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Kinetic Study of Hg^{2+} Transport Through a Liquid Membrane Containing Calix[4]arene Dinitrile Oligomer as Carrier

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*In this article, calix[4]arene dinitrile-oligomer **(1)** carrier was used as a carrier to transport Hg^{2+} ions from an aqueous solution into an aqueous receiving solution. The kinetic parameters (k_1, k_2, R_m^{max}, t_{max}, J_d^{max}, J_a^{max}) were investigated with a temperature influence, solvent, and stirring rate, and analyzed in the formation of two consecutive, irreversible first order reactions. The membrane entrance rate, k_1, and the membrane exit rate, k_2, constants were increased with the temperature and stirring rate, and found to be dependent on the solvent type in order to $CH_2Cl_2 > CHCl_3 > CCl_4$. For the maximum membrane exit flux, J_a^{max}, the activation energy was found from the slope of the linear Arrhenius relationship to be 4.78 kcal/mol, which indicates that the process is controlled by species diffusion.*

Keywords liquid membranes, mercury (II) transport, transport kinetics, calixarenes

Introduction

In recent years, liquid membrane (LM) has been widely used to study the ion transport against a concentration gradient. The ion transport through an LM plays an important role in simulating biological membrane functions and separation technologies because of high transport efficiency, excellent selectivity, and economic advantages of LM. A number of successful researches involving the transport of metal ions (1–4), rare earth elements (5, 6), drugs (7, 8), phenols (9), fructose (10), and the treatment of seawater and wastewater (11–13) through the liquid membrane have been carried out. The transport kinetics of alkali metal ions (14), copper ion (15), mercury ion (16–19), cadmium ion (20), and L-isoleucine (Ile) (21) has also been studied.

Hg^{2+} ions in wastewater are a major toxic contaminant and have been explored as being a very important environmental and technological problem. The removal of Hg^{2+} ions from wastewater is one of great importance. The use of liquid membranes in metal

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ion transport and removal processes with a mobile carrier has been proposed as a promising technology. An efficient and suitable carrier in the separation technology is needed in order to remove selectively the desired substances, particularly toxic contaminants on the donor phase side of the LM and to release them readily on the acceptor phase side. Despite the increasing industrial use Hg^{2+} ion in the world and its hazardous effects to human health (22), information about the transport of this ion across LM is quite sparse (23–26). Hence, the development of a new membrane carrier for selective removal and purification of Hg^{2+} ion from its mixtures is still a challenging problem.

In the present study on the co-transport of Hg^{2+} ion through liquid membranes calyx[4]arene dinitrile-oligomer **(1)** was used as the carrier ligand (as presented in Figure 1). The carrier was synthesized according to method in the literature (27) and used to examine various parameters that are responsible for the transport of Hg (II) ions from donor solutions to an acceptor one. The kinetics of Hg^{2+} ion transport were analyzed at different temperatures in the range of 293–308 K and at different stirring rates in various solvents, and are discussed in the form of two irreversible first order reactions.

Experimental

Materials

The chemical reagents used in these experiments were mercury (II) nitrate, dichloromethane, chloroform, CCl_4 and picric acid obtained from Merck Co. (Darmstadt, Germany). A mercury (II) picrate solution was prepared by the addition of a 1×10^{-2} M mercury (II) nitrate to a 2.5×10^{-5} M aqueous picric acid solution and shaken at 25°C for 1 h. The aqueous solutions were prepared using demineralized water.

Kinetic Procedure

Co-transport experiments were conducted using a thermostated (Grand Mark, Model W14, Grants Instruments, Cambridge, England) apparatus. Transport experiments were carried out in a U-type cell. An organic solution (20 ml) containing the ionophore was placed in the bottom of the cell and two portions of aqueous donor and acceptor solutions (10 ml) were carefully added on top. Both surface areas were $2.5\,cm^2$. The organic phase was

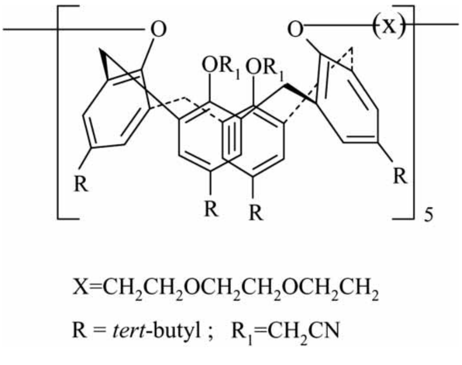

Figure 1. The structure of ligand used as carrier.

stirred at variable speeds magnetically (Chiltern Mark, Model HS 31). The initial phases consisted of the donor phase, which was an aqueous mercury (II) picrate (2.5×10^{-5} M) solution, while the membrane phase was made up by dissolving carrier **(1)** ($C_{carrier} = 10^{-3}$ M) in the organic phase. The acceptor phase consisted of doubly distilled water. Samples were taken from both water phases (acceptor and donor phases) at various intervals of time and the picrate ion concentration was analyzed by a spectrophotometric method (28). The spectrophotometric measurements were performed by means of an UV-VIS Spectrometer Shimadzu 160A. Each experimental result reported is the arithmetic mean of two independent measurements.

Results and Discussion

In previous work (16, 17), the selective transport of Hg^{2+} ions from an aqueous phase was carried out by using nitrile derivatives of calix[4]arenas as the carrier. In this work, the transport Hg^{2+} ion by calix[4]arene dinitrile-oligomer **(1)** in the LM was studied and the kinetic behavior of the transport process as a function of temperature, stirring rate and solvents was investigated.

All the measurements were carried out under exactly the same experimental conditions. A simple theoretical approach was used to obtain the consecutive kinetic equations for a transport system, which was discussed in details elsewhere (16, 17, 29–31).

In the experiments, the variation of picrate ion concentration with time was directly measured in both donor (C_d) and acceptor phases (C_a). The corresponding change of picrate ion concentration in the membrane phase was determined from the material balance between the phases. For practical reasons, the dimensionless reduced concentrations were used:

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

where C_{d0} is the initial Hg^{2+} concentration in the donor phase, while C_d, C_m and C_a represents the Hg^{2+} concentration in donor, membrane and acceptor phases, respectively. The material balance with respect to the reduced concentrations can be expressed as $R_d + R_m + R_a = 1$. From this expression, the kinetic behavior of the consecutive irreversible first order reactions can be described as follows:

$$C_d \xrightarrow{k_1} C_m \xrightarrow{k_2} C_a \tag{2}$$

where k_1 and k_2 are the apparent membrane entrance and exit rate constants, respectively. The kinetic scheme for consecutive reaction systems can be described by considering the reduced concentrations as follows:

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

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

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

where J represents the flux. Integrating of the Equations 3–5, assuming as $k_1 \neq k_2$, leads to the differential equations given as follows:

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

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

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

The maximum values of R_m and t_{max} when $dR_m/dt = 0$, can be evaluated as:

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

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

Which by considering the first-order time differentiation of Equations 6–8 leads to the following forms:

$$\left.\frac{dR_d}{dt}\right|_{\max} = -k_1\left(\frac{k_1}{k_2}\right)^{-k_1/(k_1-k_2)} \equiv J_d^{\max} \tag{11}$$

$$\left.\frac{dR_a}{dt}\right|_{\max} = k_2\left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_a^{\max} \tag{12}$$

$$\left.\frac{dR_m}{dt}\right|_{\max} = 0 \tag{13}$$

$$-\left.\frac{dR_d}{dt}\right|_{\max} = \frac{dR_a}{dt}|_{\max} \tag{14}$$

It should be noted that the system is assumed to be in steady state at $t = t_{max}$, since the concentration of Hg^{2+} ions in the membrane does not vary with time (Equation 13). Consequently, the entrance and exit fluxes are equal having opposite signs.

Here, the transport mechanism is a co-transport (ion-pair mediated diffusion) process, in which co-transport of Hg^{2+} ion with the carrier was studied over a temperature range of 293–308 K and at different stirring rates in the range of 200–400 rpm. The kinetic parameters of k_1 and k_2 from the obtained by fitting Equations 6 and 8 to this data. The calculated k_1, k_2, R_m^{max}, t_{max}, J_d^{max} and J_a^{max} values at different temperatures and different stirring rates for $CHCl_3$ solvent are presented in Tables 1 and 2, respectively. As an example, the variation of the reduced concentration of Hg^{2+} ion through the liquid membrane in $CHCl_3$ solvent at 300 rpm and 25°C is presented in Figure 2. It is seen that R_d decreases exponentially with time, accompanied by a simultaneous increase of R_a, whereas R_m presents at maximum at intermediate times. The maximum R_m values were found to lie between the 0.28 and 0.36 range. This shows that the membrane phase also had an effect on the transport. It is also seen that the t_{max} values were decreased upon increasing temperature and stirring rates. It is immediately obvious that the extraction of Hg^{2+} from the donor phase into the membrane occurs at a rate equal to the release of mercury from the membrane into the acceptor phase. Thus, it seems reasonable to assume that the extraction

Table 1

The kinetic parameters of Hg^{2+} transport using carrier **(1)** at different temperatures (stirring rate is 300 rpm; solvent is $CHCl_3$)

Temperature (K)	$k_1 \times 10^2$ (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})
293	1.25	1.75	0.31	67.29	−5.39	5.39
298	1.59	1.82	0.34	58.69	−6.26	6.26
303	1.89	2.14	0.35	49.73	−7.38	7.38
308	2.10	2.25	0.36	45.53	−7.99	7.99

or release of Hg^{2+} from its ion-paired complex is the rate-determining step of the membrane transport process.

It is clearly seen that the highest transport efficiency was reached at 308 K and 400 rpm stirring rate with the transport efficiency decreasing as these parameters decreased. As temperature and stirring rates are increased, R_m^{max} increases somewhat, t_{max} decreases, thus the Hg^{2+} ions are rapidly complexed with the ligand carrier. The membrane entrance (k_1) and exit (k_2) rate constants increase with increasing temperature as well as with stirring rate.

The variation of reduced Hg^{2+} ion concentration with time in donor and acceptor phases shown in Figures 3 and 4, respectively. Co-transport of Hg^{2+} ion experiments was studied over a temperature range of 293–308 K. R_d decreases with time, increasing the temperature, but R_a increases. The numeric analysis of Hg^{2+} transport was solved to compare with the experimental results (R_d and R_a values) by using non-linear curve-fitting as shown by the dashed lines in Figures 3 and 4; there is fairly good agreement between the theoretical curves and experimental points.

The activation energy was calculated from a plot of the maximum membrane exit flux (J_a^{max}) vs. (1/T) at 200 rpm, as presented in Figure 5.

$$\ln(J) = \ln(A) - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{15}$$

The activation energy value for carrier **(1)** in the liquid membrane was found to be 4.78 kcal/mol. As known, activation energy values are quite low for diffusion-controlled processes, whose rate constants are strongly affected by temperature. The E_a values of diffusion-controlled processes are lower than those of chemically controlled processes.

Table 2

The kinetic parameters of Hg^{2+} transport using carrier **(1)** at different stirring rates ($T = 298$ K; solvent is $CHCl_3$)

Stirring rate (rpm)	$k_1 \times 10^2$ (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})
200	0.76	1.20	0.29	103.88	−3.45	3.45
300	1.59	1.82	0.34	58.69	−6.26	6.26
400	2.29	2.42	0.36	42.52	−8.65	8.65

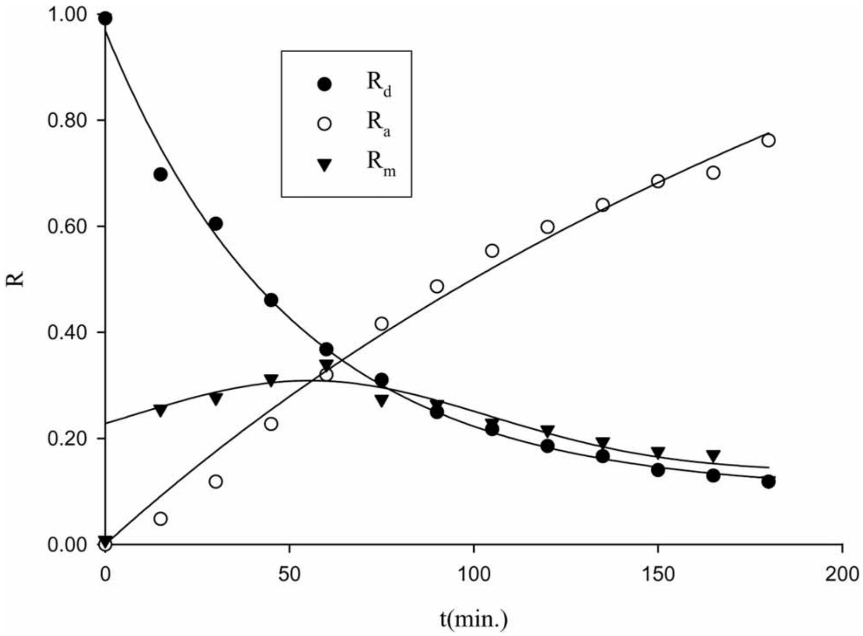

Figure 2. The changes of reduced concentrations of Hg^{2+} ion with time in co-transport through liquid membrane (T = 298 K, solvent is $CHCl_3$). (The symbols represent the experimental points; the lines are obtained from the curve-fitting program).

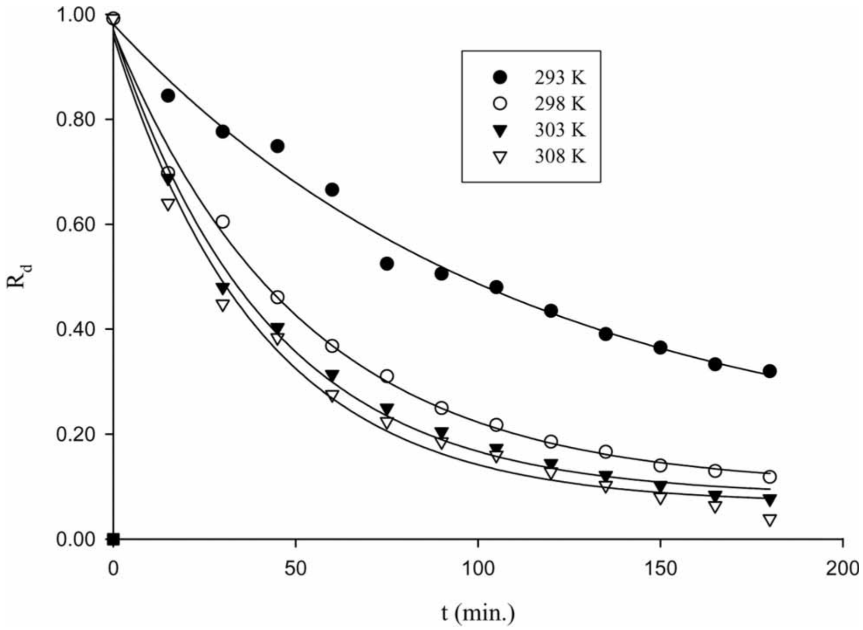

Figure 3. The changes of reduced concentrations of Hg^{2+} in the donor phase with time during co-transport through liquid membrane using of calix[4]arene dinitrile oligomer carrier at different temperatures at a stirring rate of 300 rpm. (The symbols represent the experimental points; the lines are obtained from the curve-fitting program).

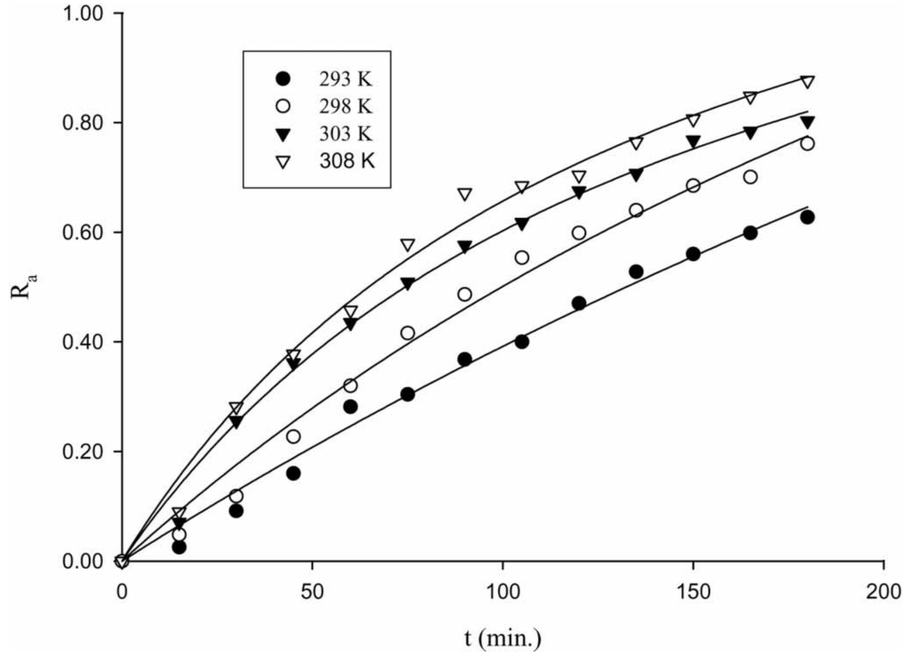

Figure 4. The changes of reduced concentrations of Hg^{2+} in the acceptor phase with time during co-transport through liquid membrane using of calix[4]arene dinitrile oligomer carrier at different temperatures at a stirring rate of 300 rpm. (The symbols represent the experimental points; the lines are obtained from the curve-fitting program).

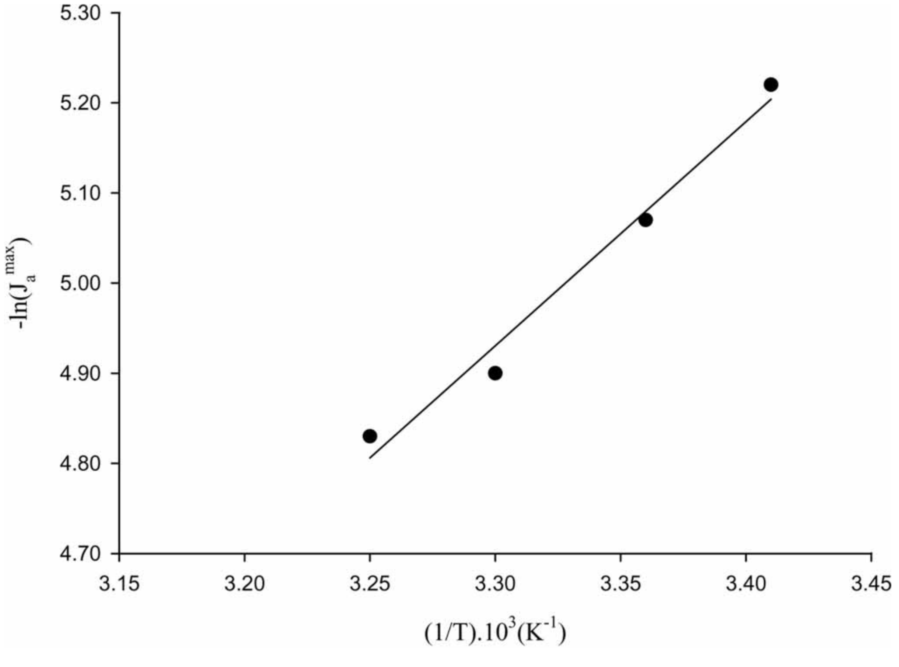

Figure 5. Arrhenius plot of Hg^{2+} ion transport at J_a^{max}.

Table 3

The kinetic parameters for Hg^{2+} transport using carrier **(1)** when different solvents are used (T = 298 K; stirring rate 300 rpm)

Solvent	$k_1 \times 10^2$ (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})
CH_2Cl_2	1.85	2.048	0.35	51.34	−7.16	7.16
$CHCl_3$	1.59	1.82	0.34	58.69	−6.26	6.26
CCl_4	0.44	0.70	0.28	178.25	−1.01	1.01

It was pointed out that the activation energies of diffusion-controlled processes are lower than 10 kcal/mol (32). The calculated activation energy for carrier **(1)** shows that the transport of Hg^{2+} ion is diffusion-controlled processes.

The present work was to investigate the physicochemical approach to co-transport of Hg^{2+} ion transport through a liquid membrane containing calix[4]arene dinitrile-oligomer **(1)** carrier. Therefore, the effect of solvents on the transport process was studied under the same conditions, and the results obtained with CH_2Cl_2 and CCl_4 are presented in Table 3, along with analogous results for $CHCl_3$. It has been observed that the membrane entrance and exit rate constants are found to vary in the order $CH_2Cl_2 > CHCl_3 > CCl_4$, and the variation of R_a values is illustrated in Figure 6. This shows that the R_a values are strongly affected by the membrane solvent system, and the higher transport efficiency

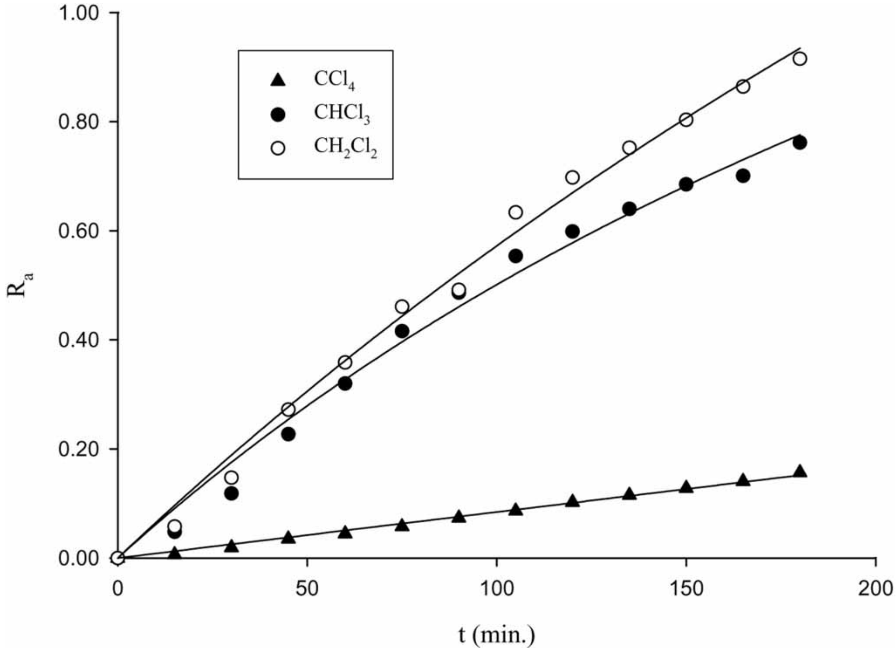

Figure 6. The changes of reduced concentrations of Hg^{2+} in the acceptor phase with time during co-transport through liquid membrane using of calix[4]arene dinitrile oligomer carrier in different solvents at a stirring rate of 300 rpm. (The symbols represent the experimental points; the lines are obtained from the curve-fitting program).

was observed with CH_2Cl_2 solvent. From this observation, the results are consistent with the literature (29), in which the efficiency of CH_2Cl_2, with respect to the R_a values, was higher than of $CHCl_3$ and CCl_4, because their viscosity values were in the reverse order. Thus, we demonstrated that the characteristics of the membrane solvents are one of the main factors in establishing transport efficiency.

Conclusions

In this study, the kinetics of Hg^{2+} ion transport has been analyzed in the formalizing of two, consecutive, irreversible first order reactions. As temperature and stirring rate increased, R_m^{max} increases, while t_{max} decreases. The membrane entrance (k_1) and exit (k_2) rate constants increase with increasing temperature and stirring rate. The activation energy value for carrier **(1)** in the liquid membrane was found to be 4.78 kcal/mol. The value of the activation energy indicates that the process is diffusionally controlled. The membrane entrance and exit rate constants depend on the solvent type and are found to be in the order $CH_2Cl_2 > CHCl_3 > CCl_4$.

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