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Sabri Alpaydin[a]; Mustafa Yilmaz[b]; Mustafa Ersoz[b]
[a] Department of Chemical Education, Faculty of Education, University of Selcuk, Meram, Konya, Turkey [b] Department of Chemistry, Faculty of Science, University of Selcuk, Kampus, Konya, Turkey

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Kinetic Study of Hg(II) Transport Through a Bulk Liquid Membrane Containing Ester Derivative of *bis*-Calix[4]arene

Sabri Alpaydin,[1,*] Mustafa Yilmaz,[2] and Mustafa Ersoz[2]

[1]Department of Chemical Education, Faculty of Education, University of Selcuk, Meram, Konya, Turkey
[2]Department of Chemistry, Faculty of Science, University of Selcuk, Kampus, Konya, Turkey

ABSTRACT

A kinetic study of Hg(II) transport from an aqueous donor solution into an aqueous acceptor solution through a bulk liquid membrane containing *N*,*N*′-*bis*[carbonylmethoxy(5,11,17,23-tetra-*tert*-butyl-25,26,27-*tris*-(ethoxycarbonyl-methoxy)calix(4)arenyl)]-1,2-diaminoethane as a carrier was studied. The kinetic parameters (k_{1d}, k_{2m}, k_{2a}, t_{max}, R_m^{max}, J_d^{max}, J_a^{max}) for the transport were investigated in terms of the effect of temperature, the stirring rate, the carrier concentration, and the type of solvent. In this study, the pseudo-first-order apparent rate constant of the interfacial transport of the Hg(II) is determined by using the

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[*] Correspondence: Sabri Alpaydin, Department of Chemical Education, Faculty of Education, University of Selcuk, Meram, Konya, Turkey; E-mail: salpaydin@selcuk.edu.tr.

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spectrophotometric method. The kinetics of the transport was analyzed in the formalism of two consecutive irreversible first-order reactions. The membrane entrance and exit rate constants were increased with increasing of temperature, stirring rate, and carrier concentration. The membrane entrance and exit rate constants depended on the type of solvent and was found to be in the order of $CH_2Cl_2 > CHCl_3 > CCl_4$. The activation energy values are calculated as 25.50 ± 2.20 and $45.62 \pm 4.38\,\mathrm{kJ\,mol^{-1}}$ for extraction and reextraction, respectively. The values of the calculated activation energy indicate that the process is diffusionally controlled by species.

Key Words: Bulk liquid membrane; Transport of mercury(II); Transport kinetics; Calixarene.

INTRODUCTION

With the expansion of industrial activities during this century, a large increase of heavy metal quantities has been observed in the environment. For this reason, laws were passed to regulate the emissions of these toxic compounds by industries. From that moment on, a great effort has been devoted to the development of recovery technologies, among others, from wastewater. In these liquid effluents, heavy metal concentrations are found in the ppm range; but, from a toxicological viewpoint, this is too high to authorize a direct dumping in the environment. The recovery of heavy metals from liquids is achieved by transfer processes, which can be divided into four groups: liquid–solid, liquid–liquid, membrane separation processes, and biological treatment. Liquid membranes have been found as the optimal solution of some toxicity metal ions from wastewater[1–10] because of their efficiency, selectivity, and economic advantages. Their efficiency is mainly due to the use of ionophores, which offer the advantage of enhancing both the efficiency (higher interfacial fluxes) and the selectivity of the separation process.

Mercury and its compounds are major toxic contaminants in wastewater and have been explored as being very important environmental and technological problems because of their direct effects on human health due to their widespread agricultural and industrial use throughout the world.[11] The transport of Hg(II) ions through liquid membranes containing a mobile carrier has been investigated by some researchers.[4–6,12,13] Particularly, selective removal of Hg(II) ions from wastewater is interesting. Hence, the development of new methods for the selective removal is a very important objective for environmental remediation. For this reason, a variety of calix[4]arene derivatives were prepared for the problem selective removal of Hg(II) ions from waste effluents.[14,15]

The aim of this study was to investigate the kinetic analysis and the effectiveness of ester derivative of *bis*-calix[4]arene (carrier 1 as presented in Fig. 1) as a selective carrier for Hg(II) ions transport through a liquid membrane. The kinetics of Hg(II) transport were analyzed at different temperatures ranges (298, 303, 308, and 313 ± 0.1 K), different stirring rates (150, 250, and 350 rpm), different concentration ranges (1×10^{-5}, 5×10^{-5}, and 1×10^{-4} M), and various solvents (CH_3Cl, CH_2Cl_2, and CCl_4), and are discussed in the form of two irreversible first-order reactions.

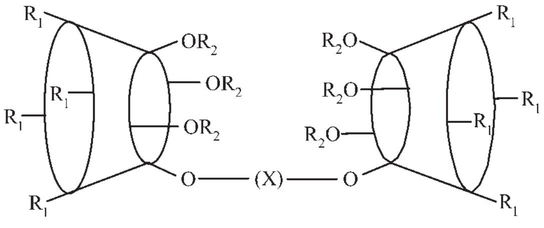
EXPERIMENTAL

Materials

The chemical reagents used in these experiments were mercury(II) nitrate, chloroform, dichloromethane, carbon tetrachloride, and picric acid (Merck Co., Darmstadt, Germany). The carrier 1 was synthesized according to a literature method.[16] Mercury(II) picrate solution was prepared by the addition of a 1×10^{-2} M mercury(II) nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and was shaken at 25°C for 1 hr. The aqueous solutions were prepared by using demineralized water.

Experimental Apparatus

A cylindrical glass cell (5.0 cm, i.d.) that holds a glass tube (3.5 cm, i.d.) vertically was used for all experiments, shown in Fig. 2. The cell was covered with aluminum foil to minimize evaporation and light exposure.



$R_2 = CH_2COOC_2H_5$
R_1 = tert-buthyl
$X = CH_2CONH(CH_2)_2NHCOCH_2$

Figure 1. The structure of ligand used as carrier 1.

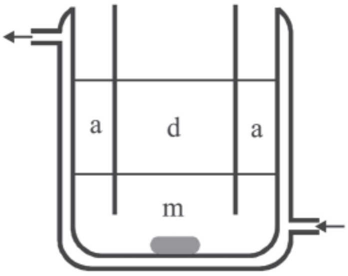


Figure 2. Schematic diagram of the apparatus for cotransport of the Hg(II): d, donor phase; a, acceptor phase; m, membrane phase.

The experiments were conducted by using a thermostated (Lauda MT 3 circulating thermostatic bath) apparatus. The membrane phase stirred by magnetic stirrer (Schott laboratory stirrer type SLR, Germany). A UV-VIS spectrophotometer (Schimadzu UV-160, Japan) was used for the determination of the Hg picrate concentration in the donor and acceptor phases at 376 nm.

Kinetic Procedures

The transport experiments were conducted by using the bulk liquid membrane apparatus presented in Fig. 2. The procedure for the preparation of samples was given in our previous works;[17] 1×10^{-2} M $Hg(NO_3)_2$ was dissolved in a 2.5×10^{-5} M solution of picric acid to convert all picric acid molecules to Hg^{2+} picrate species, and this sample was used as the donor phase. The membrane phase (50 mL), containing calixarene dissolved in organic solvent, was added to the bottom of a thermostated vessel with a 2.0-cm magnetic stirring bar inside. An open glass cylinder was inserted into the membrane. The acceptor phase, 40 mL of doubly distilled water, was placed outside the cylinder and the donor phase; 40 mL of aqueous mercury(II) picrate solution (2.5×10^{-5} M), was added very slowly to the inside. Samples were taken from both phases (donor and acceptor) at regular time intervals for a 10-hr period, and the mercury(II) picrate concentration was determined by ultra violet spectrophotometer at 376 nm. Each experimental result reported is the arithmetic mean for two independent samples and volume change by spectrophotometric method (error $<1\%$). All the measurements were carried out under exactly the same experimental conditions. Experiments were performed with no carrier present, indicating that no transport of mercury(II) picrate occurred. The consecutive kinetic equations for a transport system was used by applying a simple theoretical approach which is discussed in detail elsewhere.[12,13,17–20] The experiments were repeated at least three times.

The variation of the metal picrate concentration with time was directly measured in both the donor (C_d) and acceptor (C_a) phases. The corresponding variety of the molar quantity of Hg(II) in the membrane (n_m) was established from the material balance. The reduced dimensionless mole fractions are used for the practical point:

$$R_d = \frac{n_d}{n_{d0}} \quad R_m = \frac{n_m}{n_{d0}} \quad R_a = \frac{n_a}{n_{d0}} \tag{1}$$

where n_{d0} is the initial molar quantity of Hg(II) ions in the donor phase, while n_d, n_m, and n_a represent the molar quantity of Hg(II) ions in donor, membrane, and acceptor phase, respectively; R_d, R_m, and R_a represent the mole fraction of the Hg(II) ions in donor, membrane, and acceptor phase, respectively. The material balance can be expressed as $R_d + R_m + R_a = 1$. The results suggest that the kinetic behavior of the consecutive irreversible first-order reaction for Hg(II) ions transport can be described as follows:[20]

$$\mathrm{Hg(II)_d} \xrightarrow{k_1} \mathrm{Hg(II)_m} \xrightarrow{k_2} \mathrm{Hg(II)_a} \tag{2}$$

where k_1 and k_2 are the pseudo-first-order apparent rate constants of the membrane entrance and exit, respectively. The kinetic schema for Eq. (2) can be described by the following equations:

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

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

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

where J stands for flux. When $k_1 \neq k_2$, integrating Eqs. (3)–(5), gives:

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

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

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

where k_1 (k_{1d}) and k_2 (k_{2m}, k_{2a}) values are apparent membrane entrance and exit rate constants, respectively. The observed experimental results reveal that R_d vs. t yields a mono-exponentially decreasing curve, and R_a follows a monotonically increasing sigmoid-type curve, whereas, the time dependence of R_m present a maximum level. The actual numerical analysis was carried out by a nonlinear curve fitting. It should be mentioned that Eqs. (6)–(8) obtained here are mathematically identical to the kinetics equations given in Refs.[6,12,13]; however, the dimensionless parameters of R_d, R_m, and R_a here are defined in a molar ratio manner, rather than in a concentration–ratio manner as before,[6,12,13] and, thus, Eqs. (6)–(8) are also valid in the case of unequal volumes of d, m, and a phases.[19] Time dependence of dimensionless parameters of R_d, R_m, and R_a are defined in a molar ratio manner of Hg(II) ions in cotransport through liquid membrane with 5×10^{-5} M of carrier 1 in $CHCl_3$ at 298 K and 250 rpm are given in Fig. 3.

The maximum values of R_m (when $dR_m/dt = 0$) and t_{max} may be written as follows:

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

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

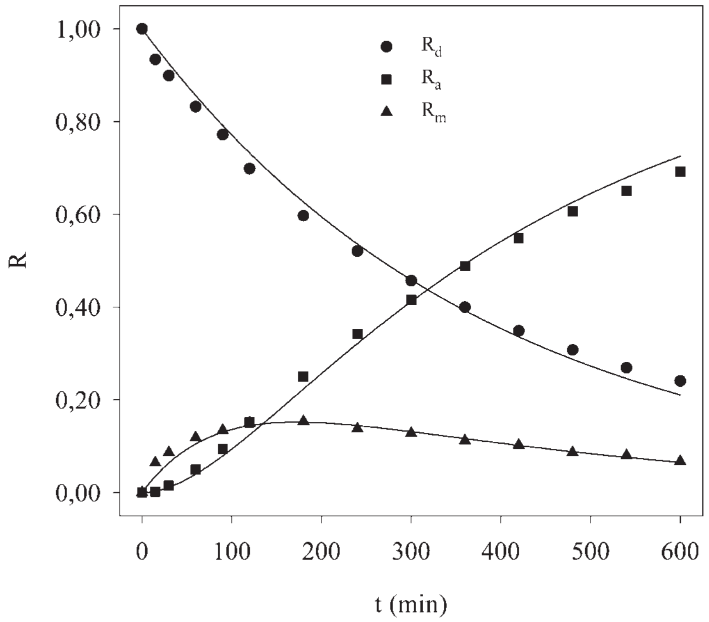


Figure 3. Time dependence of R_d, R_m, and R_a for transport of Hg(II). Membrane: 5×10^{-5} M of carrier 1 in $CHCl_3$ (298 K and 250 rpm). Theoretical curves calculated from Eqs. (6)–(8).

By considering the first-order time differentiation of Eqs. (6)–(8) at $t = t_{\max}$, one obtains:

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

$$\left.\frac{dR_{\mathrm{m}}}{dt}\right|_{\max} = 0 \tag{12}$$

$$\left.\frac{dR_{\mathrm{a}}}{dt}\right|_{\max} = -k_2\left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_{\mathrm{a}}^{\max} \tag{13}$$

We see that at $t = t_{\max}$, the system is in steady state, because the concentration of Hg(II) ions in the membrane does not vary with time [Eq. (12)]. Because the maximum entrance ($J_{\mathrm{d}}^{\max}$) and exit ($J_{\mathrm{a}}^{\max}$) fluxes are equal but having opposite signs:

$$-J_{\mathrm{d}}^{\max} = J_{\mathrm{a}}^{\max} \tag{14}$$

The actual numerical analysis was carried out by nonlinear curve fitting by using Sigma-Plot software program. The $k_{1\mathrm{d}}$ was obtained from Eq. (6) by using the donor phase data, while the $k_{2\mathrm{a}}$ may be obtained either directly from the acceptor phase data by using Eq. (8) or indirectly from the membrane phase data calculated ($k_{2\mathrm{m}}$) on the basis of Eq. (7). In both cases, the $k_{1\mathrm{d}}$ value, obtained from Eq. (6) was used in the calculations. The activation energy values were obtained from the Arrhenius equation by using the $k_{1\mathrm{d}}$ and $k_{2\mathrm{a}}$ values at different temperature.

$$\ln(k) = \ln(A) - \frac{E_{\mathrm{a}}}{RT} \tag{15}$$

RESULTS AND DISCUSSION

In a previous work,[16] it was found that carrier 1 has the desired ability of selective extraction of Hg(II). This satisfactory result was inspired to investigate the transport of Hg(II) by carrier 1 as a bulk liquid membrane and the kinetic behavior of the transport process as a function of the temperature, stirring rate, carrier concentration, and the type of solvent.

It is well known that 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 of diffusion steps and complexations/decomplexation reactions at two independent and possible different interfaces.

Effect of Carrier Concentration in Membrane on Transport of Hg(II) Ions

The transport experiments were carried out at three different initial carrier 1 concentrations 1×10^{-5}, 5×10^{-5}, and 1×10^{-4} M in $CHCl_3$ at 298 K and 250 rpm. The obtained kinetic parameters for the effect of concentration of carrier 1 are presented in Table 1. It was found that the initial carrier concentration influences the kinetic constants, as well as flux values, in full agreement with previously obtained results.[6,12,17] It is quite clear that the concentrations of carrier 1 in the organic phase have a great effect on the transport of Hg(II) and confirmed with R_m values, which is in fairly good agreement with the theoretical curves and experimental points, as presented in Fig. 4. All the curves, at three concentration of carrier 1, the highest transport efficiency was obtained with 1×10^{-4} M. It can be seen that, both kinetic constants k_{1d} and k_{2a} or fluxes are dependent on the carrier concentration and increases steadily with the initial carrier concentration, as shown in Fig. 5. It had been reported that in uncontrolled conditions, k_{1d} increases with increasing carrier concentration, showing small and fractional exponent value.[21] This obviously can be assumed from Eqs. (6)–(8) that the reduced dimensionless concentration is related with the carrier concentration. Based on the results, the carrier concentration was taken as 5×10^{-5} M for examining the effect of stirring rate, solvent type, and temperature.

In addition, a blank experiment was performed with no present carrier in the membrane. No detectable movement of the Hg(II) ions through the liquid membrane was found in the blank experiment, suggesting that the transport of the Hg(II) ions through the liquid membrane is fulfilled by the carrier.

Effect of Stirring Rate on Transport of Hg(II) Ions

To achieve effective Hg(II) transport, it is necessary to explore the effect of stirring speed on the transport process. In the present investigation, the stirring rate of the membrane phase was carried out at three different stirring rate, 150, 250, and 350 rpm at 298 K when the carrier 1 concentration was 5×10^{-5} M in $CHCl_3$. The results are presented in Table 2 and Fig. 6, indicate that the stirring rate affects the transport rate of Hg(II) through the liquid membrane. Comparing the rate constant parameters, k_{2a} rapidly increases with

Table 1. The kinetic parameters for transport of Hg(II) ions at different carrier 1 concentrations in $CHCl_3$ (298 K and 250 rpm).

Concentration (M)	$k_{1d} \times 10^3$ (min^{-1})	$k_{2a} \times 10^3$ (min^{-1})	$k_{2m} \times 10^3$ (min^{-1})	t_{max} (min)	R_{max}	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})
1×10^{-5}	2.12 ± 0.13	9.86 ± 0.40	10.01 ± 0.32	198.59	0.141	−1.39	1.39
5×10^{-5}	2.60 ± 0.16	11.07 ± 0.63	10.92 ± 0.37	171.04	0.151	−1.67	1.67
1×10^{-4}	3.17 ± 0.17	12.15 ± 0.53	11.88 ± 0.26	149.62	0.168	−1.97	1.97

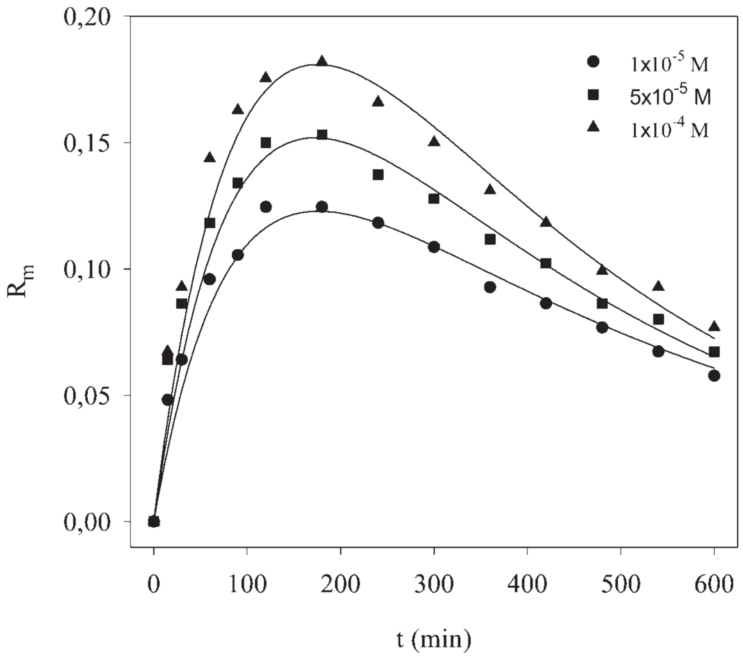


Figure 4. Time dependence of R_m for transport of Hg(II) at different carrier 1 concentration in $CHCl_3$ (298 K and 250 rpm).

increasing of stirring rate, while k_{1d} slowly increases. It was reported that the parameters, k_{1d} and k_{2a} increase with stirring speed at lower stirring speeds between 200 and 600 rpm.[22] There is an agreement with this literature, and the stirring speed was taken as 150–350 rpm. Meanwhile, R_{max} decreases with an increase of stirring rate.

Effect of Solvent on Transport of Hg(II) Ions

The effect of solvent on the transport of Hg(II) ions through the liquid membrane containing 5×10^{-5} M of carrier 1 was examined in $CHCl_3$, CH_2Cl_2, and CCl_4 at 298 K and 250 rpm. The logarithmic extraction constant of the carrier was determined as 3.05 in $CHCl_2$[16] for the carrier, which showed an effective extractant for Hg(II) ion. It also was decided to conduct experiments under the same conditions to study how different solvents affect the transport, as the nature of the solvents system passing through the liquid membranes also may have a great influence on the

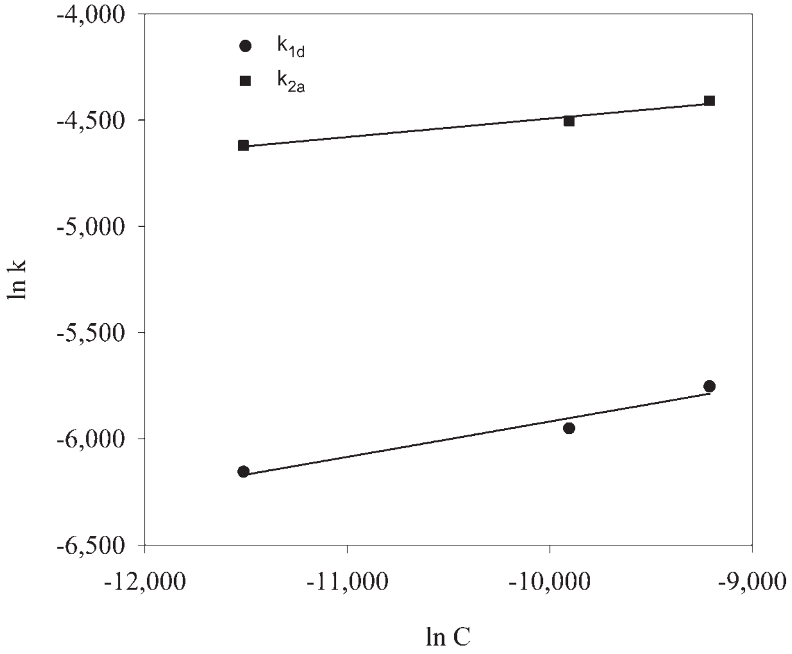


Figure 5. Concentration dependence of k_{1a} and k_{2d} for transport of Hg(II) (298 K and 250 rpm in $CHCl_3$).

efficiency of ion transport. The results are shown in Table 3, indicating that the solvent affects the transport rate of Hg(II) through the liquid membrane. As can be seen, the membrane entrance and exit rate constants, as well as the flux values, are found to vary in the order $CH_2Cl_2 > CHCl_3 > CCl_4$. The result is in good agreement with the previously published works.[6,12,23,24]

Effect of Temperature on Transport of Hg(II) Ions

The effect of temperature on the transport of Hg(II) ions through the liquid membrane containing 5×10^{-5} M of carrier 1 in $CHCl_3$ was examined at 298, 303, 308, and 313 K (250 rpm). The experimental results are collected in Table 4. It is quite obvious that k_{1d} and k_{2a} increases with an increase in the temperature. Table 4 also shows that t_{max} and R_{max} decreases with an increase of temperature. Figure 3 indicates the time dependence of the dimensionless parameters of R_d, R_m, and R_a at 298 K of Hg(II) transported in the donor,

Table 2. The kinetic parameters for transport of Hg(II) ions at different stirring rates in $CHCl_3$ (298 K and 250 rpm).

Stirring rate (rpm)	$k_{1d} \times 10^3$ (min^{-1})	$k_{2a} \times 10^3$ (min^{-1})	$k_{2m} \times 10^3$ (min^{-1})	t_{max} (min)	R_{max}	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})
150	1.99 ± 0.11	5.76 ± 0.18	5.93 ± 0.20	281.91	0.197	−1.14	1.14
250	2.60 ± 0.16	11.07 ± 0.63	10.92 ± 0.37	171.04	0.151	−1.67	1.67
350	2.95 ± 0.19	15.37 ± 1.02	14.56 ± 0.42	132.90	0.130	−1.99	1.99

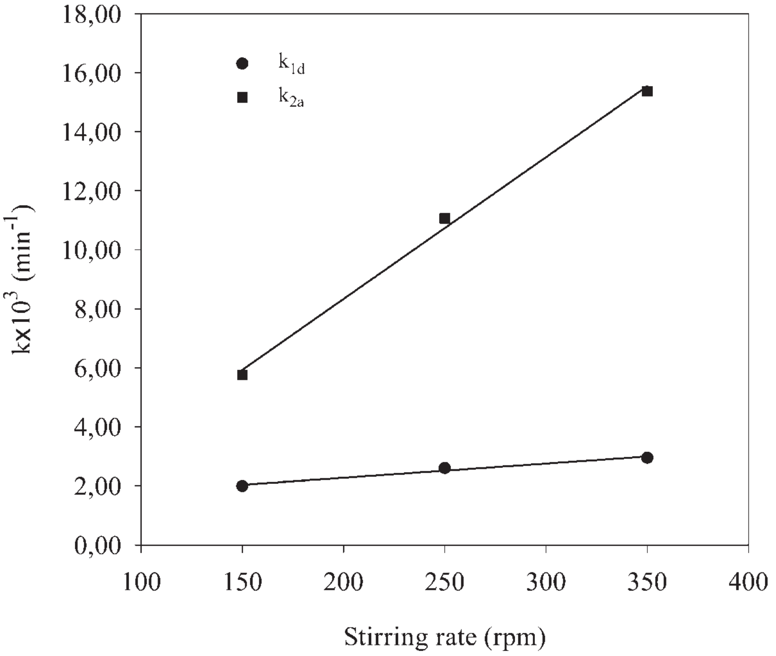


Figure 6. Stirring rate dependence of k_{1d} and k_{2a} for transport of Hg(II) $CHCl_3$ (298 K and 5 × 10^{-5} M of carrier 1 in $CHCl_3$).

membrane, and acceptor phases, respectively. Good agreement between the theoretical curves and the experimental points is shown in Fig. 3. The results suggest that the transport of the Hg(II) ions could be described by the kinetics laws of two consecutive irreversible first-order reactions in the present case. An Arrhenius-type plot is followed perfectly in Fig. 7. The activation energy values are 25.50 ± 2.20 and 45.62 ± 4.38 kJ mol^{-1} for extraction and reextraction, respectively.

CONCLUSION

The results show that the Hg(II) can be effectively transported through a liquid membrane containing *N,N′*-*bis*[carbonylmethoxy(5,11,17,23-tetra-*tert*-butyl-25,26,27-*tris*-(ethoxycarbonyl-methoxy)calix(4)arenyl)]-1,2-diaminoethane as a carrier from the aqueous solution. The investigation focused on factors influencing the Hg(II) transport, which depends on the nature of solvent,

Table 3. The kinetic parameters for transport of Hg(II) ions at 5×10^{-5} M of carrier 1 in different solvents (298 K and 250 rpm).

Solvent	$k_{1d} \times 10^3$ (min^{-1})	$k_{2a} \times 10^3$ (min^{-1})	$k_{2m} \times 10^3$ (min^{-1})	t_{max} (min)	R_{max}	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})
CH_2Cl_2	6.94 ± 0.14	16.71 ± 0.18	15.92 ± 0.52	89.94	0.222	−3.72	3.72
$CHCl_3$	2.60 ± 0.16	11.07 ± 0.63	10.92 ± 0.37	171.04	0.151	−1.67	1.67
CH_4	0.52 ± 0.14	2.23 ± 0.05	2.11 ± 0.35	835.30	0.146	−0.34	0.34

Table 4. The kinetic parameters for transport of Hg(II) ions at different temperatures, 5 × 10^{-5} M of carrier 1 in $CHCl_3$ (298 K and 250 rpm).

Temperature (K)	$k_{1d} \times 10^3$ ($\min^{-1}$)	$k_{2a} \times 10^3$ ($\min^{-1}$)	$k_{2m} \times 10^3$ ($\min^{-1}$)	t_{max} (min)	R_{max}	$J_d^{max} \times 10^3$ ($\min^{-1}$)	$J_a^{max} \times 10^3$ ($\min^{-1}$)
298	2.60 ± 0.16	11.07 ± 0.63	10.92 ± 0.37	171.04	0.151	−1.67	1.67
303	3.03 ± 0.17	16.77 ± 1.12	15.89 ± 0.59	124.53	0.124	−2.08	2.08
308	3.77 ± 0.11	22.22 ± 2.73	21.41 ± 0.87	96.15	0.118	−2.62	2.62
313	4.18 ± 0.17	27.70 ± 2.07	28.44 ± 0.74	80.40	0.108	−2.99	2.99

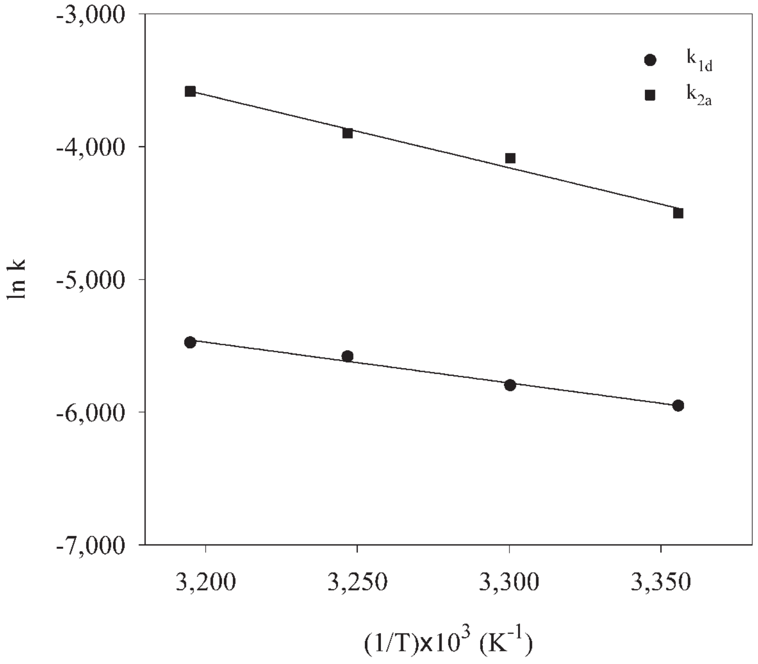


Figure 7. Arrhenius plots for transport of Hg(II) in liquid membrane. Membrane: 5×10^{-5} M of carrier 1 in $CHCl_3$ at 250 rpm.

carrier concentration, stirring rate, and temperature. The two consecutive irreversible first-order apparent rate constants, k_{1d}, k_{2m}, k_{2a}, and the flux values J_d^{max}, J_a^{max}, and also the activation energy values of interfacial transport of extraction and reextraction have been determined.

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