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Liquid Membrane Transport Kinetics of Hg (II) by Dithio Derivatized Macrotricyclic Compound

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The present study has been undertaken to investigate a process that removes inorganic mercury from waste water streams by use of a liquid membrane system in which a novel macrocyclic ligand based on dithio derivatized biscrown ether has been used as a cation carrier. The effect of temperature, stirring rate and different solvents on the kinetic parameters like k_1 , k_2 and flux values J_a^{\max} , J_d^{\max} and t_{\max} were also investigated. It was found that the membrane entrance rate constant (k_1) and the membrane exit rate constant (k_2) increased with increasing temperature and stirring rate. The membrane entrance rate constants (k_1), exit rate constants (k_2), as well as the flux values vary in the order of $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$ in different solvents study

Keywords: Macrotricyclic, transport kinetics, liquid membrane transport, mercury (II) transport, effect of temperature

1 Introduction

Supramolecular assemblies have remarkable structural variety, which allows interaction with metal centers and has received significant attention for a few decades. Hence, the synthetic supramolecular assemblies are in great demand, in the extraction and transportation of the large number of cations, anions, and neutral molecules. Many macromolecular compounds such as crown ethers (1–5), calixarenes (6–9) and cryptands (10) are used as carriers for transport process on a liquid membrane. Considerable efforts are made in the direction of transport of the metal ions across the liquid membranes over the last two to three decades. Among the separation techniques like chemical precipitation (11–13), ion exchange (14–19), reverse osmosis (20), adsorption on activated carbon (21–23) and biosorption by algae (24), the ion transport through liquid membrane is a simple, selective, efficient and cost effective technique as compared to the others. Metal ion transportation depends on various parameters like ligand structure, pH of solutions, solvent, temperature and stirring rates.

Crown ethers and calixarenes have been generally used as suitable cation carriers in liquid membrane for alkali and

alkaline earth metals (25–26), but there are only a few carriers for transportation of the toxic heavy metals. The increased concern about the environmental regulations on water pollution and the discharge of heavy metals makes it essential to develop efficient and selective technologies for their removal. Mercury is the most important pollutant of special interest because of its widespread application in agriculture and industrial areas causing adverse effects on human lung, brain, kidney and also causes neurological damage (27). Hence, the development of new methods for selective removal of Hg (II) ion for environmental remediation is a very important objective. It was considered important to have nitrogen, sulphur and oxygen in the macrocyclic compound framework for binding with metal ions like Hg (II) (28–30).

The aim of the present work was to investigate the kinetic parameters of liquid membrane transport of Hg (II) using a dithio derivatized macrotricyclic carrier, in terms of two consecutive irreversible first order reactions and effectiveness of the dithio based carrier. The extraction chemistry is basically the same as that found in liquid–liquid extraction. The kinetic parameters of mercury i.e apparent rate constants of the metal extraction and re-extraction reaction (k_1 , k_2), the maximum reduced concentration of the metal in the liquid membrane (R_m^{\max}), the time of the maximum value of R_m (t_{\max}) and the maximum entry and exit fluxes of the metal through the liquid membrane (J_d^{\max} and J_a^{\max}) of the extraction were investigated at different temperature ranges (293, 298, 303, 308K), different stirring rates (200, 300, 400 rpm) and in different solvents (CH_2Cl_2 , CHCl_3 , CCl_4).

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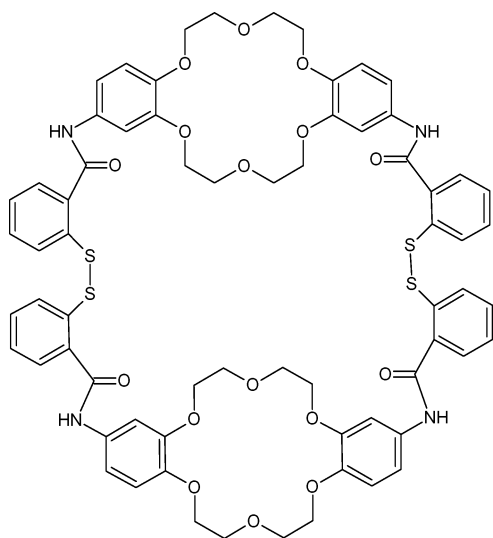


Fig. 1. The structure of dithio based macrotricyclic compound used as carrier.

2 Experimental

2.1 Reagents

All reagents and chemicals used were of analytical grade. Milli-Q water was used for preparing the stock solution of metal salts. Dilutions of the stock solution were also done by Milli-Q water. The chemical reagents used in these experiments viz. mercury (II) picrate, chloroform, dichloromethane and carbon tetrachloride were purchased from Merck. The carrier, di thio based macrotricyclic compound for membrane transport (Fig. 1) was synthesized according to our reported method (31).

2.2 Apparatus

A glass cell was used for all experiments fabricated in the workshop of Gujarat University. The experimental conditions were maintained by thermostat and magnetic stirrer.

2.3 Kinetic Procedure

The carrier was dissolved in 40 ml chloroform which was taken as the membrane phase. The donor phase (15 ml) contained mercury (II) picrate, which was adjusted to pH 4.5 with buffer solution. The acceptor phase (15 ml) contained 0.1 M HCl. Transport experiments were carried out in the U-shaped cell with the total capacity of 90 ml. Organic solution containing the carrier was placed in the bottom of the cell and two portions of the aqueous donor and acceptor solution were carefully added on top of them. The organic phase was stirred magnetically at variable speed. The whole assembly was kept in the thermostat to maintain the temperature. The mercury transport was monitored by determination of the Hg (II) concentration in both

aqueous donor and acceptor phases by UV-Vis spectral analysis. Transport of mercury was negligible in the absence of the carrier. The transport data were average of five run with the experimental error of less than 2%.

3 Results and Discussion

The liquid membrane technique contains two parts 1. Extraction of the metal ion from the aqueous donor phase to organic (liquid membrane) phase. 2. Reextraction of the metal ion from the organic (liquid membrane) phase to aqueous acceptor phase. In experiments, variation of mercury ion concentration with time was directly determined in both donor (C_d) and acceptor (C_a) phases using UV-Vis spectrometer at regular time intervals of 25 min for a total of 250 min. The corresponding change of mercury ion concentration in the membrane phase was determined from the material balance between the phases. For practical reason, the dimensionless reduced concentrations (R) were used:

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

Where C_{d0} is the initial Hg (II) concentration in the donor phase, while C_d , C_m and C_a represent the Hg (II) concentration in donor, membrane and acceptor phases, respectively. The material balance can be established as $R_d + R_m + R_a = 1$. When R_d , R_m and R_a values are inspected, the results suggest that the Hg (II) ion transport obeys the kinetic laws of two consecutive irreversible first-order reactions according to the kinetic scheme.



Where k_1 is the rate constants of the extraction of Hg (II) from aqueous donor phase to organic acceptor phase and k_2 is the rate constant of the reextraction of Hg (II) from organic membrane phase to aqueous acceptor phase. Equation 2 for consecutive irreversible reactions 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. When $k_1 \neq k_2$, integrating Equations 3 to 5 gives the following expressions:

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

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

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

Table 1. The kinetic parameters for transport of Hg (II) ions at different stirring rates (T = 298; solvent is CHCl₃)

Stirring rate (rpm)	$k_1 \times 10^2$ (min ⁻¹)	$k_2 \times 10^2$ (min ⁻¹)	R_m^{\max}	t_{\max} (min)	$J_a^{\max} \times 10^2$ (min ⁻¹)	$J_d^{\max} \times 10^2$ (min ⁻¹)
200	0.82	1.08	0.32	106.5	0.34	-0.34
300	1.32	1.81	0.31	64.2	0.56	-0.56
400	2.83	3.42	0.34	32	1.16	-1.16

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

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

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

Where by considering the first-order time differentiation of Equations 6 to 8 leads to the following forms:

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

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

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

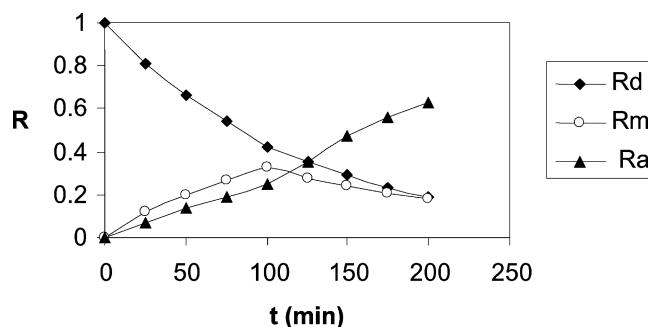
$$\left(\frac{dR_d}{dt}\right)_{\max} = \left(\frac{dR_a}{dt}\right)_{\max} \quad (14)$$

It should be noted that the system is assumed to be in steady state at $t = t_{\max}$, since the concentration of Hg (II) ions in the membrane does not vary with time Equation 13. consequently, the entrance and exit fluxes are equal having opposite signs.

$$-J_d^{\max} = J_a^{\max} \quad (15)$$

The extraction rate constant, k_1 , was obtained from Equation 6 by using donor phase concentration, while the reextraction rate constant, k_2 , was determined from the acceptor phase concentration by using Equation 8 or indirectly from the membrane phase data calculated (k_2) on the basis of Equation 7.

It is seen (Fig. 2) that R_d decreases exponentially with time, accompanied by a simultaneous increase of R_a , where as R_m was found to be maximum at intermediate time intervals. 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. The liquid membrane transport was

**Fig. 2.** Time dependence concentration of R_d , R_m and R_a of Hg (II) through liquid membrane.

studied and the kinetic behavior of the transport process as a function of temperature, stirring rate and solvents were investigated.

3.1 Effect of Stirring Rate

The influence of the stirring speed on Hg (II) ion transport was studied. The stirring rate of the membrane phase was carried out at three different stirring rates 200, 300 and 400 rpm at 298 K in CHCl₃. The experimental results summarized in Table 1 show that the membrane entrance rate constant (k_1) and exit rate constant (k_2) increases and t_{\max} decreases with increase in stirring rate.

3.2 Effect of Temperature

The effect of temperature on the transport of Hg (II) ions across the bulk liquid membrane was also investigated at 293, 298, 303 and 308 K at 200 rpm in CHCl₃, respectively. The experimental results are shown in Table 2 and Figure 3 which shows that the kinetic parameters, entrance rate constant k_1 and exit rate constant k_2 , as well as flux constant J_a^{\max} and J_d^{\max} increase with increase in the temperature; also shows that t_{\max} decreases with an increase

Table 2. The kinetic parameters for transport of Hg (II) ions at different temperatures (stirring rate, 200 rpm; solvent, CHCl₃)

Temperature (K)	$k_1 \times 10^2$ (min ⁻¹)	$k_2 \times 10^2$ (min ⁻¹)	R_m^{\max}	t_{\max} (min)	$J_a^{\max} \times 10^2$ (min ⁻¹)	$J_d^{\max} \times 10^2$ (min ⁻¹)
293	0.59	0.92	0.29	134.0	0.26	-0.26
298	0.82	1.08	0.32	106.5	0.34	-0.34
303	1.23	1.48	0.34	74	0.50	-0.50
308	1.42	2.10	0.29	58	0.61	-0.61

Table 3. The kinetic parameters for transport of Hg (II) ions with the use of different solvents (stirring rate, 200 rpm; temperature, 298 K)

Solvent	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	R_m^{\max}	t_{\max} (min)	$J_a^{\max} \times 10^2$ (min^{-1})	$J_d^{\max} \times 10^2$ (min^{-1})
CH ₂ Cl ₂	1.12	1.31	0.33	82.0	0.43	-0.43
CHCl ₃	0.82	1.08	0.32	106.5	0.34	-0.34
CCl ₄	0.32	0.89	0.20	179	0.17	-0.17

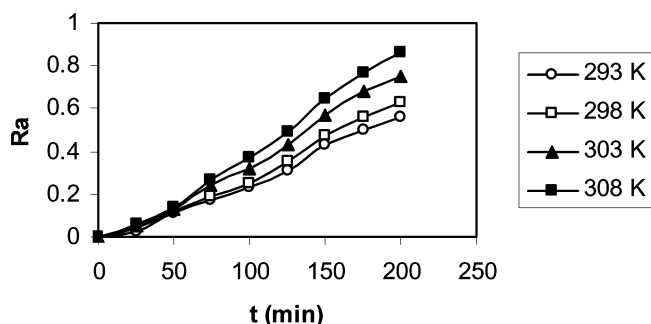


Fig. 3. Reduced concentrations of Hg (II) in the acceptor phase with the time at different temperatures.

in temperature. In the present investigation, results suggest that the transport of the Hg (II) ions could be described by the kinetic laws of two consecutive irreversible first-order reactions.

3.3 Effect of Solvent

The experiments were performed with three different solvents: CH₂Cl₂, CHCl₃ and CCl₄. As can be seen in the results (Table 3, Fig. 4), the membrane entrance and exit rate constants, t_{\max} and flux constant J_a^{\max} values are remarkably different in these solvents. The variation of R_a values for the different solvent systems is illustrated in Figure 4, indicating the role played by the nature of solvents on transport efficiency through liquid membrane. The highest transport efficiency has been obtained with CH₂Cl₂. It is also found that the membrane entrance and exit rate con-

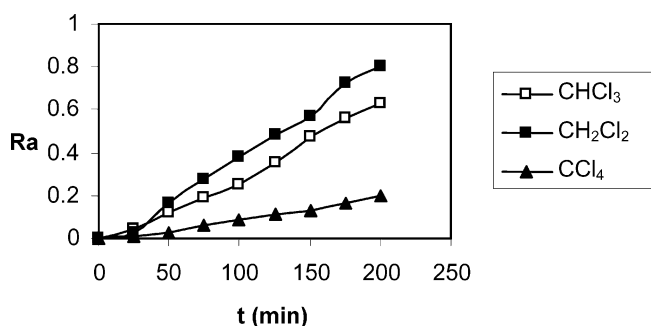


Fig. 4. Reduced concentrations of Hg(II) in the acceptor phase with the time in different solvents.

Table 4. Physicochemical characteristics of solvents used

Solvent	Dielectric constant	Refractive index	Dipole moment	Viscosity	Molar volume
CH ₂ Cl ₂	9.08	1.424	1.959	0.437	64.2
CHCl ₃	4.80	1.446	1.354	0.58	96.5
CCl ₄	2.24	1.466	0	0.969	96.5

stants, as well as the flux values, vary in the order CH₂Cl₂ > CHCl₃ > CCl₄. The physicochemical properties of these solvents are given in Table 4.

4 Conclusions

An efficient transport system for Hg (II) ions through a bulk liquid membrane system containing dithio based macrotricyclic compound as a carrier was studied. The efficiency of the transport depends on various parameters like the type of solvent, stirring speed and temperature. The two consecutive irreversible first-order apparent rate constants, k_1 , k_2 and flux values J_a^{\max} , J_d^{\max} and t_{\max} were investigated at the different parameters. Results shows that the kinetic parameters entrance rate constant k_1 and exit rate constant k_2 , increase with increase in the temperature and stirring rates.

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