Studies on the Macrocycle Mediated Transport in a Bulk Liquid Membrane System of Transition Metal Cations

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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 consisted of a buffer solution (CH_3COOH/CH_3COONa) at pH = 5 and containing an equimolar mixture of Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and Pb^{2+} metal cations. The organic phase contained the macrocyclic ligand, 1,10-dodecyl-1,10-diaza-18-crown-6 (Kryptofix 22DD) as an ionophore and the receiving phase consisted of a buffer solution (HCOOH/HCOONa) at pH = 3. The results show that the ionophore is selective for silver cation. The effects of various organic solvents on cation transport rates have been demonstrated. Among the organic solvents involving nitrobenzene (NB), chloroform ($CHCl_3$), dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE), chloroform-nitrobenzene ($CHCl_3$-NB) and chloroform-dichloromethane ($CHCl_3$-DCM) binary systems which were used as liquid membrane, a good transport efficiency and selectivity was obtained for Ag^+ cation. The sequence of transport rate for Ag^+ cation in the pure organic solvents was found to be: DCM > $CHCl_3$ > NB > 1,2-DCE. The non-linear behaviour was observed for variations of the transport rate of silver cation *versus* the composition of chloroform-nitrobenzene and chloroform-dichloromethane binary mixtures was discussed in terms of changing the chemical and physical properties of the constituents solvents when they mix with one another. The influence of fatty acids as surfactant in the membrane phase on the transport of metal cations was also investigated.

Key Words: Bulk liquid membrane transport, 1,10-dodecyl-1,10-diaza-18-crown-6, Kryptofix 22DD, Transition metal cations.

INTRODUCTION

In recent years, liquid membranes (LMs) have widely been used to study ion transport against a concentration gradient. Ion transport through the liquid membranes plays an important role in simulating biological membrane functions and separation technologies because of the high transport efficiency and excellent selectivity of the liquid membranes. A number of successful studies involving the transport of metal ions[1-4], rare earth elements[5,6], drugs[7], fructose[8] and the treatment of sea water and waste water[9,10] through the liquid membrane have been carried out. Liquid membranes can be designed as bulk liquid membranes (BLM), supported liquid membranes (SLM), emulsion liquid membranes (ELM), polymer inclusion membranes (PIMs) and activated composite membranes (ACM). Bulk liquid membranes consist of three phases: two aqueous phases as a donor or an acceptor and one organic phase in which a carrier is dissolved. The transport from an aqueous donor phase through an organic membrane phase to an aqueous acceptor phase occurs. Although a number of carriers for the transport of alkali and alkaline metal ions using

bulk liquid membranes have been used so far[11,12], relatively few carriers have been reported for the selective and efficient transport of heavy metal cations[13-15].

Active research is recently in progress on the use of macrocyclic compounds as carriers in liquid membrane systems. A characteristic of macrocyclic ligands which make them desirable membrane carriers is their high degree of cation selectivity. For example, in this paper, a good transport selectivity has been observed for Ag^+ cation over several cations by using an appropriate crown ether.

The aim of the present investigation is to study the effect of the nature of the cations and crown ether and the solvent properties of the liquid membrane on the transport of some of the transition metal cations across bulk liquid membranes. In this study, we report the results of competitive seven metal membrane transport experiments involving Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and Pb^{2+} metal cations with 1,10-dodecyl-1,10-diaza-18-crown-6 (Kryptofix 22DD) (Fig. 1) as a carrier, using nitrobenzene (NB), chloroform ($CHCl_3$), dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE), chloroform-nitrobenzene ($CHCl_3$-NB) and chloroform-dichloromethane ($CHCl_3$-DCM)

binary mixtures as liquid membrane. The effect of the stearic acid, palmitic acid and oleic acid as surfactant on transport efficiency of the metal cations was also investigated.
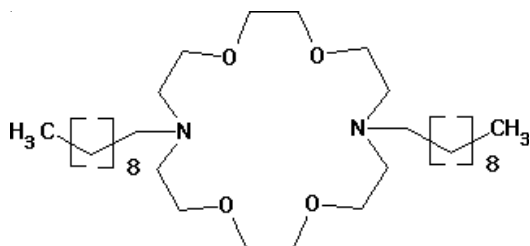

Fig. 1. Structure of 1,10-dodecyl-1,10-diaza-18-crown-6 (Kryptofix 22DD)

EXPERIMENTAL

1,10-Dodecyl-1,10-diaza-18-crown-6 (Kryptofix 22DD), silver(I) nitrate, iron(III) nitrate, cadmium(II) nitrate, sodium acetate, zinc(II) nitrate, oleic acid, chloroform, dichloromethane and 1,2-dichloroethane, nitric acid and acetic acid (all purchased from Merck). Copper(II) nitrate, cobalt(II) nitrate, lead(II) nitrate, stearic acid and nitrobenzene (all purchased from BDH). Sodium hydroxide, palmitic acid and formic acid (purchased from Riedel) were used without further purification and of the highest purity. All aqueous solutions were prepared using double distilled deionized 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-meter using a combined glass electrode. A bulk type liquid membrane cell was used in all transport experiments (Fig. 2).
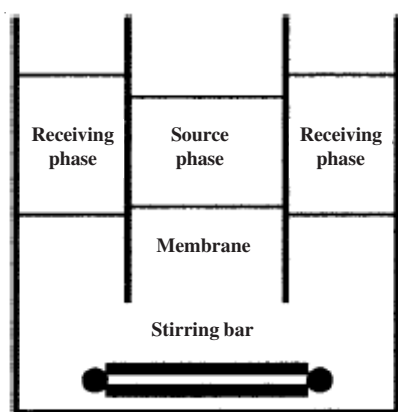

Fig. 2. Schematic diagram of the apparatus used for the extraction of metal cations with liquid membrane

Procedure: The transport experiments employed a " concentric cell" in which the aqueous source phase (10 mL) and receiving phase (30 mL) were separated by an organic phase (50 mL). Details of the cell design have been reported elsewhere[16]. The organic phase was magnetically stirred by a Teflon-coated magnetic bar at 20 rpm. The aqueous source consisted of a buffer solution (CH_3COOH/CH_3COONa) at pH = 5 containing an equimolar mixture of metal cations (0.01 M). The organic phase contained the macrocycle ionophore (0.001 M) and the receiving phase consisted of a buffer solution (HCOOH/HCOONa) at pH = 3. A pH gradient is used in order

to facilitate the transport of the metal cations across the organic membrane by counter transport of protons. All transport runs were terminated after 24 h and atomic absorption spectroscopy was used to determine the amount of each of the metal cations. The liquid membrane used in this study is represented schematically in Fig. 3.
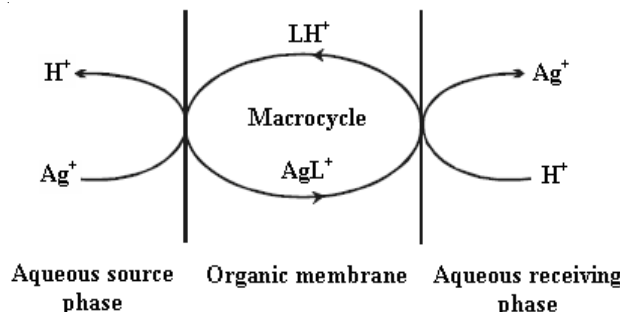

Fig. 3. Liquid membrane system for transport of Ag^+ cation

RESULTS AND DISCUSSION

Effect of solvent on transport efficiency of the metal cations: According to Izatt and coworkers[17], several parameters whose values depend on the membrane solvent can affect transport. These are the thickness of the unstirred boundary layers in the membrane (*i.e.*, the diffusion path length), diffusion coefficients of all mobile species in these boundary layers and the log K_f value for formation of the cation-ligand complex in the organic phase. Additional parameters are the partition coefficients of the macrocycle and the cation-ligand complex. The thickness of the boundary layers is a function of the rate at which the solvent is stirred, as well as, its viscosity. The partitioning of ions into the organic phase should also be affected by the dielectric constant of the medium[18].

The data for competitive transport of Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and Pb^{2+} metal cations from an aqueous source phase through nitrobenzene, chloroform, dichloromethane and 1,2-dichloroethane membranes containing diazacrown 22DD ligand are given in Table-1 and the graphical result is shown in Fig. 4.
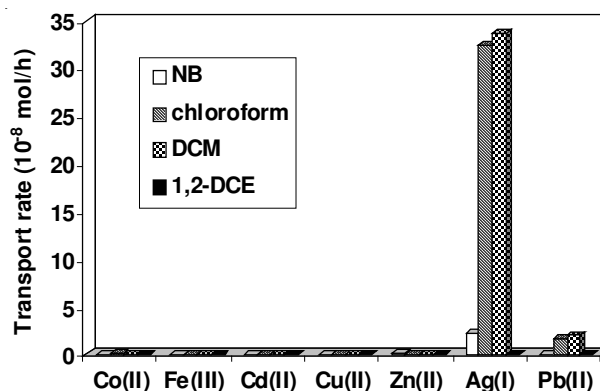

Fig. 4. Comparison of the results of metal ions transport (water/organic solvent/water) studies for diazacrown 22DD. Source phase: pH = 5 (CH_3COOH/CH_3COONa) containing metal ions at 0.01M (10 mL). Membrane phase: contains macrocyclic ionophore (0.001 M) (50 mL). Receiving phase: pH = 3 (NaOH/HCOOH) (30 mL), stirred for 24 h

TABLE-1

DATA FOR SEVEN METAL CATIONS COMPETITIVE TRANSPORT ACROSS ORGANIC SOLVENTS AS
BULK LIQUID MEMBRANE WITH DIAZACROWN 22DD

Solvent	Co^{2+}	Fe^{3+}	Cd^{2+}	Cu^{2+}	Zn^{2+}	Ag^{+}	Pb^{2+}
Nitrobenzene							
% (Receiving)[a]	–[d]	–	–	–	0.01	0.17	–
% (Membrane)[b]	–	2.93	–	–	0.21	0.18	4.81
J (mol per 24 h)[c]	–	–	–	–	0.19	2.15	–
Chloroform							
% (Receiving)[a]	0.01	–	–	–	–	2.60	0.13
% (Membrane)[b]	0.11	6.82	0.41	4.80	6.36	3.29	7.39
J (mol per 24 h)[c]	0.17	–	–	–	–	32.46	1.60
Dichloromethane							
% (Receiving)[a]	–	–	–	–	–	2.69	0.17
% (Membrane)[b]	0.11	7.46	–	–	–	5.31	6.46
J (mol per 24 h)[c]	–	–	–	–	–	33.69	2.11
1,2-Dichloroethane							
% (Receiving)[a]	–	–	–	–	–	–	–
% (Membrane)[b]	–	3.14	–	–	3.43	10.64	–
J (mol per 24 h)[c]	–	–	–	–	–	–	–

[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 $\times 10^{-8}$; [d]The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

The results show that diazacrown 22DD is a selective ionophore for Ag^{+} cation and under the employed experimental conditions, the Ag^{+} ion is transported from the source phase into the receiving phase. As is obvious from Fig. 4, the sequence of transport rate for silver ion in organic solvents is: DCM > $CHCl_3$ > NB > 1,2-DCE. According to the physicochemical properties of the solvents, these results may be attributed to the lower viscosity of DCM ($\eta = 0.39$) which leads to increase the rate of ion transfer in this organic solvent compared to the other three solvents. Moreover, the low donor number (DN) of dichloromethane (DN = 1) results in decreasing the competition between the solvent and the ligand molecules which leads to increasing the stability of the complex formed between the Ag^{+} cation and diazacrown 22DD and, therefore, increasing the rate of cation transfer in this organic solvent.

The higher polarity of the solvent results in higher solubility of the complex in membrane phase and, therefore, the transport rate of the metal cation increases. Although the dipole moment of DCM ($\mu = 1.55$) is lower than those of 1,2-DCE ($\mu = 1.86$) and NB ($\mu = 4$)[19], but the J value (transport rate) for Ag^{+} ion transport is larger in DCM with respect to the other solvents. The lower dielectric constant of DCM ($\varepsilon = 8.93$) than those of 1,2-DCE ($\varepsilon = 10.66$) and NB ($\varepsilon = 34.80$) may aid the ion-pair formation in DCM which resulting a better transfer rate in DCM membrane phase.

Effect of ionophore structure on cation transport: The selectivity and fluxes of the metal cations are strongly influenced by the nature of the macrocyclic ionophore. The relative size of the metal ion to the cavity size of the macrocyclic ligand, the kind of donor atoms and substituting groups present in the ring has an important role in the selectivity of the ligand for the metal cations[20].

For competitive transport of the seven metal cations, diazacrown 22DD was used as an ionophore. The attachment of large hydrophobic groups to the ring of the ligand, increases its lipophilicity thus increasing its solubility and effectively trapping it in the organic phase into one or both of the aqueous phases.

The J value (Table-1) for Ag^{+} ion transport with diazacrown 22DD is bigger than the other metal cations, since its size (ionic radius = 1.15 Å) is close to the cavity size of the ligand (2.6-3.2 Å) and also since the Ag^{+} cation is a softer Lewis acid than Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} metal cations[21], therefore, based on the hard and soft acid-base concept, the interaction of the silver cation with the nitrogen atom of this ligand as a soft base is stronger than the other metal cations, thus the Ag^{+} ion forms a stronger complex with this macrocyclic ligand which results in a more transport efficiency for this cation compared to the other metal cations.

Effect of surfactants on transport efficiency: The results of the influence of the stearic acid, palmitic acid and oleic acid (4.0×10^{-3} M) as surfactant in the membrane phase containing known concentration of the ionophore (1.0×10^{-3} M) and organic solvents (nitrobenzene, chloroform, dichloromethane and 1,2-dichloroethane) on the silver ion transport are given in Table-2. As expected, the efficiency of transport of Ag^{+} cation increases in the presence of fatty acids. This confirms the cooperative action of the two components as carriers. A possible explanation for this cooperative behaviour would be the existence of some proton-donor and proton-accepter interactions between surfactant (as proton donor) and nitrogen atom of diazacrown 22DD (as proton acceptor) which can impart a greater degree of lipophilicity to the ligand-cation complex, in order to facilitate the cation transport through liquid membrane.

A major role of the fatty acids 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].

As is evident from Table-2, in some cases 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 the acidic proton of carboxylic acids in these aprotic and protophobic solvents which results in formation of a weaker complex

TABLE-2
EFFECT OF SURFACTANTS ON Ag⁺ TRANSPORT ACROSS
ORGANIC SOLVENTS SYSTEM AS BULK MEMBRANE WITH
DIAZACROWN 22DD

Solvent	Fatty acid	% (Receiving)[a]	% (Membrane)[b]	J (mol per 24 h)[c]
NB	–	0.17	0.18	2.15
	Stearic acid	0.42	14.69	5.26
	Palmitic acid	0.82	10.90	10.25
	Oleic acid	0.24	8.90	3.08
CHCl₃	–	2.60	3.29	32.46
	Stearic acid	2.71	8.42	33.88
	Palmitic acid	1.00	9.27	12.55
	Oleic acid	2.74	18.92	34.28
DCM	–	2.69	5.31	33.69
	Stearic acid	2.43	16.55	30.38
	Palmitic acid	3.50	20.60	43.81
	Oleic acid	1.76	21.39	22.06
1,2-DCE	–	–[d]	10.64	–[d]
	Stearic acid	–[d]	21.03	–[d]
	Palmitic acid	–[d]	20.62	–[d]
	Oleic acid	–[d]	25.36	–[d]

[a]Per cent of silver cation in the receiving phase after 24 h; [b] Percent of silver cation in the membrane phase after 24 h; [c] All values are × 10⁻⁸; [d]The hyphenated symbols mean that the values are about zero or they are with high uncertainties.
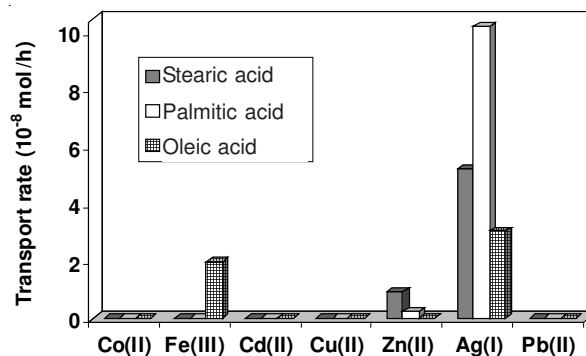

Fig. 5. Comparison of the results of metal ions transport (water/ nitrobenzene/water) studies for diazacrown 22DD. Source phase: pH = 5 (CH₃COOH/CH₃COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains macrocyclic ionophore (0.001 M) and fatty acids (0.004 M) (50 mL). Receiving phase: pH = 3 (NaOH/HCOOH) (30 mL), stirred for 24 h

between the Ag⁺ cation and the macrocyclic ligand in the presence of these fatty acids. Another possibility is the formation of micelles of fatty acids in the membrane phase which trap the ligand-cation complex and therefore, the transport decreases in the presence of these fatty acids.

The graphical results obtained for the studied metal cations transport across nitrobenzene phase containing diazacrown 22DD in the presence of the three fatty acids is shown in Fig. 5.

Effect of binary mixed solvents on transport efficiency of the metal cations: The data for competitive transport of Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and Pb^{2+} metal cations with diazacrown 22DD in CHCl₃-NB and CHCl₃-DCM binary

systems as membrane phase are summarized in Tables 3 and 4, respectively. The results show a good selectivity for Ag⁺ among the seven metal cations. The results for the transport of Ag⁺ by diazacrown 22DD in these solvent systems are shown in Fig. 6. As is seen in this Figure, the transport rate of the Ag⁺ metal cation decreases as the mole fraction of nitrobenzene increases in CHCl₃-NB binary solutions. This behaviour may be due to the lower viscosity of chloroform ($\eta = 0.58$) than that of nitrobenzene ($\eta = 1.62$) and also the higher dielectric constant of nitrobenzene ($\varepsilon = 34.80$) than that of chloroform ($\varepsilon = 4.80$).

As is evident in Fig. 6, there is a non-linear relationship between the changes of the transport rate of the Ag⁺ ion *versus* the solvent composition in CHCl₃-NB and CHCl₃-DCM binary mixtures. This behaviour may be attributed to the structural changes of the solvent systems when they are mixed with one another[23] and hence changing the structure of the solvent mixtures and, therefore, changing in solvation properties of

TABLE-3
DATA FOR SEVEN METAL CATIONS COMPETITIVE TRANSPORT ACROSS CHCl₃-NB BINARY
SYSTEMS AS BULK LIQUID MEMBRANE WITH DIAZACROWN 22DD

Solvent	Co^{2+}	Fe^{3+}	Cd^{2+}	Cu^{2+}	Zn^{2+}	Ag^+	Pb^{2+}
Pure CHCl₃							
% (Receiving)[a]	0.01	–[d]	–	–	–	2.60	0.13
% (Membrane)[b]	0.11	6.82	0.41	4.80	6.36	3.29	7.39
J (mol per 24 h)[c]	0.17	–	–	–	–	32.46	1.60
75 % CHCl₃ + 25 % NB							
% (Receiving)[a]	–	0.04	–	–	0.03	1.19	0.05
% (Membrane)[b]	–	31.35	–	–	0.78	8.38	3.44
J (mol per 24 h)[c]	–	0.59	–	–	0.41	14.94	0.60
50 % CHCl₃ + 50 % NB							
% (Receiving)[a]	–	–	–	–	0.01	0.83	–
% (Membrane)[b]	–	30.59	–	–	2.22	8.29	3.49
J (mol per 24 h)[c]	–	–	–	–	0.14	10.46	–
25 % CHCl₃ + 75 % NB							
% (Receiving)[a]	–	–	–	–	–	0.82	–
% (Membrane)[b]	0.67	3.22	–	0.27	–	13.39	7.82
J (mol per 24 h)[c]	–	–	–	–	–	10.32	–
Pure NB							
% (Receiving)[a]	–	–	–	–	0.01	0.17	–
% (Membrane)[b]	–	2.93	–	–	0.21	0.18	4.81
J (mol per 24 h)[c]	–	–	–	–	0.19	2.15	–

[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 × 10⁻⁸; [d]The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

TABLE-4
DATA FOR SEVEN METAL CATIONS COMPETITIVE TRANSPORT ACROSS CHCl$_3$-DCM BINARY
SYSTEMS AS BULK LIQUID MEMBRANE WITH DIAZACROWN 22DD

Solvent	Co^{2+}	Fe^{3+}	Cd^{2+}	Cu^{2+}	Zn^{2+}	Ag^+	Pb^{2+}
Pure CHCl$_3$							
% (Receiving)[a]	0.01	–[d]	–	–	–	2.60	0.13
% (Membrane)[b]	0.11	6.82	0.41	4.80	6.36	3.29	7.39
J (mol per 24 h)[c]	0.17	–	–	–	–	32.46	1.60
75 % CHCl$_3$ + 25 % DCM							
% (Receiving)[a]	–	–	–	–	0.01	3.26	0.19
% (Membrane)[b]	2.04	13.91	–	2.87	9.03	17.66	8.68
J (mol per 24 h)[c]	–	–	–	–	0.16	40.72	2.35
50 % CHCl$_3$ + 50 % DCM							
% (Receiving)[a]	–	–	–	–	0.02	1.65	0.09
% (Membrane)[b]	–	12.14	–	0.70	0.51	20.01	6.48
J (mol per 24 h)[c]	–	–	–	–	0.23	20.64	1.19
25 % CHCl$_3$ + 75 % DCM							
% (Receiving)[a]	–	–	–	–	0.02	1.83	0.19
% (Membrane)[b]	–	25.70	–	1.84	2.82	20.19	16.03
J (mol per 24 h)[c]	–	–	–	–	0.27	22.93	2.40
Pure DCM							
% (Receiving)[a]	–	–	–	–	–	2.69	0.17
% (Membrane)[b]	0.11	7.46	–	–	–	5.31	6.46
J (mol per 24 h)[c]	–	–	–	–	–	33.69	2.11

[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 $\times 10^{-8}$; [d] The hyphenated symbols mean that the values are about zero or they are with high uncertainties.
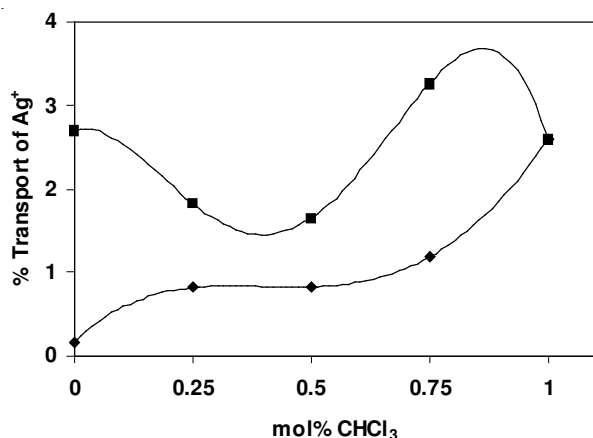

Fig. 6.   Changes of Ag$^+$ ion transport with the composition of the CHCl$_3$-NB (◆) and CHCl$_3$-DCM (■) binary system. Source phase: pH = 5 (CH$_3$COOH/CH$_3$COONa) containing metal ions at 0.01M (10 mL). Membrane phase: contains macrocyclic ionophore (0.001 M) in CHCl$_3$-NB and CHCl$_3$-DCM binary solvents (50 mL). Receiving phase: pH = 3 (NaOH/HCOOH) (30 mL), stirred for 24 h

the cyclic polyether and even the resulting complex in solutions. The interactions between some binary mixed solvents have been studied[24-28]. For example, interactions between the chloroform and nitrobenzene molecules causes the formation of an intermolecular hydrogen bond[29] in their binary solutions. These kind of interactions change some of the chemical and physical properties of each of the 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.

Conclusion

The liquid membrane transport experiments of Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ag$^+$ and Pb^{2+} metal cations using 1,10-dodecyl-1,10-diaza-18-crown-6 (Kryptofix 22DD) 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. diazacrown 22DD showed a good efficiency and selectivity for Ag$^+$ 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 > CHCl$_3$ > NB > 1,2-DCE. A good selectivity was also observed for Ag$^+$ cation in the case of using CHCl$_3$-NB and CHCl$_3$-DCM binary mixed solvents as membrane phase. The transport rate of the Ag$^+$ 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 diazacrown 22DD showed that the transport efficiency changes in the presence of fatty acids in organic phase.

REFERENCES

1. D. Nanda, M.S. Oak, M.P. Kumar, B. Maiti and P.K. Dutta, *Sep. Sci. Technol.*, **36**, 2489 (2001).
2. J. Zolgharnein, H. Shams and G. Azimi, *Sep. Sci. Technol.*, **42**, 2303 (2007).
3. P.S. Kulkarni, S. Mukhopadhyay, M.P. Bellary and S.K. Ghosh, *Hydrometallurgy*, **64**, 49 (2002).
4. M. Shamsipur, M.H. Mashhadizadeh and G. Azimi, *Sep. Purif. Technol.*, **27**, 155 (2002).
5. M. Ma, D. He, Q. Wang and Q. Xie, *Talanta*, **55**, 1109 (2001).
6. J. Dolezal, C. Moreno, A. Hrdlicka and M. Valiente, *J. Membr. Sci.*, **168**, 175 (2000).
7. S.C. Lee, *Chem. Eng. J.*, **79**, 61 (2000).

8. M. Di Luccio, B.D. Smith, T. Kida, C.P. Borges and T.L.M. Alves, *J. Membr. Sci.*, **174**, 217 (2000).
9. D. He, M. Ma and Z. Zhao, *J. Membr. Sci.*, **169**, 53 (2000).
10. A.A. Ensafi and H. Eskandari, *Sep. Sci. Technol.*, **36**, 81 (2001).
11. R.M. Izatt, J.D. Lamb, R.T. Hawkins, P.R. Brown, S.R. Izatt and J.J. Christensen, *J. Am. Chem. Soc.*, **105**, 1782 (1983).
12. R.M. Izatt, R.M. Haws, J.D. Lamb, D.V. Dearden, P.R. Brown, D.W. McBride Jr. and J.J. Christensen, *J. Membr. Sci.*, **20**, 273 (1984).
13. C. Fontàs, M. Hidalgo, V. Salvadó and E. Anticó, *Anal. Chim. Acta*, **547**, 255 (2005).
14. M. Shamsipur, O.R. Hashemi and V. Lippolis, *J. Membr. Sci.*, **282**, 322 (2006).
15. A. Safavi and S. Rastegarzadeh, *Talanta*, **42**, 2039 (1995).
16. P.S.K. Chia, L.F. Lindoy, G.W. Walker and G.W. Everett, *Pure Appl. Chem.*, **65**, 521 (1993).
17. D.W. McBride, R.M. Izatt, J.D. Lamb, J.J. Christensen, in eds.: J.L. Atwood, J.E. Davies and D.D. MacNical, Inclusion Compounds, Physical Properties and Applications, Academic Press, New York, Vol. 3, p. 598 (1984).
18. R.M. Izatt, R.L. Bruening, G.A. Clark, J.D. Lamb and J.J. Christensen, *J. Membr. Sci.*, **28**, 77 (1986).
19. K. Izutzu, Electrochemistry in Nonaqueous Solution. Wiley-VCH, Weinheim (2002).
20. G.H. Rounaghi, M.S. Kazemi and H. Sadeghian, *J. Incl. Phenom. Macrocycl. Chem.*, **60**, 79 (2008).
21. C. Kalidas, G. Hefter and Y. Marcus, *Chem. Rev.*, **100**, 819 (2000).
22. J. Kim, A.J. Leong, L.F. Lindoy, J. Kim, J. Nachbaur, A. Nezhadali, G. H. Rounaghi and G. Wei, *J. Chem. Soc. Dalton Trans.*, 3453 (2000).
23. G.H. Rounaghi and R.S. Khoshnood, *J. Incl. Phenom. Macrocycl. Chem.*, **55**, 309 (2006).
24. A. Ali, S. Hyder and A.K. Nain, *J. Molecul. Liq.*, **79**, 89 (1999).
25. M. Jozwiak, *Thermochim. Acta*, **417**, 31 (2004).
26. G.H. Rounaghi, E. Nazari, A. Ghaemi and M. Mohajeri, *J. Coord. Chem.*, **63**, 2349 (2010).
27. G.H. Rounaghi, M. Mohajeri, M. Doaei and A. Ghaemi, *J. Incl. Phenom. Macrocycl. Chem.*, **67**, 443 (2010).
28. M. Ansarifard, G.H. Rounaghi, M. Chamsaz and K. Taheri, *Asian J. Chem.*, **21**, 2799 (2009).
29. F. Kh. Tukhvatullin, A.K. Atakhodzhaev, S.A. Osmanov, I.P. Klener, A. Zhumaboev and U.N. Tashkenbaev, *Russ. Phys. J.*, **34**, 304 (1991).