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Liquid Membrane Transport of Hg(II) by an Azocalix[4]arene Derivative

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Abstract: A kinetic study of Hg(II) transport from an aqueous donor solution into an aqueous acceptor solution through a liquid membrane containing 25,26,27–tribenzoyloxy-28-hydroxy-5,11,17,23-tetra-(4-*n*-butylphenylazo)calix[4]arene ***1*** as a carrier was studied. The kinetic parameters (k_1, k_2, $R_m^{\max}$, $t_{\max}$, $J_d^{\max}$, $J_a^{\max}$) for the transport were investigated in terms of the effect of temperature, the stirring rate, the carrier concentration, and the type of solvent. The kinetics of transport was analyzed in the formalism of two consecutive irreversible first-order reactions. The membrane entrance rate, and exit rate constants were increased with increasing of temperature stirring rate, and carrier concentration. The membrane entrance rate and exit rate constants depended on the type of solvent and was found to be in order of $CH_2Cl_2 >$ $CHCl_3 >$ CCl_4. The activation energy values are calculated as 30.67 ± 2.64 and $57.33 \pm 4.90\,kj\,mol^{-1}$ for extraction and reextraction, respectively. The values of calculated activation energy indicate that the process is diffusionally controlled by species.

Keywords: Liquid membrane, transport kinetics, transport of mercury(II), calixarenes

INTRODUCTION

Nowadays heavy metals are among the most important pollutants in source and treated water and are becoming a severe public health problem. Industrial and municipal wastewaters frequently contain metal ions. Industrial waste constitutes the major source of various kinds of metal pollution in natural

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water (1). 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 waste water (2–12).

It is important that macromolecular compounds such as crown ethers, cryptands and calixarenes are used as carrier on transport processes in liquid membranes. Crown ether, (13, 14) a well-known class of macrocyclic compounds has been used for the selective transport of alkali metal ions. Another class of macrocyclic compounds, known as calixarenes, is of recent interest as selective extractants for metal ions. There are a few works, related the separation of Hg^{2+} ions in liquid membranes the using calixarenes as carrier (15–18).

According to our other works, it was firstly used on calixarene azo derivative as carrier in liquid membrane transport studies. Besides our other previous works, the effect of carrier concentration in membrane on the transport of Hg(II) ions was investigated in this study (4, 15, 16).

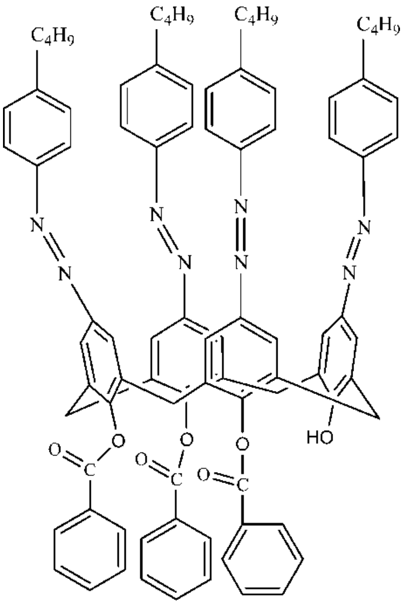
Mercury is a hazardous environmental contaminant. In Japan, 2252 people have been affected and 1043 have died due to Minamata disease for the past two decades, caused by elevated mercury pollution from a chemical plant (19). The transport of Hg(II) ions through liquid membranes containing a mobile carrier has been investigated by some researchers (20–24, 20–24). 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.

The aim of this study was to investigate the kinetic analysis and the effectiveness of azo derivative of calix[4]arene (carrier ***1*** as presented in Fig. 1). The kinetics of Hg(II) transport were analyzed at different temperatures ranges (293, 298, 303, and 308 K), different stirring rates (200, 300, 400 rpm), different concentration ranges (1×10^{-5}, 1×10^{-4}, and 1×10^{-3} M), and various solvents ($CHCl_3$, CH_2Cl_2, and CCl_4), and are discussed in the form two irreversible first order reactions.

EXPERIMENTAL

Materials

The chemical reagents used in these experiments were mercury(II) nitrate, dichloromethane, chloroform, carbontetrachloride, and picric acid (Merck products). The carrier ***1*** was synthesized according to a literature method (25). 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 hour. The aqueous solutions were prepared using demineralised water.



(1)

Figure 1. The structure of azocalix[4]arene derivative used as carrier.

Kinetic Procedure

Co-transport experiments were carried out in a U-type cell inserted inside a thermostated (Grand mark, model W14) apparatus (Fig. 2). 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 of them. Both surface areas were 2.5 cm^2. The organic phase was stirred at variable speeds magnetically (Chiltern mark, model HS 31).

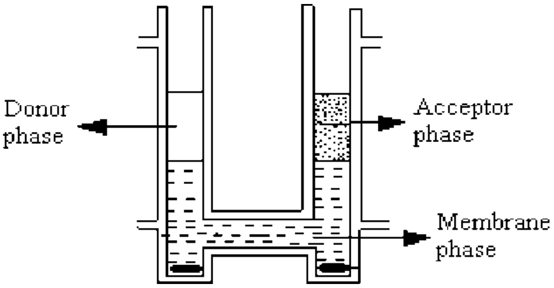


Figure 2. Schematic diagram of the apparatus for co-transport of the Hg(II).

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*** in the organic phase. The acceptor phase consisted of doubly distilled water. The pH of acceptor phase adjusted to 9 by ammonia-ammonium chloride buffer. 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. The spectrophotometric measurements were performed by means of an UV-Vis Spectrometer Shimadzu 160A. 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 (15, 17, 18, 26–29). 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. 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 reason, the dimensionless reduced concentrations were used:

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

where C_{d0} is the initial Hg(II) ion concentration in the donor phase, while C_d, C_m, and C_a represents the Hg^{2+} ion 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. When $k_1 \neq k_2$, integrating eqs. (3)–(5), gives:

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

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

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

where k_1 and k_2 are the apparent membrane entrance and exit rate constants, respectively. The kinetic parameters k_1 and k_2 were obtained by fitting eqs. (6)–(8) to this data. As an example, the variation of the reduced concentration of Hg(II) ion through the liquid membrane with 1×10^{-3} M of carrier ***1*** in $CHCl_3$ at 300 rpm and 25°C is presented in Fig. 3. The observed experimental results reveal 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 values of R_m (when $dR_m/dt = 0$) and t_{max} may be written as follows:

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

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

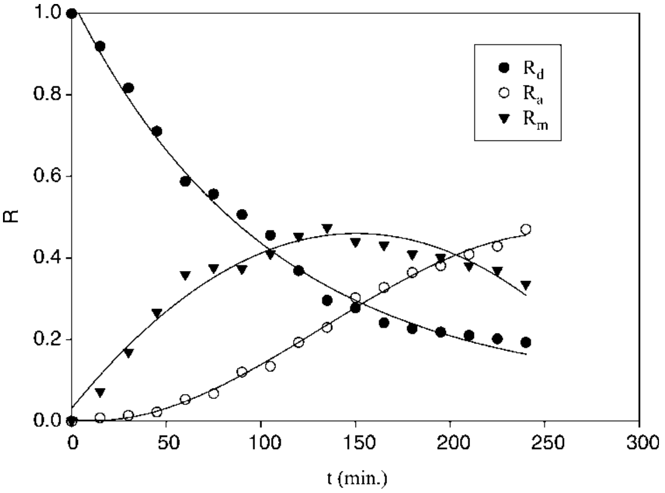


Figure 3. Time dependence of R_d, R_m, and R_a for transport of Hg(II). Membrane: 1×10^{-3} M of carrier ***1*** in $CHCl_3$ (298 K and 300 rpm). Theoretical curves calculated from eqs. (6)–(8).

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

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

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

$$\left.\frac{dR_a}{dt}\right|_{\max} = k_2\left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_a^{\max} \tag{13}$$

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_d^{max}) and exit (J_a^{max}) fluxes are equal but having opposite signs:

$$-J_d^{max} = J_a^{max} \tag{14}$$

The actual numeric analysis was carried out by nonlinear curve fitting by using Sigma-Plot software program. The kinetic parameters k_1 and k_2 were obtained by fitting eqs. (6)–(8) to this data. The activation energy values were obtained from the Arrhenius equation by using the k_1 and k_2 values at different temperature.

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \tag{15}$$

RESULTS AND DISCUSSION

In our previous reports, (4, 15, 16, 18) the transport of Hg(II) ions from aqueous phase was carried out by using derivatives of calix[4]arenes as the carrier. In this work, the transport of Hg(II) ion by derivative of azo calix[4]-arene in the liquid membrane was studied and the kinetic behavior of the transport process as a function of concentration, temperature, stirring rate, and solvents was investigated.

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}, 1×10^{-4}, and 1×10^{-3} M in $CHCl_3$ at 298 K and 300 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

Table 1. The kinetic parameters for Hg(II) ions at different carrier ***1*** concentrations in $CHCl_3$ (298 K and 300 rpm)

Concentration (M)	$k_1 \times 10^3$ (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})
1×10^{-5}	4.64	3.87	0.39	237.00	−1.51	1.51
1×10^{-4}	6.19	4.38	0.43	191.11	−1.90	1.90
1×10^{-3}	9.10	5.17	0.48	143.85	−2.46	2.46

full agreement with previously obtained results(4, 15–18). It can be seen that, both kinetic constants k_1 and k_2 or fluxes are dependent on the carrier concentration and increases steadily with the initial carrier concentration, as shown in Fig. 4. It had been reported that in controlled conditions, k_1 increases with increasing carrier concentration, showing small and fractional exponent value(7). This obviously can be assumed from eqs. (6)–(8) that the reduced dimensionless concentration is related with the carrier concentration.

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 Hg(II) ions through the liquid membrane is fulfilled by the carrier.

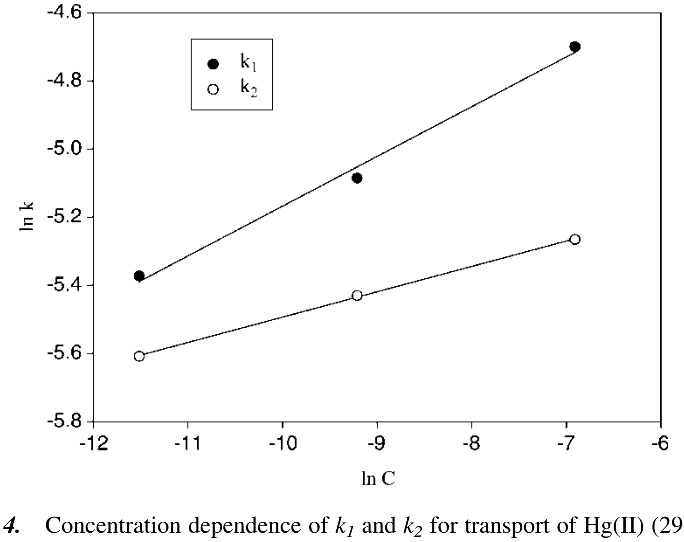


Figure 4. Concentration dependence of k_1 and k_2 for transport of Hg(II) (298 K and 300 rpm in $CHCl_3$).

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 1×10^{-3} M of carrier ***1*** in $CHCl_3$ was examined at 293, 298, 303, and 308 K (300 rpm). The experimental results are collected in Table 2. It is quite obvious that k_1 and k_2 increases with an increase in the temperature. Table 2 also shows that t_{max} and R_m^{max} decreases with an increase of temperature. The variation of Hg(II) concentration in the acceptor phase with time is given in Fig. 5 for different values of temperature. The numerical analysis of Hg(II) transport was solved to compare with the experimental results (R_a values) by using non-linear curve fitting as shown by the dashed lines in Fig. 4; there is fairly good agreement between the theoretical curves and the experimental points. It is clearly seen that the highest transport efficiency was reached at 308 K. The results suggest that the transport of the Hg(II) ions could be described by the kinetic laws of two consecutive irreversible first-order reactions in the present case. An Arrhenius-type plot is followed perfectly in Fig. 6. The activation energy values are 30.67 ± 2.64 and $57.33 \pm 4.90\,\mathrm{kj\,mol^{-1}}$ for extraction and reextraction, respectively. Founded the activation energy values results, were agree with our previous studies (30). It was pointed out the activation energies of diffusion-controlled processes are lower than 20 kcal/mol. The calculated activation energy values for carrier ***1*** show that the transport of Hg(II) ion is diffusion-controlled processes.

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, 200, 300, and 400 rpm at 298 K when the carrier ***1*** concentration was 1×10^{-3} M in $CHCl_3$. The results are presented in Table 3 and Fig. 7, indicate that the stirring rate affects the transport rate of Hg(II) through the liquid membrane. According to these results, the flux

Table 2. The kinetic parameters of Hg(II) transport using carrier ***1*** at different temperatures (stirring rate is 300 rpm; solvent is $CHCl_3$)

Temperature (K)	$k_1 \times 10^3$ (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})
293	6.95	3.50	0.50	198.94	−1.74	1.74
298	9.10	5.17	0.48	143.85	−2.46	2.46
303	11.08	7.68	0.44	107.80	−3.36	3.36
308	12.67	10.61	0.40	86.14	−4.25	4.25

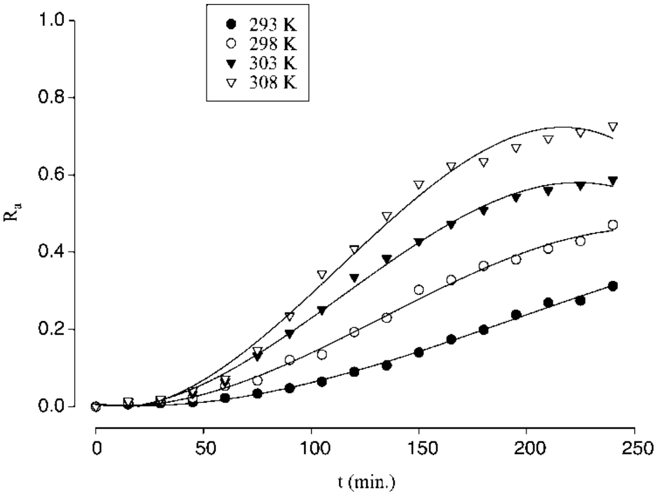


Figure 5. Time variation of reduced concentrations of Hg^{2+} in the acceptor phase during co-transport through liquid membrane using of azocalix[4]arene derivative ***1*** at different temperatures at a stirring rate of 300 rpm. (The symbols represents the experimental points, the lines are obtained from the curve-fitting program).

increases with increasing stirring rate due to decrease of the thickness of the diffusion boundary layers at both interfaces of the membrane. As shown in Fig. 7, the membrane entrance (k_1) and exit (k_2) rate constants increased by rising stirring rate.

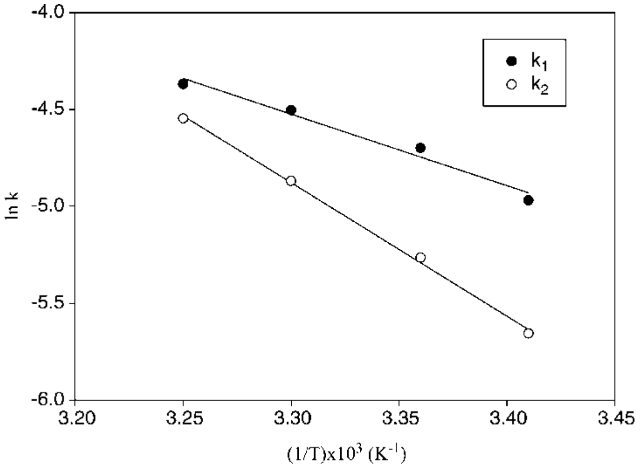


Figure 6. Arrhenius plots for transport of Hg(II) in liquid membrane. Membrane: 1×10^{-3} M of carrier 1 in $CHCl_3$ at 300 rpm.

Table 3. The kinetic parameters of Hg(II) transport using carrier ***1*** at different stirring rates (T = 298 K; solvent is $CHCl_3$)

Stirring rate (rpm)	$k_1 \times 10^3$ (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})
200	6.62	3.77	0.47	197.61	−1.79	1.79
300	9.10	5.17	0.48	143.85	−2.46	2.46
400	11.39	6.00	0.49	118.92	−2.93	2.93

Effect of Solvent on Transport of Hg(II) Ions

The present work was to investigate the physicochemical approach to co-transport of Hg(II) transport through a liquid membrane containing carrier *1*. 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 4, 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 8. This shows that the R_a values are strongly affected by the membrane solvent system, and the higher transport efficiency was observed with CH_2Cl_2 solvent. From this observation, the results are consistent with the literature (15–18), in which the efficiency of CH_2Cl_2, with

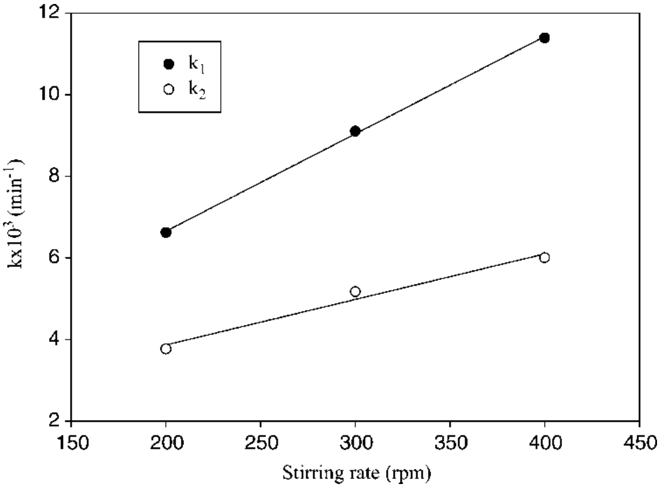


Figure 7. Stirring rate dependence of k_1 and k_2 for transport of Hg(II) (298 K and 1×10^{-3} M of carrier ***1*** in $CHCl_3$).

Table 4. The kinetic parameters for Hg(II) transport using carrier **1** when different solvents are used (298 K and 300 rpm)

Solvent	$k_1 \times 10^3$ (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})
CH_2Cl_2	14.25	5.21	0.56	111.35	−2.92	2.92
$CHCl_3$	9.10	5.17	0.48	143.85	−2.46	2.46
CCl_4	4.20	4.17	0.37	238.95	−1.54	1.54

respect to the R_a values, was higher than $CHCl_3$ 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

The kinetics of transport of Hg(II) ions through bulk liquid membrane using azocalix[4]arene derivative *1* as a carrier was examined at different carrier concentrations, different temperatures, different stirring rates and different solvents. The results show that the Hg(II) can be effectively transported through

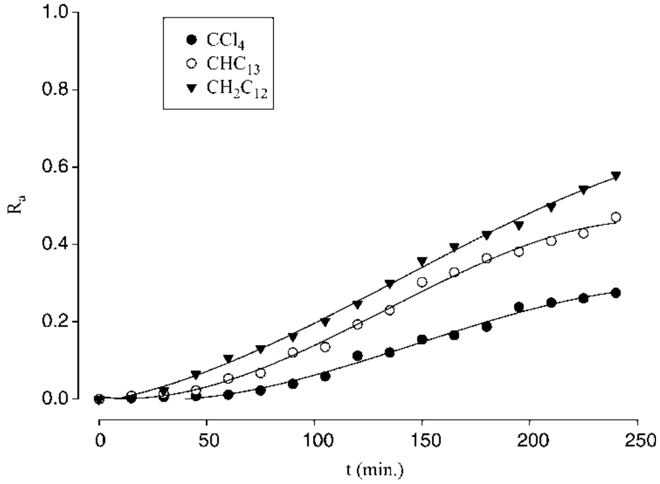


Figure 8. Time variation of reduced concentrations of Hg^{2+} in the acceptor phase during co-transport through liquid membrane using of azocalix[4]arene derivative *1* in different solvents at a stirring rate of 300 rpm. (The symbols represents the experimental points, the lines are obtained from the curve-fitting program).

a liquid membrane containing 25,26,27–tribenzoyloxy-28-hydroxy-5,11,17,23-tetra-(4-*n*-butylphenylazo)calix[4]arene as a carrier from the aqueous solution. The two consecutive irreversible first-order apparent rate constants, k_1, k_2 and the flux values J_d^{max}, J_a^{max}, and also activation energy values of interfacial transport of extraction and reextraction have been determined.

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