diazabicyclo(8,5,5)eicosan and 5,8,15,18,23,26 hexaoza-1,12-diazabicyclo-(10,8,8) octacosan, solution in toluene(Fisher) which was 3% v/v in the nonionic surfactant sorbitan monoleat (span 80 ICI Americas). Blank experiments were performed with the macrocycles absent from the toluene phase.

The macrocycles were synthesized as described previously(Jung, 1993). The source phase metal cations were 0.001 M in the NO_3^- salts for the competive metal cation. The source phase also was contanied either 0.4~0.03 M $Mg(SCN)_2$, 0.040~0.018 M MgI_2, 0.04~0.015 M $MgBr_2$, 0.28 M $MgCl_2$ or 0.4~0.28 M $Mg(CN)_2$ for Cd(II) Pb(II) Hg(II) and other transition elements transport experiments.

The receiving phase was contained either

$Mg(NO_3)_2$, MgS_2O_3, or $Li_4P_2O_7$ for the various experiments. The particular Mg^{2+} or Li^+ salts were used because the macrocycles form weaker complexes with other cations. The volume ratios of the source organic and receiving phase were 10:1:1, respectively.

The concentrations of all metal cations present in the source phase were determinde by ICP emission spectrophotometer(JOBIN YVON 70 plus) both befor and after contacting the source phase and membrane phase for a special time. The percent transport of the metals was then calcurated from the amount of disappearence from the source phase. Each ELM experiment was done in triplicate. The standard deviations between runs average about ± 5.0%.

Approximate values for the distribution coefficient between toluene and water for the macrocycles were determined equal volumes of 3.0×10^{-3}M macrocycle in toluene solution and pure water were mixed for 30 minutes using a mechanical shaker. The two phases were then allowed to separate for a minimum of 12 hours before a sample of the toluene phase was collected. This sample and a sample of the original macrocycle solution were analyzed for macrocycle concentration using a varian 3400, Gas chromatograph to obtain the macrocycle concentration peaks.

3. Result and discussion

In Table 1, the log K values for the interaction of Cd^{2+}, Pb^{2+} and Hg^{2+} with the macrocycles(Figures 2) in H_2O and methanol are given. The log K values were determined by potentiometry and solution calorimetry and these values were obtained from previous

study(Oh-Jin, Jung, 1993)

Table 1. log K values for 1:1 interaction of the macrocyclic ligands with post transition metal ions in 50% mixture solution of H_2O and CH_3OH(at 25℃ and I=0.1 mol.dm^{-3}(MeNNO$_3$)

cations	L$_1$	L$_2$	method
Cd^{2+}	6.52	4.26	potentiometry
	6.08		calorimetry
Pb^{2+}	5.85	6.59	potentiometry
Hg^{2+}	11.0	13.2	potentiometry
Zn^{2+}	4.72	2.86	potintiometry
Ni^{2+}	2.16	-	potintiometry

The order of the basicity in Table 1 was L$_2$ > L$_1$ and then it is indicating that order of the basicities are increased regulary with increase in the cavity size of macrocyclic ring. Hence, the degree of twistness of tricyclic compounds were increased in order of L$_2$ > L$_1$. The changes of the stability constants of L$_1$ and L$_2$ complex for the heavy metal ions were dependent on the basities and the cavity-size of the macrocycles because most of metal ions follow the size rule(Jung, 1993).

Especially, the stability constants of Hg(II) complexes with the macrocycles are much higher than those of Cd(II) and Pb(II) because the entropy effect is much higher than the other heavy metals by forming the complexes (Jung, 1993)

In Table 2, the approximate distribution coefficients between toluene and water are listed for some macrocycles studied. The distribution coefficient defined as the concentration of the macrocycle in the toluene devided at equilibrium, and was then calculated.

In Table 1. L$_1$ and L$_2$-macrocycles form the stable complexes with heavy metal ions(Cd^{2+}, Pb^{2+} and Hg^{2+}) to separate in this study, and the differences of these stability constants are

enough values to separate the heavy metal ions, respectively. However, the destribution coefficient of L$_1$-macrocycle in toluene-water solvent is much more than that of L$_2$. Hence, L$_1$-macrocycle having one benzene ring in macrocyclic ligand behave in hydrophobic but L$_2$ behave in hydrophilic. Therefore, we can expect that the effectiveness of this extraction is great if log K$_s$ for metal ions-macrocycle interaction is large and if the macrocycle is very insoluble in the aquous phase(Izatt et. al., 1988).

Table 2 Distribution Coefficients between Toluene and Water for Some Macrocycles

macrocycle	Destribution Coefficients $K_L=[L]_{Toluene}/[L]_{Water}$
L$_1$	908
L$_2$	0.111
Cryptand222[a]	<0.018
Cryptand221[a]	<0.014
B18C6[a]	>10

a) G. A. Clark. A Dissertation for the Degree of Doctor of philosophy, Department of Chemistry, Brigham Young Unversity, Utah, USA (1985)

An example of selective transport of neutral M$_x$A$_y$ moieties over charged species is found in the selective transport of Cd(II) over Hg(II) and Zn(II)(Izatt et al., 1988). using the emulsion liquid membrane containg dicyclohexano-18-crown-6.

In Table 3 and Figure 3 and 4, the fraction of Zn(II), Cd(II), Pb(II) and Hg(II) containing species present in aquous solution as a neutral M$_x$A$_y$ moiety, α$_2$ for varying concentrations of A^{n-}is given where A^{n-}=SCN$^-$, I$^-$ and CN$^-$, respectively. The curves in Figures 3, was calculated from the equilibrium constants for M^{m+}-A^{n-} interaction with the assumption made that [A^{n-}] >> [M^{m+}]. In the experiments performed [A^{n-}] is at least 40 times greater

than $[M^{m+}]$.

Table 3. Fraction of Cd(II), Pb(II), Hg(II) Present as MA₂ in the Source Phase as a Function of A⁻

A⁻	[A⁻]M	$a°_2$		
		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}	0.18
Br⁻	0.30	0.303	0.22	1×10^{-3}
Cl⁻	0.56	0.44	0.16	0.02
CN⁻	0.40	0.12	0.45	1.0×10^{-3}

$a°_2$: The fraction of M(m) presen as MA₂[The $a°_2$ values were calcul ated from log $\beta(H_2O)$ values for formation of MAn^{2-n}(Izatt, 1982) – Log[CN⁻]
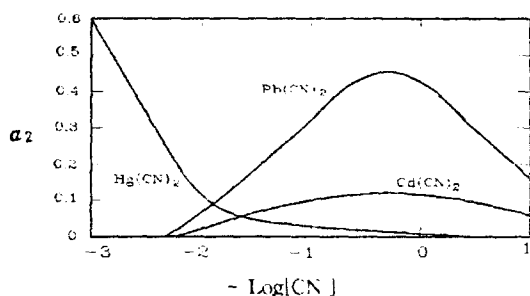

Fig. 3. Fraction of M(II) present as M(CN)₂, a_2, for Varying [CN⁻]total Where M = Pb(II), Cd(II) and Hg(II)

When A^{n-}=SCN⁻, the amount of Cd(SCN)₂ present in solution is maximized when [SCN⁻]= 0.4 M. At the same [SCN⁻], the amount of Hg(SCN)₂ present in solution is minimal, but the amount of Zn(SCN)₂ is nearly maximized and the amount of Pb(SCN)₂ present in solution is nearly minimized. Therefore, as discussed in introduction, we would expect that Cd(II) would be transproted selectively over Hg(II) and Pb(II) but that Cd(II)-Zn(II) separation would be poor in an ELM contanig 0.4 M SCN⁻ in the source phase. When A^{n-}=I⁻, the amount of CdI₂ present in solution is maximized when [I⁻]=0.04 M. At

the same [I⁻] the amount of HgI₂ and PbI₂ present in solution, is minimal. When A^{n-}=Br⁻ and Cl⁻, Cd(II)-Pb(II) and Cd(II)-Hg(II) separation are poor in an ELM containg 0.04 M-Br⁻ and 0.28 M-Cl⁻ in the source phase, respectively.

When A^{n-}=CN⁻, the amount of Cd(CN)₂ and Pb(CN)₂ in present in solution is maximized when [CN⁻]=0.04 M., At the same [CN⁻], the amount of Hg(CN)₂ present in solution is minimal. Therefore, we choose the SCN⁻ ion as the source phase for the selective transport of Cd(II) over Hg(II) and Pb(II) in an ELM containing macrocycle L₁-Toulene solution.

The experimental results with NO₃⁻, $S_2O_3^{2-}$ and $P_2O_7^{4-}$ in the receiving phase are given in Table 4.

Table 4. Competitive Transport of Cd(II), Pb(II), Hg(II) and Zn(II)

Metal cation	Co – anion	tpersent Transport [a, b]		
		Receiving phase Agent		
		NO_3^-	$S_2O_3^{2-}$	$P_2O_7^2$
Cd(II)	SCN⁻(0.4M)	70	99	75
Pb(II)	SCN⁻(0.4M)	8	14	46
Hg(II)	SCN⁻(0.4M)	2	12	8
Zn(II)	SCN⁻(0.4M)	12	8	3
Zn(II)	I⁻	3	3	7
Cd(II)	I⁻	67	87	72
Hg(II)	I⁻	12	85	37
Pb(II)	I⁻	10	36	42
Zn(II)	CN⁻	5	5	12
Cd(II)	CN⁻	72	86	16
Hg(II)	CN⁻	2	5	2
Pb(II)	CN⁻	73	84	93
Cd(II)	SCN⁻(0.04M)	–	2	–
Pb(II)	SCN⁻(0.04M)	–	8	–
Hg(II)	SCN⁻(0.04M)	–	85	–

a) Transport after 25 minutes in a 0.4 M SCN⁻, 0.037 M I⁻ or 0.4 M CN⁻/0.04 M-L₁ in toluene/0.3 M receiving phase(NO₃⁻, $S_2O_3^{2-}$ or $P_2O_7^{4-}$) emulsion membrane. Metals are present at 10^{-2} M
b) log $\beta(H_2O)$ values for formation of $M(S_2O_3)_n^{2-n}$, MI_n^{2-n} and $M(P_2O_7)^{2-}$ are as follows(Smith R. M. et al., 1976).

In Table 4. We can expect that $S_2O_3^{2-}$ is more favorable than other receiving phase(NO_3^- or I^-) when Cd(II) or Hg(II) are selectively separated from competitive transport species in SCN^- or I^- solution and that $P_2O_7^{4-}$ is the most effective as receiving phase, when Pb(II) is a selectively separated from Hg(II) or Cd(II) in CN^- solution.

In one ELM experiment, the $CdA_2(aq)$ ($A^- = SCN^-$, I^-, Br^-, Cl^- or CN^-) concentrations in the source phase were maximized ([SCN^-]= [CN^-]=0.4 M, [I^-]=0.037 M, [Br^-]=0.3 M, [Cl^-]=0.56 M) and Cd(II) transport (Izatt et al., 1987) was determined after 25 minutes of source phase contact with the emulsion. The percentage of Cd(II), Hg(II) and Pb(II) transproted as function of A^- was SCN(99), I^-(85) and CN^-(93) in each of receiving phase($S_2O_3^{2-}$ or $P_2O_7^{2-}$) solution.

The order of decreasing transport using the several A^- species is also the order of increasing degree of solvation for A^-. Hence, the choice of A^{n-} for a particular M_xA_y separation should include the consideration of this parameter.

Analogs of L_1(Figure 2) containing sufficient hydrophobic bulk for the particular membrane system were used in these experiments. The selectivity order for cation interaction with these macrocycles, Hg(II) > Cd(II) > Pb(II) > Zn(II), in both solvent extraction and homogeneous solvent is identical. If the macrocyclic carrier were the only factor in determining selectivity this would always be the selectivity order. However in the first and third line of Table 4 highly selective transport of Cd(II) over Hg(II) is seen. In this experiment, 0.4 M SCN^- is present in the source phase so that $Hg(SCN)_4^{2-}$(α_2=9.0$\times$ 10^{-2})and $Cd(SCN)_2$(α_2=0.47) are the primary

species present. The neutral $Cd(SCN)_2$ species is transported preferentially over the ionic and enhance more hydrophilic, $Hg(SCN)_4^{2-}$. The transport efficiency, i.e.) the fraction of total initial amount of Cd(II) present in the source phase which is transported was 99% for the $S_2O_3^{2-}$ receiving phase. The enhanced transport efficiency is due to the fact that free Cd^{2+} and $Cd(SCN)^-$ are the primary species present in the receiving phase where SCN^- is not excess. Hence, the concentration gradient in $Cd(SCN)_2$ can be maintained until a large fraction of the original Cd(II) present is transported(Izatt et al., 1989)

The expected macrocycle selectivity order, Hg(II) > Cd(II) is obtained with 0.04M SCN^- where Cd^{2+}(α=2$\times$$10^{-4}$ as $Cd(SCN)_2$) and $Hg(SCN)_2$ (α=0.48) are the primary species in the source phase. In this case, a Hg(II) transport efficiency of 85% was observed for the emulsion system containing macrocycle(L_1) in this experiment. In this system, $Hg(SCN)_2$ is also the primary species present in the initial H_2O soruce receiving phase upon transport. In fact, some precepitation of $Hg(SCN)_2$ in the receiving phase was observed and this enhanced the amount of transport possible.

In a study of K^+ transport by 18-crow-6 as a function of anion type in bulk liquid membrane system(Lamb et al., 1980), transport rates of the fastest(picrate ion) and slowest(F^-) systems deffered by nearly 10^8. Interactions between cations and anions can affect membrane transport rates selectivity and overall transport efficiency.
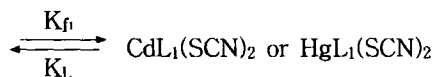
The effect of these interactions lies in the fact that transport in these systems is driven by a concentration gradient across the membrane in the transported species. This species is the neutral cation-anion ion pair.

Hence, source phase anion type and concentrations can be controlled to effect important separations. In Table 4, The results show that the transported species are also controlled by receiving phase anion types. For example, $S_2O_3^{2-}$ as a receiving phase reagent interacts strongly and quit selectively with Hg(II) and Cd(II) while the substitution of N or S donor atoms for O in the macrocycles(L_1 and L_2) enhances Hg(II) and Cd(II) selectivity over Pb(II), Zn(II) and other transition metals(Jung, 1993). Combination of these factors with controlled concentration(excess or slight excess) of SCN^- as a function of co-anion in the source phase allows virtually infinite selectivity for Cd(II) and Hg(II) over Pb(II) and many other cations as well as nearly 100% transport efficiency and extreamly rapid transported rate.
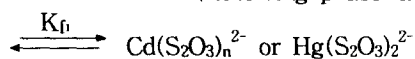
Also $P_2O_7^{4-}$ as a receiving phase reagent interacts strongly and quit selectively with Pb(II) over Cd(II), Hg(II) and many other cations when the macrocycle(L_1 and L_2) were used as carriers in this emulsion liquid membranes.

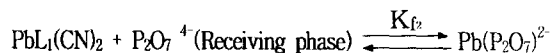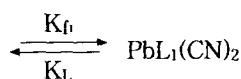Hence, we can expect the separation mechanism for competitive cations in this emulsion membrane systems as follows :

1) $Cd(SCN)_2$ or $Hg(SCN)_2$(source phase)
   + L_1(carrier in Toluene-water solution)

$$\underset{K_L}{\overset{K_{f_1}}{\rightleftarrows}} \quad CdL_1(SCN)_2 \text{ or } HgL_1(SCN)_2$$

$CdL(SCN)_2$ or $Hg(SCN)_2$ + $2S_2O_3^{2-}$
                        (Receiving phase in water)

$$\overset{K_{f_1}}{\rightleftarrows} \quad Cd(S_2O_3)_n^{2-} \text{ or } Hg(S_2O_3)_2^{2-}$$

2) $Pb(CN)_2$(source phase)
   + L_1(carrier in toluene-water solution)

$$\underset{K_L}{\overset{K_{f_1}}{\rightleftarrows}} \quad PbL_1(CN)_2$$

$$PbL_1(CN)_2 + P_2O_7^{4-}(\text{Receiving phase}) \overset{K_{f_2}}{\rightleftarrows} Pb(P_2O_7)^{2-}$$

Macrocycles, L_1 and L_2 are the same for the effect of macrocycle donor atoms but this macrocycle, L_1 is different from L_2 in the effect of macrocycle ring size and ring number.

The distribution coefficient for L_1 is expected to be more than that of L_2 since the distribution coefficient was found to increase with size for these simple macrocycles and because of attachment of hydrophobic molecule in macrocycle.

In Table 5 are listed the percentage of heavy metal ions transported accross the membrane after 25 minutes of stirring for the different macrocycles as well as the membrane to which no macrocycle was added.

Table 5. Heavy Metal Ion Transport Percent after 25 Minutes of Emulsion Stirring for Different Macrocycles

carriers	Cd(II)[a]	Pb(II)[b]	Hg(II)[c]
L_1	99	93	85
L_2	23	19	12
no macrocycle	5	5	5

a) co - anion is a 0.4 M SCN and receiving phase is a $S_2O_3^2$

b) co - anion is a 0.4 M CN and receiving phase is a $P_2O_7^{4-}$

C) co - anion is a 0.04 M SCN and receiving phase is a $S_2O_3^2$

Inhibitions of Cd(II), Pb(II) and Hg(II) transports with L_2 are also chiefly due to the small distribution coefficients of the macrocycle in toluene-water solution. Therefore, L_2-carrier is less transport than L_1 for the heavy metal ions becase the distribution coefficient of L_2 in toluene-water solution is less than that of L_1.

Cd(II) over Pb(II) and Hg(II) was effectively separated in the L_1-toluene emulsion membrane because interaction factors of Cd(II)-$S_2O_3^{2-}$ and

Cd(II)-L₁ were more fovorable than those of Hg(II) and Pb(II)-recieving phase and those of Hg(II) and Pb(II)-L₁. Despite the log K value of Hg(II)-L₁ is much larger than that of Cd(II)-L₁, efficiency of the transportation for Hg(II) are smaller than that for Cd(II) because log K values of Hg(II)-L₁ are much larger than the value of interaction between Hg(II) and receiving species($S_2O_3^{2-}$).

Acknowledgement

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거대고리 운반체에 의한 중금속이온의 에멀죤 액체막 수송

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액체막의 운반체로 사용할 새로운 2개의 거대고리화합물을 합성하였다. 이들 결과들은 이 시스템을 구성하는데 있어서 이론의 응용성을 증명하여 준다. source phase의 공존이온으로서 SCN⁻, I⁻, CN⁻ 및 Cl⁻이온을 그리고 receiving phase에서 $S_2O_3^{2-}$와 $P_2O_7^{4-}$을 이용한 액체막계로부터 중금속 이온들에 대한 선택적 수송효율을 검토하였다.

source phase의 M(II)이 Cd(SCN)₂([SCN⁻]= 0.40M), Hg(SCN)₂([SCN⁻]=0.40M), Pb(CN) ([CN⁻]= 0.40M)일때 M(II)의 수송율은 최대값을 나타낸다. 각각의 경쟁 양이온에 대한 Cd(II)이나 Pb(II)은 source phase가 $0.3M-S_2O_3^{2-}$이나 $0.3M-P_2O_7^{4-}$ 일때 가장 잘 분리된다.

이 연구의 결과에서, 이 액체막계에서 효과적인 거대고리-매질수송을 하기 위해서는 두개의 규칙이 반드시 필요하다. 첫째, toluene중으로 M^{n+}이온이 효과적으로 추출되고, 즉 만일 M^{n+}-거대고리화합물 상호작용에 대한 logK 값이 크고 수용액층에서 거대고리 화합물이 용해하지 않는다면 그 추출효과는 최대가 된다. 둘째로, receiving phase의 화학종($S_2O_3^{2-}$이나 $P_2O_7^{4-}$)과 M^{n+}의 logK값과 M^{n+}-거대고리화합물(L₁이나 L₂)의 상호작용에 대한 logK 값의 비가 충분히 크다면 receiving phase와 toluene의 접촉면으로부터 쉽게 중금속이온(Cd^{2+}, Pb^{2+} 및 Hg^{2+})들이 떨어져 나온다.

L₁(3,5-benzo-10,13,18,21-tetraoxa-1,7-diazabicyclo(8,5,5) eicosan)은 Cd^{2+}과 Pb^{2+}이온과 안정한 착물을 형성한다. 그리고 L₁은 수용액중에서 용해하기가 매우 어렵다.

그리고 Cd^{2+}-L₁이나 Pb^{2+}-L₁착물은 $Cd^{2+}-(S_2O_3)_2^{2-}$나 $Pb^{2+}-P_2O_7^{4-}$착물보다 비교적 불안정하다. 다른 한편으로 Hg^{2+}-L₁착물의 안정도는 $Hg^{2+}-(S_2O_3)^{2-}$이나 $Pb^{2+}-P_2O_7^{4-}$의 그것보다 그리고 L₂(5,8,15,18,23,26-hexaoxa-1,12-diazabicyclo(10,8,8)octacosan)의 toluene에 대한 분배계수는 L₁의 그것보다 훨씬 작다. 따라서 Hg^{2+}-L₁이나 M^{n+}-L₂(M^{n+}=Cd^{2+}, Pb^{2+}이나 Hg^{2+})의 안정도상수가 매우 큼에도 불구하고 이들 양이온의 수송량은 매우 적다.