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# Transport Study of Metal Cations Through a Bulk Liquid Membrane Using Benzo-18-crown-6 as an Ionophore

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The transport experiments of $Cr^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ag^+$ and $Pb^{2+}$ metal cations were carried out by benzo-18-crown-6 (B18C6) using chloroform ($CHCl_3$), 1,2-dichloroethane (1,2-DCE), dichlorometh-ane (DCM), nitrobenzene (NB), chloroform-nitrobenzene ($CHCl_3$-NB) and chloroform-dichloromethane ($CHCl_3$-DCM) binary mixed solvents as liquid membranes. The aqueous source phase consisted of a buffer solution ($CH_3COOH/CH_3COONa$) at pH = 5 and containing an equimolar mixture of these 7 metal cations. The organic phase contained the macrocycle ligand, benzo-18-crown-6 (B18C6) as an ionophore and the receiving phase consisted of a buffer solution (HCOOH/HCOONa) at pH = 3. The obtained results show that benzo-18-crown-6 is a highly selective ionophore for $Pb^{2+}$ cation. The sequence of transport efficiency for $Pb^{2+}$ cation in organic solvents was found to be : DCM > NB > 1,2-DCE > $CHCl_3$. The influence of the stearic acid, palmitic acid and oleic acid in the membrane phase on the ion transport was investigated. A non-linear behaviour was observed for variation of the transport rate of $Pb^{2+}$ cation *vs.* the composition of $CHCl_3$-NB and $CHCl_3$-DCM binary mixtures.

**Key Words: Bulk liquid membrane transport, Benzo-18-crown-6, $Cr^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ag^+$, $Pb^{2+}$ metal cations, Chloroform, 1,2-Dichloroethane, Dichloromethane, Nitrobenzene, Chloroform-nitrobenzene, Chloroform-dichloromethane binary mixtures.**

## INTRODUCTION

Selective removal of $Pb^{2+}$ ion for environmental remediation and in the treatment of acute and chronic lead poisoning remains an important objective[1-3]. Attempts to remove toxic heavy metal ions (*e.g.*, $Cd^{2+}$ and $Pb^{2+}$) from the environment and from biological systems have utilized a variety of separation methods such as adsorption, precipitation, solvent extraction and liquid membrane transport. Liquid membrane transport is a new separation process as a modification of solvent extraction. The simultaneous extraction and stripping operation is very attractive, because the solute of interest can move from a high concentration solution to a low concentration solution with a suitable carrier[4]. Crown ether derivatives have been widely used as suitable neutral carriers for the selective and efficient transportation of cations through liquid membranes. The efficiency of their interaction may be affected by the nature of the metal ion and by the number, distance and orientation of the donor atoms of the ligand that are structurally accessible to the complexed cation[5-7]. During the past decade, there have been some studies on $Pb^{2+}$-selective membrane transport using neutral ionophores[8-10].

In this study, the transport of $Cr^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ag^{+}$ and $Pb^{2+}$ metal cations with benzo-18-crown-6 (B18C6) (Fig. 1) as a carrier was performed using chloroform ($CHCl_3$), 1,2-dichloroethane (1,2-DCE), dichloromethane (DCM), nitrobenzene (NB), chloroform-nitrobenzene ($CHCl_3$-NB) and chloroform-dichloromethane ($CHCl_3$-DCM) binary mixtures as liquid membranes. The effect of the stearic acid, palmitic acid and oleic acid as surfactants on transport efficiency of the metal cations was also investigated.

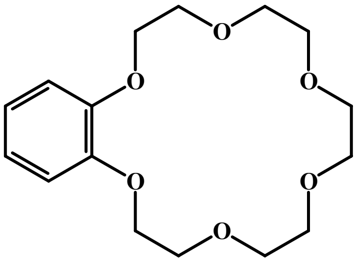

Fig. 1. Structure of benzo-18-crown-6

## EXPERIMENTAL

Benzo-18-crown-6 (Merck), chromium(III) nitrate (BDH), cobalt(II) nitrate (BDH), copper(II) nitrate (BDH), zinc(II) nitrate (Merck), cadmium(II) nitrate (Riedel), silver(I) nitrate (Merck), lead(II) nitrate (BDH), sodium acetate (Riedel), sodium hydroxide (Riedel), stearic acid (BDH), palmitic acid (Riedel) and oleic acid (Merck) were used without further purification. Formic acid (Riedel), chloroform (BDH) 1,2-dichloroethane, dichloromethane, nitrobenzene, acetic acid and nitric acid (all from Merck) were used with the highest purity. All aqueous solutions were prepared using deionized double distilled water.

A Shimadzu AA-670 atomic absorption spectrometer (AAS) was used for measurement of metal ions concentration. The pH measurements were made with a Metrohm 692 pH/ ion meter using a combined glass electrode. A bulk type liquid membrane cell was used in all transport experiments.

**Procedure:** Transport experiments were carried out at ambient temperature. A cylindrical glass cell (inside diameter 5 cm) holding a glass tube (inside diameter 2 cm), thus separating the two aqueous phases, was used (Fig. 2). The aqueous source phase (10 mL) and receiving phase (30 mL) were separated by an organic phase (50 mL). The organic phase was magnetically stirred by a Teflon-coated magnetic bar at 20 rpm. The aqueous source phase consisted of a buffer solution ($CH_3COOH$/

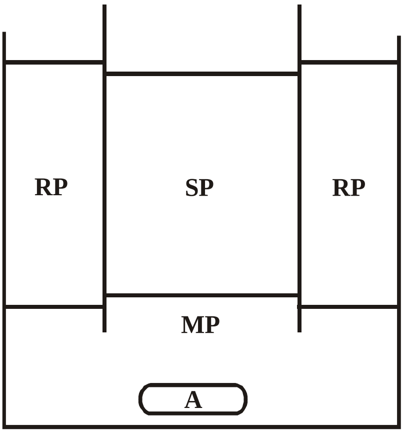

Fig. 2. Representation of the bulk type liquid membrane cell used: SP = source phase; RP = receiving phase; MP = membrane phase; A = magnetic stirrer

$CH_3COONa$) at pH = 5 containing an equimolar mixture of the metal cations (0.01 M). The organic phase (liquid membrane) contained the macrocycle ionophore (B18C6) (0.001 M) and the receiving phase consisted of a buffer solution (HCOOH / HCOONa) at pH = 3. The pH gradient is used in order to facilitate the transport of the metal ions across the organic membrane by counter transport of protons. The organic solvents: $CHCl_3$, 1,2-DCE, DCM, NB, $CHCl_3$-NB and $CHCl_3$-DMC binary mixtures were used as membrane phase. After 24 h, the metal ions concentration of both aqueous phases were measured by atomic absorption spectroscopy along with a series of standard solutions which were made similarly, in order to convert the atomic absorption signals to concentration units.

## RESULTS AND DISCUSSION

**Effect of solvent on transport efficiency of the metal cations:** The ability of the solvent molecules to compete with the donor atoms of the ligand towards the coordination sites of cation, is one of the factors that can thermodynamically influence the complexation process[11].

The data for competitive transport of $Cr^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ag^+$ and $Pb^{2+}$ metal cations from an aqueous source phase through $CHCl_3$, 1,2-DCE, DCM and NB membranes containing benzo-18-crown-6 ligand at ambient temperature are given in Table-1 and the graphical results are shown in Fig. 3.

The obtained results show that benzo-18-crown-6 is highly selective ionophore for $Pb^{2+}$ cation and under the employed experimental conditions, the $Pb^{2+}$ ion is transported from the source phase into the receiving phase. The liquid membrane used in this study is shown schematically in Fig. 4. The movement of charged species through the hydrophobic liquid membrane is accomplished by the presence of a cooperative host composed of benzo-18-crown-6. After complexation of the

TABLE-1
DATA FOR SEVEN METAL CATIONS COMPETITIVE TRANSPORT ACROSS ORGANIC SOLVENTS AS BULK LIQUID MEMBRANE WITH B18C6

| Solvent | Cr(III) | Co(II) | Cu(II) | Zn(II) | Cd(II) | Ag(I) | Pb(II) |
|---|---|---|---|---|---|---|---|
| $CHCl_3$ | | | | | | | |
| % (Receiving)[a] | –[d] | – | – | – | – | 0.21 | 5.04 |
| % (membrane)[b] | – | – | 5.08 | – | – | – | 14.12 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.26 | 6.31 |
| 1,2-DCE | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.15 | 6.43 |
| % (membrane)[b] | 1.93 | 6.67 | 1.97 | – | – | 2.76 | 12.66 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.19 | 8.03 |
| DCM | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.53 | 10.41 |
| % (membrane)[b] | 6.00 | 3.58 | 4.33 | – | – | – | 18.86 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.69 | 13.02 |
| NB | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 3.15 | 7.34 |
| % (membrane)[b] | 0.61 | 7.59 | 6.12 | – | – | 4.61 | 22.01 |
| J (mol per 24 h)[c] | – | – | – | – | – | 3.94 | 9.18 |

[a]Per cent of total metal cations in the receiving phase after 24 h; [b]Per cent of total metal cations in the membrane phase after 24 h; [c]All values are × $10^{-7}$; [d]The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

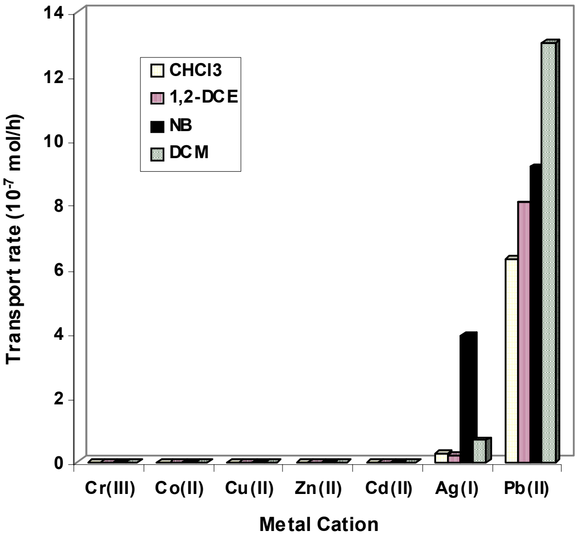

Fig. 3. Comparison of the results of metal ion transport (water/organic solvent/water) studies with B18C6. Source phase: pH = 5 ($CH_3COOH/CH_3COONa$) containing metal ions at 0.01 M (10 mL). Membrane phase: contains B18C6 (0.001 M), (50 mL). Receiving phase: pH = 3 (NaOH/HCOOH), (30 mL) stirred for 24 h at ambient temperature

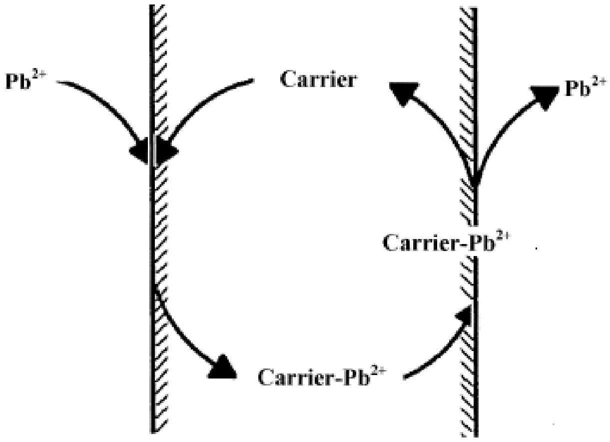

Fig. 4. Liquid membrane system for transport of $Pb^{2+}$ cation

carrier with $Pb^{2+}$ ion on the left side of the membrane, the complex diffuses down its concentration gradient. On the right side of the membrane, the metal ion would be released into the receiving phase (with pH gradient). At this stage, the free carrier diffuses back across the liquid membrane. The net result is the transport of $Pb^{2+}$ ion from the aqueous source phase to the aqueous receiving phase across the bulk organic membrane phase.

As is seen from Fig. 3, the transport of $Pb^{2+}$ ion by this ligand is varied in order: DCM > NB > 1,2-DCE > $CHCl_3$. The results for competitive metal cation transport across DCM as organic solvent are shown in Fig. 5. According to the physicochemical properties of the solvents, which are given in Table-2, may be attributed to the lower viscosity of DCM which leads to increase the rate of ion transfer in this organic solvent compared to the other 3 solvents. Although the dipole moment of DCM ($\mu = 1.55$) is lower than those of 1,2-DCE ($\mu = 1.88$) and NB ($\mu = 4$), but the $J$ value for $Pb^{2+}$ ion transport is larger in DCM with respect to 1,2-DCE. The lower dielectric constant of DCM ($\varepsilon = 8.93$) than those of 1,2-DCE ($\varepsilon = 10.44$) and NB ($\varepsilon = 34.8$) may aid the ion-pair formation in DCM which results

TABLE-2
SOME PHYSICOCHEMICAL PROPERTIES OF ORGANIC SOLVENTS USED AS LIQUID MEMBRANES[12]

| Solvent | Structure | DN [a] | AN [b] | $\mu^c$ | $\varepsilon^d$ | $\eta^e$ | $d^f$ |
|---|---|---|---|---|---|---|---|
| Chloroform | $CHCl_3$ | 4.0 | 23.1 | 1.35 | 4.80 | 0.58 | 1.479 |
| 1,2-Dichloroethane | $ClCH_2CH_2Cl$ | 0.0 | 16.7 | 1.86 | 10.66 | 0.73 | 1.250 |
| Dichloromethane | $CH_2Cl_2$ | 1.0 | 20.4 | 1.55 | 8.93 | 0.39 | 1.316 |
| Nitrobenzene | $C_6H_5NO_2$ | 4.4 | 14.8 | 4.00 | 34.80 | 1.62 | 1.198 |

[a]Donor number; [b]Acceptor number; [c] Dipole moment; [d] Dielectric constant; [e] Viscosity; [f]Density.

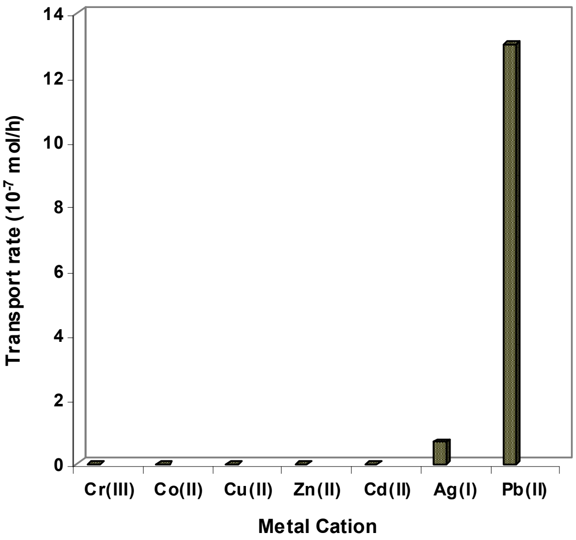

Fig. 5. The results of metal ion transport (water/DCM/water) with B18C6. Source phase: pH = 5 ($CH_3COOH/CH_3COONa$) containing metal ions at 0.01 M (10 mL). Membrane phase: contains B18C6 (0.001 M), (50 mL). Receiving phase: pH = 3 (NaOH/HCOOH), (30 mL) stirred for 24 h at ambient temperature.

in a better transfer rate in DCM membrane phase. As is evident from Table-1, the selectivity of B18C6 for $Cr^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ag^{+}$ and $Pb^{2+}$ metal cations does not depend on the identity of organic solvents that used as membrane phase.

**Effect of ionophore structure on transport efficiency of the metal cations:** The cyclic polyethers better known as crown ethers are a unique class of compounds with hydrophilic interior and lipophilic exterior capable of metal ion transport across the non-aqueous barriers[13,14].

For competitive transport of the 7 metal cations, we used benzo-18-crown-6 as an ionophore. The results showed that the transport of metal cations into the receiving phase was undetectable in absence of B18C6 in the organic liquid membranes. The attachment of phenyl 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 aqueous phases. The investigations have established that the nature of macrocyclic ionophore such as ring size, the kind of donor atoms and the substituting groups present in the polyether ring has an important effect on cation transport[15,16]. The observed $J$ values for $Pb^{2+}$ and $Ag^{+}$ transport (Table-1) show that B18C6 system preferentially transports the $Pb^{2+}$ ion into the aqueous receiving phase rather than $Ag^{+}$ ion. Although the size of $Ag^{+}$ ion (r = 1.26 Å) is bigger than the size of the $Pb^{2+}$ ion (r = 1.18 Å) and, therefore, it can attain a more convenient fit condition for the crown ether cavity (2.6-3.2 Å)[17], but since the $Pb^{2+}$ ion has a less soft character than $Ag^{+}$ ion[18], it seems according to the hard and soft acid-base concept, it can form a more stable complex with the oxygen donor atoms of B18C6 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-1, high transport rates of $Pb^{2+}$ ion rather than $Ag^{+}$ ion in 4 solvent systems are obtained in these experiments.

**Effect of surfactants on transport efficiency of the metal cations:** Surfactant systems have been recognized as very useful alternatives for improving analytical methodologies and development of new concepts in analytical chemistry[19-22]. Addition of a long chain fatty acid reduces the degree of carrier loss and also could have a cooperative effect in the uphill transport of cation through the ligand membrane. A possible reason for this cooperative behaviour would be existence of some proton donor-acceptor interaction between the lipophilic fatty acid (as proton donor) and the donor atoms of the ligand (as proton acceptor), which can impart a grater degree of lipophilicity to the crown ether-metal ion complex, in order to facilitate the cation transport through the liquid membrane[23].

In another experiment, the competitive mixed metal ion transport processes (water/organic solvent/water) employed an organic phase containing known concentrations of the ionophore ($10^{-3}$ M) and fatty acids ($4 \times 10^{-3}$ M) as surfactant. The results of the influence of the stearic acid, palmitic acid and oleic acid as surfactants in the membrane phase on the cation transport are shown in Table-3. As is evident from this Table, in most cases, the efficiency of $Pb^{2+}$ ion transport decreases in the presence of these fatty acids. As is obvious from these data, the cooperative behaviour in the presence of these long-chain hydrocarboxylic acids is decreased. This may be due to formation of hydrogen bonds between the donor atoms of the ligand and

TABLE-3
EFFECT OF SURFACTANTS ON TRANSPORT EFFICIENCY OF THE METAL CATIONS[a]

| Membrane phase | Cr(III) | Co(II) | Cu(II) | Zn(II) | Cd(II) | Ag(I) | Pb(II) |
|---|---|---|---|---|---|---|---|
| $CHCl_3$ | –[b] | – | – | – | – | 0.21 | 5.04 |
| $CHCl_3$ + stearic acid | – | – | – | – | – | 0.17 | 3.81 |
| $CHCl_3$ + palmitic acid | – | – | – | – | – | 0.16 | 3.37 |
| $CHCl_3$ + oleic acid | – | – | – | – | – | 0.20 | 5.40 |
| 1,2-DCE | – | – | – | – | – | 0.15 | 6.42 |
| 1,2-DCE + stearic acid | – | – | – | – | – | 0.24 | 8.29 |
| 1,2-DCE + palmitic acid | – | – | – | – | – | 0.08 | 5.08 |
| 1,2-DCE + oleic acid | – | – | – | – | – | 0.08 | 6.09 |
| DCM | – | – | – | – | – | 0.53 | 10.41 |
| DCM + stearic acid | – | – | – | – | – | 0.34 | 8.17 |
| DCM + palmitic acid | – | – | – | – | – | 0.64 | 8.52 |
| DCM + oleic acid | – | – | – | – | – | 0.50 | 7.98 |
| NB | – | – | – | – | – | 3.15 | 7.34 |
| NB + stearic acid | – | – | – | – | – | 1.44 | 4.70 |
| NB + palmitic acid | – | – | – | – | – | 1.95 | 5.91 |
| NB + oleic acid | – | – | – | – | – | 2.16 | 7.11 |

[a]Data for per cent of total metal cations in the receiving phase after 24 h; [b]The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

the acidic proton of carboxylic acids in these aprotic and protophobic solvents which results in formation of a weaker complex between the $Pb^{2+}$ ion and the macrocyclic ligand in the presence of these fatty acids. Another possibility is the formation of micelles of the fatty acids in the membrane phase which trap the crown-cation complex and, therefore, the transport rate of $Pb^{2+}$ ion decreases in the presence of stearic, palmitic and oleic acids.

**Effect of binary mixed solvent membranes on transport efficiency of the metal cations:** The data for competitive transport of $Cr^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ag^+$ and $Pb^{2+}$ metal cations with B18C6 ligand in $CHCl_3$-NB and $CHCl_3$-DCM binary systems as membrane phase are shown in Tables 4 and 5. The graphical results for the transport of the metal cations by B18C6 in $CHCl_3$-NB and $CHCl_3$-DCM

TABLE-4
DATA FOR SEVEN METAL CATIONS COMPETITIVE TRANSPORT ACROSS $CHCl_3$-NB BINARY SYSTEMS AS BULK MEMBRANE WITH B18C6

| Solvent | Cr(III) | Co(II) | Cu(II) | Zn(II) | Cd(II) | Ag(I) | Pb(II) |
|---|---|---|---|---|---|---|---|
| Pure $CHCl_3$ | | | | | | | |
| % (Receiving)[a] | –[d] | – | – | – | – | 0.21 | 5.04 |
| % (membrane)[b] | – | – | 5.08 | – | – | – | 14.12 |
| J (mol per 24 h) [c] | – | – | – | – | – | 0.26 | 6.31 |
| 75% $CHCl_3$ + 25% NB | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.59 | 7.55 |
| % (membrane)[b] | – | 6.33 | 19.48 | – | – | – | 24.35 |
| J (mol per 24 h) [c] | – | – | – | – | – | 0.74 | 9.43 |
| 60% $CHCl_3$ + 40% NB | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.18 | 5.07 |
| % (membrane)[b] | – | 8.68 | 5.014 | 1.78 | 6.06 | – | 15.14 |
| J (mol per 24 h) [c] | – | – | – | – | – | 0.23 | 6.33 |
| 50% $CHCl_3$ + 50% NB | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.71 | 9.61 |
| % (membrane)[b] | – | 5.38 | 5.74 | – | – | 3.08 | 22.05 |
| J (mol per 24 h) [c] | – | – | – | – | – | 0.88 | 12.01 |
| 40% $CHCl_3$ + 60% NB | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.14 | 5.66 |
| % (membrane)[b] | – | 8.77 | 4.07 | – | – | – | 9.33 |
| J (mol per 24 h) [c] | – | – | – | – | – | 0.17 | 7.08 |
| 25% $CHCl_3$ + 75% NB | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.91 | 7.78 |
| % (membrane)[b] | – | – | 3.15 | – | 4.54 | – | 16.30 |
| J (mol per 24 h) [c] | – | – | – | – | – | 1.14 | 9.73 |
| Pure NB | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 3.15 | 7.34 |
| % (membrane) [b] | 0.61 | 7.59 | 6.12 | – | – | 4.61 | 22.01 |
| J (mol per 24 h) [c] | – | – | – | – | – | 3.94 | 9.18 |

[a]Per cent of total metal cations in the receiving phase after 24 h; [b]Per cent of total metal cations in the membrane phase after 24 h; [c]All values are × $10^{-7}$; [d]The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

TABLE-5
DATA FOR SEVEN METAL CATIONS COMPETITIVE TRANSPORT ACROSS CHCL$_3$-DCM BINARY SYSTEMS AS BULK MEMBRANE WITH B18C6

| Solvent | Cr(III) | Co(II) | Cu(II) | Zn(II) | Cd(II) | Ag(I) | Pb(II) |
|---|---|---|---|---|---|---|---|
| Pure CHCl$_3$ | | | | | | | |
| % (Receiving)[a] | –[d] | – | – | – | – | 0.21 | 5.04 |
| % (membrane)[b] | – | – | 5.08 | – | – | – | 14.12 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.26 | 6.31 |
| 75% CHCl$_3$ + 25% DCM | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.22 | 6.73 |
| % (membrane)[b] | 1.05 | 4.00 | 0.79 | – | – | – | 13.76 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.28 | 8.41 |
| 60% CHCl$_3$ + 40% DCM | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.23 | 7.35 |
| % (membrane)[b] | 10.93 | 2.69 | 5.06 | 6.23 | 15.04 | – | 20.91 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.29 | 9.19 |
| 50% CHCl$_3$ + 50% DCM | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.29 | 8.06 |
| % (membrane)[b] | 5.98 | 3.60 | 0.45 | – | – | – | 20.98 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.36 | 10.08 |
| 40% CHCl$_3$ + 60% DCM | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.37 | 8.54 |
| % (membrane)[b] | 7.08 | 3.85 | 6.04 | – | 10.21 | 1.41 | 24.57 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.46 | 10.68 |
| 25% CHCl$_3$ + 75% DCM | | | | | | | |
| % (Receiving)[a] | – | – | – | – | – | 0.45 | 10.05 |
| % (membrane)[b] | – | – | – | 7.02 | – | – | 23.25 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.57 | 12.57 |
| Pure DCM | | | | | | | |
| % (Receiving)a | – | – | – | – | – | 0.53 | 10.41 |
| % (membrane)[b] | 6.00 | 3.58 | 4.33 | – | – | – | 18.86 |
| J (mol per 24 h)[c] | – | – | – | – | – | 0.69 | 13.02 |

[a]Per cent of total metal cations in the receiving phase after 24 h; [b]Per cent of total metal cations in the membrane phase after 24 h; [c]All values are × $10^{-7}$; [d]The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

binary systems are shown in Figs. 6 and 7. As is obvious from these Figures, 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 behaviour may be due to the interactions between chloroform and nitrobenzene molecules and also between chloroform and dichloromethane molecules in their binary solutions. It has been shown that in binary solutions of nitrobenzene and chloroform, the C-H vibration band in the Raman spectra shifts toward higher frequencies which has been explained by the formation of an intermolecular hydrogen bond between chloroform and nitrobenzene molecules in their binary solutions[24]. These kinds of interactions will result in changing some of the chemical and physical properties of each of solvents such as acidity, basicity, polarity and relative permittivity which will affect the log $K_f$ values for formation of the cation-ligand complex in organic membrane phase and also changing the composition of the boundary layers and therefore, changing the desolvation of the aqueous metal species as the membrane phase is varied.

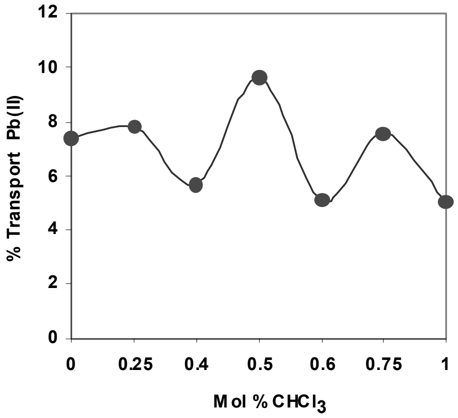

Fig.6. Changes of $Pb^{2+}$ ion transport with the composition of $CHCl_3$-NB binary mixed solvent

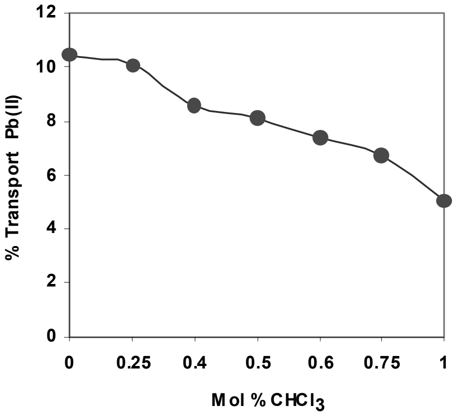

Fig. 7. Changes of $Pb^{2+}$ ion transport with the composition of $CHCl_3$-DCM binary mixed solvent

## Conclusion

The liquid membrane transport experiments of $Cr^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ag^{+}$ and $Pb^{2+}$ metal cations using benzo-18-crown-6 (B18C6) 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. B18C6 showed a good selectivity for $Pb^{2+}$ cation rather than the other metal cations and the order of the transport ability of the ligand for this metal cation in different membrane systems was found to be: DCM > NB > 1,2-DCE > $CHCl_3$. A good selectivity was also observed for $Pb^{2+}$ cation in the case of using $CHCl_3$-NB and $CHCl_3$-DCM binary mixed solvents as membrane phase. The transport rate of the $Pb^{2+}$ cation is influenced by the composition of the mixed solvent and a non-linear behaviour was observed between the transport rate and the composition of membrane systems which was discussed in terms of solvent-solvent interactions. The experimental results obtained for competitive liquid membrane transport of the studied metal cations by B18C6 showed that the transport efficiency changes in the presence of fatty acids in organic phase. The simplicity, low cost and high selectivity for $Pb^{2+}$ cation transport obtained by the used liquid membrane systems, demonstrate their potential applicability for selective removal concentration or purification of $Pb^{2+}$ cation from its mixtures with the other metal cations.

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