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

Transport of metals through a liquid membrane containing calix[4]arene derivatives as carrier

H. Korkmaz Alpoguz[a]; Shahabuddin Memon[a]; Mustafa Ersoz[a]; Mustafa Yilmaz[a]
[a] Department of Chemistry, Selcuk University, Konya, Turkey

To cite this Article Alpoguz, H. Korkmaz , Memon, Shahabuddin , Ersoz, Mustafa and Yilmaz, Mustafa(2002) 'Transport of metals through a liquid membrane containing calix[4]arene derivatives as carrier', Separation Science and Technology, 37: 9, 2201 — 2215

To link to this Article: DOI: 10.1081/SS-120003509

URL: http://dx.doi.org/10.1081/SS-120003509

SEPARATION SCIENCE AND TECHNOLOGY, 37(9), 2201–2213 (2002)

TRANSPORT OF METALS THROUGH A LIQUID MEMBRANE CONTAINING CALIX[4]ARENE DERIVATIVES AS CARRIER

H. Korkmaz Alpoguz,
Shahabuddin Memon, Mustafa Ersoz,* and
Mustafa Yilmaz

Department of Chemistry, Selcuk University, Kampus,
Konya 42031, Turkey

ABSTRACT

Co-transport of metals (Hg^{2+}, Pb^{2+}, Na^{+}) from an aqueous solution into an aqueous-receiving solution through a bulk liquid membrane containing calix[4]arene nitrile derivatives as carriers was investigated. Kinetic parameters were analyzed with consecutive irreversible first-order reactions and the effect of solvents such as CH_2Cl_2, $CHCl_3$, and CCl_4 was also examined. The transport rates show that both nitrile derivatives are efficient and selective for Hg(II) ions with respect to Na^{+} and Pb^{2+} ions and the dinitrile derivative is found to be a better carrier than the tetranitrile one. The membrane entrance- and exit rate-constants depend on the solvent type and are found to be in the order $CH_2Cl_2 > CHCl_3 > CCl_4$. A remarkable difference was also observed of the same order for fluxes.

---

*Corresponding author. E-mail: mersuz@selcuk.edu.tr

INTRODUCTION

Recently, many attempts for metal separation and recovery by liquid membranes have been afforded (1,2). It has been demonstrated that the transport mediated by mobile carriers is one of the simplest method for selective removal of an ion from aqueous solution of ionic species (3). Liquid membranes play an important role in the separation processes (4). Their efficiency and economic advantages designate them to be the optimal solution of some important problems in science and technology, such as precious metal recovery (5), toxic product (6–8) (metals, organic molecules) elimination from wastewaters, etc. Therefore, scientific research in this field continues to be very active, despite some important solution-awaiting technological problems, which at present prevent large-scale applications of liquid membranes in the chemical industry.

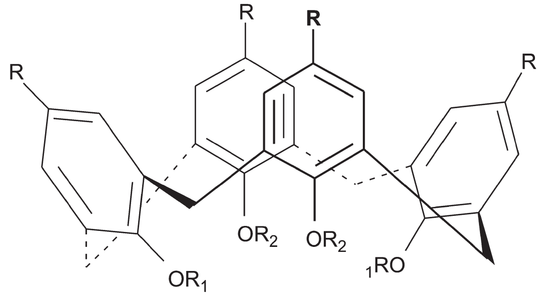
The design and synthesis of calixarenes, an important class of macrocyclic ion receptors, is very well documented in supramolecular chemistry (9–11). The highly ordered structure of calixarenes offers not only boundless possibilities for chemical modifications, but also makes them extremely useful in the study of molecular recognition in supramolecular processes. Therefore, we have chosen the calix[4]arene skeleton as a vehicle for modeling such phenomena in liquid membrane technique. In the transport system, on one hand, carrier molecules dissolved in liquid membranes have very specific and selective interacting power, on the other, the nature of solvent molecules decisively influences the metal-ion transport phenomena (3). It was reported that some solvent increases the transport efficiency, but some others decrease or may even stop completely transport flux (12). The membrane composition on the metal-ion transport efficiency was also important (13–15).

The aim of this work was to investigate the kinetic analysis and the effectiveness of two nitrile derivatives of calix[4]arene (1 and 2 shown in Fig. 1) as carriers for Hg^{2+}, Pb^{2+}, and Na^{+} ions and also to examine the solvent efficiency on the process for ion transport through bulk liquid membrane.

EXPERIMENTAL

Materials

The chemical reagents used in these experiments were mercury (II) nitrate, dichloromethane, chloroform, CCl_4, (Merck, Co., Darmstadt, Germany, 99.8%), sodium hydroxide, and picric acid, (Merck). The alkali picrates were prepared as described elsewhere (16) by stepwise addition of a $2.0 \times 10^{-2}\,M$ aqueous picric acid solution to a $0.14\,M$ aqueous solution of metal hydroxide until neutralization, which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried in vacuo for



1 R = tert-butyl; R_1= CH_2CN, R_2= H

2 R = tert-butyl; R_1, R_2= CH_2CN

Figure 1. Structure of ligands used as carrier.

24 hr. Transition metal picrates were prepared by the addition of a $1 \times 10^{-2} M$ mercury (II) nitrate to a $2.5 \times 10^{-5} M$ aqueous picric acid solution and shaken at 25°C for 1 hr. The aqueous solutions were prepared using deionized water.

Synthesis of Carriers

The carriers 5,11,17,23-tetra-*tert*-butyl-25,27-dicyanomethoxy-26,28-dihydroxy calix[4]arene **1**, and 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanomethoxy calix[4]arene **2** used in the study were synthesized according to literature methods (17).

Kinetic Procedure

Co-transport experiments were conducted using a thermostated (Grants Instruments, model W14, Cambridge, England) apparatus at 25°C. Transport experiments were carried out in a U-type cell. An organic solution (20 mL) containing the carrier was placed at the bottom of the cell and two portions of aqueous solutions (10 mL) were carefully added on top of them. Both surface areas were $2.5\,cm^2$. The organic phase was stirred at 500 rpm magnetically. (Chiltern Scientific Inst. Ltd., model HS 31, U.K.).

The initial compositions of the phases consisted of the donor phase, which was an aqueous metal picrate ($2.5 \times 10^{-5} M$) and membrane phase was made up by dissolving carrier (calix[4]arene derivatives, $C_{\text{carrier}} = 10^{-3} M$) in the organic solvent. Acceptor phase consisted of double distilled water. Samples were taken from both water phases (acceptor and donor phases) at regular time intervals and the metal picrate concentration was analyzed by a spectrophotometric method (18). Each experimental result reported is the arithmetic mean for two independent samples and volume change by spectrophotometric method (error $< 1\%$).

RESULTS AND DISCUSSION

All kinetic measurements were performed under exactly the same experimental conditions. Two different membrane systems (dinitrile calixarene and tetranitrile calixarene) involving three different solvents were investigated.

In the experiments, the variation of metal concentration with time was directly measured in both donor (C_d) and acceptor phases (C_a). The corresponding change of metal in the membrane phase was established from the material balance. In general, the reduced concentrations are used for practical reasons as follows:

$$R_d = \frac{C_d}{C_{d0}} \quad R_m = \frac{C_m}{C_{d0}} \quad R_a = \frac{C_a}{C_{d0}} \tag{1}$$

where C_{d0} is the initial metal concentration in the donor phase C_d, C_m, and C_a represents the metal concentration in donor, membrane, and acceptor phases, respectively. From this expression, the material balance can be established as $R_d + R_m + R_a = 1$. The variation of reduced concentration of Hg^{2+} ion with time through liquid membrane in CH_2Cl_2 containing dinitrile derivative is shown in Fig. 2. The obtained experimental results show that R_d decreases exponentially with time accompanied by a simultaneous increase of R_a, whereas R_m presents at maximum. From these results, the kinetic behavior for bulk liquid membrane transport process can be described by consecutive irreversible first-order reactions (12–15).

$$C_d \xrightarrow{k_1} C_m \xrightarrow{k_2} C_a$$

where C_d, C_m, and C_a represents the metal concentration in donor, membrane, and acceptor phases, respectively, k_1 and k_2 are the apparent membrane entrance and exit rate-constants, respectively. The kinetic scheme for consecutive irreversible reactions may be described by the following rate equations:

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \tag{2}$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \tag{3}$$

$$\frac{dR_a}{dt} = k_2 R_m = J_a \tag{4}$$

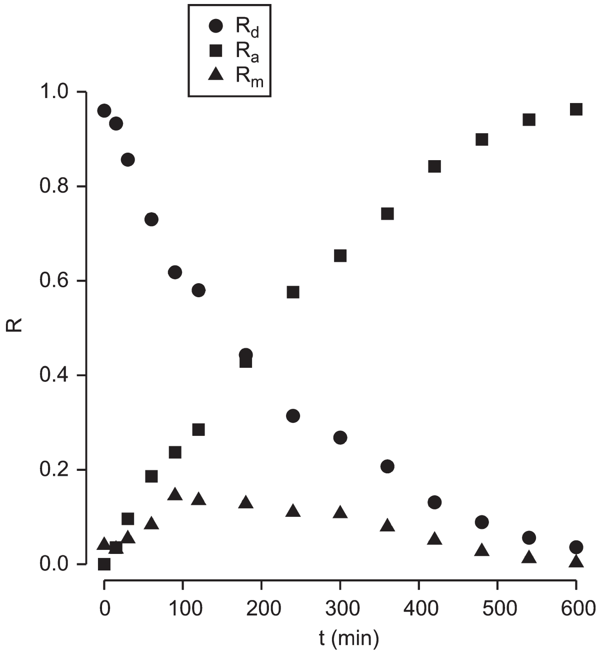


Figure 2. Variation of reduced concentrations of Hg^{2+} ion in co-transport through liquid membrane ($T = 298 \pm 0.1K$, solvent is CH_2Cl_2).

where J is the flux, when $k_1 \neq k_2$, and integrating the above differential equations gives

$$R_{\mathrm{d}} = \exp(-k_1 t) \tag{5}$$

$$R_{\mathrm{m}} = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{6}$$

$$R_{\mathrm{a}} = 1 - \frac{k_1}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \tag{7}$$

The maximum values of R_{m} and $t_{\max}$ (when $\mathrm{d}R_{\mathrm{m}}/\mathrm{d}t = 0$) can be written as

$$R_{\mathrm{m}}^{\max} = \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \tag{8}$$

$$t_{\max} = \left(\frac{1}{k_1 - k_2}\right)\ln\frac{k_1}{k_2} \tag{9}$$

By considering the first-order time differentiation (5–9) at $t_{\max}$, one obtains the following equations

$$\left.\frac{\mathrm{d}R_\mathrm{d}}{\mathrm{d}t}\right|_{\max} = -k_1\left(\frac{k_1}{k_2}\right)^{-k_1/(k_1-k_2)} \equiv J_\mathrm{d}^{\max} \tag{10}$$

$$\left.\frac{\mathrm{d}R_\mathrm{m}}{\mathrm{d}t}\right|_{\max} = 0$$

$$\left.\frac{\mathrm{d}R_\mathrm{a}}{\mathrm{d}t}\right|_{\max} = k_2\left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_\mathrm{a}^{\max} \tag{11}$$

$$-\frac{\mathrm{d}R_\mathrm{d}}{\mathrm{d}t}\Bigg| = \frac{\mathrm{d}R_\mathrm{a}}{\mathrm{d}t}\Bigg| \tag{12}$$

The numerical analysis was realized by nonlinear curve fitting using SIGMA-PLOT software program. Accordingly, k_1 rate constant was obtained from Eq. (5) and k_2 rate constant was determined by using Eq. (7) keeping k_1 constant in curve-fitting program. For the membrane systems (dinitrile calixarene and tetranitrile calixarene), with three different solvents, the membrane entrance- (k_1) and the exit rate- (k_2) constants together with $R_\mathrm{m}^{\max}$, $t_{\max}$, $J_\mathrm{d}^{\max}$, and $J_\mathrm{a}^{\max}$ values measured for Hg^{2+}, the results are presented in Table 1.

The good agreement between the theoretical curves and the experimental points for Hg^{2+} ion transport in both carriers are shown in Figs. 3 and 4 (as shown with dashed line). The results suggest that the Hg^{2+} ions transport can be described by the kinetic laws of two consecutive irreversible first-order reactions in the present case.

Table 1. The Kinetic Parameters of Hg^{2+} when Different Solvents were Used as Membrane

Ligand	Solvent	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	$R_\mathrm{m}^{\max}$	$t_{\max}$ (min)	$J_\mathrm{d}^{\max} \times 10^3$ (min^{-1})	$J_\mathrm{a}^{\max} \times 10^3$ (min^{-1})
Dinitrile	CH_2Cl_2	4.7	22.0	0.15	89.2	−3.3	3.3
	$CHCl_3$	2.5	12.48	0.13	161.1	−1.62	1.62
	CCl_4	1.6	3.56	0.23	407.9	−0.83	0.83
Tetranitrile	CH_2Cl_2	3.5	16.54	0.14	119.1	−2.32	2.32
	$CHCl_3$	1.6	12.4	0.095	189.6	−1.18	1.18
	CCl_4	0.3	0.81	0.21	1944.8	−0.17	0.17

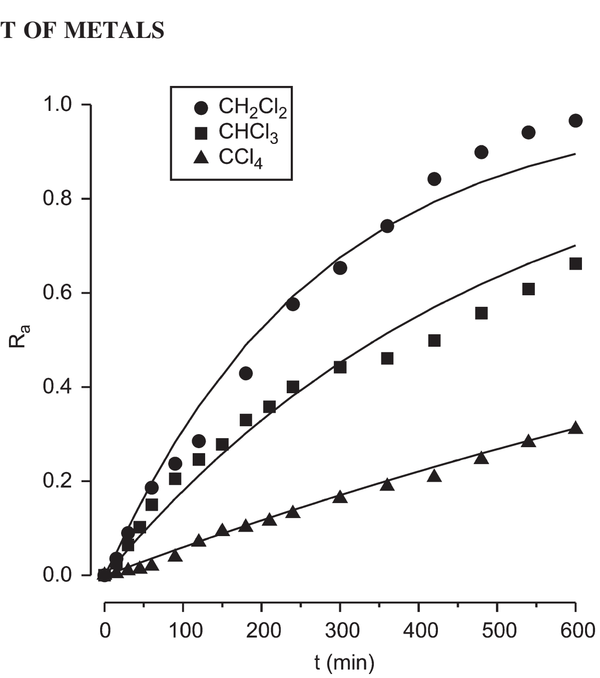


Figure 3. Time variation of reduced concentrations of Hg^{2+} in the acceptor phase during co-transport through liquid membrane using dinitrile derivative in different solvents. (The symbols represent the experimental points, the dashed lines are obtained from the curve-fitting program; $T = 298 \pm 0.1K$).

The nature of the membrane material and solvent system may have also a great influence on the efficiency of metal-ion transport. In order to check this point, appropriate experimental conditions have been set up for two different carrier systems using solvents such as dichloromethane, chloroform, and CCl_4. The results are shown in Figs. 3 and 4. It can be seen that R_a values are affected by membrane-solvent system. The transport efficiency of Hg^{2+} transport was observed to be the highest with CH_2Cl_2 solvents. Dichloromethane solvent appeared to be the most efficient one in the transport processes with respect to chloroform and carbon tetrachloride solvents. When the kinetic parameters were compared for solvents and the type of carrier system, the membrane entrance- and exit rate- constants strongly depended on solvents and seemed to be similar for ligands as shown in Table 2. In all these cases, it has been found that $k_2 > k_1$. As it is seen, the membrane entrance- (k_1) and exit rate- (k_2) constants, t_{max}, R_{max} values, and J_a^{max} values are remarkably different for the solvents. For the membrane systems, it can be seen that all the kinetic parameters that were dependent on the solvent type, were different and were always higher for dinitrile carrier. On the other hand, the obtained kinetic parameters were influenced by the type of solvent and the ligand carrier.

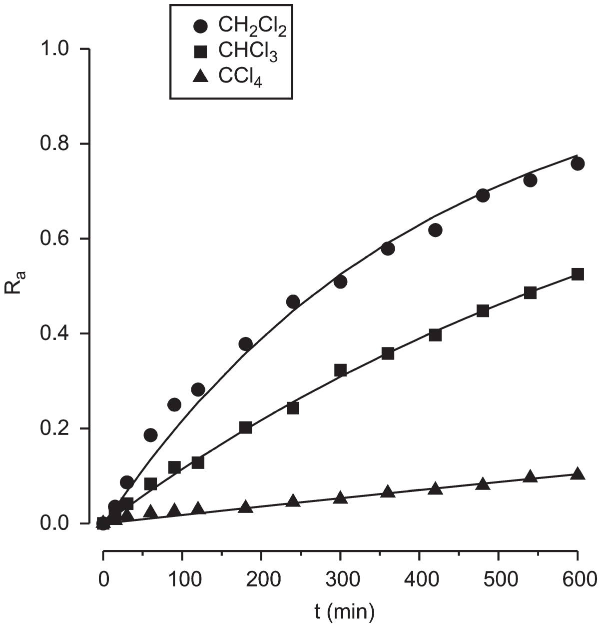


Figure 4. Time variation of reduced concentrations of Hg^{2+} in the acceptor phase during co-transport through liquid membrane using tetranitrile derivative in different solvents. (The symbols represent the experimental points, the dashed lines are obtained from the curve-fitting program; $T = 298 \pm 0.1K$).

For the systems investigated (Table 1), all the kinetic experiments were performed under the same conditions. Taking into account total fluxes obtained when Hg^{2+} ions were transported through carrier molecules, transport efficiency of dichloromethane solvent is higher than that of $CHCl_3$ and CCl_4 for the two carrier systems. These results are in agreement with Ref. (12) in which the efficiency of dichloromethane according to R_a values was higher than that of $CHCl_3$ and CCl_4.

Table 2. Physicochemical Characteristics of Solvents (12)

Solvent	ϵ_0	n_D	μ	η	V_m
CH_2Cl_2	9.08	1.424	1.959	0.437	64.2
$CHCl_3$	4.81	1.446	1.354	0.58	96.5
CCl_4	2.24	1.466	0	0.969	96.5

ϵ_0, dielectric constant (20°C); n_D, refractive index; μ, dipole moment; η, viscosity; V_m, molar volume.

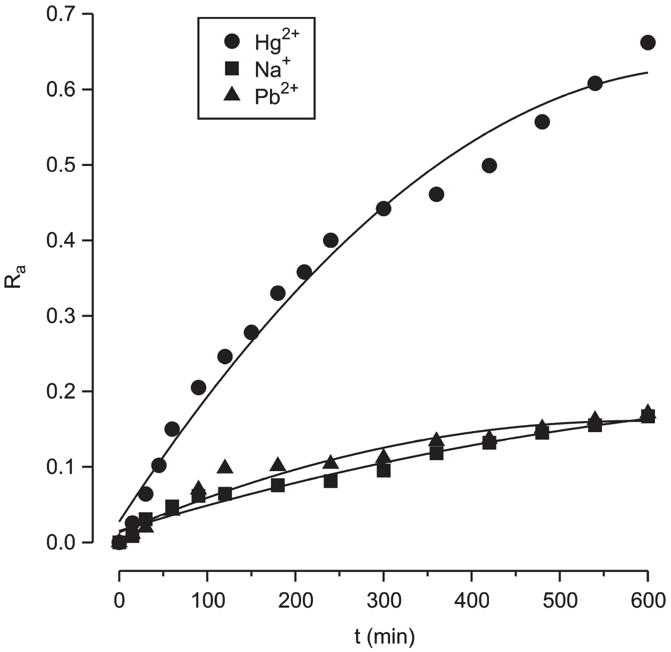


Figure 5. Time variation of reduced concentrations of metals in the acceptor phases during the co-transport through liquid membrane for dinitrile carrier. ($T = 298 \pm 0.1K$).

These observations suggest that viscosity plays a role in metal transport. It is seen from Table 2 that the transport efficiency is sensitive to the viscosity of the solvents and the viscosity values are in the order $CH_2Cl_2 > CHCl_3 > CCl_4$. The viscosity value of $CHCl_2$ compared to CCl_4 is smaller, about two-fold and its transport efficiency is higher about three-fold or higher. These results show the importance of the nature of membrane solvent in establishing transport efficiency.

The nature of the solvent of the membrane phase influences the distribution equilibrium at the interfaces between the membrane and aqueous solution. It has been reported that the solvent polarity is important in solvent extraction and the relative cation is selectively quite often sensitive to the polarity change (19,20). There was a larger effect of solvent type on transport, whereas a minimal effect of solvent type on membrane selectivity was observed (21). As shown in Table 2, the solvent type also has an effect on selectivity.

For comparing the selectivity of Hg^{2+} ion with alkali and divalent cations, experiments were carried out with Na^+ and Pb^{2+} ions by using chloroform solvent under the same experimental conditions. Time variation of reduced concentration of metals in the acceptor phase during the co-transport through liquid membrane

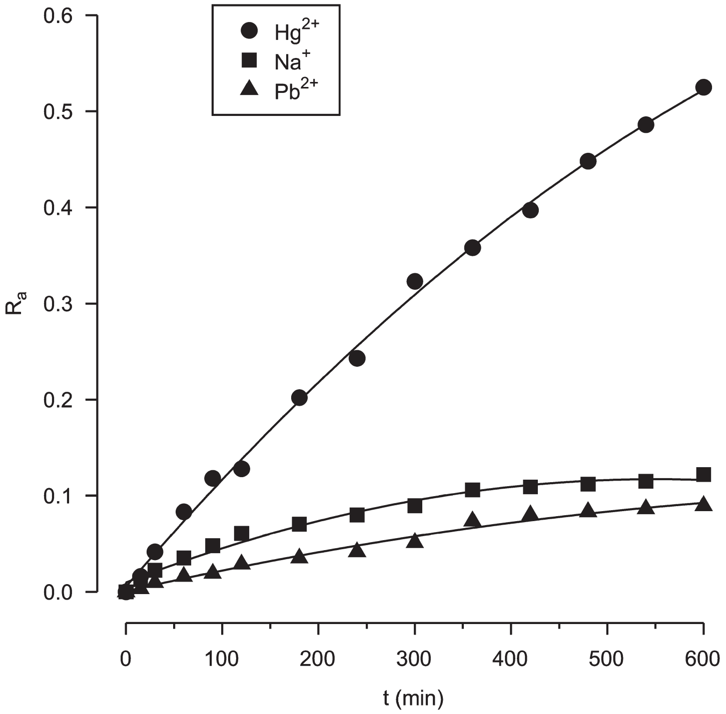


Figure 6. Time variation of reduced concentrations of metals in the acceptor phases during the co-transport through liquid membrane for tetranitrile carrier. ($T = 298 \pm 0.1\text{K}$).

for dinitrile and tetranitrile derivatives are shown in Figs. 5 and 6, respectively. The obtained kinetic parameters are given in Table 3. Table 3 shows that both carrier studied are efficient and selective for Hg^{2+} ions with respect to Na^+ and Pb^{2+} ions. Their efficiency, ranges from 1.18 (J_a^{max}) for the system tetranitrile to 1.62 for the system dinitrile, which is inferior. The dinitrile derivative is a better carrier than the tetranitrile. It should be noted, however, that the two nitrile derivatives are less efficient for Na^+ and Pb^{2+} ions. Dinitrile is a remarkable carrier in view of its selectively for Hg^{2+} ions.

It was pointed out that a ligand is a selective carrier when the most efficiently bound cation is also the one which is carried the fastest (21). On the other hand, it will be a selective receptor when the best-bound cation is the one most slowly transported. According to these definitions, dinitrile derivative is considered as a selective carrier even in the presence of other alkali or divalent cations: Hg^{2+} will be selectively transported.

Table 3. Kinetic Parameters of Metals for Carriers in $CHCl_3$ ($T = 298K$)

Ligand	Metal	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})
Dinitrile	Na^+	0.2	0.76	0.16	1597.0	−0.12	0.12
	Pb^{2+}	0.3	0.8	0.21	1961.4	−0.17	0.17
	Hg^{2+}	2.5	12.48	0.13	161.1	−1.62	1.62
Tetranitrile	Na^+	0.2	0.76	0.16	2380.9	−0.12	0.12
	Pb^{2+}	0.1	0.34	0.18	5074	−0.06	0.06
	Hg^{2+}	1.6	12.4	0.095	189.6	−1.18	1.18

CONCLUSION

The results obtained show that all the chemical kinetic parameters are influenced by the type of carrier as well as solvent. This seems to confirm that the nature of the membrane material and solvent affects mainly the initial state of diffusion. Taking into account the fluxes of metals transported through the calix[4]arene derivativized liquid membranes, the transport efficiency seems to be higher for dinitrile compound compared with the tetranitrile one. The efficiency and reproducibility of transport depend on carrier and solvent type. The structure of the carrier, the nature of cation, and the nature of the solvent have been proved to influence the transport efficiency.

REFERENCES

1. Schugerl, K.; Mohrmann, A.; Gutknecht, W.; Hauertmann, H.B. Application of Liquid Membrane Emulsion for Recovery of Metals from Mining Waste Waters and Zinc Liquors. Desalination **1985**, *53* (1–3), 197–215.
2. Izatt, R.M.; McBride, D.W., Jr. ; Brown, P.R.; Lamb, J.D.; Christensen, J.J. The Influence of Halocarbon Solvent on Macrocycle-Mediated Cation Transport Through Liquid Membranes. J. Membr. Sci. **1986**, *28* (1), 69–76.
3. Szpakowska, M.; Nagy, O.B. Membrane Material Effect on Copper Coupled Transport Through Liquid Membranes. J. Membr. Sci. **1991**, *64* (1&2), 129–143.
4. Noble, R.D.; Way, J.D. Liquid Membrane Technology. In *Liquid Membranes: Theory and Applications*; ACS Symp. Ser. No. 347, Noble, R.D., Way, J.D., Eds.; American Chemical Society: Washington, DC, 1987; 1.

5. Tavlarides, L.L.; Bae, J.H.; Lee, C.K. Solvent Extraction, Membranes, and Ion Exchange in Hydrometallurgical Dilute Metals Separation. Sep. Sci. Technol. **1987**, *22* (2–3), 581–617.
6. Kitagawa, K.; Nishikawa, Y.; Frankenfeld, J.W.; Li, N.N. Wastewater Treatment by Liquid Membrane Process. Environ. Sci. **1977**, *11* (6), 602–605.
7. Saito, K.; Uezu, K.; Hori, T.; Furusaki, S.; Suga, T.; Okamoto, J. Performance Analysis of a Fixed Bed Charged with Capillary Fiber Form Chelating Resin for Recovery of Uranium from Seawater. J. Atom. Energ. Soc. Jpn. **1988**, *30* (4), 359–364.
8. Sugiura, M.; Yamaguchi, T. Coupled Transport of Picrate Anion Through Liquid Membranes Supported by a Microporous Polymer Film. J. Colloid Interf. Sci. **1983**, *96* (2), 454–459.
9. Gutsche, C.D. *Calixarene*; Royal Society of Chemistry: Cambridge, 1989.
10. Viceos, J.; Böhmer, V. *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer: Dordrecht, 1991.
11. Atwood, J.L.; Bott, S.G. *Water-Soluble Calixarene Salts. A Class of Compounds with Solid-State Structures Resembling Those of Clays in Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer: Dordrecht, 1991.
12. Szpakowska, M.; Nagy, O.B. Copper(II) Ion Transport Through Mono and Binary Liquid Membranes. Bull. Soc. Chim. Belg. **1990**, *99* (4), 243–253.
13. Szpakowska, M.; Nagy, O.B. Application of the Competitive Preferential Solvation Theory to Facilitated Ion Transport Through Binary Liquid Membranes. J. Phys. Chem. **1989**, *93* (9), 3851–3854.
14. Szpakowska, M.; Nagy, O.B. Non-steady State vs. Steady State Kinetic Analysis of Coupled Transport Through Binary Liquid Membranes. J. Membr. Sci. **1993**, *76* (1), 27–38.
15. Szpakowska, M.; Nagy, O.B. Effect of Physicochemical Properties of Binary Liquid Membranes on Steady-State Transport of Cu(II) Ions. Polyhedron **1993**, *12* (11), 1277–1288.
16. Arnaud-Neu, F.; Schwing-Weill, M.J.; Ziat, K.; Cremin, S.; Harris, S.J.; McKervey, M.A. Selective Alkali and Alkaline Earth Cation Complexation by Calixarene Amides. N. J. Chem. **1991**, *15* (1), 33–37.
17. Collins, E.M.; McKervey, M.A.; Madigan, E.; Moran, M.B.; Owens, M.; Ferguson, G.; Harris, S.J. Chemically Modified Calix[4]arenes. Regioselective Synthesis of 1,3-(Distal) Derivatives and Related Compounds. X-Ray Crystal Structure of a Diphenol-Dinitrile. J. Chem. Soc. Perkin Trans. 1 **1991**, *12*, 3137–3142.
18. Deligöz, H.; Yilmaz, M. Liquid–Liquid Extraction of Transition Metal Cation by Calixarenes-Based Cyclic Ligands, Solvent Extr. Ion Exch. **1995**, *13*, 19–26.

19. Buschmann, H.J.; Mutihac, L. Complex-Formation Between the Macrocyclic Ligand 18-Crown-6- and Unprotonated Amines in Methanol. Thermochim. Acta **1994**, *237* (1), 203–206.
20. Buschmann, H.J.; Mutihac, L.; Mutihac, R. Physicochemical Parameters of the Transport of Amines and Amino Acids Through Liquid Membranes by Macrocyclic Ligands. Sep. Sci. Technol. **1999**, *34* (2), 331–341.
21. Lehn, J.M. *Physical Chemistry of Transmembrane, Ion Motions*; Spach, G., Ed.; Elseiver: Amsterdam, 1983; 181–207.

Received June 2001
Revised September 2001