Effect of Solvent on Competitive Bulk Membrane Transport of Transition and Post Transition Metal Cations Using Decyl-18-crown-6

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Abstract

A series of competitive metal ion transport experiments have been performed. Each involved transport from an aqueous source phase across an organic membrane phase into an aqueous receiving phase. The source phase contained equimolar concentrations of cobalt(II), nickel(II), cupper(II), zinc(II), cadmium(II), silver(I) and lead(II) metal cations. The membrane phase incorporated ionophore, decyl-18-crown-6. The membrane solvents include: chloroform, dichloromethane, 1,2-dichloroethane, nitrobenzene and chloroform–nitrobenzene binary solvents. A good transport efficiency and selectivity of Pb^{2+} transport from aqueous solutions are observed in this investigation. The selectivity order for competitive bulk liquid membrane transport of the studied transition and post transition metal cations through chloroform is: $Pb^{2+} > Co^{2+} > Ni^{2+} > Ag^+ > Cd^{2+}$, but in the case of dichloromethane, 1,2-dichloroethane and nitrobenzene as liquid membranes, the selectivity sequences were found to be: $Pb^{2+} > Co^{2+} > Cd^{2+} > Cu^{2+} > Ag^+ > Ni^{2+} > Zn^{2+}$, $Pb^{2+} > Co^{2+} > Ag^+ > Ni^{2+} > Zn^{2+}$ and $Pb^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Ag^+$, respectively. The transport rate of the metal cations in chloroform–nitrobenzene binary solvents is sensitive to the solvent composition. The transport processes were studied in absence and presence of the stearic acid and the results show that the sequence of selectivities and ion transport rates change in the presence of stearic acid.

Introduction

Transport of metal ions across a membrane plays an essential role in many biochemical processes [1] and has many useful practical applications in separation science. As artificial ligand models, several types of macrocyclic molecules have been prepared and demonstrated specifically to transport alkali, alkaline earth and organic ammonium ions with high selectivities [2–6]. In marked constract, little attention has been directed towards the transport of transition and heavy metal ions [7–11]. Information about the transport of these metal cations across liquid membranes is quite sparse. Transport of some of the metal cations by crown ethers and cryptands has been investigated [12, 13]. The stability constants of complexes have been used to understand the extraction equilibrium in different systems. As a rule, the rate of transport increases with rise in stability of the complexes, and latter decreases due to complex formation at external interface.

Large monovalent anions like picrate and perchlorate permit good transport of the metal cations through the membranes [14].

The goal of the present investigation is to study the effect of the nature of the cation and crown ether and especially the solvent properties on the liquid membrane transport. Here we report the liquid membrane transport of some of the transition and post transition metal cations using decyl-18-crown-6 (Scheme 1) as an ion carrier in various liquid membranes.
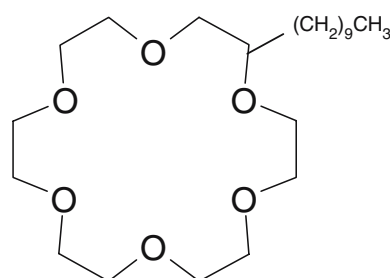
Scheme 1. Decyl-18-crown-6.

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Experimental

Reagents and solvents

Decyl-18-crown-6 (Merck), cobalt(II) nitrate (Riedel), nickel(II) nitrate (G.P.R), cupper(II) nitrate (Fluka), zinc(II) nitrate (Merck), silver(I) nitrate (G.P.R) and cadmium(II) nitrate, lead(II) nitrate, sodium acetate, sodium hydroxide all from Merck and stearic acid (BDH) were used without further purification. The solvents chloroform (Analar), dichloromethane (Merck), 1,2-dichloroethane (Merck) and nitrobenzene (Merck) with the highest purity were used as liquid membranes. Acetic acid (Merck), formic acid (Merck) and nitric acid (BDH) were used as received. All aqueous solutions were prepared using double distilled deionized water. All solvents used for the membrane phase were presaturated with water by shaking a two-phase water–organic mixture and then removing the aqueous phase.

Procedure

The transport experiments employed standardized concentric cells in which the aqueous source phase (10 cm^3) and receiving phase (30 cm^3) separated by an organic phase (50 cm^3). Details of the cell is shown in Scheme 2. For each experiment, both aqueous phases and the organic phase (liquid membrane) were stirred separately at 20 rpm using stirring paddles for the receiving phase and propellers for the source and organic phases each coupled to a single (gread) synchronous motor and the cell was enclosed by a water jacket and thermostated at 25 °C. The aqueous source phase consisted of a buffer solution at pH 4.9 ± 0.1 (6.95 cm^3 of 2 mol dm^{-3} sodium acetate solution and 3.05 cm^3 of 2 mol dm^{-3}
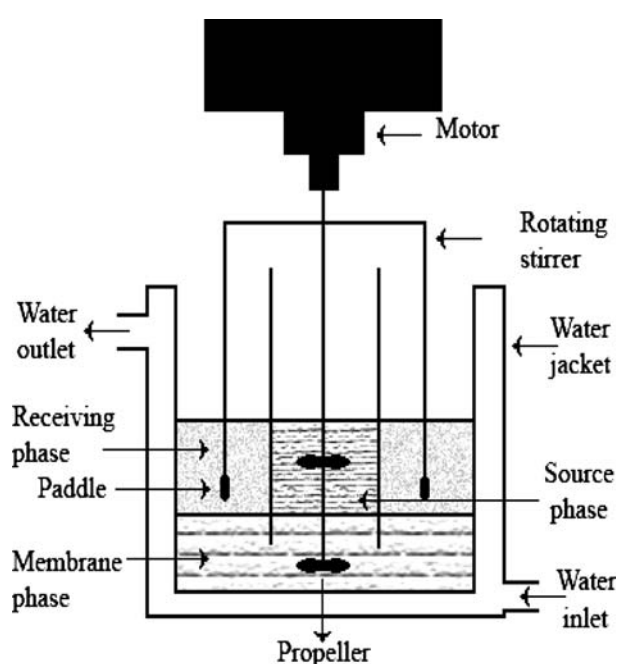
Scheme 2. Liquid membrane cell.

acetic acid made up to 100 cm^3) [15] containing an equimolar mixture of the metal ions, each at the concentration of 1.0×10^{-2} mol dm^{-3}, the total 'all-metal' concentration was 7.0×10^{-2} mol dm^{-3}. The organic phase contained the macrocycle at 10^{-3} mol dm^{-3}. The receiving phase consisted of a buffer solution at pH 3.0 ± 0.1 (56.6 cm^3 of 1 mol dm^{-3} formic acid and 10 cm^3 of 1 mol dm^{-3} sodium hydroxide made up to 100 cm^3) [15]. All transport runs were terminated after 24 h and atomic absorption spectroscopy was used to determine the amount of each metal ion transported over this period. Both source and receiving phases were analyzed (using a Shimadzo spectra AA-670 spectrometer) after each transport run. This also enabled the amount of the metal cations remaining in the membrane phase to be calculated. The transport results are quoted as the average values obtained from duplicate runs carried out parallel using different cells that had previously been shown to yield identical results within experimental error.

Results

The results for competitive transport of seven-metal cations from a source phase at pH 4.9 through four liquid membranes, chloroform, dichloromethane, 1,2-dichloroethane and nitrobenzene containing decyl-18-crown-6 into acidic receiving phase (pH = 3) are listed in Table 1. The results for competitive transport of seven-metal cations from a source phase at pH 4.9 through chloroform–nitrobenzene binary mixtures containing decyl-18-crown-6 into acidic receiving phase (pH = 3) are listed in Table 2. A pH gradient was utilized to facilitate transport of the metal ions across the membrane by counter transport of protons. The selectivity sequences for competitive transport of the studied metal cations by decyl-18-crown-6 in various organic membranes are shown in Table 3. The results in presence of stearic acid in chloroform phase are listed in Table 4. In Figures 1–3 are shown the results for competitive transition and post transition metal cations transport across organic liquid membranes. The variation of transport rate of Pb^{2+} metal cation *versus* the mole fraction of chloroform in chloroform–nitrobenzene binary solvents is shown in Figure 4. The rate of transport process for chloroform system *versus* time is shown in Figure 5.

Effect of carrier structure on the cation transport

For competitive transport of the seven metal cations we used decyl-18-crown-6 as an ionophore. The attachment of large decyl group to 18-crown-6 increases its lipophilicity thus increasing its solubility and effectively trapping it in the organic phase into one or both of the aqueous phases.

The investigations have established that the nature of a macrocyclic ionophore such as the ring size, the kind of donor atoms and substituting groups present in the

Table 1. Data for competitive transport of seven metal cations across bulk chloroform, dichloromethane, 1,2-dichloroethane and nitrobenzene membranes by decyl-18-crown-6 at 25 °C

Ionophore	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ag^+	Cd^{2+}	Pb^{2+}
Chloroform							
%(transport receiving)[a]	3.93	0.82	–	–	0.06	0.04	15.23
%(membrane)[b]	–	–	79.21	76.50	13.55	–	43.37
J (mol per 24 h)[c]	4.90	1.0	–	–	0.08	0.06	19.04
Dichloromethane							
%(transport receiving)[a]	3.27	1.58	2.06	0.75	2.01	2.10	28.62
%(membrane)[b]	–	4.41	12.65	74.40	12.08	18.16	64.00
J (mol per 24 h)[c]	4.09	1.97	2.57	0.94	2.50	2.62	35.78
1,2-Dichloroethane							
%(transport receiving)[a]	0.72	0.20	–	0.04	0.3	0.05	14.52
%(membrane)[b]	4.52	50.14	70.30	48.86	68.10	14.95	42.48
J (mol per 24 h)[c]	0.9	0.25	–	0.05	0.40	0.06	18.15
Nitrobenzene							
%(transport receiving)[a]	1.33	0.45	–	0.27	0.15	0.22	9.20
%(membrane)[b]	28.08	6.91	52.0	23.13	13.99	16.88	39.5
J (mol per 24 h)[c]	1.7	0.56	–	0.33	0.19	0.28	11.5

[a]Percent of total metal cations in the receiving phase after 24 h.
[b]Percent of total metal cations in the membrane phase after 24 h.
[c]All J values are $\times 10^{-7}$.

Table 2. Data for competitive transport of seven metal cations across bulk chloroform–nitrobenzene binary mixed solvent membranes by decyl-18-crown-6 at 25 °C

Ionophore	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ag^+	Cd^{2+}	Pb^{2+}
Pure CHCl$_3$							
%(transport receiving)[a]	3.93	0.82	–	–	0.06	0.04	15.23
%(membrane)[b]	–	–	79.21	76.50	13.55	–	43.37
J (mol per 24 h)[c]	4.90	1.0	–	–	0.08	0.06	19.04
75% CHCl$_3$–25% NB[d]							
%(transport receiving)[a]	–	0.33	–	0.11	0.09	–	11.72
%(membrane)[b]	4.64	–	6.84	21.06	7.60	15.08	34.60
J (mol per 24 h)[c]	–	0.41	–	0.14	0.11	–	14.65
50% CHCl$_3$–50% NB[d]							
%(transport receiving)[a]	–	0.40	–	0.26	0.18	–	9.43
%(membrane)[b]	10.45	–	13.45	23.82	9.57	20.50	26.00
J (mol per 24 h)[c]	–	0.50	–	0.32	0.22	–	11.79
25% CHCl$_3$–75% NB[d]							
%(transport receiving)[a]	–	–	–	–	0.45	0.05	9.32
%(membrane)[b]	19.82	12.25	19.43	29.54	20.98	28.24	41.26
J (mol per 24 h)[c]	–	–	–	–	0.56	0.05	11.65
Pure NB[e]							
%(transport receiving)[a]	1.33	0.45	–	0.27	0.15	0.22	9.20
%(membrane)[b]	28.08	6.91	52.0	23.13	13.99	16.88	39.50
J (mol per 24 h)[c]	1.7	0.56	–	0.33	0.19	0.28	11.50

[a]Percent of total metal cations in the receiving phase after 24 h.
[b]Percent of total metal cations in the membrane phase after 24 h.
[c]All J values are $\times 10^{-7}$.
[d]Composition of binary mixtures is expressed in mol% for each solvent system.
[e]NB = nitrobenzene.

ring has an important effect on cation transport [16, 17]. The results obtained in this study, show that decyl-18-crown-6 system preferentially transport the Pb^{2+} ion. Although the size of Ag^+ ion ($r = 1.26$ Å) is bigger than the size of the Pb^{2+} ($r = 1.18$ Å) ion and, therefore, it can attain a more convenient fit condition for the crown

Table 3. Selectivity sequences for competitive transport for some of the transition and post transition metal cations across bulk liquid membranes by decyl-18-crown-6

Solvent system	Selectivity order	Selectivity ratios (Pb^{2+}/Ag^+)
Pure solvents		
Chloroform	$Pb^{2+} \gg Co^{2+} > Ni^{2+} > Ag^+ > Cd^{2+}$	238
Dichloromethane	$Pb^{2+} \gg Co^{2+} > Cd^{2+} > Cu^{2+} > Ag^+ > Ni^{2+} > Zn^{2+}$	14
1,2-Dichloroethane	$Pb^{2+} \gg Co^{2+} > Ag^+ > Ni^{2+} > Zn^{2+}$	60
Nitrobenzene	$Pb^{2+} \gg Co^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Ag^+$	46
Mixed solvents		
75%CHCl$_3$–25%NB	$Pb^{2+} \gg Ni^{2+} > Zn^{2+} > Ag^+$	133
50%CHCl$_3$–50%NB	$Pb^{2+} \gg Ni^{2+} > Zn^{2+} > Ag^+$	52
25%CHCl$_3$–75%NB	$Pb^{2+} \gg Ag^+ > Cd^{2+}$	20

Table 4. Data for seven-metal cations competitive transport across a bulk chloroform membrane by decyl-18-crown-6 in presence of stearic acid at 25 °C

Ions	% Receiving[a]	% Membrane[b]	J (mol per 24 h)[c]
Co^{2+}	–	70.5	–
Ni^{2+}	–	–	–
Cu^{2+}	–	90.2	–
Zn^{2+}	–	87.74	–
Ag^+	0.15	4.77	0.19
Cd^{2+}	0.18	–	0.22
Pb^{2+}	17.77	26.08	22.2

[a]Percent of total metal cations in the receiving phase after 24 h.
[b]Percent of total metal cations in the membrane phase after 24 h.
[c]All J values are $\times 10^{-7}$.

ether cavity, but since the Pb^{2+} ion has a less soft character than Ag^+ ion [18], it seems that according to the hard and soft acid–base concept, it can form a more stable complex with oxygen donor atoms of decyl-18-crown-6 as a hard base. Moreover, the Pb^{2+} ion bears a high charge density, which results in a strong interaction with this ligand. Therefore, as shown in Table 3, high selectivity ratios of Pb^{2+} ion to Ag^+ ion are obtained in these experiments.

Effect of solvent upon fluxes and selectivity in bulk liquid membrane transport

According to Izatt and co-workers, several parameters whose values depend on the membrane solvent can affect the transport of the metal cations [19]. The data for competitive transport of the seven metal cations in different membranes, which are listed in Table 1, show that the rate of transport of the metal cations depends on the nature of the membrane solvent. As is shown in Table 3, the selectivity sequences for competitive bulk liquid membrane transport of the studied transition and post transition metal cations through chloroform, dichloromethane, 1,2-dichloroethane and nitrobenzene liquid membranesbydecyl-18-crown-6 are: $Pb^{2+} > Co^{2+} > Ni^{2+} > Ag^+ > Cd^{2+}$, $Pb^{2+} > Co^{2+} > Cd^{2+} > Cu^{2+} > Ag^+ > Ni^{2+} > Zn^{2+}$, $Pb^{2+} > Co^{2+} > Ag^+ > Ni^{2+} > Zn^{2+}$ and $Pb^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Ag^+$, respectively. As shown in Table 1, no transport was observed for some of the metal cations in liquid membrane phases. The selectivity ratios of Pb^{2+}/Ag^+ in these solvent systems are listed in Table 3, the selectivity ratio of Pb^{2+}/Ag^+ in chloroform is much bigger than the other three organic solvents. As is evident in Table 1, the rate of transport of Pb^{2+} metal cation through organic
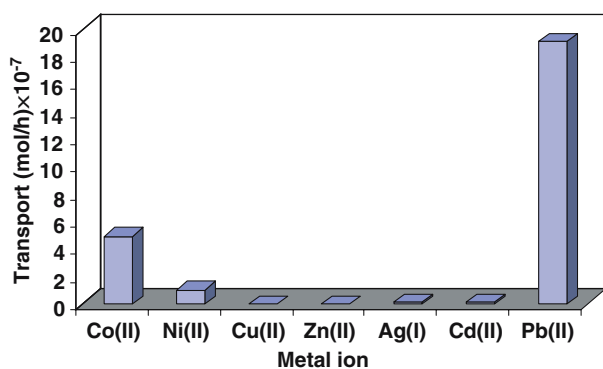

Figure 1. Results of the competitive seven metal cations transport experiment (water/chloroform/water) at 25 °C. Aqueous source phase: 10 ml, contains seven metal cations, each with initial concentration 0.01 M prepared in a buffer solution (CH$_3$COOH/CH$_3$COONa) pH 4.9. Membrane chloroform phase: 50 ml, contains ligand (0.001 M). Aqueous receiving phase: a buffer solution of (HCOOH/HCOONa), pH 3.0.
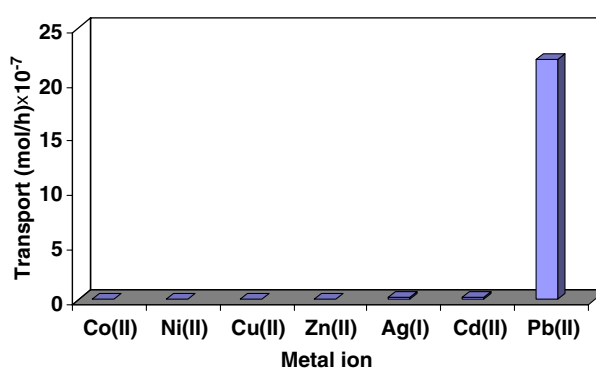

Figure 2. Results of the competitive seven metal cations transport experiment (water/chloroform–stearic acid/water) at 25 °C. Aqueous source phase: 10 ml, contains seven metal cations, each with initial concentration 0.01 M prepared in a buffer solution (CH$_3$COOH/ CH$_3$COONa) pH 4.9. Membrane chloroform phase: 50 ml, contains ligand (0.001 M) and stearic acid (0.004 M). Aqueous receiving phase: a buffer solution of (HCOOH/HCOONa), pH 3.0.
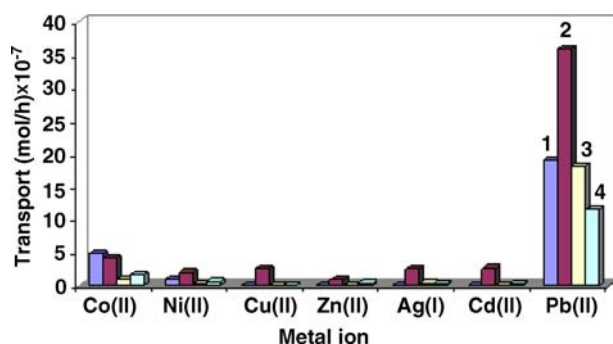
Figure 3. Comparison of the results of the competitive seven metal cations transport experiments at 25 °C in various organic membranes. Aqueous source phase: 10 ml, contains seven metal cations, each with initial concentration 0.01 M prepared in a buffer solution (CH_3COOH/CH_3COONa) pH 4.9. Membrane liquid phase: 50 ml, contains ligand (0.001 M). Aqueous receiving phase: a buffer solution of ($HCOOH/HCOONa$), pH 3.0. 1($CHCL_3$), 2(DCM), 3(1,2–DCE) and 4(NB).
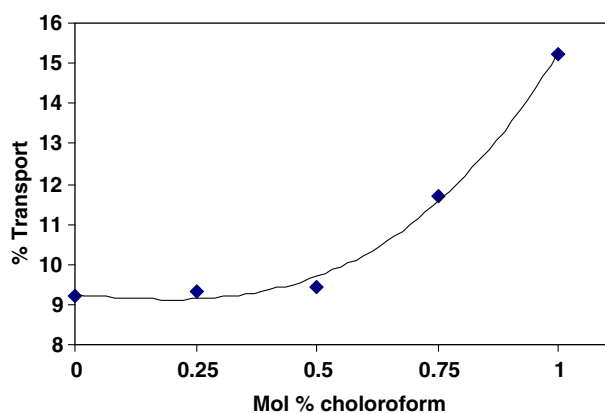

Figure 4. Changes of the transport rate of Pb^{2+} metal cation with solvent composition in chloroform–nitrobenzene binary mixed solvent.
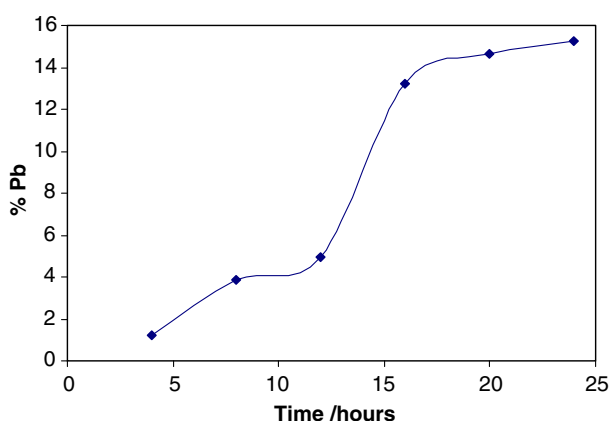

Figure 5. Amount of Pb^{2+} metal cation transported into the receiving phase and source phase *versus* time (h) for competitive bulk liquid membrane transport in chloroform.

solvents is: dichloromethane > chloroform > 1,2-dichloroethane > nitrobenzene. According to the physicochemical properties of the solvents, this result may be attributed to the lower viscosity of dichloromethane ($\eta = 0.39$) than that of chloroform ($\eta = 0.58$), 1,2-dichloroethane ($\eta = 0.73$) and nitrobenzene ($\eta = 1.62$) which leads to increase the rate of transport in this organic solvent compared to the other three solvents [20]. On the other hand, the higher dielectric constant of nitrobenzene than that of chloroform, dichloromethane and 1,2-dichloroethane can lead to destabilization of the ion pair in the organic phase leading to decrease the rate of transport of Pb^{2+} metal cation through nitrobenzene as liquid membrane.

Effect of binary mixed solvent membrane on transport efficiency of the metal cations

As is obvious from Table 2, the transport of Pb^{2+} metal cation increases as the concentration of nitrobenzene is lowered in chloroform–nitrobenzene binary mixed solvent. According to the physicochemical properties of the solvents, the lower viscosity of chloroform ($\eta = 0.58$) than that of nitrobenzene ($\eta = 1.62$) and also the higher dielectric constant of nitrobenzene than that of chloroform can result in an increase in transport rate of the Pb^{2+} metal cation as the mole fraction of nitrobenzene decreases in chloroform–nitrobenzene binary solutions. The changes of transport rate *versus* the composition of the chloroform–nitrobenzene binary solvent is shown in Figure 4. As is evident from this Figure, the transport process for the Pb^{2+} metal cation is sensitive to the solvent composition and a non-linear relationship is observed for variation of the transport rate of this metal cation with the composition of the binary mixed solvent. This behavior may be due to the interactions between the chloroform and nitrobenzene molecules in their binary mixtures [21], which may result in changing the composition of the boundary layers, and, therefore, changing the desolvation of the aqueous metal species as the membrane phase is varied.

Effect of stearic acid on transport efficiency of the metal cations

In another experiment, the competitive mixed metal ion transport processes (water–chloroform–water) employed an organic phase containing known concentrations of the ionophore and stearic acid. A major role of the stearic acid (4×10^{-3} mol dm^{-3}) is to aid the transport process by providing a lipophilic counter ion in the organic phase on proton loss to the aqueous source phase, giving rise to charge neutralization of the metal cation being transported through ion pairing or adduct formation [22, 23]. In this manner the uptake of lipophilic nitrate anions into the organic phase is avoided. An additional benefit of adding lipophilicity in the form of a long-chain hydrocarbon has been documented for systems of the above type [24]. Normally, ion pair/adduct formation serves to inhibit any bleeding of partially species from the organic membrane phase into either of

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the aqueous phases. For competitive bulk liquid membrane transport of the transition and post transition metal cations through chloroform liquid membrane by decyl-18-crown-6 in the presence of stearic acid, the selectivity order changed to: $Pb^{2+} > Cd^{2+} > Ag^+$ (Table 3) and the selectivity ratio of Pb^{2+}/Ag^+ was found to be 118. As is shown in Figure 2, no transport was observed for Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} metal cations through chloroform phase in presence of stearic acid.

Effect of time

Figure 5 shows the time dependence of Pb^{2+} metal cation transport through chloroform membrane under the optimum experimental conditions. As shown in this Figure, the transport rate of Pb^{2+} ion increases with time up to about 16 h. After this time, the transport rate of Pb^{2+} cation becomes independent of time.

Conclusion

The liquid membrane transport experiments of cobalt(II), nickel(II), cupper(II), zinc(II), cadmium(II), silver(I) and lead(II) metal cations using decyl-18-crown-6 (Scheme 1) as an ion carrier in various organic membranes showed that the rates of cation transport are strongly influenced by the nature and composition of the membrane solvents. The sequence of selectivities for competitive of the metal cations are changed by changing the membrane solvent. Decyl-18-crown-6 showed a good selectivity for Pb^{2+} ion and the order of the transport ability of the ligand for this metal cation in different membrane systems was found to be: dichloromethane > chloroform > 1,2-dichloroethane > nitrobenzene.

A good selectivity was also observed for Pb^{2+} ion in the case of using chloroform–nitrobenzene binary mixed solvents as membrane phase. The transport rate of the Pb^{2+} ion is influenced by the composition of the mixed solvent and a non-linear behavior was observed between the transport rate and the composition of this membrane system and it was found that the selectivity orders of the ion carrier for the metal cations are changed with respect to the pure organic solvent membranes.

The experimental results obtained for competitive liquid membrane transport of the studied metal cations by decyl-18-crown-6 showed that the sequence of selectivities and ion transport ability change in presence of stearic acid in chloroform phase.

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