Asian Journal of Chemistry Vol. 21, No. 5 (2009), 3577-3587

Competitive Transport Studies of Seven Metal Cations Through Bulk Liquid Membrane Using 1,4-Dioxa-7,10-dithiacyclododecane-2,3-dione

GHOLAM HOSSEIN ROUNAGHI*, MALIHE SADAT HOSSEINY and HAMID SADEGHIAN
Department of Chemistry, Factulty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran
E-mail: ghrounaghi@yahoo.com

Competitive permeation of 7 metal ions from an aqueous source phase containing equimolar concentrations of cobalt(II), copper(II), chromium(III), silver(I), cadmium(II), zinc(II) and lead(II) metal cations at pH = 5 into an aqueous receiving phase at pH = 3 through an organic phase facilitated by a new synthesized lipophilic crown ether, 1,4-dioxa-7,10-dithiacyclododecane-2,3-dione, as an ionophore was studied as bulk liquid membrane transport. The obtained results show that the ionophore is highly selective ionophore for silver ion and under the employed experimental conditions, it transport only this metal cation among the seven studied metal cations. The effects of various organic solvents on cation transport rates have been demonstrated. Among the organic solvents involving dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE), chloroform ($CHCl_3$) and nitrobenzene (NB) which were used as liquid membrane, the most transport rate was obtained for Ag(I) cation in dichloromethane. The sequence of transport rate for silver ion in organic solvents was: DCM > NB > $CHCl_3$ > 1,2-DCE. A linear relationship was observed between the transport rate of silver ion and the composition of $CHCl_3$-DCM, but a non-linear behaviour was found in the case of $CHCl_3$-NB. The influence of the stearic, palmetic and oleic acids as surfactant in the membrane phase on the transport of metal cations was also investigated.

Key Words: Bulk liquid membrane transport, Zinc(II), Lead(II), Chromium(III), Cobalt(II), Copper(II), Silver(I), Cadmium(II), Dichloromethane, 1,2-Dichloroethane, Chloroform, Nitrobenzene, 1,4-Dioxa-7,10-dithiacyclododecane-2,3-dione.

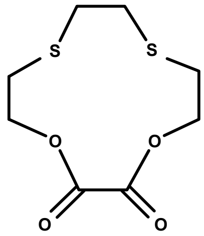
INTRODUCTION

Industry generates large amounts of wastes which can harm nature and human health. Metal ions such as silver, zinc, lead and copper are some of the harmful species found in these wastes. In order to avoid the uncontrolled waste of this type of pollutants, it is necessary to develop techniques that allow their recovery and reutilization in the productive chain. Many of the conventional separation and concentration processes used in hydrometallurgy, such as precipitation, ion exchange with resins or solvent extraction[1,2], are today reconsidered in view of their possible substitution with processes based on synthetic membranes.

Today, membrane processes are used in a wide range of applications. The membrane systems offer greater advantage in terms of energy and matter consumption, as well as, they offer more selectivity, compared to other separation systems. It is possible to use a liquid as a membrane with the advantage of higher diffusion coefficients with respect to solid membranes.

In the case of liquid membrane, a suitable complexing agent serving as the carrier for the metal ion is added to the membrane. If the added reagent is selective for a particular metal ion, a selective transport may occur. Among a wide variety of carriers used in liquid membranes, macrocyclic crown ethers and their derivatives have been demonstrated to be excellent cation carriers[3-7]. So, transport through liquid membranes can be an attractive method for simultaneous separation, concentration and purification of species of interest from aqueous systems. There have been a number of investigations of the transport of some alkali and alkaline earth metal ions[8] and also transition and post-transition metal cations[9,10] through bulk liquid membranes using various synthetic ionophores.

The goal 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 and post transition metal cations across bulk liquid membranes. In this paper, we report the results of competitive rate of seven-metal membrane transport experiments involving Cr^{3+}, Co^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, Zn^{2+} and Pb^{2+} metal cations with 1,4-dioxa-7,10-dithiacyclododecane-2,3-dione (**I**) as a carrier, using dichloromethane (DCM), chloroform ($CHCl_3$), 1,2-dichloroethane (1,2-DCE), nitrobenzene (NB), chloroform-nitrobenzene ($CHCl_3$-NB) and chloroform-dichloromethane ($CHCl_3$-DCM) binary mixtures as liquid membrane. The effect of the stearic, oleic and palmetic acids as surfactants on transport efficiency of the metal cations was also investigated.



Structure of 1,4-dioxa-7,10-dithiacyclododecane-2,3-dione (**I**)

EXPERIMENTAL

1,4-Dioxa-7,10-dithiacyclododecane-2,3-dione was prepared by a method similar to that in the literature[11]. Cobalt(II) nitrate (BDH), copper(II) nitrate (BDH), zinc(II) nitrate (Merck), silver(I) nitrate (Merck), cadmium(II) nitrate (Riedel), lead (II) nitrate (BDH), chromium(III) nitrate (BDH), sodium acetate, sodium hydroxide, palmetic acid (all from Riedel), stearic acid (BDH) and oleic acid (Merck) were used without further purification. Chloroform (BDH), 1,2-dichloroethane, dichloromethane and nitrobenzene (all from Merck) with highest purity were used as liquid membranes. Acetic acid (Merck), formic acid (Riedel) and nitric acid (Merck) were used as received. All aqueous solutions were prepared using deionized double distilled water.

Procedure: The transport experiments employed standardized concentric cells in which the aqueous source phase (10 mL) and receiving phase (30 mL) separated by an organic phase (50 mL) (Fig. 1). Details of the cell design have been reported elsewhere[12]. All transport experiments were carried out at ambient temperature. The organic layer was stirred by a Teflon-coated magnetic bar. Speed of stirrer was adjusted so that the phases did not mix with each other. Under these conditions, not only the mixing process is perfect, but also the interfaces between the organic membrane and the two aqueous phases remained flat and were well defined.

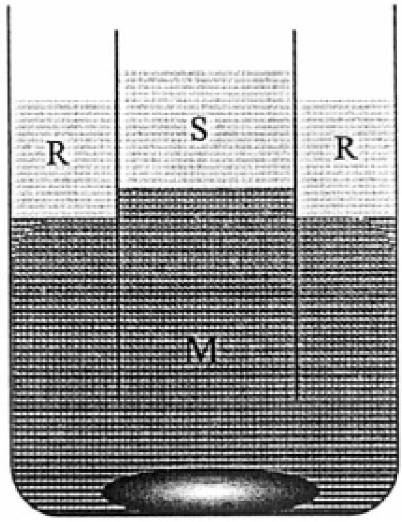


Fig. 1. Liquid membrane apparatus (S: source phase; R: receiving phase; M: liquid membrane)

The inner aqueous phase (source phase) consisted of a buffer solution at pH = 4.9 ± 0.1 (6.95 mL of 2 mol dm^{-3} sodium acetate solution and 3.05 mL of 2 mol dm^{-3} acetic acid made up to 100 mL) containing an equimolar mixture of the metal cations (0.01 M). The organic phase contained the macrocyclic ionophore (0.001 M) and the receiving phase consisted of a buffer solution at pH = 3 ± 0.1 (56.6 mL of 1 mol dm^{-3} formic acid and 10 mL of 1 mol dm^{-3} NaOH made up to 100 mL)[13]. In the course of the transport experiment, after 24 h, samples of both aqueous phases were analyzed for metal content by atomic absorption spectroscopy (Shimadzu-670). The metal ion transport arrangement used in the present investigation is represented schematically in Fig. 2.

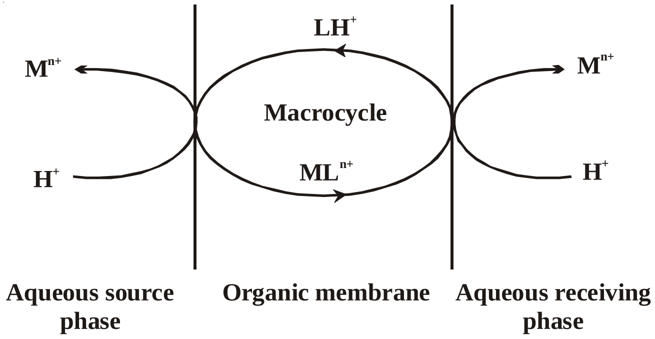


Fig. 2. Diagram illustrating the system used in the current study for the transport of a metal ion across a membrane phase

RESULTS AND DISCUSSION

Effect of carrier structure on cation transport: 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 ring has an important effect on cation transport[3,14]. Chelating agents containing sulfur atoms as coordination sites possess great affinity toward d^{10} transition metal ions like Ag^+. Thus the formation of thiacrown ether complexes with metal cations may be attributed to the affinity of the metal ion for sulfur atom. Of course, the relative sizes of the metal ion and cavity of the macrocyclic ligand can also play an important role in the selectivity of the resulting complex[15].

For competitive transport of the 7 metal cations, 1,4-dioxa-7,10-dithiacyclododecane-2,3-dione is used as an ionophore. Since the Ag^+ cation is a softer Lewis acid than the other metal cations, therefore, based on the hard and soft acid-base concept, the interaction of the Ag^+ cation with the sulfur atoms of this ligand as a soft base is stronger than the other metal cations. The results obtained in this study (Fig. 3), show that the macrocyclic ligand (**I**) forms a stronger complex with Ag^+ cation with respect to the other metal cations and therefore, transports effectively the Ag^+ ion from the source phase into receive phase.

Effect of solvent upon fluxes and selectivity: According to Izatt and coworkers[16], 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 composition of the boundary layers is a function of the mutual water-solvent solubilities. The partitioning of ions into the organic phase should also be affected by the dielectric constant[17].

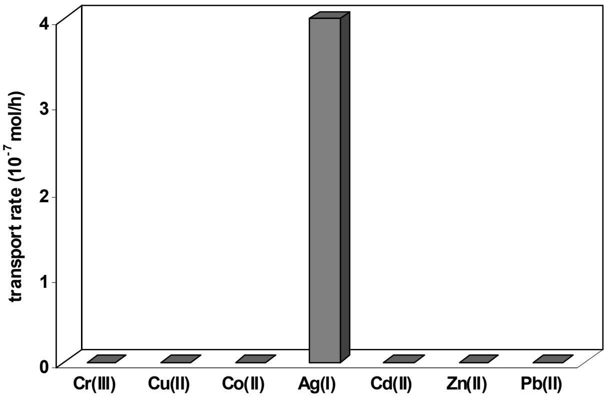


Fig. 3: The results of metal ion transport (water/nitrobenzene/water) studies for ligand (**I**). Source phase: pH = 5.0 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains macrocyclic ionophore (**I**) (0.001 M) (50 mL). Receiving phase: pH = 3.0 (NaOH/HCOOH) (30 mL), stirred for 24 h

The data for competitive transport of Cr^{3+}, Co^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, Zn^{2+} and Pb^{2+} metal cations from an aqueous source phase through dichloromethane, chloroform, 1,2-dichloroethane and nitrobenzene membranes containing macrocyclic ligands (**I**) are shown in Table-1. As is seen from Fig. 4, the rate of transport of silver ion by this ligand varied in order: DCM > NB > $CHCl_3$ > 1,2-DCE. According to the physicochemical properties of the solvents, this result may be attributed to the lower viscosity of dichloromethane (η = 0.39) than those of chloroform (η = 0.58), 1,2-dichloroethane (η = 0.73) and nitrobenzene (η =1.62) which leads to increase the rate of transport in this organic solvent compared to the other three solvents[18].

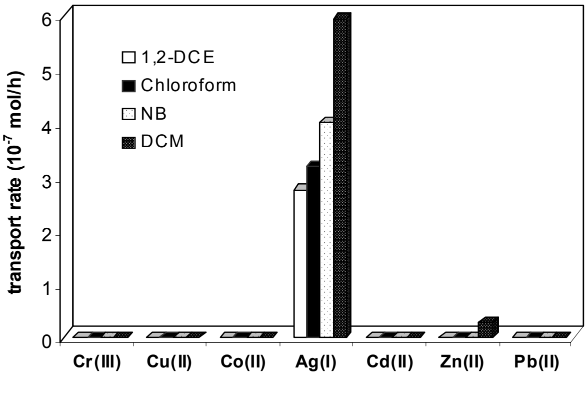


Fig. 4. Comparison of the results of metal ion transport (water/organic solvent/water) studies for ligand (I). Source phase: pH = 5.0 (CH_3COOH/CH_3COONa) containing metal ions at 0.01M (10 mL). Membrane phase: contains macrocyclic ionophore (**I**) (0.001 M) (50 mL). Receiving phase: pH = 3.0 (NaOH/HCOOH), (30 mL) stirred for 24 h

TABLE-1
DATA FOR 7-METAL IONS COMPETITIVE TRANSPORT ACROSS ORGANIC SOLVENTS AS BULK MEMBRANE WITH MACROCYCLIC IONOPHORE (**I**)

Solvent	Cr(III)	Cu(II)	Co(II)	Ag(I)	Cd(II)	Zn(II)	Pb(II)
DCM							
% (Receiving)[A]	–[D]	–	–	4.76	–	0.23	–
% (Membrane)[B]	–	7.43	1.99	26.38	–	3.43	8.95
J (mol per 24 h)[C]	–	–	–	5.94	–	0.28	–
$CHCl_3$							
%(Receiving)[A]	–	–	–	2.55	–	–	–
%(Membrane)[B]	–	3.06	1.057	23.43	–	–	7.28
J (mol per 24 h)[D]	–	–	–	3.18	–	–	–
NB							
%(Receiving)[A]	–	–	–	3.20	–	–	–
%(Membrane)[B]	–	–	3.58	13.16	2.76	–	–
J (mol per 24 h)[C]	–	–	–	4.00	–	–	–
1,2-DCE							
%(Receiving)[A]	–	–	–	2.20	–	–	–
%(Membrane)[B]	1.91	3.25	1.22	15.53	–	–	4.85
J (mol per 24 h)[C]	–	–	–	2.75	–	–	–

[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.

Although the viscosity of nitrobenzene is higher than that of chloroform and 1,2-dichloroethane, but the *J*-value for Ag^+ transport is larger in nitrobenzene with respect to chloroform and 1,2-dichloroethane. The higher polarity of nitrobenzene ($\mu = 4$)[19] compared to the other two organic solvents results in higher solubility of the complex of Ag^+ with this ligand in membrane phase and therefore, the transport rate of Ag^+ in this organic phase is higher than $CHCl_3$ and 1,2-DCE. On the other hand, the higher dielectric constant of 1,2-dichloroethane ($\varepsilon = 10.1$) than that of chloroform ($\varepsilon = 4.8$) can lead to destabilization of the ion pair in organic phase leading to decrease the rate of transport of Ag^+ metal cation through the 1,2-DCE as liquid membrane.

Effect of binary mixed solvents upon fluxes and selectivity: The results of transport from a source phase containing seven metal cations through chloroform-dichloromethane and chloroform-nitrobenzene binary mixtures containing macrocyclic ligand are listed in Tables 2 and 3. As is obvious from Fig. 5, the rate of transport of Ag^+ is sensitive to the composition of $CHCl_3$-NB binary solution and a non-linear relationship is observed for variation of the transport rate of this metal cation with the composition of this binary mixed solvent. This behaviour may be due to the interactions between the chloroform and nitrobenzene molecules, as the formation of an intermolecular hydrogen bond[20] in their binary mixtures, which may result in changing some of the chemical and physical properties of each of the solvents in their binary solutions.

TABLE-2
DATA FOR 7-METAL IONS COMPETITIVE TRANSPORT ACROSS $CHCl_3$-NB BINARY SYSTEMS AS BULK MEMBRANE WITH MACROCYCLIC IONOPHORE (**I**)

Solvent	Cr(III)	Cu(II)	Co(II)	Ag(I)	Cd(II)	Zn(II)	Pb(II)
Pure $CHCl_3$							
%(Receiving)^{A}	–^{D}	–	–	2.55	–	–	–
%(Membrane)^{B}	–	3.06	1.057	23.43	–	–	7.28
J (mol per 24 h)^{C}	–	–	–	3.18	–	–	–
75%$CHCl_3$ + 25%NB							
%(Receiving)^{A}	–	–	–	3.30	–	–	–
%(Membrane)^{B}	2.32	–	2.660	15.01	–	–	3.71
J (mol per 24 h)^{C}	–	–	–	4.12	–	–	–
60%$CHCl_3$ + 40%NB							
%(Receiving)^{A}	–	–	–	3.36	–	–	–
%(Membrane)^{B}	–	–	1.990	10.02	–	–	4.09
J (mol per 24 h)^{C}	–	–	–	4.19	–	–	–
50%$CHCl_3$ + 50%NB							
%(Receiving)^{A}	–	–	–	3.08	–	–	–
%(Membrane)^{B}	15.84	–	2.530	19.71	–	–	7.57
J (mol per 24 h)^{C}	–	–	–	3.85	–	–	–
40%$CHCl_3$ + 60%NB							
%(Receiving)^{A}	–	–	–	2.31	–	–	–
%(Membrane)^{B}	–	1.64	1.420	14.53	1.34	–	4.14
J (mol per 24 h)^{C}	–	–	–	2.89	–	–	–
25%$CHCl_3$ + 75%NB							
%(Receiving)^{A}	–	–	–	2.92	–	–	–
%(Membrane)^{B}	3.79	–	4.500	17.46	0.18	4.71	3.70
J (mol per 24 h)^{C}	–	–	–	3.65	–	–	–
Pure NB							
%(Receiving)^{A}	–	–	–	3.20	–	–	–
%(Membrane)^{B}	–	–	3.580	13.16	2.76	–	–
J (mol per 24 h)^{C}	–	–	–	4.00	–	–	–

^{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.

As is evident from Fig. 6, the transport rate of Ag^+ increases as the concentration of chloroform is lowered in $CHCl_3$-DCM binary mixed solvent. According to the physicochemical properties of the solvents, the higher viscosity of chloroform than that of dichloromethane can result in a decrease in transport rate of the Ag^+ as the mole fraction of $CHCl_3$ increases in $CHCl_3$-DCM binary solutions. A linear relationship is observed between the transport rate of Ag^+ metal cation with the composition of this binary mixture (Fig. 6). This probably reveals that there is no significant interaction between the chloroform and dichloromethane molecules that could affect the chemical and physical properties of each of these solvents in their binary mixtures.

TABLE-3
DATA FOR 7-METAL IONS COMPETITIVE TRANSPORT ACROSS $CHCl_3$-DCM BINARY SYSTEMS AS BULK MEMBRANE WITH MACROCYCLIC IONOPHORE (**I**)

Solvent	Cr(III)	Cu(II)	Co(II)	Ag(I)	Cd(II)	Zn(II)	Pb(II)
Pure $CHCl_3$							
%(Receiving)^A	–^{D}	–	–	2.55	–	–	–
%(Membrane)^B	–	3.06	1.057	23.43	–	–	7.28
J (mol per 24 h)^C	–	–	–	3.18	–	–	–
75%$CHCl_3$ + 25%DCM							
%(Receiving)^A	–	–	–	3.31	–	–	–
%(Membrane)^B	3.55	4.56	4.500	15.01	0.72	–	6.50
J (mol per 24 h)^C	–	–	–	4.13	–	–	–
60%$CHCl_3$ + 40%DCM							
%(Receiving)^A	–	–	–	3.48	–	–	–
%(Membrane)^B	2.45	–	3.070	15.60	1.70	–	5.57
J (mol per 24 h)^C	–	–	–	4.35	–	–	–
50%$CHCl_3$ + 50%DCM							
%(Receiving)^A	–	–	–	3.74	–	–	–
%(Membrane)^B	2.41	–	4.030	16.72	2.76	–	3.36
J (mol per 24 h)^C	–	–	–	4.67	–	–	–
40%$CHCl_3$ + 60%DCM							
%(Receiving)^A	–	–	–	4.02	–	–	–
%(Membrane)^B	10.52	–	0.680	17.59	1.16	2.27	5.73
J (mol per 24 h)^C	–	–	–	5.02	–	–	–
25%$CHCl_3$ + 75%DCM							
%(Receiving)^A	–	–	–	3.97	–	–	–
%(Membrane)^B	–	4.15	–	8.85	2.05	–	1.91
J (mol per 24 h)^C	–	–	–	4.96	–	–	–
Pure DCM							
%(Receiving)^A	–	–	–	4.76	–	0.23	–
%(Membrane)^B	–	7.43	1.990	26.38	–	3.43	8.95
J (mol per 24 h)^C	–	–	–	5.94	–	0.28	–

^{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.

Effect of surfactants on transport efficiency: It has been found that a major role of the fatty acids is to aid the transport process by increasing in lipophilicity of crown-cation complex through some proton-donor and proton-acceptor interactions between surfactant (as proton donor) and oxygen atoms of ligand (as proton acceptor) which can facilitate the cation transport through liquid membrane[21] and also serve to inhibit any bleeding of partially species from the organic membrane phase into either of the aqueous phases.

The results of the influence of the stearic acid, palmetic acid and oleic acid as surfactant (0.004 M) in the membrane phase containing dichloromethane, chloroform, 1,2-dichloroethane and nitrobenzene on the silver ion transport are given in

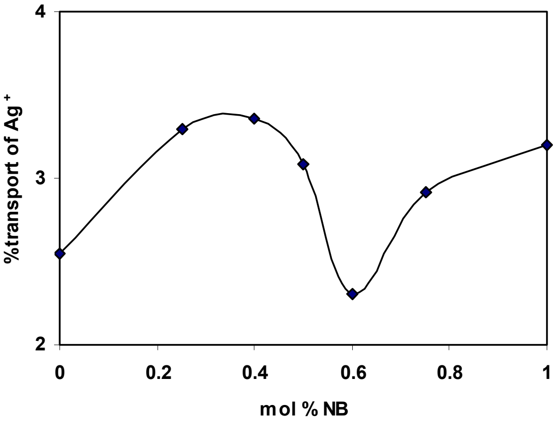


Fig. 5. Changes of Ag^+ ion transport with the composition of the $CHCl_3$-NB binary system. Source phase: pH = 5.0 (CH_3COOH/CH_3COONa) containing metal ions at 0.01M (10 mL). Membrane phase: contains macrocyclic ionophore (**I**) (0.001M) in $CHCl_3$-NB binary solvents (50 mL). Receiving phase: pH = 3.0 (NaOH/ HCOOH) (30 mL), stirred for 24 h

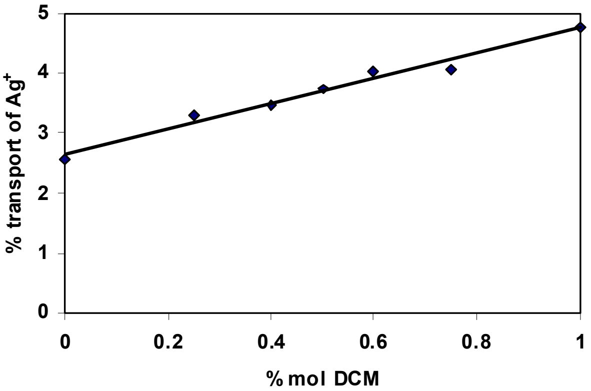


Fig. 6. Changes of Ag^+ ion transport with the composition of the $CHCl_3$-DCM binary system. Source phase: pH = 5.0 (CH_3COOH/CH_3COONa) containing metal ions at 0.01M (10 mL). Membrane phase: contains macrocyclic ionophore (**I**) (0.001M) in $CHCl_3$-DCM binary solvents (50 mL). Receiving phase: pH = 3.0 (NaOH/HCOOH) (30 mL), stirred for 24 h

Table-4. 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 the acidic proton of carboxylic acids in these aprotic and protophobic solvents which results in formation of a weaker complex between the Ag^+ 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 crown-cation complex and therefore, the transport of Ag^+ decreases in the presence of stearic, palmetic and oleic acids.

TABLE-4
EFFECT OF SURFACTANTS ON SILVER ION TRANSPORT ACROSS ORGANIC SOLVENTS SYSTEM AS BULK MEMBRANE WITH MACROCYCLIC IONOPHORE (**I**)

Solvent	Fatty acid	%(Receiving)^A	%(Membrane)^B	J (mol per 24 h)^C
DCM	–	4.76	26.38	5.74
	Stearic acid	4.18	27.27	5.22
	Palmetic acid	4.38	18.62	5.48
	Oleic acid	4.42	22.41	5.53
$CHCl_3$	–	2.55	23.43	3.18
	Stearic acid	2.32	23.04	2.89
	Palmetic acid	2.71	18.88	3.38
	Oleic acid	2.34	22.10	2.92
NB	–	3.20	13.16	4.00
	Stearic acid	2.60	10.96	3.25
	Palmetic acid	1.82	12.27	2.27
	Oleic acid	2.90	14.32	3.61
1,2-DCE	–	2.20	15.53	2.75
	Stearic acid	1.44	21.83	1.80
	Palmetic acid	1.40	21.17	1.75
	Oleic acid	1.28	18.41	1.59

^{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}.

Conclusion

A transport system for seven metal cations through a bulk liquid membrane containing a new synthesized ligand, 1,4-dioxa-7,10-dithiacyclododecane-2,3-dione, as ion carrier was studied and was found that this ligand is an excellent carrier for selective transport of Ag^+. This study demonstrates that the rates of cation transport are strongly influenced by the nature of organic phase and the transport rate of Ag^+ in dichloromethane phase is greater than in nitrobenzene, chloroform and 1,2-dichloroethane liquid membranes. A good selectivity was also observed for Ag^+ cation in the case of using chloroform-nitrobenzene ($CHCl_3$-NB) and chloroform-dichloromethane ($CHCl_3$-DCM) binary mixed solvents as membrane phase. A linear behaviour was observed between the transport rate of silver(I) cation and the composition of $CHCl_3$-DCM membrane system, but a non-linear relationship was observed for the case of $CHCl_3$-NB system. The results obtained for competitive liquid membrane transport of the studied metals in the presence of stearic acid, palmetic acid and oleic acid as surfactant in different organic phases show that transport rate of silver ion decreases in the presence of these fatty acids.

ACKNOWLEDGEMENT

The authors acknowledge the support of this work by Ferdowsi University of Mashhad, Mashhad, Iran.

REFERENCES

1. R.D. Noble and S.A. Stern, Membrane Separation Technology: Principles and Applications, Elsevier, Amsterdam (1995).
2. G.M. Ritcey and A.W. Ashbrook, Solvent Extraction, Part II, Elsevier, Amsterdam (1979).
3. J.D. Lamb, R.M. Izatt, D.G. Garrick, J.S. Bradshaw and J.J. Christensen, *J. Membr. Sci.*, **9**, 83 (1981).
4. Y. Hasegawa, M. Miyata and S. Yoshida, *Bull. Chem. Soc. (Japan)*, **59**, 3003, (1986).
5. T.M. Flyes, *J. Membr. Sci.*, **24**, 229 (1985).
6. F. Wilman, W.F. Van Straaten and F. De Jong, *Recl. Trav. Chim. Pays Bas*, **112**, 273 (1993).
7. R.M. Izatt, D.V. Dearden, P.R. Brown, J.J. Bradshaw and J.J. Christensen, *J. Am. Chem. Soc.*, **7**, 105, 1785 (1993).
8. R.A. Bartsch, E. Jeon, W. Walkowiak and W. Apostoluk, *J. Membr. Sci.*, **159**, 123 (1999).
9. G.H. Rounaghi and R.S. Khoshnood, *J. Incl. Phenom. Macro. Chem.*, **55**, 309 (2006).
10. G.H. Rounaghi and M.S. Kazemi, *Asian J. Chem.*, **20**, 366 (2008).
11. S.M. Sayedi, A. Sadeghian, H. Sadeghian, A. Hazrathoseyni and M. Sadeghian, *Phosphorus Sulfur Silicon Rel. Elem.*, **182**, 265 (2007).
12. P.S.K. Chia, L.F. Lindoy, G.W. Walker and G.W. Everett, *Pure. Appl. Chem.*, **65**, 521 (1993).
13. D.D. Perrin and B. Dempsey, Buffer for pH and Metal Ion Control, Chapman and Hall, London, p. 132 (1979).
14. M.C. Shen, Z.L. Wang, Q.H. Luo Gao and G.Y. Lu, *Acta Chim. Sin.*, **49**, 718 (1991).
15. K. Saito, S. Murakami, A. Muromatsu and E. Sekido, *Polyhedron*, **12**, 1587 (1993).
16. D.W. McBride, R.M. Izatt, J.D. Lamb and 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. 3, 598 (1984).
17. R.M. Izatt, R.L. Bruening, G.A. Clark, J.D. Lamb and J.J. Christensen, *J. Membr. Sci.*, **28**, 77 (1986).
18. H.K. Alpogus, S. Memon, M. Erosoz and M. Yilmaz, *New J. Chem.*, **26**, 477 (2002).
19. K. Izutzu, Electrochemistry in Nonaqueous Solution, Wiley-VCH (2002).
20. F. Kh. Tukhvatullin, A.K. Atakhodzhaev, S.A. Osmanov, I.P. Klener, A. Zhumaboev and U.N. Tashkenbaev, *Russ. Phys. J.*, 304 (1991).
21. Sh. Dadfarnia and M. Shamsipur, *Bull. Chem. Soc. (Japan)*, **65**, 2779 (1992).

(*Received*: 9 June 2008; *Accepted*: 10 February 2009) AJC-7229