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Mechanism and Kinetics of Copper(II) Transport through a Liquid Membrane Containing a Dithiophosphonate Derivative as Carrier

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The transport of Cu(II) ions from an aqueous solution into an aqueous receiving solution through a bulk liquid membrane containing a dithiophosphonate derivative (**1**) as a carrier was examined. The kinetic parameters were analyzed assuming 2 consecutive, irreversible first-order reactions. The influence of temperature and stirring rate on the kinetic parameters (k_1 , k_2 , R_m^{max} , t_{max} , J_d^{max} and J_a^{max}) was also investigated. The membrane entrance rate, k_1 , and the membrane exit rate, k_2 , increased with increasing temperature and stirring rate. For the maximum membrane exit flux, J_a^{max} , the activation energy was determined from the slope of the linear Arrhenius relationship to be 8.70 kcal mol⁻¹, which indicates that the process is controlled by species diffusion.

Key Words: Co-transport, Copper(II) transport, Transport kinetics, Liquid membranes, Temperature effects, Diffusional rate-determining step, Dithiophosphonates.

Introduction

In recent years, the liquid membrane has widely been used to study ion transport against a concentration gradient. Ion transport through the liquid membrane plays an important role in simulating biological membrane functions and separation technologies because of the high transport efficiency, excellent selectivity and economic advantages of the liquid membrane. A number of successful studies involving the transport of metal ions¹⁻⁵, rare earth elements^{6,7}, drugs^{8,9}, phenols¹⁰, fructose¹¹ and the treatment of seawater and wastewater¹²⁻¹⁴ through the liquid membrane have been carried out. Selective transport of transition metal ions through liquid membranes has become increasingly noteworthy. A number of carriers for heavy metal ions and in particular Cu(II), which is both vital and toxic to many biological systems, have been reported¹⁵⁻²⁰.

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Organophosphorus and dithiolato derivatives such as phosphates, phosphinates, phosphonates, dithiophosphates, dithiophosphinates and dithiophosphonates are important compounds because of their agricultural and industrial applications. These compounds have been utilized as additives for lubricants, antioxidants, flotation agents for ores, solvent extraction reagents, insecticides and pesticides^{21–24}.

We report an investigation of co-transport of the Cu^{2+} ion through liquid membranes. *O*-(1,3-Bis(piperidino-2-propyl)-4-methoxyphenyl)dithiophosphonate **1** is the carrier ligand as presented in Figure 1. The kinetics of Cu^{2+} ion transport were analyzed at different temperatures as well as at different stirring rates in CHCl_3 .

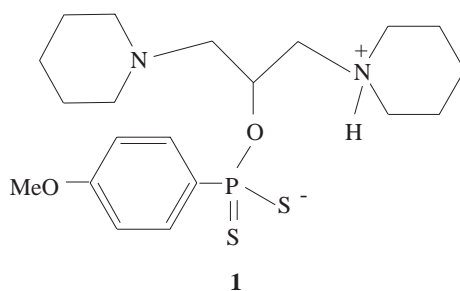


Figure 1. The proposed structure of the ligand used as carrier.

Experimental

Materials

The chemical reagents used in these experiments were copper(II) nitrate (Merck), chloroform (Merck), and picric acid (Merck). Copper(II) picrate solution was prepared by the addition of 1×10^{-2} M copper(II) nitrate to a 2.5×10^{-5} M aqueous picric acid solution and shaking 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 2 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 magnetically at variable speeds (Chiltern, model HS 31).

The initial phases consisted of the donor phase, which was an aqueous copper(II) picrate (2.5×10^{-5} M) solution, while the membrane phase was made up by dissolving carrier (**1**) ($C_{\text{carrier}} = 10^{-3}$ M) in the CHCl_3 . The acceptor phase consisted of doubly distilled water. Samples were taken from both water phases (acceptor and donor phases) at various intervals and the picrate ion concentration was analyzed using a spectrophotometric method²⁵. Each experimental result reported is the arithmetic mean of 2 independent measurements.

Results and Discussion

There are no studies in the literature regarding dithiophosphonate derivatives as a transport carrier, although there are studies with phosphonate derivatives^{26–28}. Those studies show that phosphonate derivatives is selective transport to Eu(III) and amino acids, as in aqueous media. Some studies of Cu(II) transport through the liquid membrane using different carrier ligands exist in the literature^{2,17,20,29}. Gholivand and Khersandipoor have studied the selective and efficient uphill transport of Cu(II) through a bulk liquid membrane using *N*-ethyl-2-aminocyclopentene-1-dithiocarboxylic acid as carrier¹⁷. We investigated the transport of the Cu²⁺ ion by carrier **1** in the bulk liquid membrane and the kinetic behavior of the transport process as a function of temperature and stirring rate.

The liquid membrane technique contains 2 processes in a single stage: extraction of the metal ion from the aqueous donor solution to the organic phase containing the carrier molecules (membrane) and a reextraction of this metal ion from the membrane to the aqueous acceptor phase. The overall transport process consists of a mixture of diffusion steps and complexation/decomplexation reactions at 2 independent and possibly different interfaces.

The mechanism of the ion pair mediated transport (co-transport) is given in Figure 2. L represents the ligand carrier. At the interface between donor and membrane, the metal picrate ion pair forms a complex with the ligand, and then the [LM]⁺Pic⁻ complex diffuses through the membrane. At the interface between membrane and acceptor, the carrier ion pairs are decomplexed and M⁺Pic⁻ is liberated into the acceptor phase. Finally, the ligand carrier diffuses back across the membrane aqueous boundary layers.

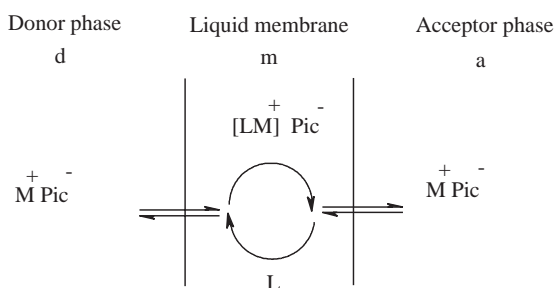


Figure 2. Mechanism of the ion pair mediated transport (co-transport) through liquid membrane M: Metal, Pic: Picrate salt, L: Ligand, [L-M]⁺Pic⁻: ion pair.

It has been reported that the transport process of the Cu (II) ions obeys the kinetic laws of consecutive irreversible first-order reactions^{20,29,30}. 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, as discussed in detail elsewhere^{30–37}.

The variation of picrate ion concentration with time was determined for both donor (C_d) and acceptor phases (C_a). If a 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 reasons, and are thus represented as described below.

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 in picrate ion concentration in the

membrane phase was determined from the material balance between the phases. For practical reasons, dimensionless reduced concentrations were used:

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

where C_{d0} is the initial Cu^{2+} concentration in the donor phase, while C_d , C_m and C_a represent the Cu^{2+} concentrations in the 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:



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.

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

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

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

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 a steady state at $t = t_{max}$, since the concentration of Cu^{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 the Cu^{2+} ion through a liquid membrane with carrier **1** was studied over a temperature range of 293 to 308 K and at different stirring rates in the range 300 to 500 rpm. The kinetic parameters k_1 and k_2 were obtained by fitting equations (6) and (8) to these data. The k_1 , k_2 , R_m^{\max} , t_{max} , J_d^{\max} and J_a^{\max} values calculated at different temperatures and different stirring rates are presented in Tables 1 and 2, respectively. Time variation of the reduced concentration of Cu^{2+} ions at 400 rpm and 25 °C is illustrated in Figure 3. It can be seen that R_d decreases exponentially with time, accompanied by a simultaneous increase in R_a , whereas R_m is presents at the maximum level at intermediate times. The maximum R_m values were found to lie between 0.17 and 0.33. This clearly indicates that the membrane phase plays a role in the transport. The other important factor is that the t_{max} values also decreased with increasing temperature and stirring rates.

Table 1. The kinetic parameters of Cu^{2+} transport using carrier **(1)** at different temperatures (stirring rate is 400 rpm).

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	1.08	3.55	0.18	482.11	-6.41	6.41
298	1.71	3.70	0.238	387.90	-8.81	8.81
303	2.18	4.74	0.241	303.82	-11.20	11.20
308	2.76	4.85	0.27	269.67	-13.10	13.10

Table 2. The kinetic parameters of Cu^{2+} transport using carrier **(1)** at different stirring rates ($T = 298$ K).

Stirring Rate (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})
300	0.96	3.45	0.17	513.55	-5.86	5.86
400	1.716	3.70	0.238	387.90	-8.81	8.81
500	4.06	5.14	0.33	218.40	-16.70	16.70

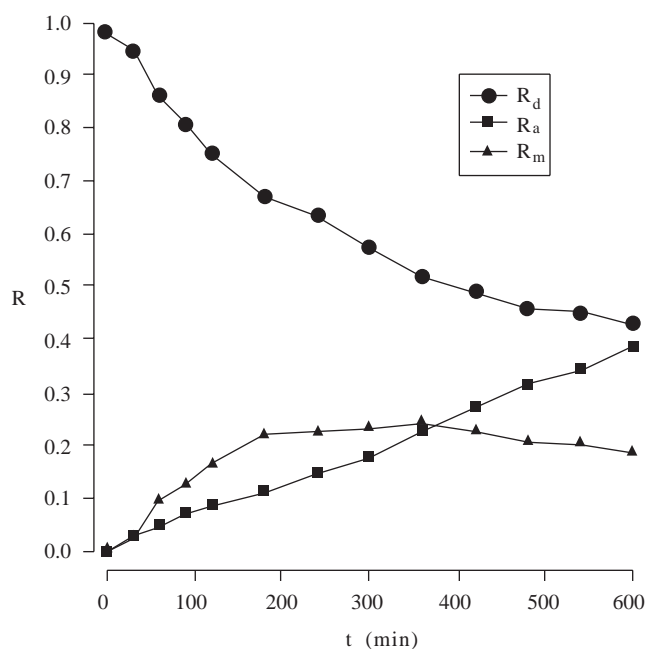


Figure 3. Time variation of reduced concentration of Cu^{2+} ion in co-transport through a liquid membrane ($T = 298 \text{ K}$).

The effect of temperature on the co-transport of Cu^{2+} is presented in Figure 4. The reduced concentration of Cu^{2+} in the acceptor phase with time increases exponentially, particularly at higher temperatures. In other words, transport efficiency was higher at higher temperatures and stirring rates. As a result, when temperature and stirring rate were increased, R_m^{max} increased, while t_{max} decreased.

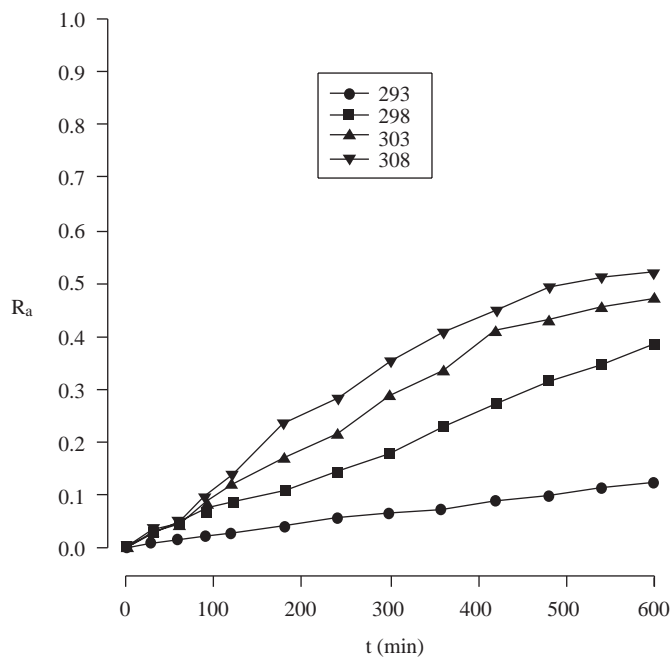


Figure 4. Time variation of reduced concentrations of Cu^{2+} in the acceptor phase during co-transport through a liquid membrane using the dithiophosphonate derivative (**1**) at different temperatures at a stirring rate of 400 rpm.

The activation energy was calculated by plotting the maximum membrane exit flux (J_a^{max}) versus T^{-1} at 400 rpm, as presented in Figure 5.

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

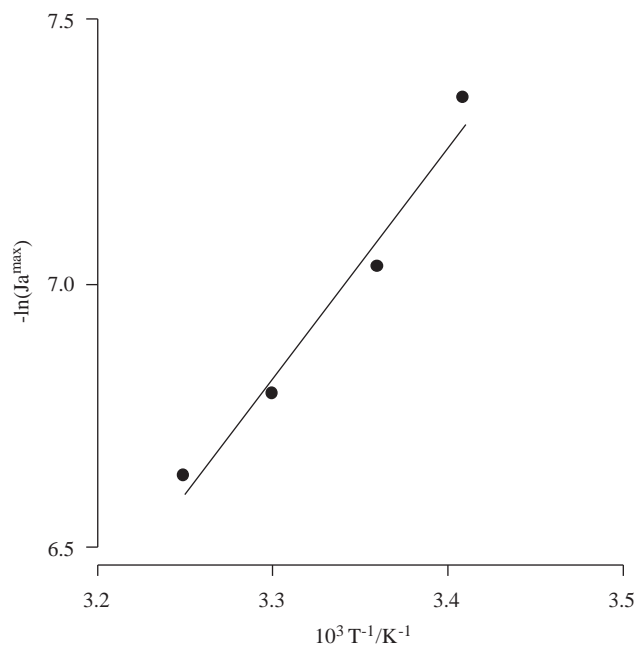


Figure 5. Arrhenius plot of Cu^{2+} ion transport at J_a^{max} .

The activation energy value for carrier **1** in the liquid membrane was 8.70 kcal/mol. 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 has been reported that the activation energies of diffusion-controlled processes are lower than 10 kcal/mol³⁸. The calculated activation energy for carrier **1** shows that the transport of the Cu^{2+} ion is a diffusion-controlled process.

Conclusions

The kinetics of transport of Cu^{2+} ions through bulk liquid membrane (chloroform) using dithiophosphonate derivative (**1**) as a carrier was examined at different temperatures and different stirring rates. As temperature and stirring rate increased, R_m^{max} increased while t_{max} decreased. The membrane entrance (k_1) and exit (k_2) rate constants increase with increasing temperature and stirring rate. It is expected that the temperature and stirring effects are mainly exerted on the maximum complexation and decomplexation between the Cu^{2+} picrate and ligand carrier at the aqueous-organic interfaces.

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