Transport of Metal Ions Across Bulk Liquid Membrane With MacroCycle Compounds

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Abstract

The transport experiments of Pb^{2+},Cd^{2+} and Zn^{2+} metal cations were performed by dibenzo-18- crown -6 , dicyclo18-crown-6 , kryptofix 2.2.2 and diaza 18-crown -6 using 1,2- Dichtoro ethane , chloroform and carbon tetra chloride as liquid membrane , The aqueous source phase consisted of 10^{-3}M of Metals nitrate in 10 ml of double distilled deionized water at PH = 5.2 – 5.5 and the receiving phases consisted of 10 ml double distilled deionizer water at PH = 3.2-3.7 . The effects of operating conditions , stirring speed , type of carrier structure and solvents in the feed and strip phase were studied . From the results that the transport rate of Pb^{2+}, Cd^{2+} and Zn^{2+} metal cations can be enhanced by increasing stirring speed but not very high , dicyclohexyl-18-crown-6 is the best carrier structure and du to the effect cyclohexhl which is electron donating group, 1,2- di chloro ethane was found the best set solvent according to permeability and flux data du to its polarity constants Also , the transport rate efficiency observed of cations the selectivity of cations is Pb^{2+} , Cd^{2+} and Zn^{2+} which are appreciable with the value of its hydration energy and the Pearson's Hard Soft Acid Base principle (HSAB).

Keywords: Bulk Liquid Membrane, Crown Ethers, Diaza -18-Crown -6

الخلاصة

تم دراسة أنتقال ألايونات الموجبة للفلزات Zn^{2+} , Cd^{2+} , Pb^{2+} بأستخدام ثنائي بنزو 18- كراون-6 ,ثنائي سايكلو هكسيل-18- كراون-6,ثنائي أزا-18- كراون - 6,كريبتوفكس 2.2.2,وكان غشاء السائل المستخدم 2,1- ثنائي كلورو أيثان ,كلوروفورم,رباعي كلوريد الكاربون . وتضمن الطور المائي المصدر 0.001 مولاري من نترات الفلزات المذابة في 10 مل من الماء المقطر اللاأيوني عند pH =5.2-5.5الطور المائي المستقبل 10مل من الماء المقطر اللاأيوني عند PH =3.2-3.7 . وقد درست الظروف المؤثرة على العمل مثل سرعة التحريك,نوع الناقل ,نوع المذيب في الطورين المغذي والمستقبل,ومن النتائج وجد أنه بألامكان تحسين سرعة أنتقال ألايونات الموجبة للفلزات Pb^{2+} , Cd^{2+}, Zn^{2+} بزيادة سرعة التحريك بحدود(100) دورة بالثانية وأستخدام 2,1-ثنائي كلوروأيثان كأفضل مذيب لثابت قطبيته المتعادل والثنائي سايكلوهكسيل18-كراون -6كأفضل ناقل لاحتوائه مجموعة السايكلو الدافعة

للالكترونات ,كما لوحظ أن كفأة وأنتقائية سرعة النقل للايونات الموجبة للفلزات Pb^{2+} , Cd^{2+} , Zn^{2+} تتوافق مع قيم طاقة التميؤ للايونات ومبدأ حامض قاعدة صلدة لينة لبيرسون .

مفاتيح الكلمات : الغشاء السا ئل الضخم , كراون أيثر ,ثنائي أزا-18-كراون-6

Introduction

Liquid-Liquid extraction is at present a separation technique , most frequently used in chemistry both on a laboratory and industrial . Solvent extraction deals with the transport chemical substances from one phase into another , which is classified into solvation , chelating , ion- pair extraction and synergistic .(1-3)

Transport of metal ions across liquid membrane (LMs) is a powerful tool . recently , many attention have been attributed to liquid membrane (LM) technique to the specific characteristics , LMs can carry out simultaneous extraction and stripping processes in the same stage , and it has benefits of no equilibrium mass transfer and uphill effect (4,5) .

First group macro cyclic compounds are crown ethers which contain oxygen , sulfur and nitrogen as donor atoms (6) . The stability of the crown ether – metal ion complex is dependent on the number of ether donor atoms of particular importance is the size and shape of the cavity relative to the cation size due to differences in polarizability , nitrogen containing crown ethers (aza crowns) and sulfur containing crown ethers (thia crown) display different ionic selectivity than oxygen-containing crown ethers (7) .

$$M^{2+}_{aq} + 2NO_3^{-}{}_{aq} + n\,L_{org} \leftrightarrow ML_n(NO_3)_{2\,org}$$

$$K_{ex.} = [ML_n(NO_3)_2]_{org} / [M^{2+}]_{aq} + [NO_3^{-}]_{aq} + [L^{n}]_{org}$$

$$ML_n(NO_3)_{2\,org} \leftrightarrow M_{aq} + n\,L_{org} + 2NO_3^{-}{}_{aq}$$

$$K_{b\,ex} = [ML_n(NO_3)_2]_{org} / [M]_{aq} + [n\,L]_{org} + [2NO_3^{-}]_{aq}$$

The main concept associated with molecular recognition is the " lock and key " concept proposed by Emil fisher at the end of the nineteenth century (8) .

The supra molecular architectures have been applied in various field of science and technology (9) based on exploiting the presence of a cavity that allow for host – guest behavior of various cyclo phanes with their luminescent or electronic properties (10)

Experimental

Reagents :

Inorganic chemicals , Pb(II) , Cd(II) and Zn(II) nitrate were of analytical grade form (BDH)company . The organic reagents DB18C6 , DCH18C6 , DA-18-C6 were purchased from SIGMA-ALDRICH and Kryptofix 2.2.2 from MERIC company . The organic solvents dichloroethane , chloroform,1,2- dichloro ethane were purchased from (BDH) company . Aqueous solutions were prepared with double distilled water with a conductivity of 0.1 MS. cm^{-1} .

Transport experiment conditions *:*

Membrane experiment conditions . Source phase solutions consisted of 0.01M $Pb(NO_3)_2$,$Cd(NO_3)_2.4H_2O$and$Zn(NO_3)_2.6H_2O$in10 ml of double distilled deionized water at PH 5.2 -5.5 , Receiving Phase consist of 10 ml of double distilled water at PH=3.2-3.7 and membrane phase consisted of 0.01M from dicyclo hexyl-18-crown-6 , dibenzo-18-Crown-6,diaza-18-

Crown-6 and kryptofix 2.2.2in40mlof1,2-dichloroethane, chloroform and carbon tetrachloride. .

The receiving and feeding phases were sampled every 30 min and monitored using flame and flameless atomic absorption Spectrophotometer.Each experiment was performed in U-tube set up in a thermostatic room at $24 \pm 2 C^{\circ}$ as shown in fig(1), lastly the macro cyclic crown ethers which are used in the liquid membrane were recovered by washing the extraction liquid membrane phase five times using doubled distilled deionized water and the organic solvent then distilled using simple distillation setup to obtain the dried macro cyclic ethers.Puritywas checked by measuring the melting points and the infrared spectra .

Fig 1: U-shape setup

Flux and Permeability calculations :

Flux and Permeability parameters were calculated using the equations (11,12)

$$J_M = \frac{CxV}{AxT}$$

C : Concentration of cation in the source or receiving phase in (mol.L^{-1})

V : volume of receiving phase (L) .

A : the effective area of membrane (m^2)

T : time (Sec) .

$P = J_M/C_i$

J_M= Flux of cation

C_i = initial concentration of cation (10^{-3}M)

P= permeability

Results and Discussion

3.1-Liquid membrane kinetic. :

The variation of ion concentration with time was determined for both donor (C_d) and acceptor phases (C_a). If a corresponding change ofion concentration in the membrane phase was not directly determined, it was calculatedfrom the material balance between the phases. In general, the dimensionless reduced concentrations areuseful for practical reasons, and are thus represented as described below.In the experiments, the variation of ion concentration with time was directly measured inboth donor (C_d) and acceptor phases (C_a). membrane phase was determined from the material balance between the phases. For practical reasons,

dimensionless reduced concentrations were used:

$$R_d = C_d / C_{d0} \quad R_m = C_m/C_{d0} \quad R_a = C_a / C_{d0} \qquad \textbf{(1)}$$

where Cd0 is the initial ion concentration in the donor phase, while Cd, Cm and Ca represent the ion concentrations in the donor, membrane, and acceptor phases, respectively. With respect to the reduced concentrations, the material balance can be expressed as

$R_d + R_m + R_a = 1$. From this expression, the

kinetic behavior of the consecutive irreversible1rst-order reactions are described in the following relation:

$$C_d \rightarrow C_m \rightarrow C_a \qquad \textbf{(2)}$$

where k_1 and k_2 are the apparent membrane entrance and exit rate constants, respectively. The kinetic scheme for consecutive reaction systems can be described by considering the reduced concentrations as follows:

$$dR_d /dt = -k_1 R_d = J_d \qquad \textbf{(3)}$$

$$dR_m /d t = k_1 R_d - k_2 R_m \qquad \textbf{(4)}$$

$$dR_a /d t = k_2 R_m = J_a \qquad \textbf{(5)}$$

where J represents the flux. Integration of eqns. (3)-(5), assuming that $k_1 = k_2$, leads to the differentialequations.

$$R_d = \exp(-k_1 t) \qquad \textbf{(6)}$$

$$R_m = k_1/k_2 - k_1[\exp(-k_1 t) - \exp(-k_2 t)] \qquad \textbf{(7)}$$

$$Ra = 1 - k_1/k_2 - k_1[k_2 \, exp (-k_1 t) - k_1 \, exp (-k_2 t)] \qquad \textbf{(8)}$$

The maximum values of R_m and t_{max}, when $dR_m /dt = 0$, can be evaluated as

$$R^{max}_{m=} (k_1/k_2)^{-k_2 = (k_1 - k_2)} \qquad \textbf{(9)}$$

$$t_{max} = (1/k_1 - k_2) \, ln k_1/k_2 \qquad \textbf{(10)}$$

which, by considering the1rst-order time diferentiation of eqns. (6)-(8), leads to the following forms:

$$dR_d /dt_{\max} = -k_1(k_1/k_2)^{-k_1/(k_1 - k_2)} = J^{\max}_d \qquad \textbf{(11)}$$

$$dR_a /dt = -k_2(k_1/k_2)^{-k_2/(k_1 - k_2)} = J^{\max}_a \qquad \textbf{(12)}$$

$$dR_m /dt_{\max} = 0 \qquad \textbf{(13)}$$

$$- dR_d /d t_{\max} = dR_a /d t_{\max} \qquad \textbf{(14)}$$

It should be noted that the system is assumed to be in a steady state at t = t*max*, since the concentration of ions in the membrane does not vary with time [eqn. (13)]. Consequently, the entrance and exit fluxes are equal and have opposite signs(13).

Studying factors effecting on the transport of Pb^{2+} and Zn^{2+} cations .

Effect of stirring :

The stirring rates have significant influence on the transport of Pb^{2+} , Cd^{2+} , Zn^{2+} ions through Bulk Liquid Membrane from feed phase to the stripping phase . The transport experiments were carried out at three different stirring speed 80, 100 and150 rpm . As shown in fig (2,3and4) and table (1and2) .

The transport efficiency increase with increasing stirring speed , however, at higher stirring speeds not only the hydrodynamic , instabilities at the membrane – aqueous interface arose , part of the carrier was lost this carrier penetration confer adverse effect on the transport efficiency (14,15).

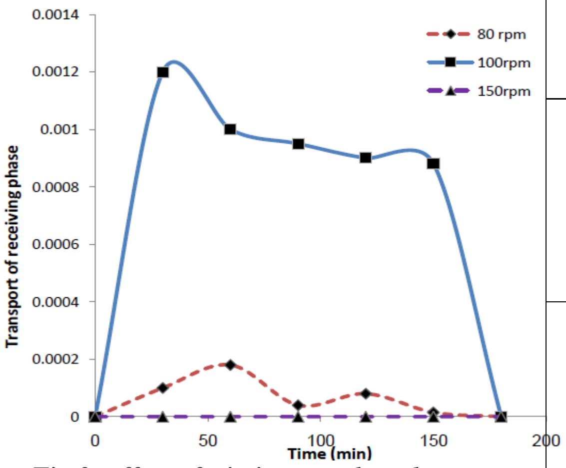


Fig 2 :effect of stirring speed on the transport rate of Pb^{2+} ion

Table 1: Effect of stirring speed on flux and permeability of Pb^{2+} , Cd^{2+} , Zn^{2+} ion in the source phase

Stirring Speed	**P b(II)**	**C d(II)**	**Zn(II)**
80 rpm J/ mol m^2.sec	1.881 x10^{-7}	1.934 x10^{-7}	1.179 x10^{-7}
Per/ mol/sec	1.881 x10^{-1}	1.934 x10^{-1}	1.179 x10^{-1}
K_{ex}	1.100 x10^{-3}	1.300 x10^{-4}	6.102 x10^{-5}
100 rpm J/ mol m^2.sec	1.669 x10^{-7}	1.669 x10^{-7}	1.373 x10^{-7}
Per/ mol/sec	1.669 x10^{-1}	1.921 x10^{-1}	1.378 x10^{-1}
K_{ex}	1.350 x10^{-3}	1.800 x10^{-4}	6.512 x10^{-5}
150 rpm J/ mol m^2.sec	1.438 x10^{-7}	1.438 x10^{-7}	0.374 x10^{-7}
Per/ mol/sec	1.438 x10^{-1}	1.168 x10^{-1}	0.374 x10^{-1}
K_{ex}	1.000 x10^{-3}	1.000 x10^{-4}	6.310 x10^{-5}

Table 2 : Effect of stirring speed on flux and permeability of Pb^{2+} , Cd^{2+} , Zn^{2+} ion in the receiving phase

Stirring Speed	**P b (II)**	**C d(II)**	**Zn(II)**
80 rpm J/ mol m^2.sec	1.994 x10^{-10}	7.366 x10^{-11}	6.52 x10^{-15}
Per/ mol/sec	1.994 x10^{-4}	7.366 x10^{-5}	6.52 x10^{-9}
$K_{b\ ex}$	1.953 x10^{-5}	2.810 x10^{-6}	5.312 x10^{-7}
100 rpm J/ mol m^2.sec	7.527 x10^{-10}	4.185 x10^{-11}	3.395 x10^{-14}
Per/ mol/sec	7.527 x10^{-2}	4.185 x10^{-5}	3.395 x10^{-8}
$K_{b\ ex}$	2.060 x10^{-5}	3.600 x10^{-6}	5.63 x10^{-7}
150 rpm J/ mol m^2.sec	4.516 x10^{-11}	1.674 x10^{-11}	-
Per/ mol/sec	4.516 x10^{-5}	1.674 x10^{-5}	-
$K_{b\ ex}$	1.523 x10^{-5}	2.750 x10^{-6}	-

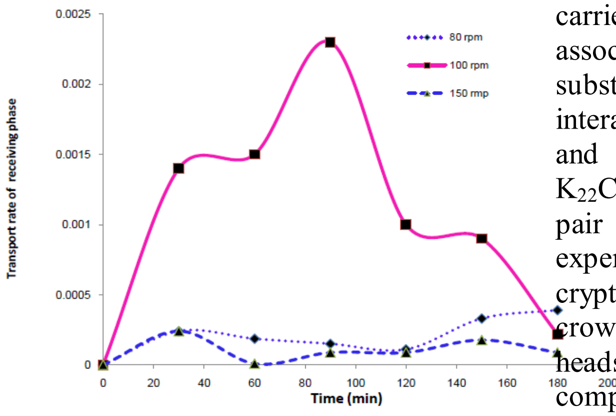


Fig 3 :effect of stirring speed transport rate of Cd $^{2+}$ion

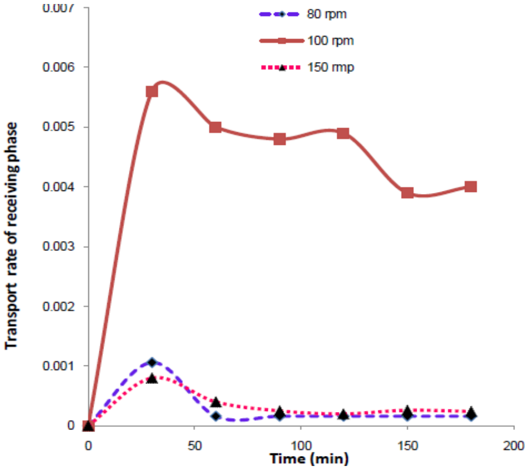


Fig 4 : effect of stirring speed on the transport rate of Zn^{2+} ion

Effect of type of carrier :

The nature of macrocyclic ionophore such as the ring size , the kind and number of donor atoms , and also the substituting groups present in the ring has an important effect on cation transport **(16,17)** .

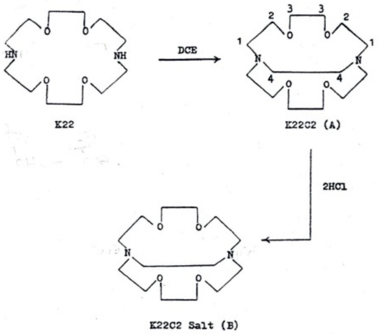
The characteristic of the crown ethers , can be used as carriers for both cationic and anionic forms of metal ions**(18)** According to pearson's HSAB principles ,as shown in table (4) , the substitutions of some oxygen atom by sulfur or nitrogen atom should results in an increase in the complex stability of Pb^{+2} ion with diaza-18-crwon 6 as carrier , but a major problem associated with the use of aza – substituted crown ether is the interactions with the solvent 1,2-DCE and the formation of the compound $K_{22}C_2$ and will be decrease the ion-pair stability in the transport experiment .**(19)** On the other hand the cryptand (2.2.2) is a cage type bicycle crown compounds, whose two bridge heads consist of two N groups , these compounds bind metal ion light into space in their lattice **(20)** , from the thermodynamic reason , by which strong complex agents retain the metal ion in the membrane also beside the kinetic factors : strong complex agents frequently show a slow rate of decomplexation .**(21,22)**

However , DCH18C6 complex with Pb^{2+} ion more stable than DB18C6 due to substituent group which is enhance the electron density inside the cavity negatively charge on oxygen atom by cyclohexyl group when the benzene group act as electron with drawing group which will be reduce the charge density on the oxygen atoms .

In such cases the selectivity of the system is not due to cavity size of crown ether , because , the Crwon ethers display selectivity in complexation mainly based on cavity and ion size . As observed from table (7) the ionic radius of cadmium ion , Cd^{+2} (r=0.97A) is smaller thane Pb^{2+} (r=1.18A),and the ionic radius of Zn^{2+} is smaller than the radius of Cd^{+2} and Pb^{2+} ions So , they can't attain a convenient fit condition for the cavity size of 18-crwon – 6 (2.6-3.2 Ȧ) and for Crypt[2.2.2] is (2.8Ȧ) from the table (5,6) and figure (5,6,7).The values of J&per. and lipophilicity of the macro cyclic compounds are :

DC18C6>DB18C6>DA 18 C6 > cryp[2.2.2]

in this trend the extraction constant will be decreased .



Table(4) Classification of some metal ions and ligands as hard and soft acids and bases (23)

Electrophiles	Nucleophiles
Hard acids H$^+$,Li$^+$,Na$^+$,K $^+$, Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} Al ,Sc ,Ga Cr^{3+} , Co^{3+} , Fe^{3+} ,Ce^{3+} Si $^{4+}$, Ti^{4+} ,Cr^{4+} , Th^{4+}	**Hard bases** H_2O ,OH$^-$, F$^-$,PO$_4$, SO^{2-} CO_3^{2-} ,ClO$_4$ $^{2-}$, NO_3^-, Cl$^-$ ROH, RO$^-$,R_2O ,NH ,RNH CH_3^-,N_2H_4
Soft acids Cu$^+$,Ag$^+$,Au$^+$,Ti $^+$,Hg$^+$ Cd $^{2+}$,Hg^{2+} , Pd^{2+} ,Pt^{2+} Ti^{3+} Pt^{3+}	**Soft bases** R_2 S , RS$^-$,$S_2O_3^{2-}$, CN$^-$ I$^-$,SCN$^-$, R_3 P ,R_3 As H$^-$,R$^-$
Border line Fe^{2+} , Co^{2+} ,Ni $^{2+}$,Cu^{2+} ,Zn^{2+} P b $^{2+}$, Sn^{2+} ,R u $^{2+}$, Os^{2+} Sb^{3+} ,Bi^{3+} ,Rh^{3+} ,Ir^{3+}	**Border line** C l$^-$, Br$^-$,N_3^- ,NO_2^- ,SO_3^{2-} $PhNH_2$

Table 5 : Effect of type of carrier on flux and permeability of Pb^{2+} , Cd^{2+} , Zn^{2+} ions in the receiving phase

Type of carrier	P b(II)	C d(II)	Zn(II)
DB18C6			
J/ mol m^2.sec	1.507×10^{-10}	3.515×10^{-11}	1.110×10^{-13}
Per/ mol/sec	1.507×10^{-4}	3.515×10^{-5}	1.110×10^{-7}
K ex	1.760×10^{-5}	3.012×10^{-6}	5.340×10^{-7}
DCH18C6			
J/ mol m^2.sec	7.527×10^{-10}	4.185×10^{-11}	3.395×10^{-14}
Per/ mol/sec	7.527×10^{-4}	4.185×10^{-5}	3.395×10^{-8}
K_{ex}	2.060×10^{-5}	3.600×10^{-6}	5.630×10^{-7}
DA18C6			
J/ mol m^2.sec	9.974×10^{-11}	6.586×10^{-7}	6.904×10^{-12}
Per/ mol/sec	9.974×10^{-5}	6.586×10^{-4}	6.904×10^{-6}
K_{ex}	2.000×10^{-5}	2.570×10^{-6}	5.390×10^{-7}
Cryp2.2.2			
J/ mol m^2.sec	1.816×10^{-9}	2.828×10^{-11}	3.163×10^{-13}
Per/ mol/sec	1.816×10^{-3}	2.828×10^{-5}	3.163×10^{-10}
K_{ex}	1.240×10^{-5}	2.020×10^{-6}	4.390×10^{-7}

Table 6 : Effect of type of carrier on flux and permeability of Pb^{2+} , Cd^{2+} , Zn^{2+} ions in the source phase

Type of carrier	P b(II)	C d(II)	Zn(II)
DB18C6			
J/ mol m^2.sec	6.758 $x10^{-8}$	2.235 $x10^{-7}$	1.164 $x10^{-7}$
Per/ mol/sec	6.758 $x10^{-2}$	2.235 $x10^{-1}$	1.164 $x10^{-1}$
K_{ex}	1.00 $x10^{-3}$	1.312 $x10^{-4}$	6.120 $x10^{-5}$
DCH18C6			
J/ mol m^2.sec	$1.669*10^{-7}$	1.921 $x10^{-7}$	1.373 $x10^{-7}$
Per/ mol/sec	$1.669*10^{-1}$	1.921 $x10^{-1}$	1.373 $x10^{-1}$
K_{ex}	$1.350*10^{-3}$	1.800 $x10^{-4}$	6.512 $x10^{-5}$
DA18C6			
J/ mol m^2.sec	$2.738*10^{-9}$	5.356 $x10^{-4}$	7.192 $x10^{12}$
Per/ mol/sec	$2.738*10^{-3}$	5.356 $x10^{-5}$	7.192 $x10^{-4}$
K_{ex}	$0.897*10^{-3}$	1.00 $x10^{-4}$	5.900 $x10^{-5}$
Cryp2.2.2			
J/ mol m^2.sec	$1.352*10^{-9}$	7.384 $x10^{-8}$	1.872 $x10^{-8}$
Per/ mol/sec	$1.352*10^{-1}$	7.384 $x10^{-2}$	1.872 $x10^{-2}$
K_{ex}	$0.751*10^{-3}$	0.812 $x10^{-4}$	5.512 $x10^{-5}$

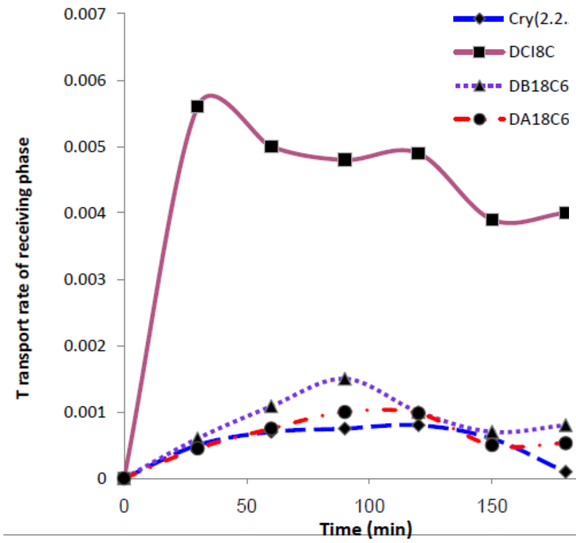


Fig 5 : effect of type of carrier on rate transport of Pb^{2+} ion

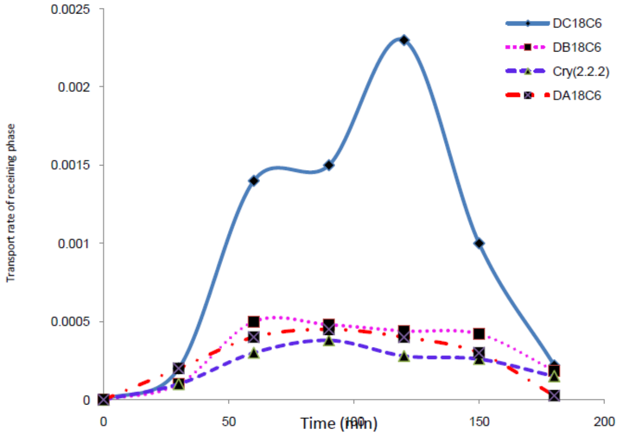


Fig6 :effect of type of carrier on transport rate of Cd^{2+} ion

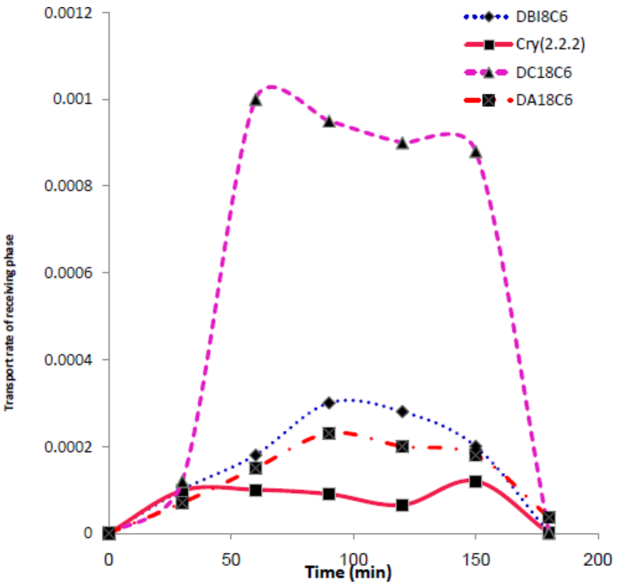


Fig 7 :effect of type of carrier on transport rate of Zn^{2+} ion

3. Effect of solvent : The selection of a suitable organic in BLM is one of the most critical factors in membrane function , and its characteristics largely effect the extraction efficiency of membrane systems three chlorinated organic solvents of various polarities have been chosen for this stage of the project .

According to free energy of transfer which can be represented by the equation**(24)** :

$$\Delta G_{tr} = \Delta G_{sol} - \Delta G_h$$

ΔG_{tr} **: free energy of transfer**

ΔG_{sol} **: free energy of solvation**

ΔG_h **: free energy of hydration**

The free energy hydration of ions should be smaller than its free energy of salvation to assist transport process from source phase to receiving through liquid membranephase. The selectivity of ions transport increase adversely with the values of its hydration energy which is dependent on the radius of ion, As shown in table(7)

In the present work , from table (8)DCE membrane is largely effective than chloroform and carbon tetrachloride may du to its moderate dipole moment and dielectric constant and then solvates ions better with increase value of K_{ex} at left membrane boundary and decrease the de complexation coefficient of ion – pair complex at the right membrane **(26)** as shown in table(9,10).

The electrostatic ion – dipole interaction plays significant role in the complexations of crown ethers with cations .

The more stable complexes of liquids are electrostatic model , in which an ion pair requires little energy to separate of general ionic compounds in organic solvents required a small amount of energy for solvation and the over coming the mutual attraction of the ion pairs and the hydration energy the last but not least temperature effecting on the transport and diffusion process by increase the rate constants of reactions and diffusion coefficient as shown in fig (8,9,10) at the same decrease the extraction process by decreasing the K_{ex} .

Table (7) Hydration Energies of mono valiant and divaliant ions[25]

Ion	hydration energy ΔG in KJ /mol.	Ionc Radius of metal cations
Cd^{2+}	-1755	0.97
Hg^{2+}	-1760	1.89
Pb^{2+}	-1425	1.18
H^{+}	-1050	0.47
Na^{+}	-365	1.94
Ca^{2+}	-1505	1.05
Zn^{2+}	-1770	0.7

Table (8) some physico chemical properties of organic solvent used as liquid membrane (27,28)

Solvent Structure	μ^a	ε^b	η^c	D^d	10^2mass fraction w^e	DN^f	AN^g
$CHCl_3$	1.35	4.80	0.58	1.47	0.087	4.0	23.1
$ClCH_2CH_2Cl$	1.86	10.66	0.73	1.25	0.188	0.0	16.7
CH_2Cl_2	1.55	8.93	0.39	1.31	0.176	1.0	20.4
$C_6H_5NO_2$	4.00	34.80	1.62	1.19	0.165	4.4	14.8

[a] Dipolemoment; [b] Dielectric constant; [c] Viscosity; [d] Density; [e] Water solubility in organic solvent; [f] Donor number; [g] Acceptor number

Table 9: Effect of type of solvent on flux and permeability of Pb^{2+}, Cd^{2+}, Zn^{2+} ions in the receiving phase

Type of solvent	P b(II)	C d(II)	Zn(II)
1,2-D-C-E			
J/ mol m^2.sec	7.527×10^{-10}	4.185×10^{-11}	3.395×10^{-14}
Per/ mol/sec	7.527×10^{-4}	4.185×10^{-3}	3.395×10^{-9}
$K_{b\ ex}$	2.060×10^{-5}	3.600×10^{-6}	5.630×10^{-7}
$CHCl_3$			
J/ mol m^2.sec	3.312×10^{-9}	9.208×10^{-10}	-
Per/ mol/sec	3.312×10^{-3}	9.208×10^{-4}	-
$K_{b\ ex}$	2.220×10^{-5}	3.260×10^{-6}	-
CCl_4			
J/ mol m^2.sec	1.044×10^{-10}	2.100×10^{-11}	-
Per/ mol/sec	1.044×10^{-4}	2.100×10^{-3}	-
$K_{b\ ex}$	2.160×10^{-5}	2.790×10^{-6}	-

Table 10 : Effect of type of solvent on flux and permeability of Pb^{2+} , Cd^{2+} , Zn^{2+} ion in the source phase

Type of solvent	P b(II)	C d(II)	Zn(II)
1,2-D.C.E			
J/ mol m^2.sec	1.669 $x10^{-7}$	7.384 $x10^{-6}$	1.373 $x10^{-7}$
Per/ mol/sec	1.669 $x10^{-1}$	7.38 $x10^{-1}$	1.378 $x10^{-1}$
K_{ex}	1.350 $x10^{-3}$	1.800 $x10^{-4}$	6.512 $x10^{-5}$
$CHCl_3$			
J/ mol m^2.sec	1.652 $x10^{-7}$	1.242 $x10^{-6}$	1.177 $x10^{-7}$
Per/ mol/sec	1.652 $x10^{-4}$	1.242 $x10^{-1}$	1.1775 $x10^{-1}$
K_{ex}	1.000 $x10^{-3}$	1.00 $x10^{-4}$	5.900 $x10^{-5}$
CCl_4			
J/ mol m^2.sec	1.649 $x10^{-7}$	1.686 $x10^{-6}$	1.213 $x10^{-8}$
Per/ mol/sec	1.649 $x10^{-1}$	1.686 $x10^{-1}$	1.2138 $x10^{-2}$
K_{ex}	0.800 $x10^{-3}$	0.800 $x10^{-4}$	5.612 $x10^{-5}$

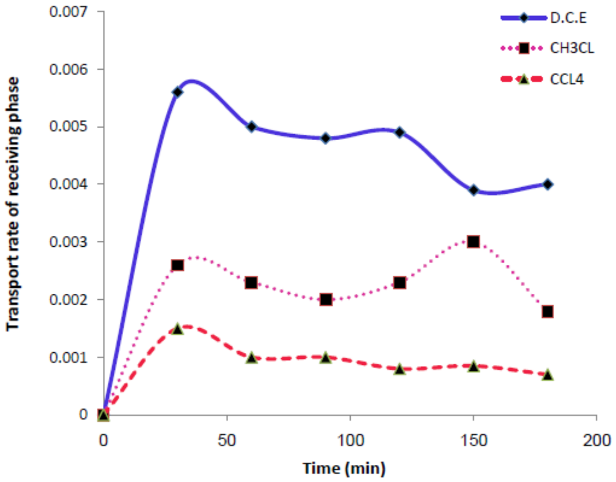


Fig 9:effect of type of solvent on transport rate of Pb^{2+} ion

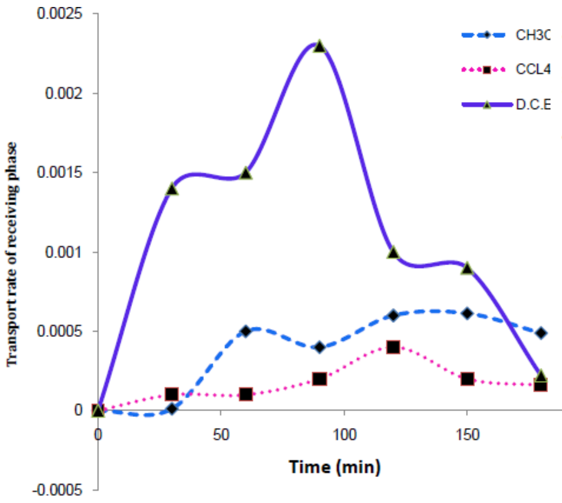


Fig 8:effect of type of solvent on transport rate of Cd^{2+} ion

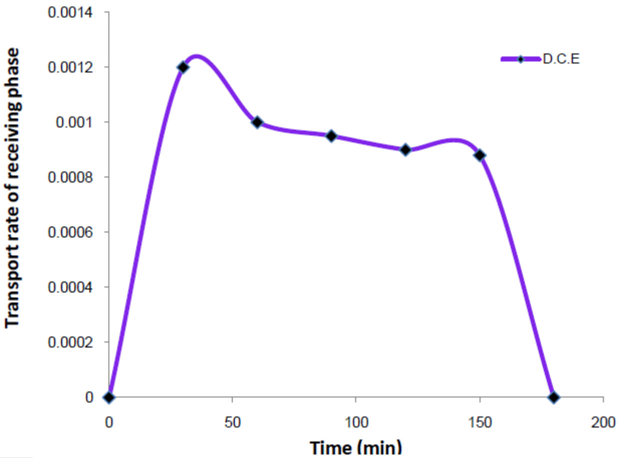


Fig 10 : effect of type of solvent on transport rate of Zn^{2+} ion

Effect of temperature :

Transport studies were carried out at varying temperature to evaluate the activation energy transport of the transport of ions .

The activation energy for transport is often [29,30] considered , its determined from A rrhenious equation given by plot log K VS. 1000 is illustrated in below equation [31]:

$$\text{Log K} = \log A - \frac{E_a}{RT}$$

Where :

K = rate constant .

A = Pre – exponential factor or frequency factor .

Ea = Activation energy .

R = gas constant .

T = temperature / K

From Figure (12,14,16) , activation energy values are low for diffusion – control processes , the rate constants are strongly affected by temperature [32] as shown in fig(11,13,15). High activation energies can be attributed to mechanism of site-site jumping and slow kinetics of decomplexation [33] .

An increase of the operating temperature apparently enhances the flux as shown in table (11,12) .

Table 11 : Effect of type of Temperature on the flux and permeability of Pb^{2+} , Cd^{2+} , Zn^{2+} ions in the receiving phase

Temperature	P b(II)	C d(II)	Zn(II)
298K			
J/ mol m^2.sec	6.24 $\times10^{-10}$	1.054 $\times10^{-11}$	5.465 $\times10^{-12}$
Per/ mol/sec	6.24 $\times10^{-4}$	1.054 $\times10^{-5}$	5.465 $\times10^{-6}$
$K_{b\ ex}$	1.850 $\times10^{-5}$	2.940 $\times10^{-6}$	5.52 $\times10^{-7}$
303K			
J/ mol m^2.sec	7.527 $\times10^{-10}$	4.185 $\times10^{-11}$	3.395 $\times10^{-14}$
Per/ mol/sec	7.527 $\times10^{-4}$	4.185 $\times10^{-5}$	3.395 $\times10^{-8}$
$K_{b\ ex}$	2.060 $\times10^{-5}$	3. 600 $\times10^{-6}$	5.630 $\times10^{-7}$
313K			
J/ mol m^2.sec	3.760 $\times10^{-10}$	1.489 $\times10^{-11}$	5.175 $\times10^{-12}$
Per/ mol/sec	3.760 $\times10^{-4}$	1.489 $\times10^{-4}$	5.175 $\times10^{-6}$
$K_{b\ ex}$	1.050 $\times10^{-5}$	2.643 $\times10^{-6}$	5.164 $\times10^{-7}$

Table 12 : Effect of type of Temperature on flux and permeability of Pb^{2+} , Cd^{2+} , Zn^{2+} ions in the source phase

Temperature	P b(II)	C d(II)	Zn(II)
298K			
J/ mol m^2.sec	2.314 $\times10^{-10}$	7.1980 $\times10^{-11}$	6.040 $\times10^{-12}$
Per/ mol/sec	2.314 $\times10^{-4}$	7.1980 $\times10^{-4}$	6.040 $\times10^{-6}$
K_{ex}	1.000 $\times10^{-3}$	1.221 $\times10^{-4}$	6.100 $\times10^{-5}$
303K			
J/ mol m^2.sec	1.669 $\times10^{-7}$	1.921 $\times10^{-7}$	1.373 $\times10^{-7}$
Per/ mol/sec	1.669 $\times10^{-1}$	1.921 $\times10^{-1}$	1.373 $\times10^{-1}$
K_{ex}	1.350 $\times10^{-3}$	1.800 $\times10^{-4}$	6.512 $\times10^{-5}$
313K			
J/ mol m^2.sec	6.274 $\times10^{-11}$	6.605 $\times10^{-11}$	6.887 $\times10^{-12}$
Per/ mol/sec	6.274 $\times10^{-5}$	6.605 $\times10^{-4}$	6.887 $\times10^{-6}$
K_{ex}	0.600 $\times10^{-3}$	1.00 $\times10^{-4}$	6.010 $\times10^{-5}$

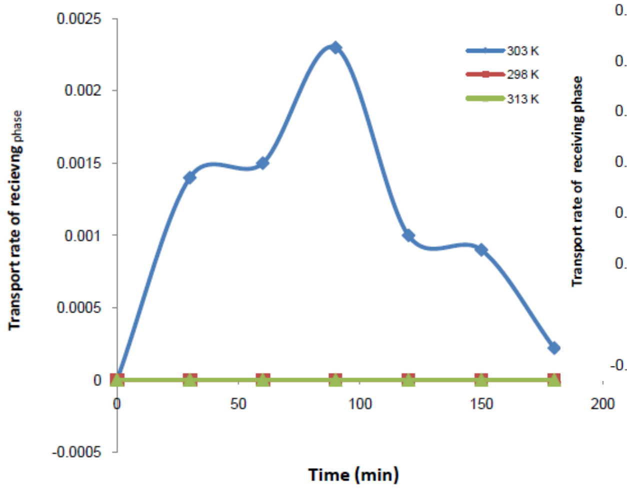


Fig 11 :Effect of temperature on transport rate of Cd $^{2+}$ion

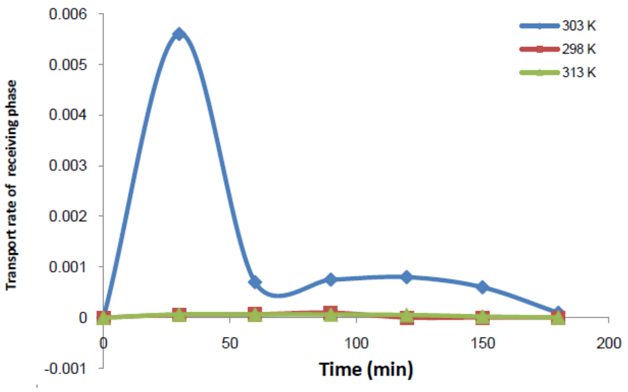


Fig 13 : Effect of temperature on the transport rate of Pb^{2+} ion

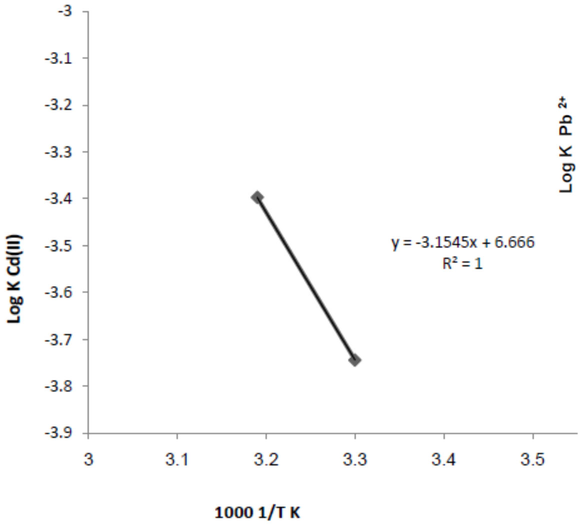


Fig 12 :Effect of temperature on the Log K Cd^{2+}ion

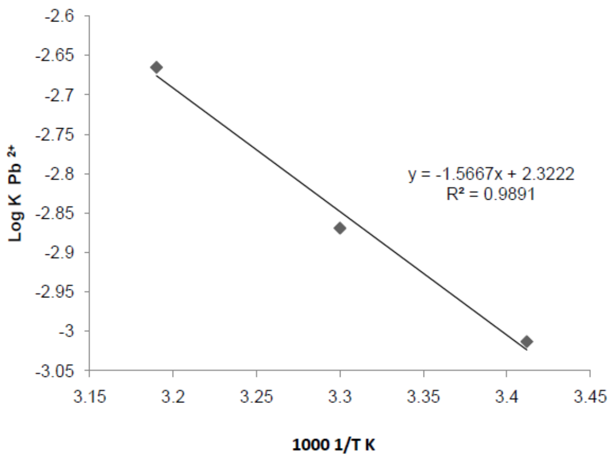


Fig 14 :Effect of temperature on Log K Pb^{2+}ion

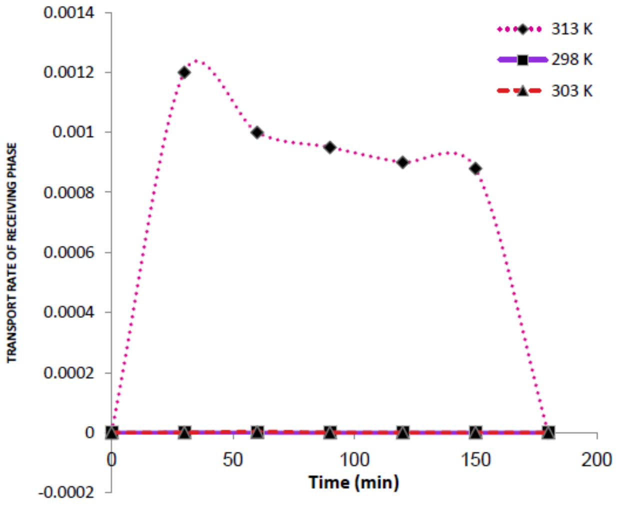


Fig 15 : Effect of temperature on the transport of Zn^{2+} ion

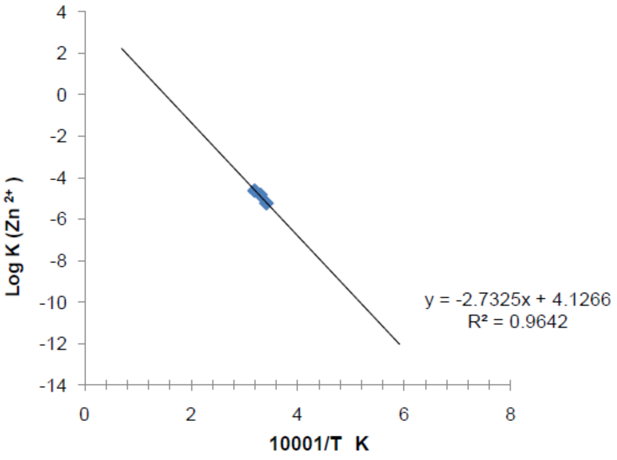


Fig 16 :Effect of temperature on Log K Zn^{2+} ion

Conclusion

Liquid membrane transport has attracted world wide attentions and much work has been directed towards developing methods for its application to the separation of various metal ions , reduces the difficulties encountered in solvent extraction , decreasing the solvent inventory requirement and also allows the use of expensive and highly selective extract ants .

The results have reflected incomplete transport system , the rate determining step which is the diffusion of the carrier nitrate complex across the thin film layers . The transport efficiency of ions increased with increasing stirring speed due to minimize the diffusion effect . How ever , at higher stirring speeds the interface stability and the area of the interlace were changed .

Crown ether is the one of best carrier used in liquid membrane system . the size cavity reflected on the selection binding characteristics of their on the separation of metal ions . The carrier DCH18C6 due to gave better transport results electron donating bonds in cyclohexyl groups , these single bounds allow for 3 – dimensional vibrations and rotations , our suggestion about carrier structures is increased lipophilicity was a accomplished by introduction of alkyls aryl or aralkyl groups on the ring of crown ether . As found in calyx[n] arene and lariat ethers which are bind cations forming stable complex in the membrane phase and faster releasing of cation in the receiving phase .

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Abbreviation :

BLM : Bulk liquid membrane .

DB18C6 : Dibenzo18-crown-6.

DCH18C6 : Dicyclohexye18-crown-6 .

DA18C6 : DiAza18-crown-6 .

Cry(2.2.2) : Kryptofix 2.2.2 .

1,2-D.C.E.: 1,2- dichloroethane.

K_{ex} : Extraction constant.

$K_{b\ ex}$: Back extraction constant.

rpm : rate per minute .

Per : Permeability.

J : Flux.