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Transport Kinetics of Hg^{2+} Through Bulk Liquid Membrane Using Calix[4]arene Ketone Derivative as Carrier

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ABSTRACT

In this article, calix[4]arene ketone derivative 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 influence of temperature, the 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 temperature and stirring rate and found to be dependent on the solvent type in the order $CH_2Cl_2 >$ $CHCl_3 > CCl_4$.

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The activation energy was obtained as 5.28 kcal/mol from the slope of the Arrhenius plot for the case of maximum membrane exit flux, J_a^{max}. This value indicates that the process is controlled by species diffusion.

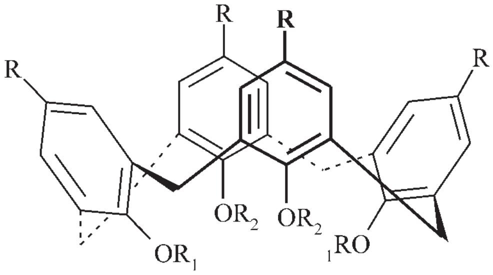
Key Words: Liquid membrane; Transport kinetics; Temperature effects; Diffusional rate-determining step; Calixarenes.

INTRODUCTION

Liquid membranes play an attractive role in separation science.[1] Their efficiency and economic advantages designate them as the optimal solution of some important problems, such as precious metal recovery particularly for permselective applications, toxic product (metals, organic molecules) elimination from wastewaters, etc. Of the three types of liquid membranes, namely, bulk (BLM), supported (SLM), and emulsion (ELM), SLM and ELM have more potential for use in industrial applications, whereas BLM is useful on a laboratory scale to evaluate new means of improving the efficiency of separation processes.[2] Although many carriers on the transport of alkali and alkaline earth metal ions through the BLM have been reported so far,[2–5] relatively few carriers have been reported for the selective and efficient transport of transition or heavy-metal ions.[6–8] Calix[*n*]arenes have been made in the design and synthesis of artificial receptors for cations, anions, and neutral organic molecules.[9–14] Various applications of calixarenes refer to purification, chromatography, catalysis, enzyme mimics, ion selective electrodes, phase transfer, transport across membranes, ion channels, and self-assembling monolayers.[15–18]

As known, the assay of mercury and its compounds has been of special interest because of their widespread agricultural and industrial use and also their hazardous effects on human health.[19] Particularly selective removal of Hg^{2+} ions is interesting from environmental remediation. In spite of the great potential of membrane transport for selective removal, a few studies for removal of Hg^{2+} have been reported.[20–26] From this point of view, a variety of calix[4]arene derivatives were synthesized for selective extraction of Hg^{2+} ions from the waste effluents.[27–29]

We report here an investigation of co-transport of Hg^{2+} ion through liquid membranes. Diacetonyloxy-5,11,17,23-tetra-*tert*-butyl-26,28-dihydroxycalix[4]arene is the carrier ligand (as presented in Fig. 1), which was synthesized according to method.[30] The kinetics of Hg^{2+} ion transport was analyzed at different temperatures as well as at different stirring rates in various solvents.



R = tert-butyl; $R_1 = CH_2COCH_3, R_2 = H$

Figure 1. The structure of ligand used as carrier.

EXPERIMENTAL

Materials

The chemical reagents were analytical grade, mercury(II) nitrate dichloromethane, chloroform, CCl_4, and picric acid obtained from Merck Co. (Darmstadt, Germany). 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 hr. The aqueous solutions were prepared using demineralized water.

Kinetic Procedure

Co-transport experiments were preformed using a thermostated (Grand mark, model W14, Grants Instruments, Cambridge, England) apparatus. Transport experiments were carried out in a conventional U-type cell. An organic solution (20 mL) containing the carrier was placed in the bottom of the cell and two aqueous solutions (donor and acceptor, 10 mL each) were carefully added on top of the organic solution. Both surface areas were $2.5\,cm^2$. The organic phase was magnetically stirred at variable speeds (Chiltern mark, model HS 31).

The procedure for the preparation of samples was given in the literature;[31] 1×10^{-2} M $Hg(NO_3)_2$ was dissolved in 2.5×10^{-5} M solution of picric acid in order to convert all picric acid molecules to Hg^{2+}-picrate species, and this sample was used as the donor phase. The membrane phase consists of the carrier (10^{-3} M), which was dissolved in the organic solution.

The acceptor phase consisted of doubly distilled water. Preliminary experiments with only picric acid in the source phase were performed to control the transport of picric acid using identical conditions, indicating no picric acid transport. Samples from both water phases (acceptor and donor phases) were taken at various time intervals. The picrate ion concentration in both phases was determined by a spectrophotometric (Shimadzu 160 A Model Spectrofotometer) method.[32] The concentration of Hg^{2+} was also determined to confirm the carried-through liquid membrane, by atomic absorption spectrophotometer (AAS); nearly the same results were observed as before. Each experimental result reported is the arithmetic mean of two independent measurements.

RESULTS AND DISCUSSIONS

In our previous reports,[25,26] the selective transport of Hg^{2+} ions from aqueous phase was carried out by using nitrile derivatives of calix[4]arenes as the carrier. In this work, the transport of Hg^{2+} ion by calix[4]arene ketone derivative in the BLM was studied and the kinetic behavior of the transport process as a function of temperature, stirring rate, and solvents was investigated. A simple theoretical approach was used to obtain the consecutive kinetic equations for a BLM transport system, which was discussed in details.[25,26]

The variation of picrate ion concentration with time was determined for both donor (C_d) and acceptor phases (C_a). If corresponding change of picrate ion concentration in the membrane phase was not directly determined, it was calculated from the material balance between the phases. In general, the dimensionless reduced concentrations are useful for practical reason, thus they are represented as follows:

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

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

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

where k_1 and k_2 are the apparent membrane entrance and exit rate constants, respectively. The kinetic scheme for consecutive reaction systems was described in detail in previous works.[25,26,33]

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 500–800 rpm. The kinetic parameters of k_1 and k_2 from the obtained data were calculated by fitting equations as described in the literature,[25,26,33] and the data for $CHCl_3$ solvent are presented in Tables 1 and 2. Time variation of the reduced concentration of Hg^{2+} ion for $CHCl_3$ solvent at 500 rpm and 25°C is illustrated in Fig. 2, in which R_d decreases exponentially accompanied by a simultaneous increase of R_a, whereas R_m presents as maximum at intermediate times. The maximum R_m values for all experimental conditions studied were found to be between 0.3 and 0.7, as given in Tables 1–4. This clearly indicates that the membrane phase plays a role in the transport. The other important factor is that the t_{max} values were also decreased upon increasing the temperature and the stirring rates.

The final value of R_d after 600 min of reaction time is expressed with R_d^{fin}. Then, permeability degree ($R_p = 1 – R_d^{fin}$) values can be obtained and are given in Table 3 for different temperatures. It should be emphasized that R_p must be as high as possible in order to have a correct analysis. The case $R_p = 1$ shows that the numerical analysis which applies to experimental values with very

Table 1. The kinetic parameters of Hg^{2+} transport using carrier at different temperatures (stirring rate is 500 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)	$J_d^{max} \times 10^4$ (min^{-1})	$J_a^{max} \times 10^4$ (min^{-1})
293	2.15	1.07	0.51	664.40	−5.16	5.16
298	2.16	1.59	0.42	537.50	−6.05	6.05
303	2.17	1.86	0.40	497.63	−7.37	7.37
308	2.18	2.10	0.37	468.97	−7.86	7.86

Table 2. The kinetic parameters of Hg^{2+} transport using the carrier 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)	$J_d^{max} \times 10^4$ (min^{-1})	$J_a^{max} \times 10^4$ (min^{-1})
500	2.16	1.59	0.42	537.50	−6.05	6.05
650	2.18	2.63	0.33	417.01	−8.78	8.78
800	2.19	2.94	0.32	392.59	−9.27	9.27

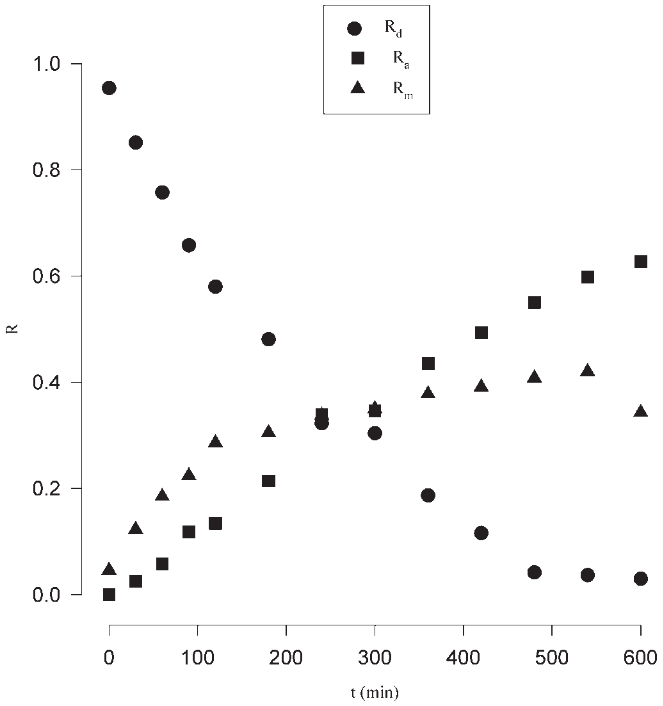


Figure 2. The changes of reduced concentrations of Hg^{2+} ion with time in co-transport through liquid membrane ($T = 298 \pm 0.1$ K, solvent is $CHCl_3$).

small standard errors. As can be seen from Table 3, greater value for R_p (0.99) was obtained. This is verified by a good correlation between experimental and theoretical data.

The effect of temperature on the co-transport of Hg^{2+} is presented in Fig. 3. It is seen that the reduced concentration of Hg^{2+} in the acceptor phase

Table 3. Distribution of Hg^{2+} ion in donor, membrane, and acceptor phases in co-transport ($t = 600$ min; solvent is $CHCl_3$; stirring rate is 500 rpm).

T (K)	R_d	R_m	R_a	R_p
293	0.17	0.37	0.46	0.83
298	0.03	0.34	0.63	0.97
303	0.02	0.31	0.67	0.98
308	0.01	0.22	0.77	0.99

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Table 4. The kinetic parameters for Hg^{2+} transport using carrier (1) when different solvents are used ($T = 298$ K; stirring rate is 500 rpm).

Solvent	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max} \times 10^4$ (min^{-1})	$J_a^{max} \times 10^4$ (min^{-1})
CH_2Cl_2	2.17	1.92	0.39	489.61	−7.49	7.49
$CHCl_3$	2.16	1.59	0.42	537.50	−6.05	6.05
CCl_4	2.09	0.44	0.66	944.33	−2.90	2.90

with time increases exponentially, particularly at higher temperature. In other words, transport efficiency was higher at higher temperatures and higher stirring rates. Comparing the experimental results for R_a values with the theoretical curves, the numeric analysis was solved by using of nonlinear curve-fitting program, as shown by the dashed lines in Fig. 3. It is seen from Fig. 3 that there is good agreement between the theoretical curves and the experimental points. As a result, when temperature and stirring rate were

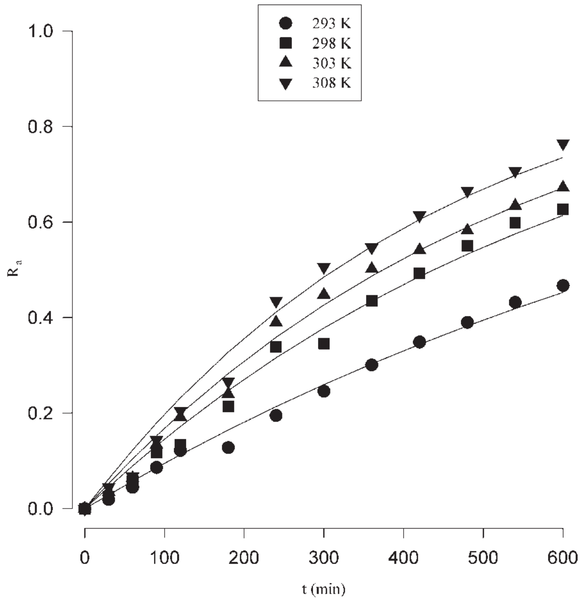

Figure 3. The changes of reduced concentrations of Hg^{2+} in the acceptor phase with time during co-transport through liquid membrane using of calix[4]arene ketone derivative at different temperatures at a stirring rate of 500 rpm. (The symbols represent the experimental points, the lines are obtained from the curve-fitting program.)

increased, $R_{\mathrm{m}}^{\max}$ increased somewhat, while $t_{\max}$ decreased. This suggests that the Hg^{2+} ions are rapidly complexed with the ligand carrier. Moreover, the kinetic parameters, membrane entrance (k_1) and exit (k_2) rate constants, also increase with increasing temperature as well as stirring rate. It was pointed out that the temperature and stirring effects are mainly exerted on the maximum complexation and decomplexation between Hg^{2+} picrate and ligand carrier at the aqueous–organic interfaces.[25]

The activation energy of co-transport of Hg^{2+} in the BLM systems was obtained by plotting the maximum membrane exit flux ($J_{\mathrm{a}}^{\max}$) values vs. $(1/T)$ at 500 rpm, by using Eq. (3). The activation energy of Hg^{2+} was calculated as 5.28 kcal/mol from the slope of the curve, as presented in Fig. 4.

$$\ln(J) = \ln(A) - \frac{E_{\mathrm{a}}}{R}\left(\frac{1}{T}\right) \tag{3}$$

As known, activation energy values are quite low for diffusion-controlled processes, whose rate constants are strongly affected by temperature. Comparing the E_{a} values of diffusion-controlled processes and chemically

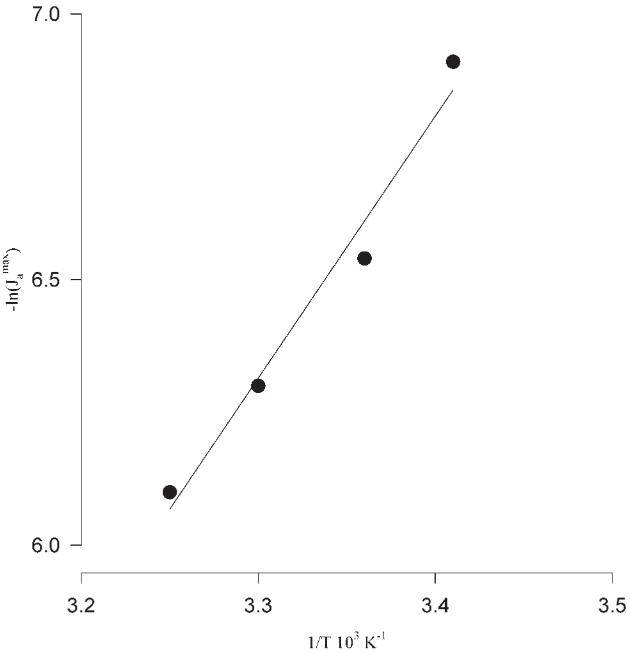

Figure 4. Arrhenius plot of Hg^{2+} ion transport at $J_{\mathrm{a}}^{\max}$.

controlled processes, the values of diffusion-controlled processes are always lower. It was pointed out that the activation energies of diffusion-controlled processes are lower than 10 kcal/mol.[34] This states that the transport of Hg^{2+} ion is a diffusion-controlled process.

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 ketone derivative 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 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 Fig. 5. 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,[35] in which the efficiency of

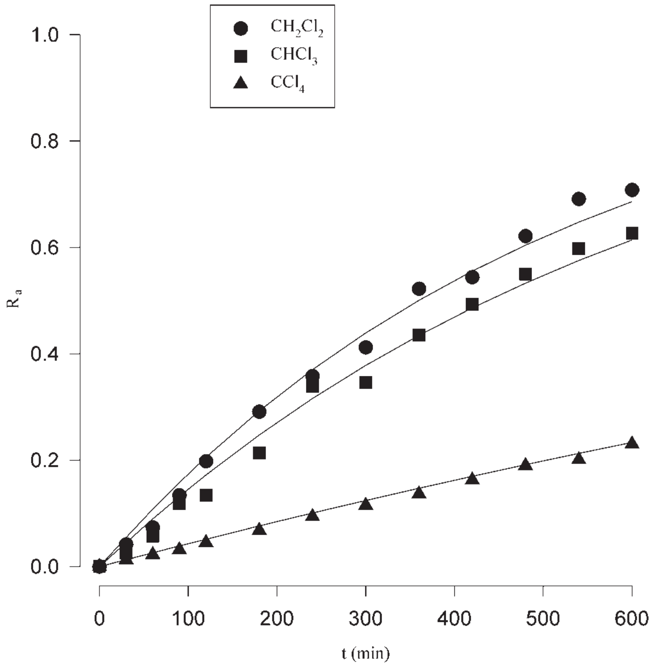

Figure 5. The changes of reduced concentrations of Hg^{2+} in the acceptor phase with time during co-transport through liquid membrane using of calix[4]arene ketone derivative in different solvents at a stirring rate of 500 rpm. (The symbols represent the experimental points, the lines are obtained from the curve-fitting program.)

dichloromethane 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 solvent are one of the main factors in establishing transport efficiency.

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