Asian Journal of Chemistry Vol. 21, No. 9 (2009), 6701-6709

Competitive Bulk Liquid Membrane Transport of Transition and Post Transition Metal Cations Using (2,3-Diphenylquinoxaline)-4',4''-dithiotriethylene glycol

G.H. ROUNAGHI*, E. RAZAVIPANAH, M.M. RIAZI, M. RAHIMIZADEH,
M. BAKAVOLI, E. REZAEI SERESHT and M.M. ESFAHANI
Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran
Fax: (98)(511)8796416; Tel: (98)(511)7626388
E-mail: ghrounaghi@yahoo.com

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), copper(II), zinc(II), silver(I) and lead(II) metal cations and the source and receiving phases being buffered at pH = 4.9 and 3.0, respectively. The membrane phase incorporated a new synthesized ionophore, (2,3-diphenylquinoxaline)-4',4''-dithio triethylene glycol. The membrane solvents include: dichloromethane, chloroform, 1,2-dichloroethane and chloroform-1,2-dichloroethane binary solvents. The obtained results show that the selectivity and the efficiency of transport for these heavy metal cations change with the nature of the organic solvents which were used as liquid membranes in these experiments. A good transport efficiency and selectivity of silver ion transport from aqueous solutions were observed in this investigation. The transport rate of the silver ion in chloroform-1,2-dichloroethane 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 transport rates change in the presence of the stearic acid.

Key Words: Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Pb^{2+}, (2,3-Diphenylquinoxaline)-4',4''-dithio triethylene glycol, Liquid membrane transport, Dichloromethane, Chloroform, 1,2-Dichloroethane, Binary solvents.

INTRODUCTION

A great deal of research work on ion transport published in last three decades[1-5] testifies to the increasing interest existing among chemists, chemical engineers and biologists in understanding the transport processes occurring across the natural and artificial membranes. The separation of chemical species from a complex mixture is often an important process in industry and chemical analysis, therefore, the transport of metal ions across a membrane 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[6-8]. The main advantage of liquid membrane transport of metal ions over their classical solvent extraction methods is that the amounts of organic solvent and metal ion carrier are remarkably reduced[9]. Information about the transport of transition and post transition metal cations across liquid membranes is quite sparse.

Transport of some of the metal cations by crown ethers has been investigated[10-12]. 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[13]. The target 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 results of study of competitive bulk liquid membrane transport of the transition and post transition metal cations using (2,3-diphenylquinoxaline)-4',4"-dithio triethylene glycol (Fig. 1) as an ion carrier in various liquid membranes.

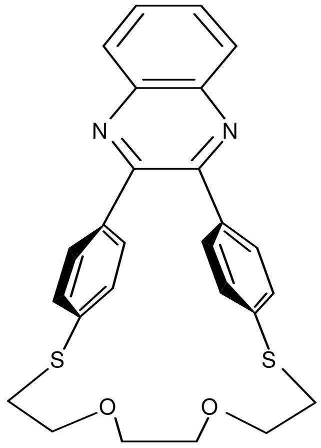

Fig. 1. (2,3-Diphenylquinoxaline)-4',4"-dithio triethylene glycol

EXPERIMENTAL

Cobalt(II) nitrate, nickel(II) nitrate, copper(II) nitrate, zinc(II) nitrate, silver(I) nitrate and lead(II) nitrate, sodium acetate and sodium hydroxide (all from Merck) and stearic acid (Fluka) were used without further purification. The solvents chloroform, 1,2-dichloroethane and dichloromethane (Merck), with the highest purity were used as liquid membranes. Acetic acid, formic acid and nitric acid (all from Merck), 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.

Synthesis of (2,3-diphenylquinoxaline)-4',4''-dithio triethylene glycol: This compound was synthesized according to a procedure developed in our laboratory starting from triethylene glycol ditosylate and 2,3-*bis*(4-mercaptophenyl)quinoxaline. Yield 41 %; m.p. > 300 ºC; IR (KBr, ν_{max}, cm^{-1}): 665, 761, 784, 816, 923, 946, 1013, 1091, 1170, 1190, 1219, 1352, 1397, 1490, 1555, 1586, 1663, 2923; ^{1}H NMR (CDCl$_3$): δ = 3.04 (t, 4H, J = 7 Hz), 3.45-3.8 (m, 8H), 7.32 (d, 4H, J = 12 Hz), 7.46 (d, 4H, J = 12Hz), 7.77 (dd, 2H, J = 4.7 Hz), 8.13 (dd, 2H, J = 4. 7 Hz); M$^+$ = 460; Anal. Calcd. for $C_{26}H_{24}N_2O_2S_2$: C, 67.80; H, 5.25; N, 6.08; S, 13.92. Found: C, 67.79; H, 4.92; N, 6.06; S, 14.14.

Procedure: The transport experiments employed a standardized concentric cell (Fig. 2). The standardized concentric cell is consist of an aqueous source phase (10 mL) and receiving phase (30 mL) which is separated by an organic phase (50 mL). For each experiment, both aqueous phases and the organic phase (liquid membrane) were stirred separately at 20 rpm using stirring paddles for the receiving phases 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 mL of 2 mol dm^{-3} sodium acetate solution and 3.05 cm^3 of 2 mol dm^{-3} acetic acid made up to 100 dm^{-3})[14] 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 6.0 × 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 mL of 1 mol dm^{-3} formic acid and 10 cm^3 of 1 mol dm^{-3} sodium hydroxide made up to 100 dm^{-3})[14]. The atomic absorption spectrometer which was used for the measurement of metal ions concentrations in both aqueous phases was a Shimadzu AA-670 instrument. pH measurements were made with a Metrohm 632 pH-meter using a combined glass electrode. All transport experiments were carried out at ambient temperature and all transport runs were terminated after 24 h. A similar transport experiment was carried out in the absence of the carrier for reference.

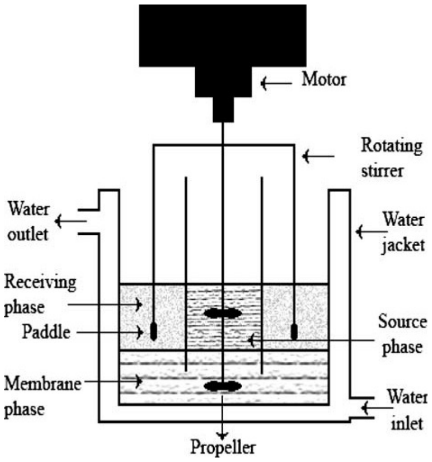

Fig. 2 Liquid membrane cell

RESULTS AND DISCUSSION

The results for competitive transport of six-metal cations from a source phase at (pH = 4.9) through three liquid membranes chloroform, dichloromethane and 1,2-dichloroethane containing (2,3-diphenylquinoxaline)-4',4''-dithiotriethylene glycol into acidic receiving phase (pH = 3) are listed in Table-1. The results for competitive transport of six-metal cations from a source phase at (pH = 4.9) through chloroform-1,2-dichloroethane binary mixtures containing (2,3-diphenylquinoxaline)-4',4''-dithio triethylene glycol 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 results in presence of stearic acid in chloroform and 1,2-dichloroethane phase are listed in Table-3. Figs. 3-5 showed the results for competitive transition and post transition metal cations transport across organic liquid membranes. The variation of transport rate of Ag^+ metal cation *versus* the mole fraction of chloroform in chloroform-1,2-dicoloroethane binary solvents is shown in Fig. 6.

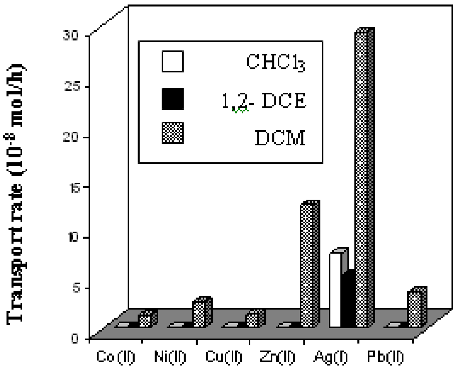

Fig. 3. Comparison of the results of metal ion transport (water/organic solvent/water) studies for (2,3-diphenylquinoxaline)-4',4''-dithio triethylene glycol. Source phase: pH = 4.9 (CH_3COOH/ CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains ligand (0.001 M) (50 mL). Receiving phase: pH = 3.0 (HCOOH/HCOONa), (30 mL) stirred for 24 h; enclosed in a water jacket at 25 °C

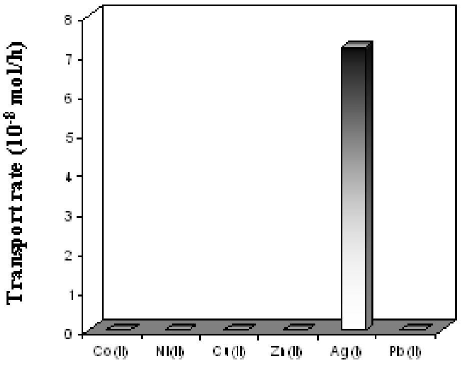

Fig. 4. Results of metal ion transport (water/ chloroform/water) studies for (2,3-diphenylquinoxaline)-4',4''-dithio triethylene glycol. Source phase: pH = 4.9 (CH_3COOH / CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains ligand (0.001 M) (50 mL). Receiving phase: pH = 3.0 (HCOOH/ HCOONa), (30 mL) stirred for 24 h; enclosed in a water jacket at 25 °C

Effect of carrier structure on the cation transport: For competitive transport of the six metal cations, we used (2,3-diphenylquinoxaline)-4',4''-dithiotriethylene glycol as an ionophore. 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[15,16]. The results obtained in this study show that (2,3-diphenylquinoxaline)-4',4''-dithiotriethylene glycol system preferentially transport the Ag^+ cation. Since the Ag^+ cation is a

TABLE-1
DATA FOR COMPETITIVE TRANSPORT OF SIX METAL CATIONS ACROSS BULK CHLOROFORM, DICHLOROMETHANE AND 1,2-DICHLOROETHANE MEMBRANES BY (2,3-DIPHENYLQUINOXALINE)-4',4''-DITHIO TRIETHYLENE GLYCOL AT 25 °C

Membrane	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ag^{+}	Pb^{2+}
Chloroform						
% (transport receiving)[a]	—	—	—	—	0.57	—
% (membrane)[b]	—	—	—	—	—[d]	—
J (mol per 24 h)[c]	—	—	—	—	0.72	—
Dichloromethane						
% (transport receiving)[a]	0.08	0.20	0.10	1.00	2.33	0.30
% (membrane)[b]	13.16	0.98	—	—	12.57	—
J (mol per 24 h)[c]	0.11	0.24	0.12	1.20	2.91	0.34
1,2-Dichloroethane						
% (transport receiving)[a]	—	—	—	—	0.41	—
% (membrane)[b]	—	—	—	—	3.79	—
J (mol per 24 h)[c]	—	—	—	—	0.51	—

[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 J values are × 10^{-7}. [d] The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

TABLE-2
DATA FOR COMPETITIVE TRANSPORT OF SIX METAL CATIONS ACROSS BULK CHLOROFORM-1,2-DICHLOROETHANE BINARY MIXED SOLVENT MEMBRANES BY (2,3-DIPHENYLQUINOXALINE)-4',4''-DITHIO TRIETHYLENE GLYCOL AT 25 °C

Membrane	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ag^{+}	Pb^{2+}
Pure $CHCl_3$						
% (transport receiving)[a]	—	—	—	—	0.57	—
% (membrane)[b]	—	—	—	—	—	—
J (mol per 24 h)[c]	—	—	—	—	0.72	—
75 % $CHCl_3$-25% 1,2-DCE[e]						
% (transport receiving)[a]	—	—	—	—	0.75	—
% (membrane)[b]	—	—	—	—	3.65	—
J (mol per 24 h)[c]	—	—	—	—	0.93	—
50 % $CHCl_3$-50% 1,2-DCE[e]						
% (transport receiving)[a]	—	—	0.12	0.10	0.87	0.26
% (membrane)[b]	—	—	—[d]	—[d]	0.13	—[d]
J (mol per 24 h)[c]	—	—	0.15	0.12	1.10	0.32
25 % $CHCl_3$-75% 1,2-DCE[e]						
% (transport receiving)[a]	—	—	—	0.15	0.76	0.14
% (membrane)[b]	—	—	—	—[d]	1.24	—[d]
J (mol per 24 h)[c]	—	—	—	0.18	0.94	0.17
Pure 1,2-DCE						
% (transport receiving)[a]	—	—	—	—	0.41	—
% (membrane)[b]	—	—	—	—	3.79	—
J (mol per 24 h)[c]	—	—	—	—	0.51	—

[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 J values are × 10^{-7}. [d] The hyphenated symbols mean that the values are about zero or they are with high uncertainties. [e] Composition of binary mixtures is expressed in mol% for each solvent system, 1,2-DCE = 1,2-Dichloroethane.

TABLE-3
EFFECT OF STEARIC ACID ON SIX-METAL IONS COMPETITIVE TRANSPORT ACROSS A BULK CHLOROFORM AND 1,2-DICHLOROETHANE MEMBRANE WITH MACROCYCLE LIGAND (2,3-DIPHENYLQUINOXALINE)-4',4''-DITHIO TRIETHYLENE GLYCOL AS IONOPHORE AT 25 °C

Membrane	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ag^{+}	Pb^{2+}
Chloroform						
%(transport receiving)[a]	0.097	0.05	0.06	0.10	0.19	0.19
%(membrane)[b]	13.90	3.34	0.17	4.10	22.0	—
J(mol per 24 h)[c]	0.12	0.06	0.08	0.11	0.23	0.23
1,2-Dichloroethane						
%(transport receiving)[a]	0.044	—	0.07	—	1.31	0.26
%(membrane)[b]	9.94	—	—	—	—	—
J(mol per 24 h)[c]	0.06	—	0.09	—	1.64	0.33

[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 J values are × 10^{-7}.

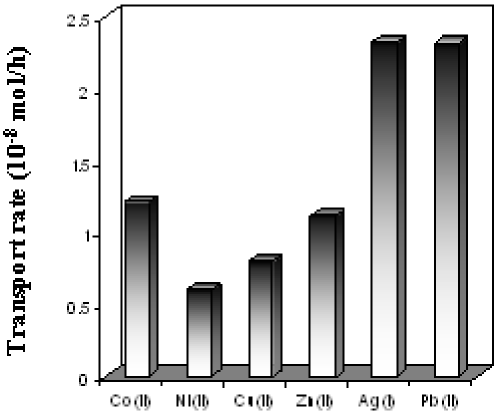

Fig. 5. Results of metal ion transport (water/chloroform-stearic acid/water) studies for (2,3-Diphenylquinoxaline)-4',4''-dithio triethylene glycol. Source phase: pH = 4.9 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains ligand (0.001M) and stearic acid (0.004) (50 mL). Receiving phase: pH = 3.0 (HCOOH/HCOONa), (30 mL) stirred for 24 h; enclosed in a water jacket at 25 °C

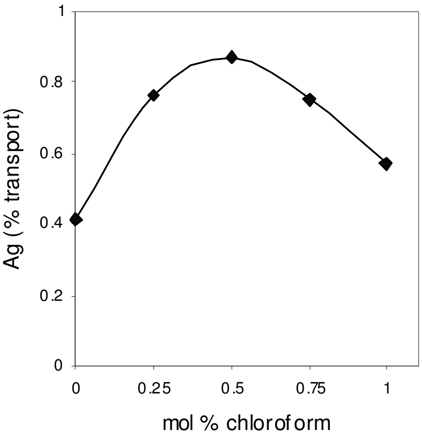

Fig. 6. Changes of silver(I) ion transport with the composition of the $CHCl_3$-1,2-DCE binary systems. Source phase: pH = 4.9 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains (2,3-diphenylquinoxaline)-4',4''-dithio triethylene glycol (0.001 M) (50 mL) in $CHCl_3$-1,2-DCE binary solvents. Receiving phase: pH = 3.0 (HCOOH/ HCOONa), (30 mL) stirred for 24 h; enclosed in a water jacket at 25 °C

softer Lewis acid than lead(II), zinc(II), cupper(II), nickel(II) and cobalt(II) metal cations[17], therefore, based on the hard and soft acid base concept, the interaction of the Ag^+ cation with the nitrogen and sulfur atoms of this ligand as a soft base is stronger than the other metal cations. In addition, the interaction of π-electron system present in aromatic ring with Ag^+ may be effective on complexation between Ag^+ and this ligand.

Effect of solvent upon fluxes and selectivity in bulk liquid membrane transport: According to Atwood and co-workers[18], several parameters whose values depend on the membrane solvent can affect the transport of the metal cations. The effect of the nature of the organic solvent as liquid membrane on the metal cation transport was investigated. As is evident in Fig. 3, the transport rates of most of the metal cations in dichloromethane are greater than in chloroform and 1,2- dichloroethane. According to the physicochemical properties of the solvents which are given in Table-4, this result may be attributed to the lower viscosity of dichloromethane than that of chloroform and 1,2-dichloroethane which leads to increase the rate of transport in this organic solvent compared to the other solvents[19]. On the other hand, according to the physicochemical properties of the solvents which are given in Table-4, the higher dielectric constant of 1,2-dichloroethane than that of chloroform and dichloromethane can lead to destabilization of the ion pair in the organic phase, leading to decrease the rate of transport of Ag^+ through 1,2-dichloroethane as liquid membrane.

TABLE-4
SOME OF PHYSICO-CHEMICAL PROPERTIES OF ORGANIC SOLVENTS USED AS LIQUID MEMBRANES [Ref. 25]

Solvent	Structure and molecular weight	DN^a	AN^b	μ^c	ε^d	η^e	d^f
Chloroform	$CHCl_3$ 119.38	4	23.1	1.35	4.8	0.58	1.479
1,2-Dichloroethane	$ClCH_2CH_2Cl$ 98.96	0	16.7	1.86	10.66	0.73	1.250
Dichloromethane	CH_2Cl_2 84.93	1	20.4	1.55	8.93	0.39	1.316

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

Effect of binary mixed solvents upon fluxes and selectivity: Data for competitive transport of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and Pb^{2+} metal cations with (2,3-diphenyl quinoxaline)-4',4''-dithio triethylene glycol ligand in chloroform-1,2-dicoloroethane binary systems as membrane phase are shown in Table-2. As is evident in Fig. 6, the change of the transport rate of the Ag^+ ion *versus* the solvent composition in chloroform-1,2-dicoloroethane binary mixture is not monotonic. This behaviour may be related to the interactions between chloroform and 1,2-dicoloroethane molecules in their binary solutions, which result in changing 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. In addition, the composition of the boundary layers and also the partition coefficients of the ligand and the cation-ligand complex may change with the composition of the binary mixed solvent[18].

Effect of stearic acid on transport efficiency of the metal cations: In another experiment the influence of the stearic acid on transport rates of Co^{2+}, Ni^{2+}, Cu^{2+},

Zn^{2+}, Ag^+ and Pb^{2+} metal cations with the synthesized ligand, (2,3-diphenylquinoxaline)-4',4"-dithiotriethylene glycol in $CHCl_3$ and 1,2-dichloroethane as a membrane phase was investigated and the results are summarized in Table-3. As is obvious from this Table, in most cases the transport rate of the metal cations increases in the presence of stearic acid. It has been observed that in some systems that carrier has nitrogen atom in its structure like amino and imino groups the carrier alone is not an effective carrier for the transport of metal cation through the bulk liquid membrane. This is mainly due to the considerable solubilities of the free and complexed forms of carrier into aqueous phases. This problem can be overcome by appending long chain aliphatic groups to the carrier backbone to increase the lipophilicity of the system. Addition of a long chain fatty acid to the organic phase also decreases the extent of carrier bleeding into the aqueous phases[20].

Conclusion

Competitive of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and Pb^{2+} metal cations transport experiments across dichloromethane, chloroform and 1,2-dichloroethane bulk liquid membranes have been performed using a new synthesized ligand, (2,3-diphenyl quinoxaline)-4',4"-dithio triethylene glycol as an ionophore. The results show that the rate of cation transport is 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. (2,3-Diphenylquinoxaline)-4',4"-dithio triethylene glycol showed a good selectivity for Ag^+ cation in all solvents and also the highest transport efficiency was observed for Ag^+ ion under the employed experimental conditions. 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. The transport rate of Ag^+ *versus* the solvent composition in chloroform-1,2-dichloroethane binary mixture is not monotonic which was discussed in term of solvent-solvent interactions between chloroform and 1,2-dichloroethane molecules in their binary mixtures. The experimental results obtained for competitive liquid membrane transport of the studied metal cations by (2,3-diphenyl quinoxaline)-4',4"-dithio triethylene glycol showed that the sequence of selectivites and ion transport ability change in the presence of stearic acid in chloroform and 1,2-dichloroethane membrane phases.

ACKNOWLEDGEMENT

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

REFERENCES

1. D.W. McBride, R.M. Izatt, J.D. Lamb and J.J. Christensen, in eds.: J.L. Atwood, J.F.D. Davies and D.D. MacNicol, Inclusion Compounds, Academic Press, Orlando, FL, Vol. 3, pp. 571-628 (1984).
2. R. Marr and A. Kopp, *Int. Chem. Eng.*, **22**, 44 (1982).
3. F. Guyon, N. Parthasarathy and J. Buffle, *Anal. Chem.*, **71**, 819 (1999).

4. F.Z. El Aamran, A. Kumar, L. Beyer, A. Florido and A.M. Sastre, *J. Membr. Sci.*, **152**, 263 (1999).
5. R.M. Goering, C.N. Bowman, C.A. Koval, R.D. Noble and M.E. Ashley, *J. Membr. Sci.*, **172**, 49 (2000).
6. E.M. Choy, D.F. Evans and E.L. Cussler, *J. Am. Chem. Soc.*, **96**, 7085 (1974).
7. J.D. Lamb, R.M. Izatt, P.A. Robertson and J.J. Christensen, *J. Am. Chem. Soc.*, **102**, 2452 (1980).
8. J. Rebek and R.V. Wattley, *J. Am. Chem. Soc.*, **102**, 4853 (1980).
9. T. Araki and H. Tsukube, Liquid Membranes: Chemical Applications, CRC Press, Boca Raton, FL (1990).
10. A. Safavi and E. Shams, *Talanta*, **48**, 1167 (1999).
11. G.H. Rounaghi and M.S.Kazemi, *J. Incl. Phenom. Macrocycl. Chem.*, **55**, 347 (2006).
12. G.H. Rounaghi and R. Sanavi, *J. Incl. Phenom. Macrocycl. Chem.*, **55**, 309 (2006).
13. S.M. Khopkar, Analytical Chemistry of Macrocyclic and Supramolecular Compounds, Narosa, India, p. 282 (2005).
14. D.D. Perrin and B. Dempsey, Buffers for pH and Metal Ion Control, Chapman and Hall, London, p. 132 (1979).
15. J.D. Lamb, R.M. Izatt, D.G. Garrick, J.S. Bradshaw and J.J. Christensen, *J. Membr. Sci.*, **9**, 83 (1981).
16. M.C. Shen, Z.L. Wang, Q.H. Luo, X. Gao and G.Y. Lu, *Acta Chim. Sin.*, **49**, 718 (1991).
17. C. Kalidas, G. Hefter and Y. Marcus, *Chem. Rev.*, **100**, 819 (2002).
18. J.L. Atwood, J.E.D. Davies and D.D. Macnicol, Inclusion Compounds: Physical Properties and Applications, Academic Press, New York, p. 589 (1984).
19. H.K. Alpoguz, S. Memon, M. Ersoz and M. Yilmaz, *New J. Chem.*, **26**, 447 (2002).
20. M. Akhond and J. Tashkhourian, *Bull. Korean Chem. Soc.*, **24**, 489 (2003).

(*Received*: 22 July 2008; *Accepted*: 16 July 2009) AJC-7681