

Transport of Hg^{2+} through bulk liquid membrane using a bis-calix[4]arene nitrile derivative as carrier: kinetic analysis

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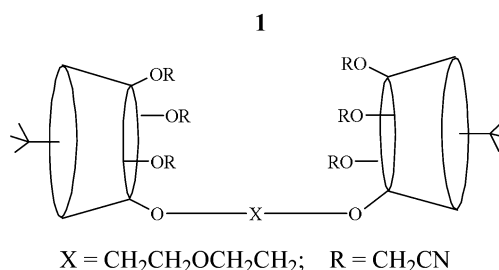
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The transport of $\text{Hg}(\text{II})$ ions from an aqueous solution into an aqueous receiving solution through a bulk liquid membrane containing a bis-calix[4]arene nitrile derivative (**1**) as a carrier was examined. The kinetic parameters were analyzed assuming two consecutive, irreversible first-order reactions. The influence of temperature, the solvent and stirring rate on the kinetic parameters (k_1 , k_2 , R_m^{\max} , t_{\max} , J_d^{\max} , J_a^{\max}) has also been investigated. The membrane entrance rate, k_1 , and the membrane exit rate, k_2 , increased with increasing temperature and stirring rate. The membrane entrance and exit rate constants are found to vary in the order $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$. For the maximum membrane exit flux, J_a^{\max} , the activation energy was found from the slope of the linear Arrhenius relationship to be $9.95 \text{ kcal mol}^{-1}$, which indicates that the process is controlled by species diffusion.

Hg^{2+} ions in waste water 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 waste water is one of great importance. The use of liquid membranes in metal 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 liquid membrane and to release them readily on the acceptor phase side. The transport of $\text{Hg}(\text{II})$ ions through liquid membranes containing a mobile carrier has been investigated by some researchers.^{1,2}

It is well known that the assay of mercury and its compounds is of special interest because of their widespread agricultural and industrial use throughout the world and also for their hazardous effects on human health.³ Hence, the development of new methods for the selective removal of Hg^{2+} ions for environmental remediation is a very important objective. However, despite the great potential of membrane transport for selective removal, there are only a few reports on membrane transport studies in liquid membranes.^{4–7} In recent years, we have been involved in the synthesis of calixarenes for selective removal of toxic metals especially $\text{Hg}(\text{II})$ ions from the aqueous phase. For this reason, a variety of calix[4]arene derivatives was prepared for the problem of selective extraction of $\text{Hg}(\text{II})$ ions from waste effluents.^{8–10}

In the present study on the co-transport of Hg^{2+} ion through liquid membranes, 2,2'-bis[5,11,17,23-tetra-*tert*-butyl-26,27,28-tris(cyanomethoxy)calix[4]arene] diethyl ether (**1**) was used as the carrier ligand. The carrier was synthesized according to the literature method⁸ and used to examine various parameters that are responsible for the transport of $\text{Hg}(\text{II})$ ions from donor solutions to 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 (Merck), dichloromethane (Merck), chloroform (Merck), CCl_4 (Merck) and picric acid, (Merck). Mercury(II) picrate solution was prepared by the addition of a $1 \times 10^{-2} \text{ M}$ mercury(II) nitrate solution to a $2.5 \times 10^{-5} \text{ M}$ aqueous picric acid solution and shaken at 25°C for 1 h. The aqueous solutions were prepared using demineralized water.

Kinetic procedures

Co-transport experiments were conducted using a thermostated (Grand model W14) apparatus. Transport experiments were carried out in a U-shaped 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 stirred at variable speeds magnetically (Chiltern model HS 31).

The initial phases consisted of the donor phase, which was an aqueous mercury(II) picrate ($2.5 \times 10^{-5} \text{ M}$) solution, while the membrane phase was made up by dissolving the carrier **1** ($C_{\text{carrier}} = 10^{-4} \text{ M}$) 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.¹¹ Each experimental result reported is the arithmetic mean of two independent measurements.

Results and discussion

In earlier reports^{12,13} the nitrile derivatives of calix[4]arenes have been found to transport Hg^{2+} ions selectively from the aqueous phase. In this work we have investigated the transport of Hg^{2+} ion by carrier **1** in the bulk liquid membrane and the kinetic behavior of the transport process as a function of temperature, stirring rate and solvent.

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 detail elsewhere.^{14–18}

In the experiments, the variation of picrate ion concentration with time was directly measured in both the donor (C_d) and acceptor (C_a) phases. The corresponding change of picrate ion concentration in the membrane phase was determined from the material balance between the phases. The concentration of Hg^{2+} in the membrane is half of the picrate concentration. For practical reason, the following dimensionless reduced concentrations were used:

$$R_d = \frac{C_d}{C_{d0}} \quad R_m = \frac{2C_m}{C_{d0}} \quad R_a = \frac{C_a}{C_{d0}} \quad (1)$$

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. The material balance with respect to the reduced concentrations can be expressed as $R_d + R_m + R_a = 1$. From these expressions, the kinetic behavior of the consecutive irreversible first-order reactions can be described as follows:



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:

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \quad (3)$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \quad (4)$$

$$\frac{dR_a}{dt} = k_2 R_m = J_a \quad (5)$$

where J represents the flux. Integration of eqns. (3)–(5), assuming that $k_1 \neq k_2$, leads to the differential equations given as follows:

$$R_d = \exp(-k_1 t) \quad (6)$$

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

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

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

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

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

which by considering the first-order time differentiation of eqns. (6)–(8) leads to the following forms:

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

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

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

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

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 [eqn. (13)]. Consequently, the entrance and exit fluxes are equal and have opposite signs.

Co-transport of Hg^{2+} ion through a liquid membrane with carrier **1** 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 k_1 and k_2 were obtained by fitting eqns. (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 at 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 500 rpm and 25 °C is presented in Fig. 1. 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 0.3 and 0.4. This shows that the membrane phase has an effect on the transport. It is also seen that the t_{\max} values decreased upon increasing the temperature and the stirring rates. It is immediately obvious that the extraction of Hg^{2+} from the donor phase into the organic

Table 1 The kinetic parameters of $\text{Hg}(\text{II})$ transport using carrier **1** at different temperatures (stirring rate is 500 rpm; solvent is CHCl_3)

	Temperature/K			
	293	298	303	308
$10^3 k_1/\text{min}^{-1}$	2.3	3.8	5.4	6.0
$10^3 k_2/\text{min}^{-1}$	3.1	3.72	4.32	6.34
R_m^{\max}	0.32	0.37	0.41	0.36
t_{\max}/min	373.1	266.1	206.6	162.1
$10^3 J_d^{\max}/\text{min}^{-1}$	−0.97	−1.38	−1.77	−2.28
$10^3 J_a^{\max}/\text{min}^{-1}$	0.97	1.38	1.77	2.28

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

	Stirring rate/rpm		
	500	650	800
$10^3 k_1/\text{min}^{-1}$	3.8	6.8	12.0
$10^3 k_2/\text{min}^{-1}$	3.72	7.3	9.28
R_m^{\max}	0.37	0.36	0.42
t_{\max}/min	266.1	142.0	94.5
$10^3 J_d^{\max}/\text{min}^{-1}$	−1.38	−2.59	−3.9
$10^3 J_a^{\max}/\text{min}^{-1}$	1.38	2.59	3.9

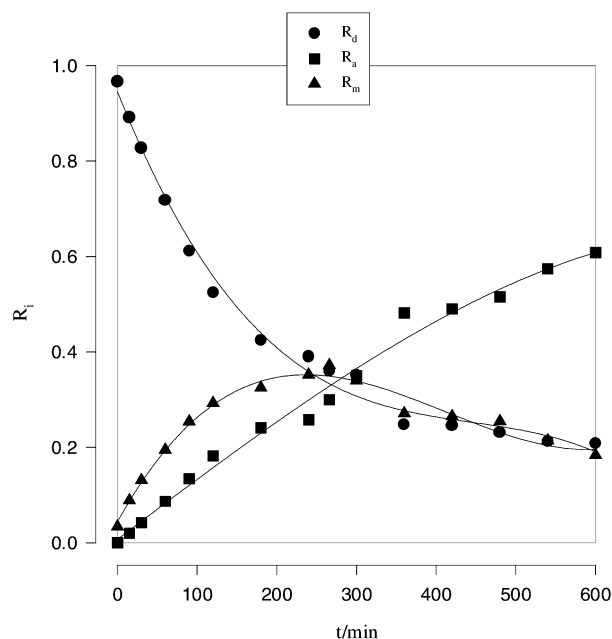


Fig. 1 Time variation of reduced concentrations of Hg^{2+} ion in co-transport through a liquid membrane ($T = 298 \pm 0.1$ K, solvent is CHCl_3).

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

The variation of Hg^{2+} concentration in the acceptor phase with time is given in Fig. 2 for different values of T . The numerical analysis of Hg^{2+} 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. 2; there is fairly good agreement between the theoretical curves and the experimental points. It is clearly seen that the highest transport

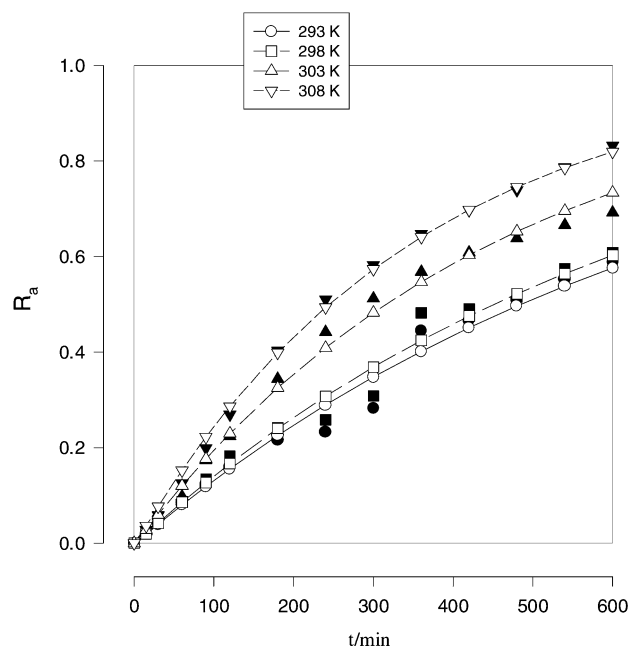


Fig. 2 Time variation of reduced concentrations of Hg^{2+} in the acceptor phase during co-transport through a liquid membrane using the bis-calix[4]arene nitrile derivative **1** at different temperatures at a stirring rate of 500 rpm. (The open symbols represent the experimental data and the filled symbols have been obtained from the curve-fitting program.)

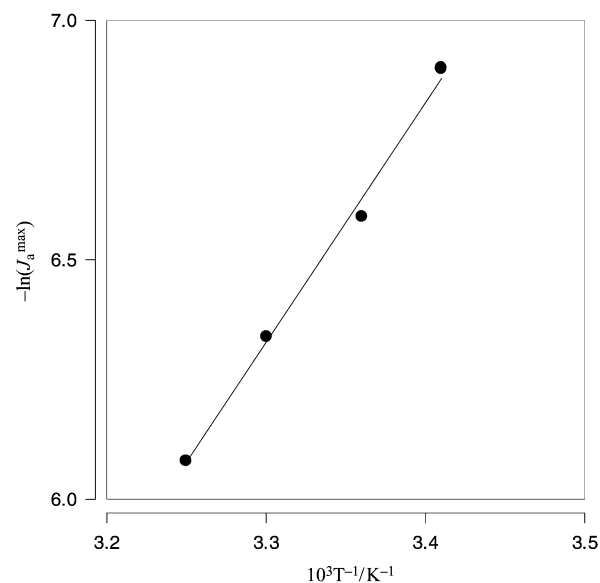


Fig. 3 Arrhenius plot of Hg^{2+} ion transport at J_a^{\max} .

efficiency was reached at 308 K and 800 rpm stirring rate, with the transport efficiency decreasing as these parameters decreased. As T and stirring rate are increased, R_m^{\max} increases somewhat while 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. It is expected 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. On the other hand, the maximum membrane entrance exit fluxes takes place in the reaction zones of ionic interfaces.

The activation energy was calculated from a plot of the maximum membrane exit flux (J_a^{\max}) versus T^{-1} at 500 rpm, as presented in Fig. 3.

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

The activation energy for carrier **1** in the liquid membrane was found to be $9.95 \text{ kcal mol}^{-1}$. 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. It was pointed out that the activation energies of diffusion-controlled processes are lower than 10 kcal mol^{-1} .¹⁹ The calculated activation energy for carrier **1** shows that the transport of Hg^{2+} ion is a diffusion-controlled process.

The present work was initiated with the aim of using a physicochemical approach to Hg^{2+} ion transport through a liquid membrane containing carrier **1**. It was decided to also

Table 3 The kinetic parameters for $\text{Hg}(\text{II})$ transport using carrier **1** when different solvents are used ($T = 298$ K; stirring rate 500 rpm)

	Solvent		
	CH_2Cl_2	CHCl_3	CCl_4
$10^3 k_1/\text{min}^{-1}$	5.9	3.8	0.5
$10^3 k_2/\text{min}^{-1}$	5.62	3.72	0.52
R_m^{\max}	0.38	0.37	0.36
t_{\max}/min	173.6	266.1	1961
$10^3 J_d^{\max}/\text{min}^{-1}$	−2.14	−1.38	−0.19
$10^3 J_a^{\max}/\text{min}^{-1}$	2.14	1.38	0.19

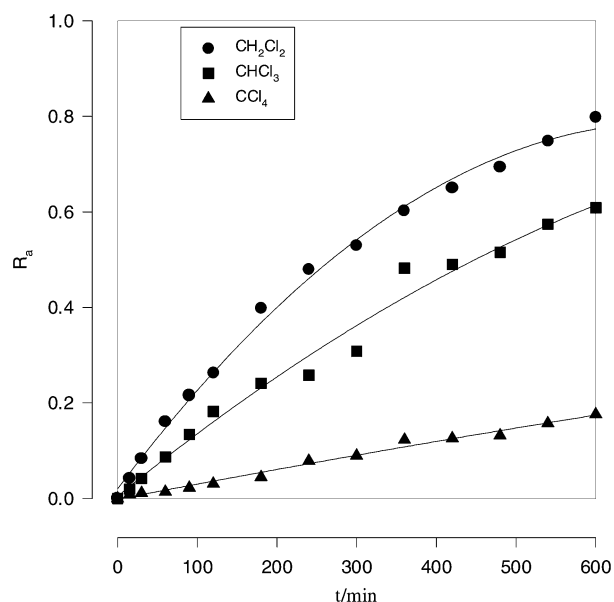


Fig. 4 Time variation of reduced concentrations of Hg^{2+} in the acceptor phase during co-transport through a liquid membrane using the bis-calix[4]arene nitrile derivative **1** in different solvents at a stirring rate of 500 rpm. (The symbols represent the experimental points, the lines are obtained from the curve-fitting program [eqn. (8)]. $T = 298 \pm 0.1 \text{ K}$.)

conduct experiments under the same conditions to study how different solvents affect the transport, as the nature of the solvent system passing through the liquid membranes may also have a great influence on the efficiency of ion transport. The results obtained with CH_2Cl_2 and CCl_4 are presented in Table 3, along with the analogous results for CHCl_3 . As can be seen, the membrane entrance and exit rate constants, t_{max} and $J_{\text{a}}^{\text{max}}$ values are remarkably different in the various solvents. The membrane entrance and exit rate constants are found to vary in the order $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$. But in all cases, it is not possible to state whether k_1 or k_2 is higher.

The variation of R_{a} values for the different solvent systems is illustrated in Fig. 4; showing that the R_{a} values are strongly affected by the choice of membrane solvent system. The transport efficiency was observed to be highest with CH_2Cl_2 . This result is in agreement with those in ref. 20, in which the efficiency of dichloromethane, based on the R_{a} values, was higher than that of CHCl_3 and CCl_4 . The physicochemical properties of the solvents are given in Table 4.

Table 4 Physicochemical characteristics^a of solvents used

	Solvent		
	CH_2Cl_2	CHCl_3	CCl_4
ϵ_0	9.08	4.81	2.24
n_D	1.424	1.446	1.466
μ	1.959	1.354	0
η	0.437	0.58	0.969
V_m	64.2	96.5	96.5

^a ϵ_0 : dielectric constant (20°C); n_D : refractive index (20°C); μ : dipole moment (D); η : viscosity (cP); V_m : molar volume (M^{-1}).

These observations suggest that viscosity is playing a major role in ion transport, as well as the polarity. Thus, we have shown that the nature of the membrane solvent is one of the main factors in establishing transport efficiency.

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