

Study of Bulk Membrane Transport of Some Heavy Metal Cations Using Three Macrocyclic Ligands Containing Oxygen and Nitrogen Heteroatoms

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Abstract

The transport experiments of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Ag⁺ and Pb²⁺ metal cations were carried out by dibenzo-18-crown-6 (DB18C6), dibenzyl-diaza-18-crown-6 (Dibenzyl-diaza-18C6) and di-*tert*-butyl-dibenzo-18-crown-6 (Di-*tert*-butyl-DB18C6) using chloroform (CHCl₃), 1,2-dichloroethane (1,2-DCE) and nitrobenzene (NB) organic solvents as liquid membranes. The source phase contained equimolar concentration of these metal cations and the source and receiving phases being buffered at pH = 5 and pH = 3, respectively. The obtained results show that the selectivity and the efficiency of transport for these heavy metal cations change with the nature of the ligand and also the organic solvents, which were used as liquid membranes in these experiments. A good selectivity was observed for silver (I) ion by dibenzyl-diaza-18C6 in all membrane systems. Dibenzo-18C6 and di-*tert*-butyl-DB18C6 showed the highest transport efficiency for cobalt (II) ion. The effect of stearic acid on transport efficiency was also investigated and the results show that the efficiency of transport of the heavy metal cations increases in the presence of this organic acid.

Introduction

The industrial importance of metal ion separation has made the study of metal ion transport behaviour an area of increasing research interest. Metal ion transport involves the transfer of metal cations from an aqueous source phase into an aqueous receiving phase through a liquid membrane. The liquid membrane technique has been emerging as a method for the selective separation of the metal cations. It has several advantages such as, the extraction, stripping and regeneration operation are combined in single step [1–3].

In recent years several researches have been carried out in the design and preparation of bulk liquid membranes [4–6] for the efficient and selective transport of some transition and heavy metal cations using different crown ether derivatives as ion carriers [7, 8]. There remains very considerable potential for development of new ligand systems that can bind selectively to a particular metal ion and separate it from a solution of mixed metal ions.

In this study, we discuss the transport of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Ag⁺ and Pb²⁺ metal cations

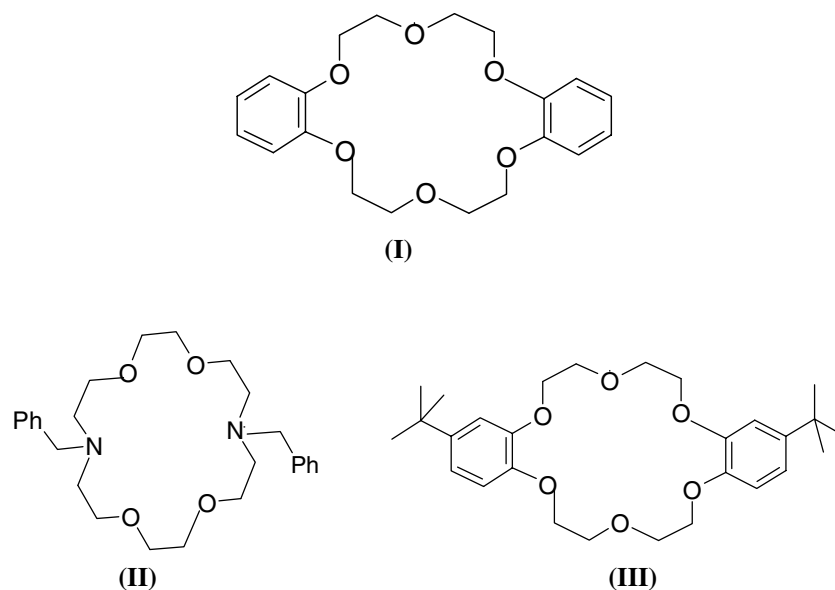
with macrocyclic ligands **I–III** (Scheme 1) as carriers using chloroform (CHCl₃), 1,2-dichloroethane (1,2-DCE) and nitrobenzene (NB) organic solvents as liquid membranes. The effect of stearic acid on transport efficiency for transport of the metal cations was also investigated. The attachment of hydrophobic groups to carriers **I–III**, increase their lipophilicity and thus increasing their solubility in the organic phase and, therefore, prevents their leaching from the organic phase into one or both of the aqueous phases.

Experimental

Reagents and solvents

Dibenzo-18-crown-6 (DB18C6) (Aldrich), dibenzyl-diaza-18-crown-6 (dibenzyl-diaza-18C6) (Merck), di-*tert*-butyl-dibenzo-18-crown-6 (di-*tert*-butyl-DB18C6) (Merck), cobalt (II) nitrate (Riedel), nickel (II) nitrate (G.P.R), copper (II) nitrate (Fluka), zinc (II) nitrate (Merck), silver (I) nitrate (G.P.R), cadmium (II) nitrate, lead (II) nitrate, sodium acetate, sodium hydroxide (all from Merck) and stearic acid (BDH) were used without further purification.

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Scheme 1. I – Dibenzo-18-Crown-6; II – Dibenzyldiaza-18-Crown-6; and III – Di-*tert*-butyl-dibenzo-18-Crown-6.

Chloroform (Analar), nitric acid (BDH) and 1,2-dichloroethane, nitrobenzene, acetic acid, formic acid (all from Merck) were used with the highest purity.

Procedure

All aqueous solutions were prepared using deionized double distilled water. The organic solvents: chloroform, 1,2-dichloroethane and nitrobenzene, which were used as membrane phase, were presaturated with water by shaking a two-phase mixture and then removing the aqueous phase. The transport experiments employed a 'concentric cell' in which the aqueous source phase (10 cm³) and receiving phase (30 cm³) were separated by an organic phase (50 cm³). Details of the cell design have been reported elsewhere [9]. Both aqueous and organic phases were stirred separately at 20 rpm, and the cell was enclosed by a water jacket and thermostated at 25 °C. The aqueous source consisted of a buffer solution (CH₃COOH/CH₃COONa) at pH=5 contain-

ing an equimolar mixture of the 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 ions across the organic membrane by counter transport of protons. All transport runs were terminated after 24 h and atomic absorption spectroscopy (Shimadzu-670) was used to determine the amount of each of the metal cations. The metal ion transport arrangements used in the present investigation is represented schematically in Figure 1.

Results and discussion

The data for competitive transport of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Ag⁺ and Pb²⁺ metal cations from an aqueous source phase through chloroform, 1,2-dichloroethane and nitrobenzene membranes con-

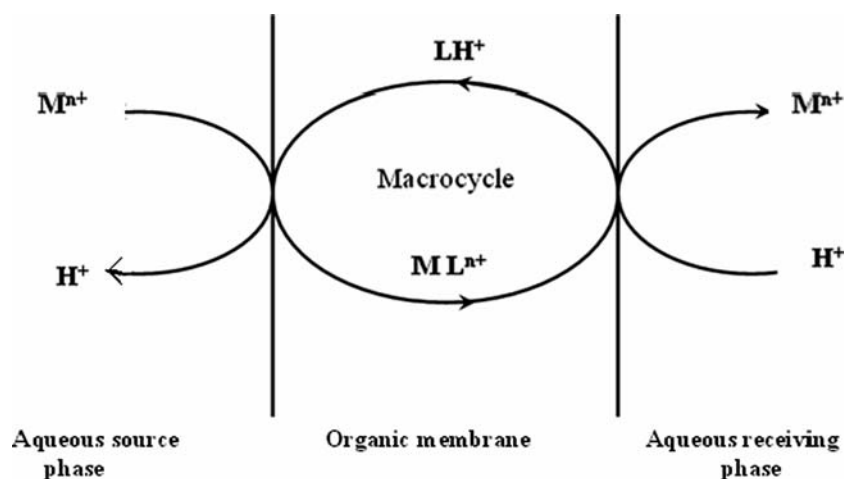


Figure 1. A diagram illustrating the system used in the current study for the transport of a metal ion across a membrane phase.

Table 1. Data for seven-metal ions competitive transport across a bulk chloroform membrane employing macrocycles of types I–III as ionophores at 25 °C

Ionophore	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
<i>I</i>							
%(Receiving) ^a	0.52	- ^d	-	0.11	0.17	0.18	0.29
%(Membrane) ^b	-	-	13.26	9.4	5.15	36.63	2.92
J(mol per 24 h) ^c	6.58	-	-	1.21	2.07	2.24	3.58
<i>II</i>							
%(Receiving) ^a	-	-	-	-	1.08	1.37	0.67
%(Membrane) ^b	-	-	-	-	-	-	-
J(mol per 24 h) ^c	-	-	-	-	13.47	17.16	8.36
<i>III</i>							
%(Receiving) ^a	0.77	-	0.55	0.12	0.04	0.24	-
%(Membrane) ^b	18.68	7.64	10.99	20.06	8.89	8.35	16.62
J(mol per 24 h) ^c	9.63	-	6.89	1.50	0.44	3.63	-

^aPercent of total metal cations in the receiving phase after 24 h.

^bPercent of total metal cations in the membrane phase after 24 h.

^cAll values are $\times 10^{-8}$.

^dThe hyphenated symbols mean that the values are about zero or they are with high uncertainties.

Table 2. Data for seven-metal ions competitive transport across a bulk 1,2-dichloroethane membrane employing macrocycles of type I–III as ionophores at 25 °C

Ionophore	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
<i>I</i>							
%(Receiving) ^a	- ^d	-	-	0.41	0.10	0.13	-
%(Membrane) ^b	5.27	3.15	19.23	18.97	6.44	-	9.67
J(mol per 24 h) ^c	-	-	-	5.11	1.26	1.63	-
<i>II</i>							
%(Receiving) ^a	-	-	0.16	0.06	0.19	0.31	0.17
%(Membrane) ^b	-	4.72	18.61	17.30	14.14	21.69	19.07
J(mol per 24 h) ^c	30.00	-	2.20	0.75	2.33	3.83	2.00
<i>III</i>							
%(Receiving) ^a	1.51	-	-	0.49	0.05	0.24	-
%(Membrane) ^b	-	1.07	10.18	18.89	0.46	8.35	9.80
J(mol per 24 h) ^c	18.81	-	-	6.09	0.63	3.63	-

^aPercent of total metal cations in the receiving phase after 24 h.

^bPercent of total metal cations in the membrane phase after 24 h.

^cAll values are $\times 10^{-8}$.

^dThe hyphenated symbols mean that the values are about zero or they are with high uncertainties.

taining macrocyclic ligands I–III at 25 °C are shown in Tables 1, 2 and 3, respectively.

A plot of transport rate for the studied metal cations with ligand II is presented in Figure 2. As is seen from this Figure, the order of the transport rate (*J* value) of these metal cations in CHCl₃ organic phase is: Ag⁺ > Cd²⁺ > Pb²⁺ but in the case of 1,2-dichloroethane and nitrobenzene is: Ag⁺ > Cd²⁺ > Pb²⁺ > Cu²⁺ > Zn²⁺. No metal–ion transport was observed for Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ cations through CHCl₃ and also for Co²⁺ and Ni²⁺ cations through DCE and NB membrane phases under the conditions employed in these experiments.

The *J* value for silver ion transport with dibenzyl-diaza-18-crown-6 ligand (ligand II) is bigger than the

other metal cations, since its ionic size (ionic radius = 1.15 Å) is very close to the cavity size of this ligand (2.6–3.2 Å) [10], and also since the Ag⁺ cation is a softer Lewis acid than Cd²⁺, Pb²⁺, Zn²⁺, Cu²⁺, Ni²⁺ and Co²⁺ metal cations [11], therefore, based on the Hard and Soft acid–base concept, the interaction of the Ag⁺ cation with the nitrogen atom of this ligand as a soft base is stronger than the other metal cations, thus the Ag⁺ forms a stronger complex with this ligand which results in a more transport efficiency for this cation compared to the other 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 Figure 2, the transport rates of most of the metal cations in CHCl₃ are greater

Table 3. Data for seven-metal ions competitive transport across a bulk nitrobenzene membrane employing macrocycles of type I–III as ionophores at 25 °C

Ionophore	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
<i>I</i>							
%(Receiving) ^a	- ^d	-	-	0.27	0.13	0.15	-
%(Membrane) ^b	5.27	-	5.42	13.57	-	-	-
J(mol per 24 h) ^c	-	-	-	3.41	1.61	1.88	-
<i>II</i>							
%(Receiving) ^a	-	-	0.26	0.18	0.47	0.76	0.30
%(Membrane) ^b	26.51	2.38	16.30	12.78	15.13	17.48	13.04
J(mol per 24 h) ^c	-	-	3.23	2.31	5.85	9.54	3.74
<i>III</i>							
%(Receiving) ^a	2.04	-	-	0.16	0.13	0.17	0.15
%(Membrane) ^b	-	0.99	10.38	6.97	-	3.04	7.68
J(mol per 24 h) ^c	25.51	-	-	2.01	1.65	2.11	1.93

^aPercent of total metal cations in the receiving phase after 24 h.

^bPercent of total metal cations in the membrane phase after 24 h.

^cAll values are $\times 10^{-8}$.

^dThe hyphenated symbols mean that the values are about zero or they are with high uncertainties.

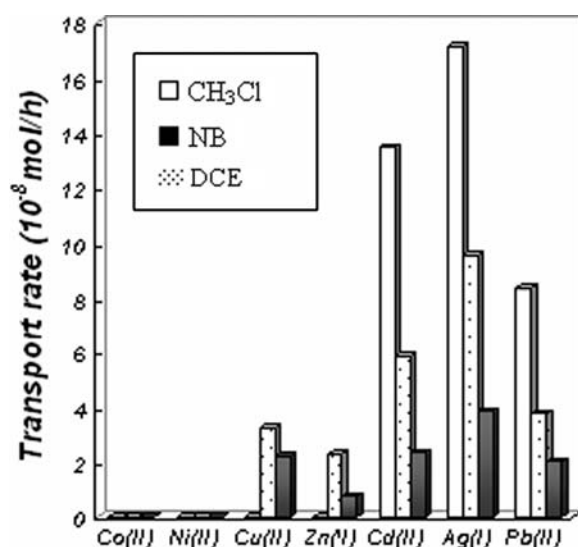


Figure 2. Comparison of the results of metal ion transport (water/organic solvent/water) studies for ligand II. Source phase: pH = 5.0 (2 M CH₃COOH/2 M CH₃COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains macrocycle II (0.001 M) (50 mL). Receiving phase: pH = 3.0 (1 M NaOH/1 M HCOOH), (30 mL) stirred for 24 h; enclosed in 25 °C water jacket.

than in 1,2-dichloroethane and nitrobenzene. According to the physicochemical properties of the solvents which are given in Table 4, this result may be attributed to the lower viscosity of chloroform than 1,2-dichloroethane and nitrobenzene which leads to increase the rate of ion transfer in this organic solvent [12].

The ligands I and III which contain only oxygen donor atoms, show the highest transport efficiency for Co²⁺ ion (Tables 1–3). Hard coordination site like oxygen atom of these crown compounds seems to generate great affinity towards some of the transition-metal cations such as Co²⁺ ion as hard acids. This result is in agreement with the stability of the complex formed between the Co²⁺ ion and ligand I in CHCl₃ [13], therefore, the substantial thermodynamic stability of cobalt

Table 4. Some physicochemical properties of organic solvents used as liquid membranes [17]

Solvent	DN ^a	AN ^b	μ^c (D)	η^d (cp)
Chloroform	0	23.1	1.354	0.58
1,2-dichloroethane	0	16.7	1.86	0.73
Nitrobenzene	4.4	14.8	4.00	1.62

^aDonor number; ^bAcceptor number; ^cDipole moment; ^dViscosity.

(II) complex of I strongly aids its transfer into the organic phase.

Comparison of the transport data which are listed in Tables 1–3, show that di-*tert*-butyl-dibenzo-18-crown-6 is a more efficient ionophore than dibenzo-18-crown-6 for transport of Co²⁺ ion which may be due to more lipophilicity of di-*tert*-butyl-DB18C6 due to the presence of *t*-butyl groups in this macrocyclic ligand [14].

The rate of transport of cobalt (II) ion by di-*tert*-butyl-dibenzo-18-crown-6 in membrane phase is varied in order: nitrobenzene > 1,2-dichloroethane > chloroform. The higher polarity of nitrobenzene compared to chloroform and 1,2-dichloroethane (Table 4), may result in higher solubility of the (di-*tert*-butyl-DB18C6 Co²⁺) complex in membrane phase and, therefore, the transport rate of cobalt (II) ion in this organic phase is bigger than the other two organic solvents [15].

Large anions, such as NO₃⁻ are highly polarizable and interact to a fair extent by dispersion forces (London forces) with the chloroform molecules, which are more polarizable than nitrobenzene molecules [16] (see Table 4). On the other hand, as is shown in the Table 4, since the acceptor number of nitrobenzene is lower than the other two organic solvents, it results in an increase in free energy of solvation of the co-anion (NO₃⁻) with the cationic species in this solvent which can relate the ion transport inversely to the negative free energy of solvation of the co-anion [17], therefore, it is expected that the

Table 5. The effect of stearic acid on seven-metal ions competitive transport across a bulk chloroform membrane with macrocycle ligands of I–III as ionophores at 25 °C

Ionophore	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
<i>I</i>							
%(Receiving) ^a	2.13	1.43	0.15	0.35	0.23	0.20	0.23
%(Membrane) ^b	- ^d	-	8.71	73.87	77.76	8.78	0.06
J(mol per 24 h) ^c	2.66	1.79	0.19	0.44	0.28	0.25	0.28
<i>II</i>							
%(Receiving) ^a	1.86	-	1.75	0.32	3.05	4.89	0.33
%(Membrane) ^b	1.34	17.10	24.13	-	9.32	19.58	34.36
J(mol per 24 h) ^c	2.33	-	2.18	0.41	3.81	6.12	0.50
<i>III</i>							
%(Receiving) ^a	-	0.08	-	0.15	0.04	-	-
%(Membrane) ^b	9.92	-	5.60	12.89	90.51	-	0.76
J(mol per 24 h) ^c	-	0.10	-	0.19	0.05	-	-

^aPercent of total metal cations in the receiving phase after 24 h.

^bPercent of total metal cations in the membrane phase after 24 h.

^cAll values are $\times 10^{-7}$.

^dThe hyphenated symbols mean that the values are about zero or they are with high uncertainties.

rate of transport of the cobalt (II) ion in nitrobenzene to be larger than in chloroform and 1,2-dichloroethane.

The influence of the stearic acid on the transport rates of the Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ and Pb^{2+} metal cations with ligands I, II and III in CHCl_3 as a membrane phase was investigated and the results are summarized in Table 5. The graphical results obtained for the studied metal ion transport across chloroform phase containing ligand I in the presence and absence of stearic acid are shown in Figures 3 and 4, respectively.

As expected, the efficiency of transport of most heavy metal cations increases in the presence of stearic acid. A major role of the stearic acid 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 for-

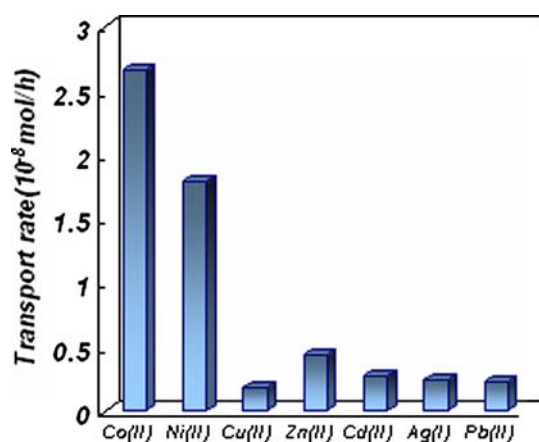


Figure 3. The results of metal ion transport (water/chloroform/water) studies for ligand I. Source phase: pH=5.0 (2 M CH_3COOH /2 M CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains macrocycle of I (0.001 M) (50 mL). Receiving phase: pH=3.0 (1 M NaOH /1 M HCOOH) (30 mL), stirred for 24 h; enclosed in 25 °C water jacket.

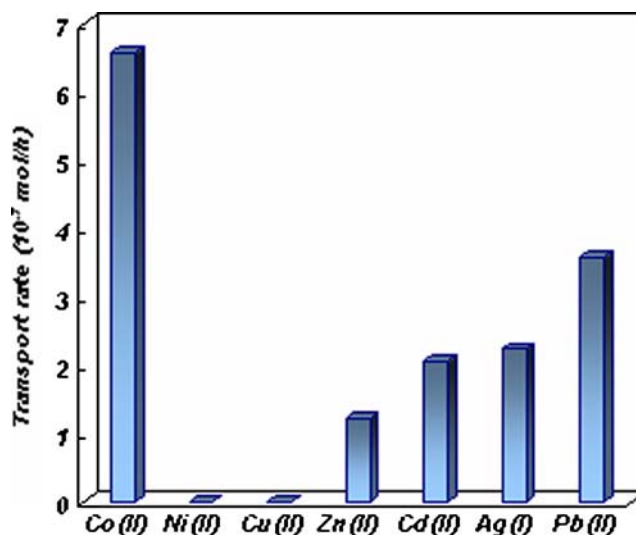


Figure 4. The results of metal ion transport (water/chloroform/water) studies for ligand I. Source phase: pH=5.0 (2 M CH_3COOH /2 M CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains macrocycle I (0.001 M) and stearic acid 0.004 M (50 mL). Receiving phase: pH=3.0 (1 M NaOH /1 M HCOOH) (30 mL), stirred for 24 h; enclosed in 25 °C water jacket.

mation [18]. Namely, ion pair/adduct formation serves to inhibit any bleeding of partially hydrophilic species (such as the protonated ionophore and/or its corresponding charged metal ion complex) from the organic membrane phase into either of the aqueous phases [19].

Conclusion

Competitive metal ion transport experiments provide a means for documenting selectivity in metal ion complex bonding. Competitive of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ and Pb^{2+} metal ions transport experiments across CHCl_3 , 1,2-DCE and NB bulk liquid membranes

have been performed using macrocyclic ligands **I–III** as ionophores. The results show that the selectivities and fluxes of the studied metal cations by macrocyclic ligands **I–III** are strongly influenced by variation of the organic solvent as membrane phase and the transport rates of most of the metal cations in chloroform phase are greater than that in 1,2-dichloroethane and nitrobenzene liquid membranes.

The heavy metal ion transport behaviour in this study also shows that the transport ability is influenced by the size-fit condition and the nature of the donor atoms present in the polyether rings, as well as the lipophilicity of the system. A good selectivity is achieved for Ag^+ ion by dibenzyl-diaza-18C6 in all cases, and highest transport efficiency was observed for Co^{2+} ion under the employed experimental conditions.

References

1. M.H. Mashahadzadeh, R. Mohyaddini, and M. Shamsipur: *Sep. Purif. Technol.* **39**, 161 (2004).
2. P.R. Danesi: *Sep. Sci. Technol.* **19**, 857 (1984).
3. L.L. Tavlarides, J.H. Bae, and C.K. Lee: *Sep. Sci. Technol.* **22**, 581 (1987).
4. A.J.B. Kemperman, D. Bargeman, Th. Van den Boomgaard, and H. Strathmann: *Sep. Sci. Technol.* **31**, 2733 (1996).
5. N.K. Djane, I.A. Bergdha, A. Schutz, G. Jöhanson, and L. Mathiasson: *Analyst* **122**, 1073 (1997).
6. M. Shamsipur, G. Azimi, and S.S. Madaeni: *J. Membr. Sci.* **165**, 217 (2000).
7. A. Jabbari, M.R. Mousavi, and M. Shamsipur: *Ind. J. Chem.* **38A**, 808 (1999).
8. A. Jabbari, H. Chaldavi, and M. Shamsipur: *Sep. Sci. Technol.* **34**, 2421 (1999).
9. P.S.K. Chia, L.F. Lindoy, G.W. Walker, and G.W. Everett: *Pure Appl. Chem.* **65**, 521 (1993).
10. M. Hiraoka: *Crown Compounds Their Characteristics and Applications*, Elsevier Scientific, Amsterdam (1982), pp. 74.
11. C. Kalidas, G. Heftor, and Y. Marcus: *Chem. Rev.* **100**, 828 (2000).
12. H.K. Alpogus, S. Memon, M. Erosoz, and M. Yilmaz: *New J. Chem.* **26**, 477 (2002).
13. J. Zhou and X. Wu: *He Huaxue Yu Fanshe Huaxue* **6**, 78 (1984).
14. S.S. Lee, I. Yoon, K. Park, J.H. Jung, L.F. Lindoy, A. Nezhadali, and G.H. Rounaghi: *J. Chem. Soc. Dalton Trans.* 2180 (2002).
15. W. YuHwang and J. ShongShin: *J. Chinese Chem. Soc.* **47**, 1215 (2000).
16. K. Izutzu: *Electrochemistry in Non-aqueous Solutions*, Wiley-VCH, (2002), pp. 85.
17. R.L. Bruening, G.A. Clark, and J.D. Lamb: *J. Membrane Sci.* **77** (1986).
18. J. Kim, A.J. Leong, L.F. Lindoy, J. Kim, J. Nachbaur, A. Nezhadalis, G.H. Rounaghi, and G. Wei: *J. Chem. Soc. Dalton Trans.* 3453 (2000).
19. L.F. Lindoy and D.S. Baldwin: *Pure Appl. Chem.* **61**, 904 (1989).