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Bulk Liquid Membrane Transport of Hg(II) by a Crown Ether Derivative

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A kinetic study of Hg(II) transport from an aqueous donor solution into an aqueous acceptor solution through a liquid membrane containing 4′-nitrobenzo [15-cown-5] (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, stirring rate, and carrier concentration. 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 the temperature stirring rate, and carrier concentration. The activation energy values are calculated as 20.33 ± 2.10 and 115.90 ± 10.5 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), crown ether

Introduction

The use of liquid membranes containing a carrier has been proposed as an alternative to solvent extraction processes for the selective separation and concentration of metals from dilute aqueous solutions. In liquid membrane technology, the extraction, stripping and regeneration operations are combined in a single stage (1, 2).

Generally, there are three ways to realize liquid membrane processes: bulk liquid membrane, emulsion liquid membrane and supported liquid membrane. The advantages of bulk liquid membranes are their simplicity and the availability of constant mass transfer area. As a result, these membranes find their use in small-scale operations and are a popular choice in applications that are in developmental stages (3).

Synthesis macrocyles have been known for over 75 years, although a real spate of publications in this area occurred in the 1960's (4). During this period, more than ten thousand macrocylic compounds were reported, and since then their number has increased markedly from year to year (5). Crown ethers have been found to be powerful extracting agents for alkali metal salts (6). They are also accepted to be model compounds to mimic antibiotics in cation transport through lipid membranes (7).

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Also, crown ether derivatives were used in metal cation transport through liquid membranes (8–10). The addition of crown ether substituents to various coordination compounds causes an increase in their solubility in common organic solvents and in water (11).

The aim of this study was to investigate the kinetic analysis and the effectiveness of derivative of crown ether (carrier **1** as presented in Figure 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), and different concentration ranges (1×10^{-5}, 1×10^{-4}, and 1×10^{-3} M), and are discussed in the form two irreversible first order reactions.

Experimental

Materials

The chemical reagents used in these experiments were mercury (II) nitrate (Merck), chloroform (Merck) and picric acid, (Merck). The carrier **1** was synthesized according to a literature method (12). 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 dematerialized water.

Kinetic Procedure

Transport experiments were carried out using our previous method with a U-type cell (13–15).

Results and Discussion

In our previous reports (13–15), 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 crown ether in the liquid membrane was studied and the kinetic behavior of the transport process as a function of concentration, temperature, and stirring rates was investigated.

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.

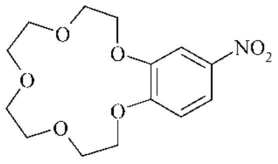

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Figure 1. The structure of crown ether derivative used as carrier.

For practical reasons, 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 parameters of k_1 and k_2 from the obtained data were calculated by fitting equations as described in the literature (13–15). The kinetic scheme for consecutive reaction systems was described in detail in previous work (13–15).

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 Figure 2. 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.

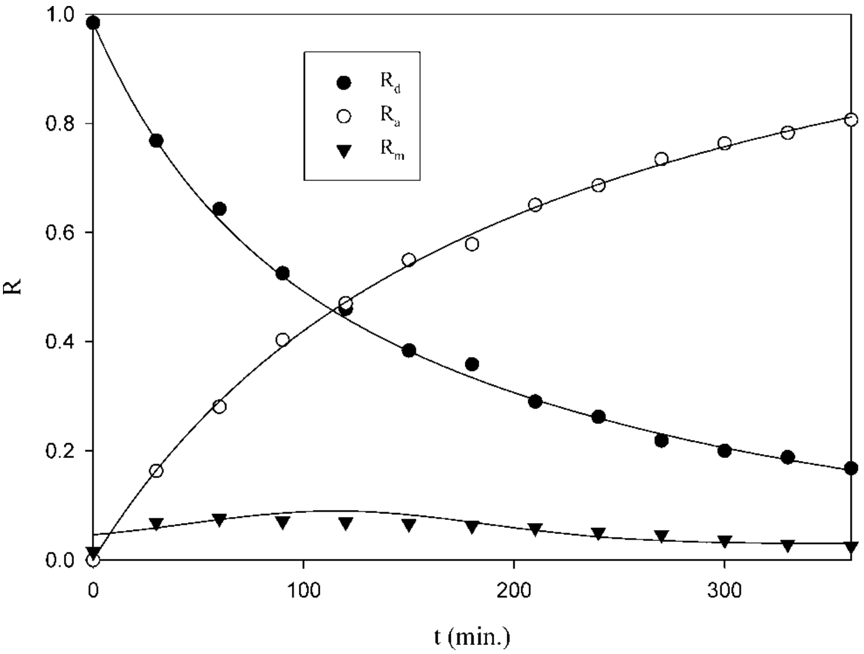

Figure 2. Time dependence of R_d, R_m, and R_a for transport of Hg(II). Membrane: 1×10^{-3} M of carrier **1** in $CHCl_3$ (298 K and 300 rpm). (The symbols represents the experimental points, the lines are obtained from the curve-fitting program).

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})	$k_2 \times 10^2$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max} \times 10^3$ (min^{-1})	$J_a^{max} \times 10^3$ (min^{-1})
1×10^{-5}	4.05	2.16	0.13	95.46	−2.75	2.75
1×10^{-4}	4.87	2.33	0.09	56.84	−3.69	3.69
1×10^{-3}	6.09	6.38	0.07	40.73	−4.75	4.75

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 full agreement with previously obtained results (13–15). 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 Figure 3. It had been reported that in controlled conditions, k_1 increases with increasing carrier concentration, showing small and fractional exponent value (16). This obviously can be assumed that the reduced dimensionless concentration is related with the carrier concentration.

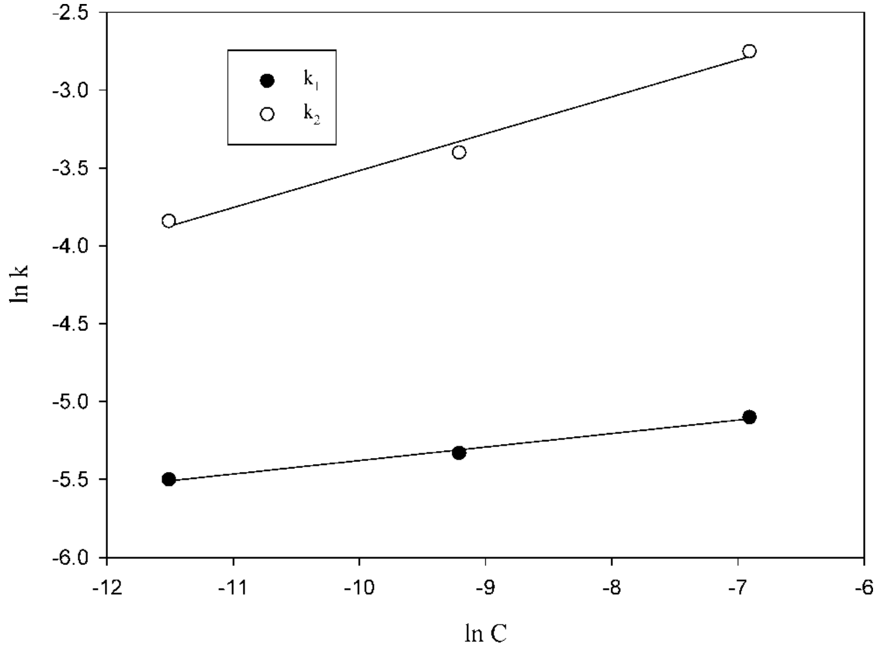

Figure 3. Concentration dependence of k_1 and k_2 for transport of Hg(II) (298 K and 300 rpm in $CHCl_3$).

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})	$k_2 \times 10^2$ (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	4.74	2.55	0.13	81.17	−3.22	3.22
298	6.09	6.38	0.07	40.73	−4.75	4.75
303	6.41	14.15	0.04	22.90	−5.53	5.53
308	7.17	22.72	0.03	15.70	−6.40	6.40

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.

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

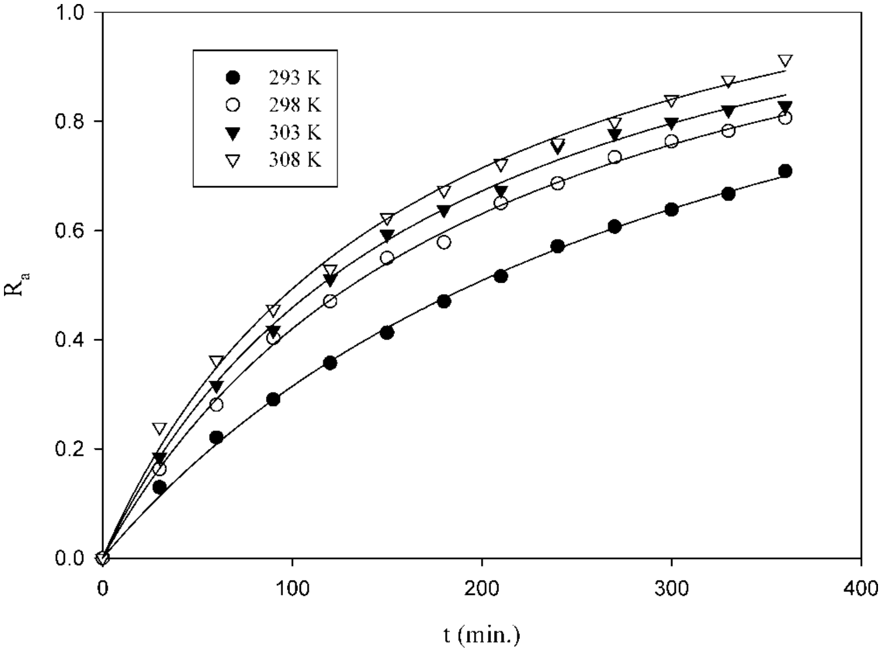

Figure 4. Time variation of reduced concentrations of Hg^{2+} in the acceptor phase during co-transport through liquid membrane using of crown ether derivative **1** at different temperatures at a stirring rate of 300 rpm. (The symbols represents the experimental points, the lines are obtained from the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

(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 Figure 4 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 Figure 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.

The activation energy values were obtained from the Arrhenius equation by using the k_1 and k_2 values at different temperature.

$$ln(k) = ln(A) - \frac{E_a}{RT} \tag{3}$$

An Arrhenius-type plot is followed perfectly in Figure 5. The activation energy values are 20.33 ± 2.10 and 115.90 ± 10.5 kj mol^{-1} for extraction and reextraction, respectively.

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

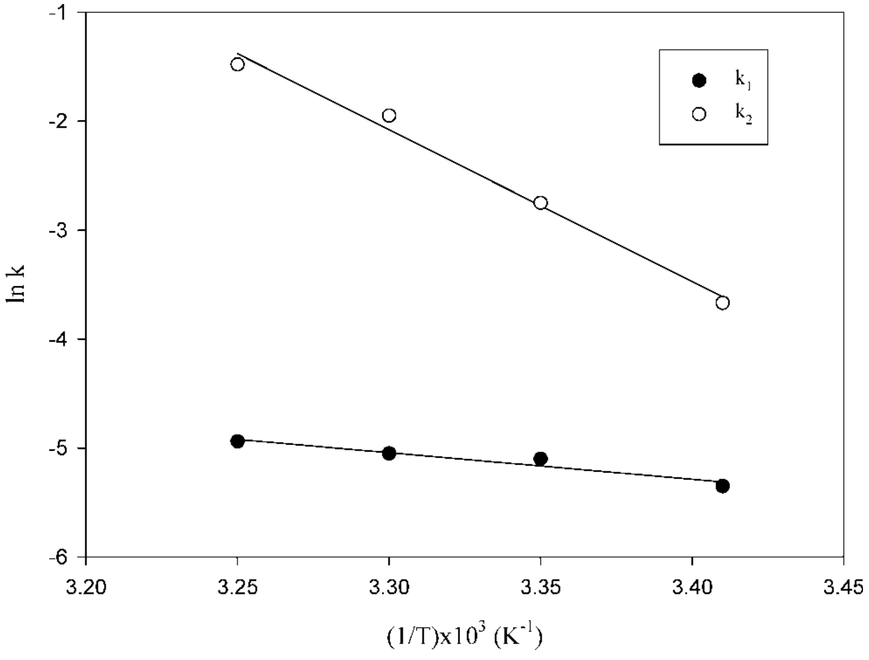

Figure 5. Arrhenius plots for transport of Hg(II) in liquid membrane. Membrane: 1×10^{-3} M of carrier **1** in $CHCl_3$ at 300 rpm.

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})	$k_2 \times 10^2$ (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	4.01	3.63	0.08	68.29	−3.05	3.05
300	6.09	6.38	0.07	40.73	−4.75	4.75
400	7.91	10.05	0.06	27.46	−6.36	6.36

phase was carried out at three different stirring rates, 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 Figure 6, and indicate that the stirring rate affects the transport rate of Hg(II) through the liquid membrane. As shown in Figure 6, the membrane entrance (k_1) and exit (k_2) rate constants increased by the rising stirring rate.

Conclusions

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

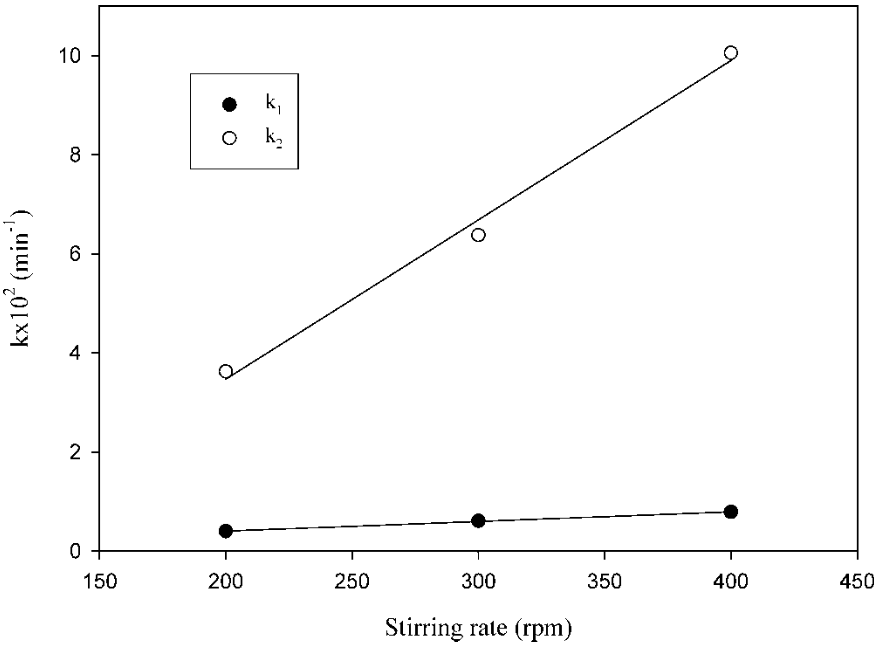

Figure 6. Stirring rate dependence of k_1 and k_2 for transport of Hg(II) (298 K and 1×10^{-3} M of carrier **1** in $CHCl_3$).

transported through a liquid membrane containing 4′-nitrobenzo [15-cown-5] 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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