This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Selective and Efficient Liquid Membrane Transport of Thallium (III) Ion by Potassium-dicyclohexyl-18-crown-6 as Specific Carrier

Javad Zolgharnein[a]; Hassan Shams[a]; Gholamhassan Azimi[a]
[a] Department of Chemistry, Faculty of Science, Arak University, Arak, Iran

To cite this Article Zolgharnein, Javad , Shams, Hassan and Azimi, Gholamhassan(2007) 'Selective and Efficient Liquid Membrane Transport of Thallium (III) Ion by Potassium-dicyclohexyl-18-crown-6 as Specific Carrier', Separation Science and Technology, 42: 10, 2303 — 2314

To link to this Article: DOI: 10.1080/01496390701446563

URL: http://dx.doi.org/10.1080/01496390701446563

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Separation Science and Technology, 42: 2303–2314, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701446563

Selective and Efficient Liquid Membrane Transport of Thallium (III) Ion by Potassium-dicyclohexyl-18-crown-6 as Specific Carrier

Javad Zolgharnein, Hassan Shams, and Gholamhassan Azimi
Department of Chemistry, Faculty of Science, Arak University,
Arak, Iran

Abstract: Potassium-dicyclohexyl-18-crown-6 was used as a selective and efficient carrier for the uphill transport of thallium (III) ion as $[TlCl_4]^-$ complex ion through a chloroform bulk liquid membrane. By using oxalate anion as a metal ion acceptor in the receiving phase, the amount of thallium (III) transported across the liquid membrane after 120 min was 96 ± 2%. The selectivity and efficiencies of thallium transport from aqueous solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Co^{3+}, Mn,$^{2+}$ Cr^{3+}, Mg^{2+}, Ca^{2+}, K^+, Na^+, and Fe^{3+} ions were investigated. In the presence of Na_3PO_4 (0.01 M) at $pH = 3$ as a suitable precipitation agent in the source phase, the interfering effect of Pb^{2+} ion were diminished drastically.

Keywords: Potassium-dicyclohexyl-18-crown-6, bulk liquid membrane, thallium (III) ion, oxalate

INTRODUCTION

The highly toxic behavior of thallium compounds in contact with human, environmental, and biological systems, causes so much effort to prevent its pollution effects (1). Thallium is introduced into the environment mainly as a waste from the production of zinc, cadmium, and lead by the combustion of coal (2). Thallium(III) is usually present in lead(II), cadmium(II), indium

Received 13 November 2006, Accepted 26 February 2007
Address correspondence to Javad Zolgharnein, Department of Chemistry, Faculty of Science, Arak University, Arak, Iran. Fax: (+98) 861 4173406; E-mail: j-zolgharnein@araku.ac.ir

(III), or zinc (II) compounds as a trace constituent (3, 4). Thallium (III) forms very stable complex species and has the highest coordination number CN = 8 in its chelates with polyaminopolycarboxilic acids (5). Also thallium (III) forms alloys with a number of metals such as silver, lead, and antimony. Therefore, because of its importance from the environmental pollution view, the separation of thallium (III) from the other metal ions has been a subject of great analytical interest (3). Unfortunately, there are few papers on the separation of thallium (III) (1–4). Among the separation methods ion-transport is a highly selective, efficient, simple, and inherently a reaction-based method with facile controllable carrier reaction conditions (6–8). It has also the major advantage of the extraction since stripping and regeneration operations are combined in one single step (9). To the best of our knowledge, there is no report about thallium (III) ion–transport through bulk liquid membrane. So, we have been interested in designing a system for the transport of thallium (III) ion through bulk liquid membrane using macroclic polyethers as selective carriers (6–9).

In this study, we describe a new selective and efficient liquid membrane system containing potassium-dicyclohexyl-18-crown-6 for the selective transport of thallium (III) ion as $[TlCl_4]^-$ counter ion. The receiving phase contains the oxalate anion which was found to play an important role in the ion- transport process (7–11).

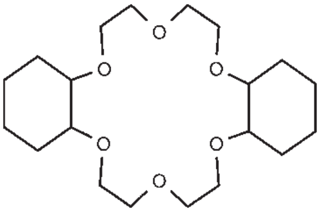
EXPERIMENTAL

Reagents and Chemicals

Reagent grade benzo-15-crown-5 (B15C5), 4-nitrobenzo-15-crown-5 (NB15C5), phenylaza-15-crown-5 (PhA15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dibenzopyridino-18-crown-6 (DBPY18C6), dicyclohexyl-18-crown-6 (DC18C6, Scheme 1),decyl-18-crown-6 (decyl-18C6), and were all purchased from Merck and were used as received. Analytical grade potassium chloride, oxalic acid, thallium (III) nitrate, and the nitrate salts of other cations (all from Merck) were of the highest purity available and used without any further purification, except for vacuum drying over P_2O_5. Extra pure chloroform (Merck) was used for the organic phase. Doubly distilled deionized water was used throughout.

Apparatus

A bulk liquid membrane cell was used in this study (12). A Perkins Elmer 3800 atomic absorption spectrophotometer was used for all the measurements of the metal concentrations in the aqueous phases. The atomic absorption measurements were made under recommended conditions for each metal



Scheme 1. Structure of ion-carrier DC18C6 (**I**).

ion. A digital pH meter, Metrohm model 722, equipped with a combined glass-calomel electrode was used for the pH adjustments.

Procedure

A cylinder glass cell (inside diameter 4.0 cm) holding a glass tube (inside diameter 2.0 cm), thus separating the two aqueous phases, was used. The inner aqueous phase (source phase, SP, 5 ml) contained thallium (III) nitrate (2.0×10^{-4} M) potassium chloride (1.0×10^{-1} M). The outer aqueous phase (receiving phase, RP, 10 ml) contained oxalic acid (1.0×10^{-2} M). The membranes phase (MP) containing 20 ml of 1.0×10^{-3} M DC18C6 in chloroform layer below these aqueous phases, and bridged the two aqueous phases. The organic layer was magnetically stirred by a Teflon-coated magnetic bar (2.0 cm × 5 mm) at 120 rpm. The experimental set-up is shown in Fig. 1. Under these conditions, not only the mixing process is uniform but also the interfaces between the organic membrane and the two aqueous phases remained flat and well-defined. Determination of the metal ion concentration in both aqueous phases was carried out by AAS. Reproducibility was confirmed as 2% or better. A similar transport experiment was carried out in the absence of the carrier for reference. No transport of any metal ions occurred in the absence of the ion carrier DC18C6. All experiments were carried out at 25°C.

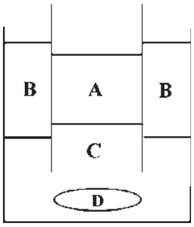


Figure 1. Representation of the bulk type liquid membrane cell used: (A) source phase, (B) receiving phase, (C) membrane phase, (D) magnetic stirrer.

RESULTS AND DISCUSSION

The complexing ability of ordinary crown ethers towards charged heavy metal ions such as Tl (III) is quite low (13, 14). So that designing the liquid membrane transport of the thallium (III) ion by using such crown ethers is impossible. But thallium (III) strongly binds to unidentate ligands such as Cl^- and I^- to form charged ionic species $[TlCl_4]^-$ or $[TlI_4]^-$ (15). Therefore the $[TlCl_4]^-$ can be readily introduced to the organic phase. Previously 18-crown-6 has been used as a carrier for both cationic and anionic forms of metal ions, but low lipophilicity of it caused substantial bleeding from the membrane phase into the aqueous phase and the efficiency of membrane gradually decreased (16, 17). To overcome this, and enhance the efficiency of the carrier, we chose dicyclohexyl-18-crown-6 as a carrier in the form of K^+−dicyclohexyl-18-crown-6 for the liquid membrane transport of the thallium (III) ion. The potassium ion was used as the co-transported cation of the thallium (III) ion because of its good fitness into the 18-crown-6 ring (13). Consequently, the amount of complex cation available to form an ion-pair with $[TlCl_4]^-$ will be greatest in the case of K^+ resulting in the largest extent of partitioning into the organic layer (18). However, in the presence of excess chloride ion, Tl (III) ion will form a relatively stable and bulky anion $[TlCl_4]^-$ with $\log \beta_4 = 16.3$ and low hydration energy (19), which can easily accompany K^+-18-crown-6 cations into the membrane phase.

The influence of the concentration of KCl in the source phase on thallium (III) ion transport was investigated and the results are shown in Fig. 2. It is evident that the percentage of transported thallium (III) ion increases with increasing the concentration of KCl. Maximum transport

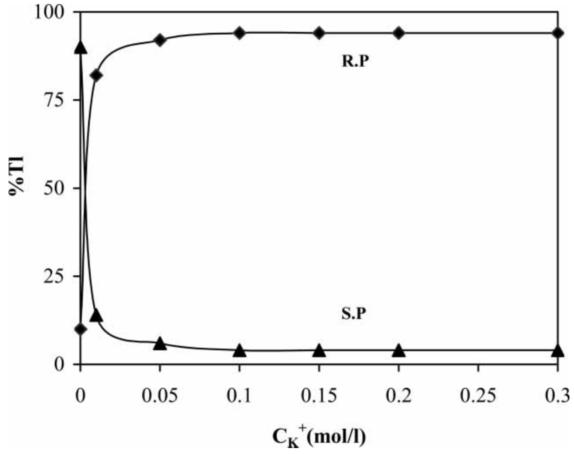


Figure 2. Effect of potassium chloride concentration in the source phase on thallium (III) ion transport. The experiment conditions as in Table 1 except for oxalic acid.

occurs when the concentration of the salt is equal 0.1 M. A further increase in the concentration of potassium chloride has no considerable effect on the transport efficiency. It is interesting to note that, in the absence of KCl, the transport of thallium (III) ions via [Tl(III)-DC18C6]$(NO_3)_3$ ion pairs into the membrane are negligible.

The percentages of thallium (III) ion transported in the presence of different stripping agents obtained under similar experimental conditions are listed in Table 1. The use of $C_2O_4^{2-}$ ion as stripping ligand in the receiving phase caused a large enhancement in the efficiency of Tl(III) ion transport when compared with the case of other receiving agents such as citrate, tartarate, EDTA, NaBr, and NaI.

The effect of oxalic acid concentration in the receiving phase on thallium (III) ion transport was investigated and the results are shown in Fig. 3. Noteworthy, the absence of a metal ion acceptor in the receiving phase resulted in negligible thallium (III) transport. As expected, it was found that the nature and composition of the ligand used as a scavenger for the transported metal ion in the receiving phase could have a significant effect on the efficiency and selectivity of transport (16, 20–23).

In this study we also verified the best pH region of the source and receiving phase for the quantitative transport of Tl(III) ion was studied. The pH values were adjusted by addition of 0.1 M HNO_3 and sodium hydroxide. As shown in Table 2, it was found that at pH = 3 of the source phase, the transport of thallium (III) ions into receiving phase is maximum and for the receiving phase in a wide pH range (1–6), the transport of thallium (III) into the receiving phase is quantitative and variation of pH caused negligible change in the transport efficiency. The pH = 3 the for source phase is due to very low solubility product of $Tl(OH)_3$.

Table 1. Effect of the receiving agent on thallium (III) transport

Stripping agent	Percentage transported in to receiving phase	Percentage remaining in the source phace
EDTA	90	4
Tratraic acid	93	4
NaI	2	28
Oxalic acid	95	4
NaBr	8	7
Citric acid	33	5

Conditions: Source phase: 5 ml of 2.0×10^{-4} M Tl(III), 0.1 M KCl, Membrane phase: 20 ml of 1.0×10^{-3} M DC18C6 in chloroform, Receiving phase: 10 ml of 1.0×10^{-2} M stripping agent, Time of transport: 120 min.

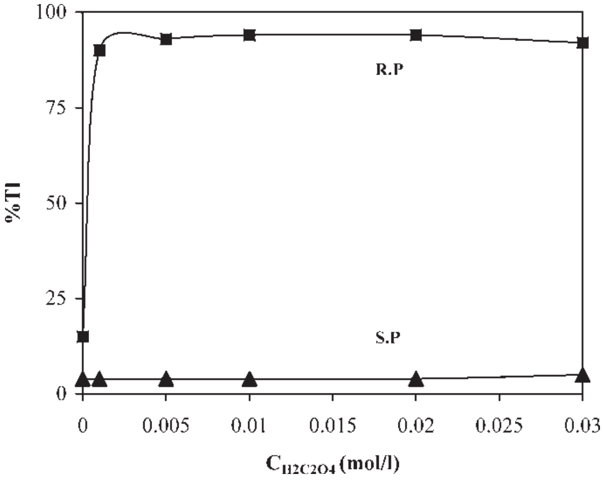


Figure 3. Effect of oxalic acid concentration in the receiving phase on thallium (III) ion transport from chloroform membrane. The experiment conditions as in Table 1, except for oxalic acid.

As we anticipated, the nature of the macrocyclic crown ether used as carrier in the organic membrane phase was found to have a pronounced effect on the permeability of the membrane system designed for thallium (III) ion transport. Under the same experimental condition, we also verified some other crown ethers as carriers for the transport of $[TlCl_4]^-$ anions in the presence of K^+ ions. The results are shown in Table 3. As can be seen decyl-18C6, 18C6, and DC18C6 are the most suitable carriers for the anionic transport of thallium (III), mainly due to their proper cavity size for

Table 2. Effect of pH of receiving phase on thallium (III) ion transport

pH of receiving phase	percentage transported into receiving phase	Percentage remaining in the source phase
1	94	5
2	95	4
3	**96**	**3**
4	95	4
5	94	5
6	90	4
7	72	5
8	46	4

Experimental conditions as in Table 1.

Table 3. Effect of the carrier structure on the thallium (III) ion transport

[a]Carrier	Percentage transported into receiving phase	Percentage remaining in the source phase
B15C5	40	55
NB15C5	3	97
PhA15C5	43	55
18C6	92	6
DB18C6	12	88
DBPY18C6	42	53
DC18C6	95	4
decyl-18C6	88	9

Experimental conditions as in Table 1.

[a] Membrane phase: 20 ml of 1.0×10^{-3} M of each carrier in chloroform.

K^+ ion (13). Consequently, they show the highest stability of the complexes in the series. Some increased transport efficiency of DC18C6 over those of others as mentioned before is related to the lower solubility of the former crown ether in the aqueous phases. It is worth mentioning that, in the case of DB18C6 and DBPY18C, despite their proper cavity size for K^+ ions' showed much lower transport efficiency in comparison with the three other 18-crowns used. This is due to the diminished stability of their K^+ complexes because of the substitution of benzo and benzo pyridyl groups, respectively (24). However, in the case of the macrocycle of smaller ring sizes such as B15C5, PhA15C5, and NB15C5 the improper cavity size for K^+ decreases the stability of the complex, and the transport of the thallium (III) ion through the liquid membrane diminishes drastically.

The effect of concentration of DC18C6 in the membrane phase on the transport of thallium (III) ion was studied and the results are shown in Fig 4. It is obvious that the percentage transport of thallium (III) ion increases with increasing concentration of macrocycle in chloroform. Maximum transport occurs at a concentration $\approx 1.0 \times 10^{-3}$ M. A further excess of carrier does not have any considerable effect on the thallium (III) ion transport.

The time dependence of thallium (III) ion transport through the liquid membrane proposed under the optimal experimental conditions was investigated and the results are shown in Fig 5. It can be seen that the extraction of thallium (III) ion from the source phase into the organic membrane occurs with a higher rate than releasing it into the receiving phase. It is found that under the optimum conditions, the transport of thallium (III) ion from the source phase into the receiving phase after 120 minutes equals 96%. The reproducibility of thallium (III) ion transport was investigated

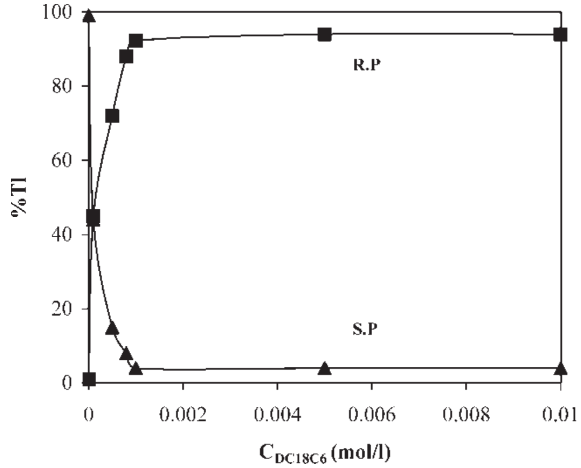


Figure 4. Effect of DC18C6 concentration in the membrane phase on thallium (III) ion transport from chloroform membrane. The experiment conditions as in Table 1.

and the percent of metal ions transported after 120 min obtained from six replicate measurements was found to be (96 ± 2)%.

In order to further study the selectivity of the membrane system for the thallium (III) ion, the percentage transport of thallium (III) ion and M^{n+} cations, which were present with thallium (III) ion in equimolar concentration, into receiving phase were determined and the results are summarized in

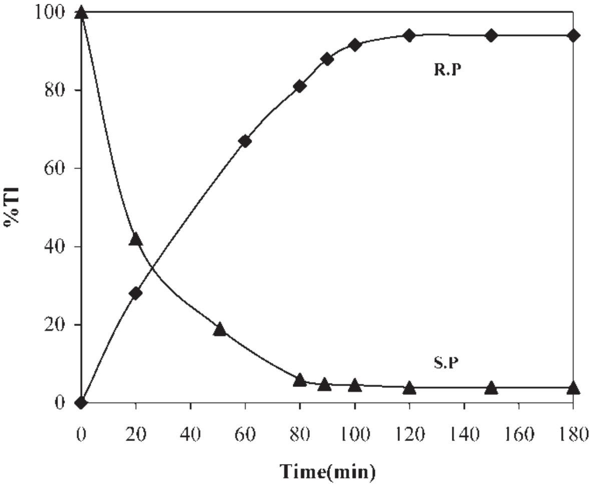


Figure 5. Time dependence of thallium(III) ion transport from chloroform membrane. The same conditions as mentioned in Table 1. Liquid membrane system for transport of Tl(III) ions.

Table 4. Amounts of cations transported from various cation mixtures through the liquid membrane

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1		
Tl(III)	94	4
Co^{2+}	0	100
Ni^{2+}	0	100
Cd^{2+}	0	100
Mixture 2		
Tl(III)	91	5
Mn^{2+}	0	99
Zn^{2+}	1	98
Mixture 3		
Tl(III)	92	4
Fe(III)	1	99
Cr^{3+}	0	100
Mixture 4		
Tl(III)	92	4
Mg^{2+}	1	99
Ca^{2+}	0	100
Mixture 5		
Tl(III)	92	4
Na^{+}	4	96
K^{+}	2	98
Mixture 6		
Tl(III)	95	4
Al^{3+}	0	100
Mixture 7		
Tl(III)	94	4
Pb^{2+}	83	5
Cu^{2+}	0	100
[a]Mixture 8		
Tl(III)	95	4
Pb^{2+}	8	12
Cu^{2+}	0	100

Experimental conditions as in Table 1.

[a] After addition of 1.0×10^{-2} M Na_3PO_4 at pH = 3 to the source phase.

Table 4. As shown among a variety of cations studied, only Pb^{2+} ions show some potential interfering effect. This is expected because of stronger complex formation between Pb^{2+} with DC18C6 than others (13, 25). As can be seen from Table, 4 (mixtures 7 and 8) the interference effects of

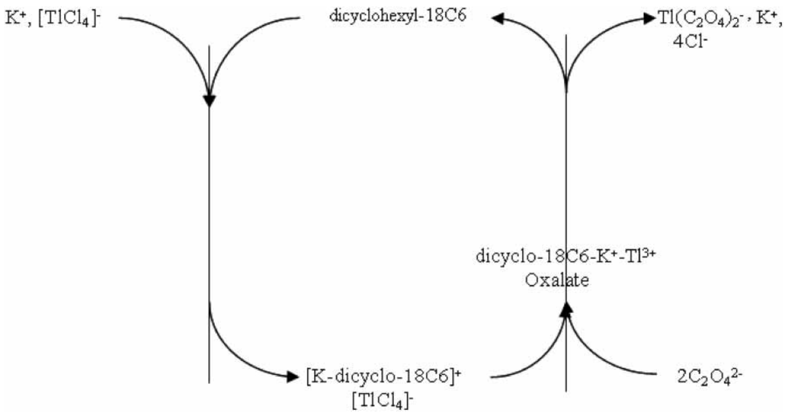


Figure 6. Liquid membrane system for transport of Tl(III) ions.

Pb^{2+} can be eliminated in the addition of Na_3PO_4 (0.01M) at $pH = 3$ as a proper masking agent to the source phase. The high selectivity of thallium (III) ion transport over the other cations used can be primarily related to the higher stability of the chloride complex of Tl(III) ion compared to those of the other metal ions used (15). On the other hand, the high affinity of oxalate for thallium (III) ions over most of the other cations tested is another important factor in determining the selectivity of Tl(III) ion transport. It is interesting to note that, under optimal experimental conditions, most of the other M^{n+} cations used revealed no measurable interfering effect even when the excess amount of $M^{n+}/$ Tl (III) ≥ 200 was employed.

A proposed mechanism of thallium (III) ion transport across the liquid membrane is presented in Fig. 6. The transport process follows this sequence of steps (17) at the source phase–membrane interface, the K^+-DC18C6 complex is formed. Since the $[TlCl_4]^-$ complex anion is less hydrated than other anions present in the source phase, it will form an ion pair with the potassium-crown complex cation. Partitioning of (K^+-DC18C6) ($TlCl_4^-$) complex into the organic membrane. Diffusion of the [K^+-DC18C6] $[TlCl_4]^-$ across the membrane. The release of Tl(III) and Cl^- into a receiving phase containing the oxalate anion with high affinity for complexes with thallium (III) ion. Diffusion of DC18C6 back across the membrane to the source phase-membrane interface where the cycle is repeated.

CONCLUSION

The results obtained in this study showed that we could selectively transport the thallium (III) ion through a liquid membrane. The proposed system is a selective transport of thallium (III) ion as $[TlCl_4]^-$ using of K^+-DC18C6 as carrier. The interfering effect of Pb^{2+} ion can be diminished by adding Na_3PO_4 (0.01 M) into the source phase and adjusting pH to 3. At optimum conditions (96 ± 2)% thallium (III) ion is transported into the receiving phase after 120 minutes.

REFERENCES

1. Chung, N.H., Nishimoto, J., Kato, O., and Tabata, M. (2003) Selective extraction of thallium (III) in the presence of gallidium (III), indium (III), bismuth (III) and antimony (III) by salting out of an aqueous mixture of 2-propranol. *J. Anal. Chim. Acta.*, 477: 243–249.
2. Hassanien, M.M., Abou-El-Sherbini, Kh. S., and Mostafa, G.A.E. (2003) A novel tetrachlorothallate (III)-PVC membrane sensor for the potentiometric of thallium (III). *Talanta*, 59: 383–392.
3. Kalyanaraman, S. and Khopkar, S.M. (1978) Solvent extraction separation of thallium (III) with mesityl oxide. *J. Anal. Chim. Acta*, 97: 181–184.
4. Sienko, M.J. and Plane, R.A. (1974) *Chemical Principles*; McGraw-Hill: London.
5. Chen, B., Lubal, P., Musso, S., and Andregg, G. (2000) Equilibria with the thallium (III) triethylenetetaminexhexaacetate anion $[Tl(ttha)]^{3-}$ in aqueous solution. *J. Anal. Chim. Acta.*, 406: 317–323.
6. Zoltov, Y.A. (1997) *Macrocyclic Compounds in Analytical Chemistry*; Jon Wiley & Sons Inc.: New York.
7. Zolgharnein, J., Hosseini, Sh., Azimi, G., and Sangi, M.R. (2003) Highly selective and efficient membrane transport of silver as $AgBr_2^-$ ion using K^+-decyl-18-crown-6 as carrier. *J. Analytical Sciences* (JPN), 19: 871–875.
8. Visser, H.C., Reinhoudt, D.N., and Jong, F.de. (1994) Carrier-mediated transport through liquid membrane. *Chem. Soc. Rev.*, 75–81.
9. Lamb, J.D., Christensen, J.J., Izatt, S.R., Bedke, K., Astin, M.S., and Izatt, R.M. (1980) Effects of salts concentration and anion on the rate of carrier—faciltated transport of metal cation through bulk liquid membranes containing crown ethers. *J. Am. Chem. Soc.*, 102: 3399–3403.
10. Mashahadizadeh, M.H., Mohyaddini, R., and Shamsipur, M. (2004) Selective and efficient liquid membrane transport of Au(III) by tetrathia-12-crown-4 as specific carrier. *J. Sep. Purif. Technol.*, 39: 161–166.
11. Jabari, A., Esmaeili, M., and Shamsipur, M. (2001) Selective transport of mercury as $Hg\ Cl_4^{2-}$ through a bulk liquid membrane using K^+-dicyclohexyl-18-crown-6 as carrier. *J. Sep. Purif. Technol.*, 24: 139–145.
12. Lamb, J.D., Christensen, J.J., Oscarson, J.L., Nielsen, B.L., Asay, B.W., and Izatt, R.M. (1980) The relationship between complex stability constants and rate of cation transport through liquid membrane by macrocyclic carriers. *J. Am. Chem. Soc.*, 102: 6820–6824.
13. Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., and Christensen, J.J. (1985) Therodynamic and kinetic data for cation-macrocycle Interaction. *J. Chem. Rev.*, 85: 271–339.
14. Izatt, R.M., Pawlak, K., Bradshaw, J.S., and Bruening, R.L. (1991) Therodynamic and kinetic data for macrocycle Interaction with cations and anions. *J. Chem. Rev.*, 911: 721–2085.
15. Martell, A.E. and Smith, R.M. (1976) *Critical Stability Constants*; Plenum Press: New York; Vol. 4.

16. Shamsipur, M. and Mashahdizadeh, M.H. (2000) Highly efficient and selective membrane transport of silver (I) using hexathia-18-crown-6 as a specific ion carrier. *J. Sep. Purif. Technol.*, 20: 147–153.
17. Izatt, R.M., Clark, G.A., and Christensen, J.J. (1985) Transport of $AgBr_2^-$ in an emulsion liquid membrane using M^{n+}-DC18C6 carriers $M^{n+} = Li^+$, Na^+, K^+, or Mg^{2+}. *J. Membr. Sci.*, 24: 1–5.
18. Izatt, R.M., McBride, D.W., Christensen, J.J., Bradshaw, J.S., and Clark, G.A. (1985) Cation transport at 25°C from binary $Tl^+–M^{n+}$ and $K^+–M^{n+}$ nitrate in a $H_2O–CHCl_3–H_2O$ liquid membrane system containing a series of macrocyclic polyether carriers. *J. Membr. Sci.*, 22: 31–46.
19. Laurie (1987) *Handbook of Analytical Chemistry*; Mir: Moscow.
20. Sirlin, C., Burgard, M., Leroy, M.J.F., and Prevost, M. (1990) Silver nitrate refining using supported liquid membranes. *J. Membr. Sci.*, 54: 299–305.
21. Kinnear, K.I., Lockhart, J.C., and Rushton, D.J. (1990) Selectivity in transport. *J. Chem. Soc. Dalton. Trans.*, 4: 1365–1373.
22. Lachowiez, E. (1992) Study of the transport of silver across a supported liquid membrane containing sulphide podand. *J. Talanta*, 39: 1031–1037.
23. Izatt, R.M., Lamb, J.D., Bruning, R.L., Wang, C., Edge, N., and Bradshaw, J.S. (1993) *J. Sep. Sci. Technol.*, 28: 383–395.
24. Zolgharnein, J., Tahmasebi, H., Habibi, M., and Amani, S. (2004) Competitive potentiometric study of a series of 18-crown-6 with some alkali and alkaline earth metal ions in methanol using Ag^+/Ag electrode. *J. Incl. Phenom.*, 49: 231–234.
25. Zolgharnein, J., Azimi, G., and Habibi, M. (2004) Competitive potentiometric study of a series of 18-crown-6 with Pb^{2+}, Ag^+, and Tl^+ ions in methanol using Ag^+/Ag electrode. *J. Polish. Chem.*, 78: 795–802.