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Kinetics of Mercury(II) Transport Through a Bulk Liquid Membrane Containing Calix[4]arene Derivatives as Carrier

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ABSTRACT

The kinetics of transport of mercury (II) ions through a bulk liquid membrane (chloroform) containing calix[4]arene nitrile derivatives as a carrier was examined at different temperatures and different stirring rates. The kinetics of mercury (II) transport could be analyzed in the formalism of two, consecutive, irreversible first-order reactions. The influence of temperature and stirring rate on kinetic parameters also have been investigated. The membrane entrance rate, k_1, and the membrane exit rate, k_2, increased with increasing temperature and increasing stirring rate. For maximum membrane exit fluxes, J_a^{max}, the activation energies were found as 1.923 ± 0.15 and 2.112 ± 0.2 kj/mol, for ligand carrier 1 and 2, respectively. The values for the found activation energy indicate that the process is controlled by species diffusion.

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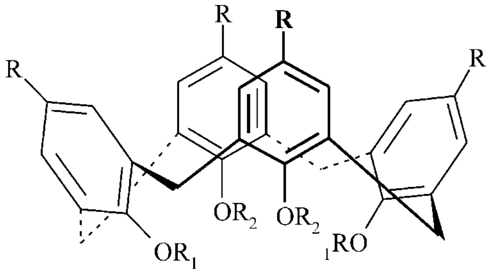
Key Words: Co-transport; Mercury (II) transport; Transport kinetics; Liquid membranes; Temperature effects; Diffusional rate-determining step; Calixarenes.

INTRODUCTION

Several techniques have been developed for the separation of ionic species from solution. Among all other mechanisms of transport of ionic species, liquid membranes has been demonstrated as one of the simplest method for the selective removal of ions from a solution, depending upon the nature of carrier molecule. Therefore, much attention has been paid in recent years to the design and synthesis of new carrier reagents for the selective extraction of ions from the bulk. The design and synthesis of calixarenes, an important class of macrocyclic ion receptors, is very well documented in supramolecular chemistry.[1−3] 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. For these reasons we have chosen the calix[4]arene skeleton as a vehicle for modeling such phenomena in liquid membrane technique.

However, many studies have been made by different groups regarding cation separation techniques. Szpakowska studied coupled transport of copper II ions through liquid membranes (n-octane) containing Acorga P-50 as a carrier.[4] Antures et al. used the multivariate calibration method PLS (partial least squares) in the investigation of K^+ transport through a chloroform membrane by using mixtures of three isomeric organic anions as counter ions.[5] Yaftian et al. have used calixarenes with pendant amide and phosphine oxide functionalities and used these extractive agents and carriers for silver (I) ions.[6] Arnaud-Neu et al. studied cation complexation by chemically modified calixarenes and transport of alkali cations by p-tert-butylcalix[n]arene esters and amides.[7] Dozol and coworkers presented excellent work about removal of cesium from high-salinity acidic or alkaline liquid waste by using crowncalix[4]arenes in supported liquid membranes and in the extraction process.[8]

In this study our aim was to investigate the effectiveness of two nitrile derivatives of calix[4]arene (1 and 2, as presented in Fig. 1) as selective carriers for Hg^{2+} transport through a bulk liquid membrane and examine the kinetic behavior of the transport process at different temperatures and at the different stirring rates. Because of the toxic nature of mercury,[9] we have



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

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

Figure 1. The structure of ligands used as carrier.

concentrated our studies over the selective extraction of Hg^{2+} cations, so as to provide a solution to prevent contaminating the environment (public streams and resources). Thus the carriers 5,11,17,23-tetra-tert-butyl-25, 27-dicyanomethoxy-26, 28-dihydroxycalix[4]arene,[1] 5,11,17,23-tetra-tert-butyl-25, and 26,27,28-tetracyanomethoxycalix[4]arene[2] used in the study were synthesized according to literature methods[10] and the kinetic analysis of Hg(II) cation was investigated by using chloroform.

EXPERIMENTAL

Materials

The chemical reagents used in these experiments were mercury (II) nitrate (Merck 99%), chloroform, (Merck $>99\%$) and picric acid (Merck). Mercury (II) picrate solution was prepared by the addition of 1×10^{-2} M mercury (II) nitrate to 2.5×10^{-5} M aqueous picric acid solution and shaken at 25°C for 1 hour. The aqueous solutions were prepared using demineralized water.

Kinetic Procedure

Cotransport experiments were conducted using a thermostated (GRAND mark, model W14) apparatus. Transport experiments were carried out in a U-type cell. A chloroform solution (20 mL) containing the ionophere was placed in 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 variable speeds by a magnetically (CHILTERN mark, model HS 31).

The initial compositions of the phases consisted of the donor phase, which was aqueous Mercury (II) picrate (2.5×10^{-5} M) and the membrane phase was made up by dissolving carrier (calix[4]arene derivatives, $C_{carrier} = 10^{-3}$ M) in chloroform. Acceptor phase consisted of double distilled water. Samples were taken from both water phases (acceptor and donor phases) at regular time intervals and the mercury (II) picrate concentration was analyzed by a spectrophotometric method.[11] Each experimental result reported is the arithmetic mean for two independent samples and volume change by spectrophotometric method (error $< 1\%$).

RESULTS AND DISCUSSION

In previous work [13–16] in this laboratory, it was found that nitrile derivatives of calix[4]arene 1 and 2 has the desired ability of selective extraction and transport of Hg^{2+}. In this work we have investigated transport of Hg^{2+} by calix[4]arene derivatives as a bulk liquid membrane and the kinetic behavior of the transport process as a function of the stirring rates and temperature.

The liquid membrane technique contains two processes in a single stage: extraction of metal ion from the aqueous donor solution to the organic phase containing the carrier molecules (membrane) and a reextraction of this metal ion from the membrane to the aqueous acceptor phase. The overall transport process consists of a mixture diffusion steps and complexations/decomplexation reactions at two independent and possible different interfaces.

The mechanism of the ion pair mediated transport is given in Fig. 2. L represents the ligand carrier. At the interface between donor and membrane, metal picrate ion pair forms complex with ligand, then the $[LM]^+Pic^-$ complex diffuses through the membrane. At the interface between membrane and acceptor, the carrier ion pairs are decomplexed and M^+Pic^- is liberated into the acceptor phase. Finally, the ligand carrier diffuses back across the membrane aqueous boundary layers.

All the kinetic measurements were carried out under the same experimental conditions. To obtain kinetic equations for a transport system, simple theoretical approach was used and discussed in detail elsewhere.[17–20] In this study, the kinetic behavior of Hg^{2+} ion transport through liquid

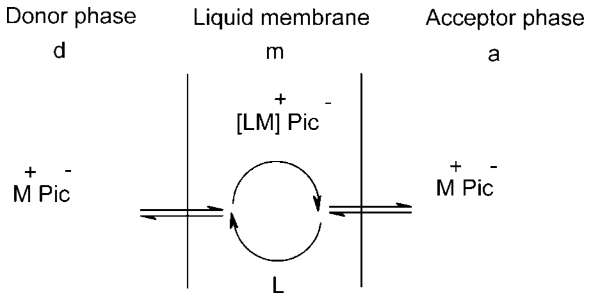


Figure 2. Mechanism of the ion pair-mediated transport through liquid membrane. M: metal; Pic: picrate salt; L: ligand; $[\text{L-M}]^+\text{Pic}^-$: ion pair.

membrane defined by two consecutive irreversible first-order reactions and their kinetic equations can be written as follows:

$$C_d \xrightarrow{k_1} C_m \xrightarrow{k_2} C_a \tag{1}$$

where C_d, C_m and C_a represent the Hg^{2+} concentrations in interface donor, membrane, and acceptor phases, respectively, and k_1 and k_2 are the apparent membrane entrance and exit rate constants, respectively. Variation of Hg^{2+} concentration with time was directly measured in both donor and acceptor phase. The corresponding change of Hg^{2+} concentration in the membrane phase (C_m) was established from the material balance between donor and acceptor phases. For practical reasons, it was better to use dimensionless reduced concentrations [17–20];

$$R_d = \frac{C_d}{C_{d0}} \quad R_m = \frac{C_m}{C_{d0}} \quad R_a = \frac{C_a}{C_{d0}} \tag{2}$$

where C_{d0} is the initial (at t = 0) Hg^{2+} concentration in the donor phase with this dimensionless notation. Thus the material balance can be expressed as simplified form:

$$R_d + R_m + R_a = 1.$$

Time dependence of reduced concentration of Hg^{2+} ion, R_d, R_m, and R_a phases in cotransport through liquid membranes with nitrile derivatives of calix[4]arene 1 and 2 at 25°C and 500 rpm are given in Figs. 3 and 4, respectively. It can be seen from Fig. 3 that R_d decreases exponentially with time; R_a increases exponentially, whereas time dependence of R_m

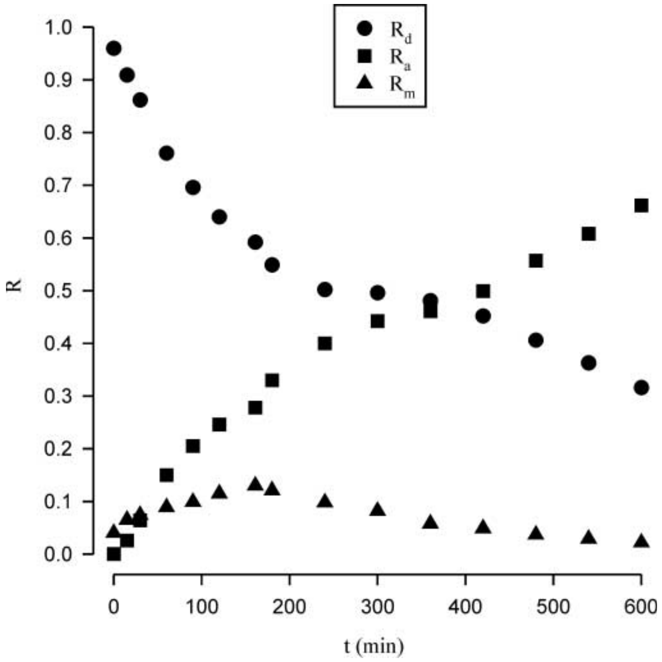


Figure 3. Time dependence of reduced concentration of Hg^{2+} ions, R_d, R_m, and R_a phases in cotransport through liquid membranes with carrier 1 (T = 298 ± 0.1 K).

presents a maximum for carrier 1. In the case of carrier 2, R_d decreases polinomally with time and Ra increases polinomally. R_a values were also calculated by numerical analysis (nonlinear curve fitting) using a Curve-fitting program (Sigma Plot), as shown by dashed line in Figs. 3 and 4.

The kinetic behavior scheme for consecutive reaction systems can be described by using reduced concentrations as given below:

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \tag{3}$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \tag{4}$$

$$\frac{dR_a}{dt} = k_2 R_m = J_a \tag{5}$$

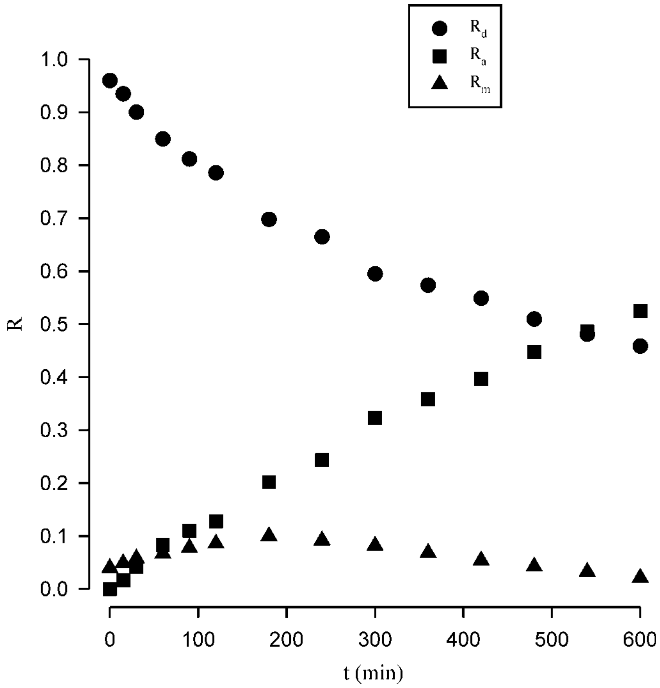


Figure 4. Time dependence of reduced concentration of Hg^{2+} ions, R_d, R_m, and R_a phases in cotransport through liquid membranes with carrier 2 (T = 298 ± 0.1 K).

Integration of this system for assuming as $k_1 = k_2$ leads to the following differential equations:

$$R_d = \exp(-k_1 t) \tag{6}$$

$$R_m = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{7}$$

$$R_a = 1 - \frac{k_1}{k_2 - k_1}\left[k_2\, exp(-k_1 t) - k_1\, exp(-k_2 t)\right] \tag{8}$$

The maximum value of R_m:

$$R_m^{\max} = \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \tag{9}$$

and t_{max} can be evaluated when $dR_m/dt = 0$ as follows:

$$t_{\max} = \left(\frac{1}{k_1 - k_2}\right) \ln \frac{k_1}{k_2} \tag{10}$$

An exponential type curve was obtained by plotting of R_a vs. t, which has an inflection point (when $d^2R_a/dt^2 = 0$):

$$R_a^{\inf} = 1 - \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \left(1 + \frac{k_1}{k_2}\right) \tag{11}$$

occurring at:

$$t_{\inf} = t_{\max} \tag{12}$$

Considering the first-order time differentiation of Eqs. (8–10) leads to the final forms of flux equations;

$$\left.\frac{d\,R_d}{dt}\right|_{\max} = -k_1 \left(\frac{k_1}{k_2}\right)^{-k_1/(k_1-k_2)} \equiv J_d^{\max} \tag{13}$$

$$\left.\frac{dR_a}{dt}\right|_{\max} = k_2 \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_a^{\max} \tag{14}$$

$$\left.\frac{dR_m}{dt}\right|_{\max} = 0 \tag{15}$$

$$-\frac{dR_d}{dt}|_{\max} = \frac{dR_a}{dt}|_{\max} \tag{16}$$

It should be emphasized that at $t = t_{\max} = t_{\inf}$, the system is in steady state because the concentration of Hg^{2+} ions in the membrane does not vary with time (Eq.16). Because the fluxes of entrance and exit are equal, they have opposite signs.

The numerical analysis was realized by nonlinear curve fitting using Sigma-Plot software program. Accordingly k_1 rate constant was obtained from Eq. (6), and k_2 rate constant was determined by using Eq. (8) and keeping k_1 constant with curve-fitting program. The kinetic parameters, k_1, k_2, R_m^{max}, t_{max}, J_d^{max} or J_a^{max} obtained at different temperatures for carriers 1 and 2 are presented in Table 1. In Figs. 3 and 4, the variation of Hg^{2+} concentration in

Table 1. The kinetics parameters of carriers at different temperatures (stirring rate is 500 rpm).

Ligand	Temp. (K)	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})
1	298	2.5	1.25	0.13	161.1	-1.62	1.62
	303	4.0	1.82	0.139	106.7	-2.54	2.54
	308	5.4	2.5	0.142	78.2	-3.54	3.54
	318	6.2	2.79	0.15	69.3	-4.19	4.19
2	298	1.6	1.24	0.10	189.6	-1.18	1.18
	303	2.8	1.47	0.13	139.5	-1.89	1.89
	308	3.9	1.99	0.132	101.9	-2.62	2.62
	318	5.3	2.09	0.16	87.8	-3.32	3.32

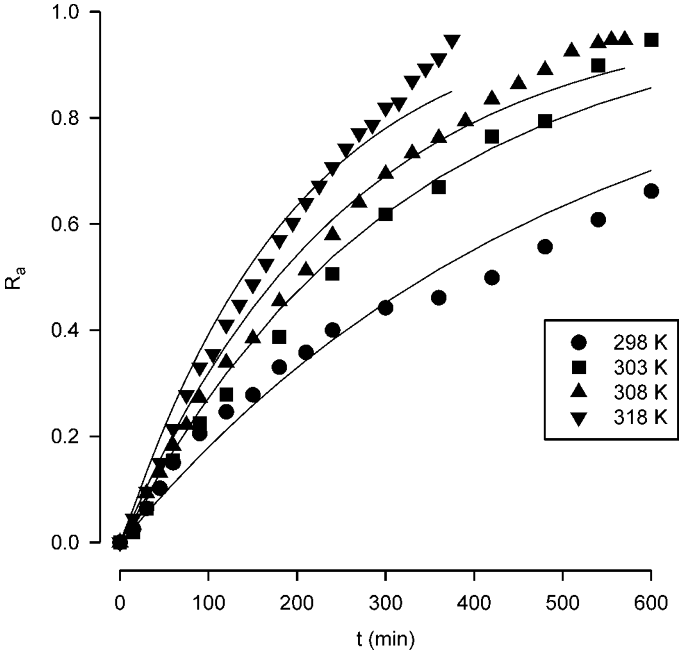


Figure 5. Time variation of reduced concentration of Hg^{2+} ions in the acceptor phase (R_a) during cotransport through liquid membranes with carrier 1 at different temperatures.

acceptor phase shows fairly good agreement between the theoretical curves and the experimental points.

The R_m values were reached at maximum level within 3 hours, and it can be seen from Table 1 that R_m values for carrier 1 is somewhat higher than that of carrier 2. The t_{max} was also obtained in a short time for carrier 1. The remarkable effect was observed with stirring rates as well as temperature.

The variation of normalized Hg^{2+} ion concentration with time in donor, membrane, and acceptor phases at different temperatures for nitrile derivatives of calix[4]arene 1 and 2 carriers are shown in Figs. 5 and 6, respectively. Cotransport of Hg^{2+}ion with calix[4]arene carriers were executed at a temperature of range of 298 to 318 K and at different stirring rates in the range of 500 to 800 rpm. The highest transport efficiency was reached at 318 K and a stirring rate of 800 rpm. When the temperature efficiency was compared, the lowest temperature efficiency was observed at

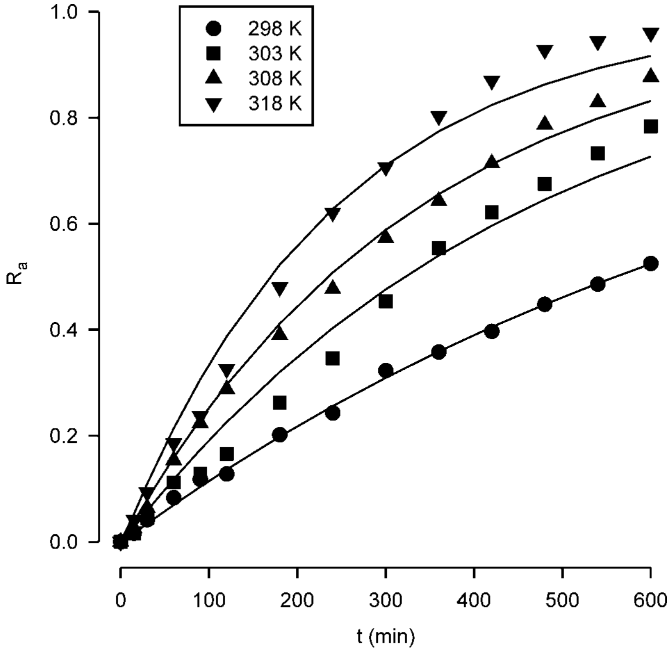


Figure 6. Time variation of reduced concentration of Hg^{2+} ions in the acceptor phase (R_a) during cotransport through liquid membranes with carrier 2 at different temperatures.

298 K. When the transport efficiency of both carriers was compared, the highest transport efficiency was obtained for carrier 1.

At cotransport of Hg^{2+} ions, the highest R_a values, the fluxes, and the kinetic parameters are obtained at higher temperature and the highest stirring rate, as seen in Table 2. Activation energies are calculated from different temperatures at the rate 500 rpm. The kinetic parameters such as (k_1) the membrane entrance and the exit rates (k_2) increases with the increase of temperature as well as stirring rates. The kinetic parameters obtained for carriers 1 and 2 at different stirring rates are also given in Table 2.

It can be pointed out that the temperatures and stirring rates have an effect on the kinetic constant. The transport of Hg^{2+} ions was carried out with the consecutive irreversible reactions. The calculating of activation energy with respect to the membrane entrance and exit rates is not the corrected procedure as pointed out by Kobya et al.[19] Therefore, the activation energy values were calculated from the maximum membrane exit flux (J_a^{max}) versus (1/T) plots, as presented Fig. 7.

$$\ln(J) = \ln(A) - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{17}$$

The calculated activation energy values for membrane were found to be 1.923 ± 0.15 kj/mol and 2.112 ± 0.20 kj/mol for carriers 1 and 2, respectively. It is expected that the temperature and stirring effect are mainly exerted on the maximum complexation and decomplexation rates between Hg^{2+} picrate and ligand carrier at the aqueous-organic interfaces. On the other hand, the maximum membrane entranceexit fluxes take places in the reaction zones of ionic interfaces.

Table 2. The kinetic parameters of carries at different stirring rates (T = 298 ± 0.1 K).

Ligand	Rates (rpm)	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})
1	500	2.5	1.25	0.13	161.1	−1.62	1.62
	650	6.3	2.82	0.15	68.4	−4.23	4.23
	800	9.1	3.6	0.16	51.1	−5.76	5.76
2	500	1.6	1.24	0.10	189.6	−1.18	1.18
	650	4.2	2.07	0.14	96.8	−2.9	2.9
	800	5.2	2.13	0.155	87.6	−3.3	3.3

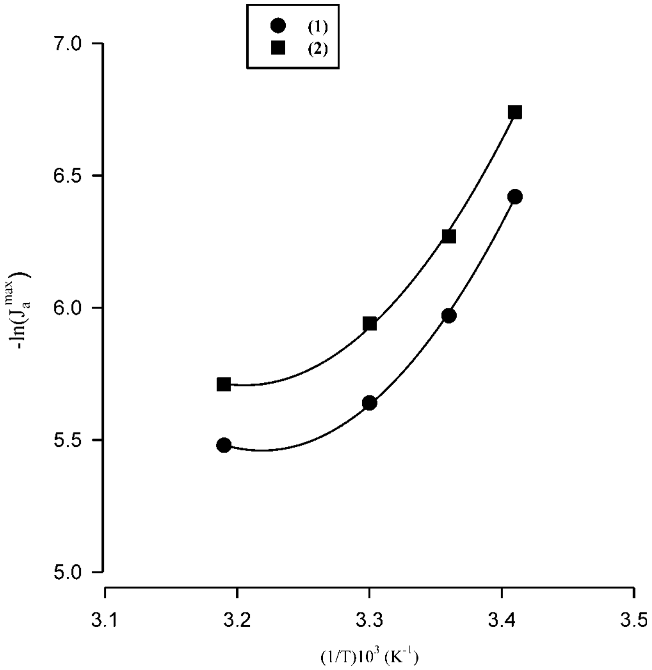


Figure 7. Arrhenius plot of Hg^{2+} ion transport at J_a^{max}.

It is well-known that the activation energy values are quite low for diffusion-controlled processes,[21] which were affected strongly by temperature on actual rate constants. When the activation energy values are compared between chemically controlled processes and diffusion-controlled processes, the E_a values are lower for diffusion-controlled processes. The obtained data for activation energy show that the transport of Hg^{2+} ion by calix[4]arene derivatives is a diffusion-controlled processes. It was reported that, for diffusion controlled processes, values are lower than 2.392 kj/mol, thus it is believed that the transport of Hg^{2+} ions is diffusion-controlled.[18]

For the membrane systems, it can be seen that the R_m^{max} values seem to be similar, but there is a difference for the membrane entrance (k_1) and exit rate constants (k_2) and J_{max} values, which is always higher for carrier 1. The obtained kinetic rate constants k_1 and k_2 were plotted as a function of the stirring rate, as presented in Fig. 8. It can be seen that the membrane entrance and exit rate constants for carrier 2 is higher, but there is a remarkable difference for membrane entrance rate constants for both carrier.

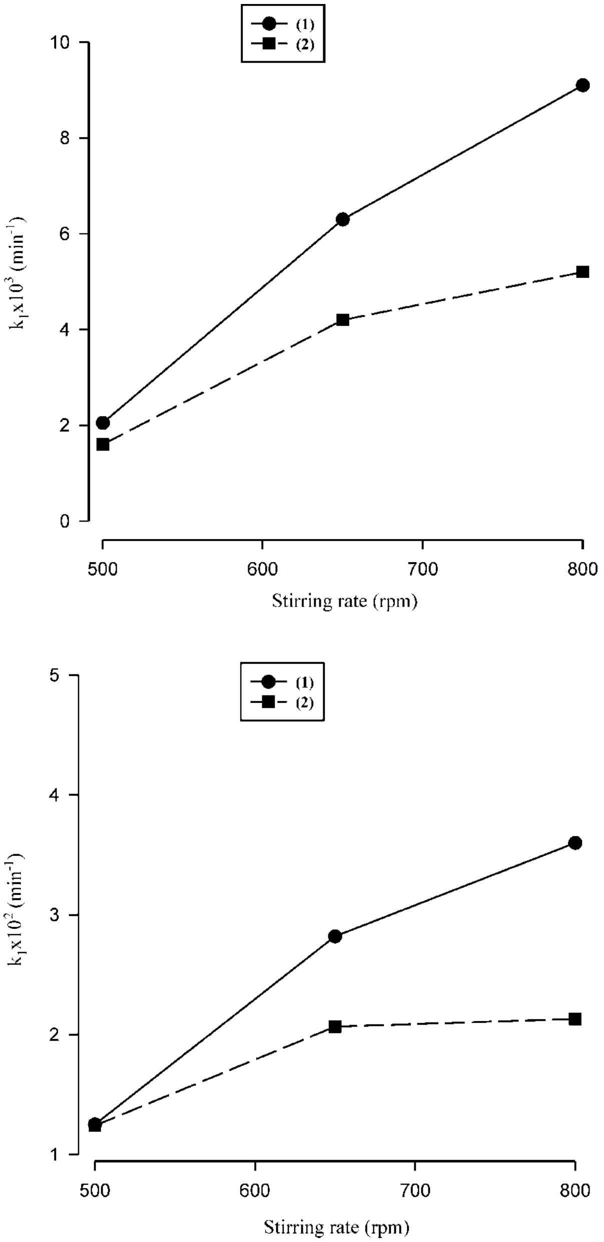


Figure 8. The effect of stirring rate on the membrane entrance and membrane exit rate constants.

From the results, it is assumed that the membrane permeation rate constant k_1 and k_2 is influenced by the type of carrier. This seems to confirm that the nature of the membrane material affects mainly the initial state of diffusion. Taking into account the fluxes obtained when the Hg^{2+} ions were transported through the calix[4]arene derivativized liquid membranes, the transport efficiency seems to be higher for compound 1 compared with compound 2.

The Hg^{2+} ions are effectively removed from aqueous solution with liquid membrane processes by calix[4]arene nitrile derivatives. Temperature and stirring rates has an important effect on the transport process and it is observed that the kinetic parameters: transport rate and fluxes increased with increasing temperature and stirring rates. In addition to temperature and mixing velocity, an investigation on the pH of different organic solvents and different receiver phases and especially physicochemical specialties of phases may be useful. Moreover, when temperature and mixing velocity are increased, R_m^{max} and t_{max} decreases, thus the Hg^{2+} ions are rapidly complexed with the ligand carrier. The calculated activation energy indicate that the process for Hg^{2+} transport with calix[4]arene nitrile derivatives is membrane diffusion controlled.

The present study shows the primary importance of the nature of the carrier in establishing transport efficiency. Striking variations of the kinetic parameters with the ligand carrier, temperature, and mixing velocity were observed. Further studies involving a greater variety of systems are still necessary to establish definitely the advantages of multicomponent membranes compared with single ligand carrier systems. Therefore, additional experiments involving supported liquid membrane systems, electrical potential application, or multicomponent membrane systems are under investigation.

In conclusion, nitrile derivatized and, therefore, the calix[4]arene-based transport system that is specific for Hg^{2+}, could be a potential method for the practical use of Hg^{2+} separation—particularly because it has the advantage of high-precision efficiency and selectivity and resources. We can conclude that the calix[4]arene derivatives are excellent carriers for the efficient transport of mercury. The efficiency and reproducibility of transport depend on type of carrier, temperature, and stirring rate.

REFERENCES

1. Gutsche, C.D. *Calixarenes*; Royal Society of Chemistry: Cambridge, 1989.
2. Viceos, J.; Böhmer, V. Calinarenes; *A Versatile Class of Macrocyclic Compounds*; Kluwer: Dordrecht, 1991.

3. Atwood, J.L.; Bott, S.G. *Water-soluble Calixarene Salts. A Class of Compounds with Solid-State Structures Resebling Those of Clays in Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer: Dordrecht, 1991.
4. Szpakowska, M. Coupled transport of copper through different types of liquid membranes containing Acorga P-50 as carrier. J. Membr. Sci. **1996**, *109* (1), 77–86.
5. Antures, A.M.; Volpe, P.L.O.; Poppi, R.J. Utilization of multivariate calibration methods for the study of K^+ transport through hydrophobic liquid membranes by using isomeric anions. Sep. Sci. Technol. **1999**, *34* (2), 289–303.
6. Yaftian, M.R.; Burgard, M.; El Bachiri, A.; Matt, D.; Wesser, C.; Dieleman, C.B. Calix[4]arenes with pendant amide and phosphine oxide functionalities:use as extractive agents and carriers for silver(I) Ions. J. Inc. Phenom. Mol. Recog. In Chem. **1997**, *29* (2), 137–151.
7. Arnaud-Neu, F.S.; Guerra, L.; McGregor, W.; Ziat, K.; Schwing-Weill, M.J.; Barret, G.; McKervey, M.A.; Marrs, D.; Seward, E.M. Cation complexation by chemically modified calixarenes. Part 7. Transport of alkali cations by p-tert-butylcalix[n]arene esters and amides. J. Chem. Soc. Perkin Trans. **1995**, *2* (1), 113–118.
8. Dozol, J.F.; Simon, N.; Lamare, V.; Rouquette, H.; Eymard, S.; Tournois, B.; De Marc, D. DCC/DESD/SEP Macias. R.M. A solution for cesium removal from high-sailinity acidic or alkaline liquid waste: the crown-calix[4]arenas. Sep. Sci. Technol. **1999**, *34* (6–7), 877–909.
9. Safavi, A.; Shams, E. Selective and efficient transport of Hg (II) through bulk liquid membrane using methyl red as carrier. J. Membr. Sci. **1998**, *144* (1–2), 37–43.
10. 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. **1991**, *1* (12), 3137–3142.
11. Hamada, F.; Fukugaki, T.; Murai, K.; Orr, G.W.; Atwood, J.L. Liquid–liquid extraction of transition and alkali-metal cations by a new calixarene-diphenylphosphine calix[4]arene methyl-ether. J. Inclusion Phenom. Mol. Recog. Chem. **1991**, *10* (1), 57–61.
12. Deligöz, H.; Yilmaz, M. Liquid–liquid Extraction of transition metal cation by calixarenes-based cyclic ligands. Solvent Extr. Ion Exch. **1995**, *13*, 19–26.
13. Memon, S.; Uysal, G.; Yilmaz, M. Selective complexation of Hg^{2+} by biscalix[4]arene nitriles. Sep. Sci. Technol. **2000**, *35* (8), 1247–1256.

14. Memon, S.; Yilmaz, M. Synthesis of complexation studies of 1,3-dialkylated p-tert-butylcalix[4]arene telomers. React. Func. Polym. **2000**, *44* (3), 227–233.
15. Alpoguz, H.K.; Memon, S.; Ersoz, M.; Yilmaz, M. Transport of metals through a liquid membrane containing calix[4]arene derivatives as Carrier. Sep. Sci. Technol. **2002**, *37* (9), 2201–2213.
16. Alpoguz, H.K.; Memon, S.; Ersoz, M.; Yilmaz, M. Transport of Hg^{2+} through bulk liquid membrane using biscalix[4]arene nitrile derivative as carrier:kinetic analysis. New J. Chem. **2002**, *26* (4), 477–480.
17. Szpakowska, M.; Nagy, O.B. Copper (II) Ion transport mono and binary liquid membranes. Bull. Soc. Chim. Belg. **1990**, *99* (4), 243–253.
18. Szpakowska, M. Kinetics of coupled transport of Cu (II) ions through liquid membranes composed of technical solvents and paraffin mixtures. J. Membrane Sci. **1994**, *92* (3), 267–273.
19. Kobya, M.; Topçu, N.; Demircioğlu, N. Kinetic analysis of coupled transport of thiocyanate ions through liquid membranes at different temperatures. J. Membr. Sci. **1997**, *130* (1–2), 7–15.
20. Szpakowska, M.; Naggy, O.B. Non-steady State vs. Steady state kinetic analysis of coupled ion transport through binary liquid membranes. J. Membr. Sci. **1993**, *76* (1), 27–38.
21. Lazarova, Z.; Boyadzhiev, L. Kinetic aspects of Copper (II) transport across liquid membrane containing LIX-860 as a carrier. J. Membr. Sci. **1993**, *78* (3), 239–245.

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