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Kinetics of Cadmium(II) Transport through a Liquid Membrane Containing Tricapryl Amine in Xylene

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ABSTRACT

Coupled transport of Cd(II) ions through a supported liquid membrane containing tricapryl amine in xylene has been examined. The influences of stirring rate, carrier concentration, stripping agent, and H^+ concentration in the feed solution were investigated. The transport of Cd(II) ions is coupled by cotransport of protons. The kinetics of Cd(II) transport could be analyzed in the formalism of two consecutive irreversible first-order reactions. The pseudofirst-order apparent rate constants of interfacial reactions in membrane transport were determined with bulk liquid membrane at various temperatures. The activation energy values are 14.7 $kJ \cdot mol^{-1}$ for extraction and 12.4 $kJ \cdot mol^{-1}$ for stripping.

Key Words. Liquid membrane; Cadmium ions; Tricapryl amine; Transport kinetics

INTRODUCTION

Cadmium is one of the main toxic pollutants characterized by a long environmental persistence and biological "half-time" which accounts for its bioaccumulation in individuals (1). The removal of Cd(II) ions from wastewater is therefore of great significance. Liquid membrane transport mediated with a mobile carrier has been proposed as a promising technology for its separation and enrichment from wastewater (2–4). Much work has been done in these studies toward developing new technologies and investigating the effects of

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experimental parameters on the transport of Cd(II) ions. The experimental results were evaluated mostly in terms of the permeability coefficient, the permeation rate, and the enrichment factor. In order to gain a clear idea of the transport of Cd(II) ions and to devise an efficient liquid membrane system for treating cadmium wastewater, the kinetics of coupled transport of Cd(II) ions through a liquid membrane containing tricapryl amine [N_{235}, $N(C_nH_{2n+1})_3$, $n = 8–10$] in xylene was analyzed by considering both extraction and stripping. In the present paper the permeation rate of Cd(II) through a supported liquid membrane has been studied as a function of stirring rate, carrier concentration, stripping agent, and H^+ concentration in the feed phase. The effect of temperature on its transport through a bulk liquid membrane has been investigated systematically, and the pseudofirst-order apparent rate constants of the interfacial reaction for extraction and stripping in the membrane have been determined. It is well known that temperature can influence the stabilities of emulsion liquid membranes and supported liquid membrane (5). We believe this investigation will significantly increase understanding of the transport process of Cd(II) ions through liquid membranes. Up to now, kinetic studies of cadmium-coupled transport in liquid membranes has been little reported in the literature.

THEORETICAL TREATMENT

Reactions at the Feed Side

$CdCl_2 \cdot 2.5H_2O$ was used in this study. It will ionize in an aqueous phase to form Cd^{2+} ions:

$$CdCl_2 \Leftrightarrow Cd^{2+} + 2Cl^- \tag{1}$$

The Cd^{2+} ions will further react with Cl^- ions present in the aqueous phase:

$$2H^+ + Cd^{2+} + 4Cl^- \Leftrightarrow H_2CdCl_4 \Leftrightarrow 2H^+ + CdCl_4^{2-} \tag{2}$$

In a HCl solution, N_{235} (R_3N) accepts a proton to form a neutral species. The Cd(II) ions in HCl can be extracted as $(R_3NH)_2CdCl_4$. The overall reaction at the feed side membrane interface is

$$2H^+_{aq} + CdCl^{2-}_{4aq} + 2R_3N_{org} = (R_3NH)_2CdCl_{4org} \tag{3}$$

Reaction at the Stripping Side

In the stripping phase the reaction at the stripping side of the membrane in the presence of CH_3COONH_4 will be

$$(R_3NH)_2\,CdCl_{4org} + 2CH_3COO^-_{aq} = 2R_3N_{org} + CdCl^{2-}_{4aq} + 2CH_3COOH_{aq} \tag{4}$$

This shows the transport of Cd(II) ions is coupled by a cotransport flow of protons. H^+ and Cl^- concentration gradients are the most often used driving forces. The mechanism of coupled transport of Cd(II) ions through a liquid membrane is schematically described in Fig. 1.

Variation of Cd(II) concentration with time was directly measured in both the donor (C_d) and acceptor (C_a) phase in the experiments. The corresponding change of cadmium concentration in the membrane (C_m) was established from the material balance. For practical reasons, the reduced concentrations are used:

$$R_d = C_d/C_{d0}, \qquad R_m = C_m/C_{d0}, \qquad R_a = C_a/C_{d0}$$

where C_{d0} is the initial Cd(II) concentration in the donor phase at $t = 0$. Obviously, we have $R_d + R_m + R_a = 1$. Our experimental results (as shown in later sections) reveal that R_d decreases monoexponentially with time, R_a follows a monotonically increasing sigmoid-type curve, while the time dependence of R_m presents a maximum. These results suggest that Cd(II) ions transport obeys the kinetic laws of two consecutive irreversible first-order reactions according to the kinetic scheme (6)

$$d \xrightarrow{k_1} m \xrightarrow{k_2} a$$

where d, m, and a stand for Cd(II) ions in the donor, membrane, and acceptor phases, respectively. It was found that the presence of an important proton gra-

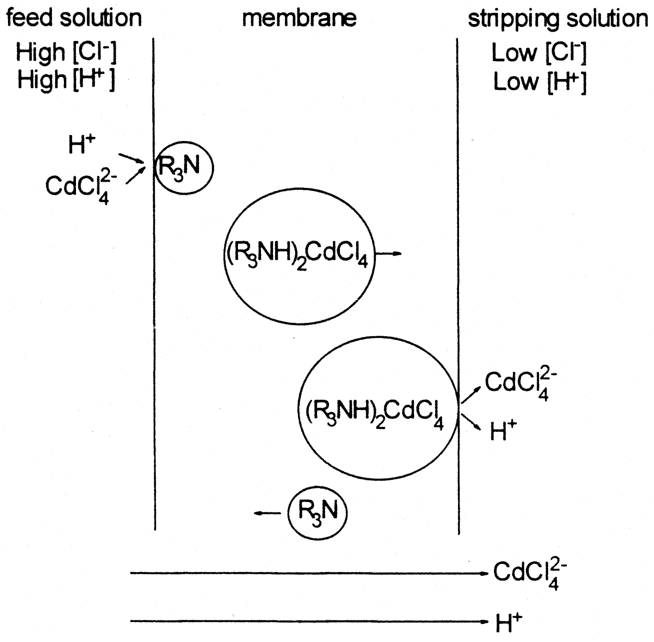

FIG. 1 Schematic description of cotransport.

dient drives the whole transport process to completion without any back leakage of cadmium(II) ions. Therefore, the above kinetic scheme may be described by the following equations (6):

$$dR_d/dt = -k_1R_d \equiv J_d \tag{5}$$

$$dR_m/dt = k_1R_d - k_2R_m \tag{6}$$

$$dR_a/dt = k_2R_m \equiv J_a \tag{7}$$

where J stands for flux, and k_1 and k_2 are the pseudofirst-order apparent rate constants of the interfacial Reactions (3) and (4). When $k_1 \neq k_2$, integrating the above differential equations gives

$$R_d = \exp(-k_1t) \tag{8}$$

$$R_m = \frac{k_1}{k_2 - k_1}\left[\exp(-k_1t) - \exp(-k_2t)\right] \tag{9}$$

$$R_a = 1 - \frac{1}{k_2 - k_1}\left[k_2\exp(-k_1t) - k_1\exp(-k_2t)\right] \tag{10}$$

It can be seen that R_d vs t yields a decreasing monoexponential curve whereas the time variations of both R_m and R_a are biexponential. The actual numerical analysis was carried out by nonlinear curve fitting.

According to Eq. (9), R_m increases at first, then decreases with time, i.e., it has a maximum (when $dR_m/dt = 0$):

$$t_{\max} = \frac{\ln(k_1/k_2)}{k_1 - k_2} \tag{11}$$

$$R_m^{\max} = (k_1/k_2)^{-k2/(k1-k2)} \tag{12}$$

By considering first-order time differentiation of Eqs. (8)–(10) at $t = t_{\max}$, one obtains

$$\left.\frac{dR_d}{dt}\right|_{\max} = -k_1\left(\frac{k_1}{k_2}\right)^{-k_1/(k_1-k_2)} \equiv J_d^{\max} \tag{13}$$

$$\left.\frac{dR_m}{dt}\right|_{\max} = 0 \tag{14}$$

$$\left.\frac{dR_a}{dt}\right|_{\max} = k_2\left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_a^{\max} \tag{15}$$

and

$$-\left.\frac{dR_d}{dt}\right|_{\max} = +\left.\frac{dR_a}{dt}\right|_{\max} \tag{16}$$

Equation (16), together with the fact that at $t = t_{\max}$ the Cd(II) concentration in the membrane does not vary, i.e., $dR_m/dt\,|_{\max} = 0$, defines the condition in which the transport kinetics follow a steady-state regime.

A plot of the moles of Cd(II) ions transported to the stripping phase against time in SLM experiments was made for each carrier-containing system. At steady state the data were fitted to a straight line, the slope of which gave the values of J (7).

EXPERIMENTAL

Materials

All the reagents used in the present work were of analytical grade. They were supplied by Hunan Chemical Reagent Corporation. N_{235} is a commercial extractant and was used without any further purification. It is a product of the Dalian Chemical Reagent Factory.

A microporous polypropylene membrane was used as a solid support. The film was obtained from the Hunan Plastic Research Institute. It was a 0.02-mm thick film with a nominal porosity of 51% and an effective pore size of 0.03 μm.

Cd(II) stock solution: A stock solution of Cd(II) was prepared by dissolving $CdCl_2 \cdot 2.5H_2O$ in deionized water. It was analyzed by EDTA titration using Eriochrome black T as indicator.

Cd(II) feed solution: A known amount of the Cd(II) stock solution was diluted with water to a given extent after adding a calculated amount of the desired HCl and NaCl.

Stripping solution: It was prepared by taking the required amount of CH_3COONH_4 and diluting it with deionized water to a known concentration.

N_{235} solutions: They were prepared by taking the calculated amount of extractant and diluting it with xylene.

All the experiments were carried out using deionized water saturated with xylene.

Flux Measurement

Bulk liquid membrane (BLM): The transport experiments were carried out using a thermostat ($t = 30 \pm 0.1$°C) as presented in Fig. 2. The aqueous feed solutions (40.00 mL) consisted of 8.9×10^{-4} M Cd^{2+}, 0.1 M HCl, and 0.4 M NaCl. The feed solution was placed in the left part (b) of the vessel and stirred at 600 rpm. The stripping solution, which consisted of 0.50 M CH_3COONH_4 (40.00 mL) and was located in the right part (a) of the vessel, was stirred at

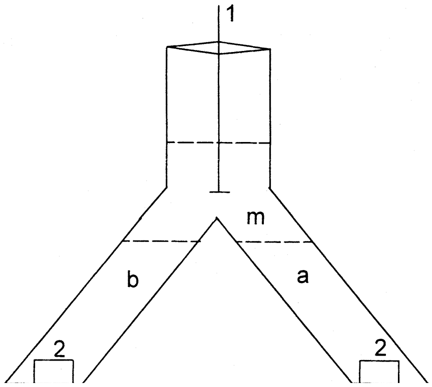

FIG. 2 Apparatus used for coupled transport of Cd(II) through liquid membrane: (a) stripping phase, (b) feed phase, (m) membrane phase, (1) glass stirrer, (2) magnetic stirrer.

600 rpm. The membrane phase (30.00 mL), which contained 0.08 M N_{235} dissolved in xylene, was added on the top of the feed and stripping phase and stirred at 600 rpm. The interface surfaces were as follows: $S_{\text{feed phase-membrane}} = 5.90\ \text{cm}^2$, and $S_{\text{membrane-stripping phase}} = 5.90\ \text{cm}^2$.

Supported liquid membrane (SLM): The experiments were performed at 30 ± 0.1°C with a simple diffusion cell. The diffusion cell consisted of two Perspex half cells. The two half cells were separated by a membrane with an area of 18 cm^2. The membrane was impregnated with the carrier dissolved in xylene and clamped between the two half cells. The aqueous feed solutions (140 mL) consisted of 8.90×10^{-4} M Cd^{2+}, 0.1 M HCl, and 0.4 M NaCl. The stripping solution (140 mL) consisted of 0.50 M CH_3COONH_4. The pH of the stripping solution was measured with a pH meter, and the H^+ concentration of the feed solution was analyzed by acid-base titration using methyl orange as indicator.

In the BLM and SLM transport experiments the samples were taken from the feed and stripping solutions at scheduled time intervals and analyzed for cadmium content with a spectrophotometry (8). The fluxes obtained were reproducible to within about ±10%.

RESULTS AND DISCUSSION

Solvent Extraction

In order to clarify the mechanism of transport of Cd(II) ions through the liquid membrane, extraction and stripping experiments were performed. Equal volumes of known concentrations of Cd(II) solution in water and N_{235} in xylene were taken in a separating funnel and thoroughly shaken. The extraction equilibration time was 1 minute. After equilibration, variations of H^+ concentration in the feed and stripping solutions were as shown in Table 1. The experimental data in Table 1 reveal that the concentrations of H^+ and Cd(II) ions diminish in the feed phase and increase in the stripping phase. The results in Table 1 demonstrate that the transport of Cd(II) ions is coupled by the cotransport flow of protons. The schematic description of the cotransport of Cd(II) is shown in Fig. 1.

Supported Liquid Membrane Experiments

Influence of Stirring Rate

The effect of stirring speed of the feed solution on Cd(II) ions transport was investigated. The experimental data indicate that beyond 530 rpm the flux of Cd(II) ions through the supported liquid membrane becomes independent of the stirring rate when the stirring speed of the stripping solution is 600 rpm. We can then assume that when rpm > 530, the thickness of the aqueous diffusion films reaches a constant limiting value. Consequently, all subsequent experiments were carried out at a stirring rate of 600 rpm in the feed and stripping solutions.

TABLE 1
Variation of Concentration of H^+ and Extraction Percentage of Cd(II) in Extraction and Stripping Experiments[a]

Composition of feed phase (M)	H^+ concentration in feed phase (M)		Percentage of extraction for Cd(II)	pH in stripping phase		Percentage of stripping for Cd(II)
	$t = 0$	$t = 10$ min		$t = 0$	$t = 30$ min	
2.23×10^{-3} Cd^{2+} 0.090 HCl 0.41 NaCl	0.090	0.017	98.8	6.87	5.89	92.1
8.90×10^{-4} Cd^{2+} 0.042 HCl 0.45 NaCl	0.042	2.1×10^{-4}	96.8	6.87	6.17	99.8
8.90×10^{-4} Cd^{2+} 0.096 HCl 0.04 NaCl	0.096	0.015	98.2	6.87	5.88	92.8

[a] Organic phase: 0.16 M N_{235}-xylene. Stripping solution: 0.50 M CH_3COONH_4. Phase ratio (V/V): 1:1. Extraction time: 10 minutes. Stripping time: 30 minutes. Temperature: 24–26°C.

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Effect of Stripping Agent

The effect of stripping agents on the transport of Cd(II) ions through the liquid membrane were examined. When the feed solution was as given above, the stripping phase contained 0.05 or 0.10 M NaOH and the concentration of N_{235} was 0.08 M, $Cd(OH)_2$ precipitate was observed in the stripping solution. As is known from Ref. 2, the use of ammonium acetate as a stripping agent effectively avoids the formation of $Cd(OH)_{2(s)}$ precipitate. Consequently, amonium acetate was used as a stripping agent in our later transport experiments.

Effect of HCl Concentration in Feed Solution

It is quite clear from Fig. 3 that the transport of Cd(II) ions through a liquid membrane is influenced by the H^+ concentration in the feed solution. The transport experiments were made at six different concentrations of H^+ ions in solutions (0.01, 0.03, 0.05, 0.1, 0.3, and 0.5 M) for 0.08 M N_{235} in the membrane. The experiments verified that the flux of cadmium ions increases from 0.01 to 0.05 M HCl in the feed solution, and a decrease in the values of *J* was observed above 0.05 M HCl. This shows the importance of protons in the feed phase. If the amount of protons increases up to 0.1, 0.3, or 0.5 M, Reaction (2)

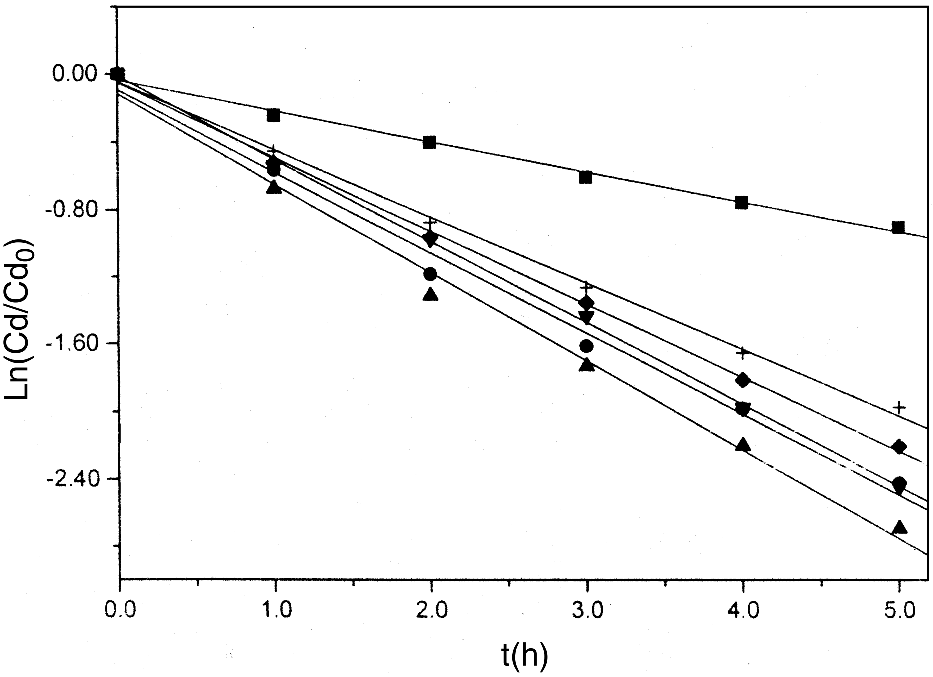

FIG. 3 Plot of ln (Cd/Cd_{0}) of Cd(II) in feed phase versus time at different concentrations of HCl in the feed. Carrier: 0.08 M; stripping: 0.5 M CH_3COONH_4; temperature: 30°C. (■) 0.01 M, (●) 0.03 M, (▲) 0.05 M, (▼) 0.10 M, (◆) 0.30 M, (■) 0.50 M.

will shift backward and there may be difficulties in dissociating $CdCl_4^{2-}$ from H_2CdCl_4. This causes a decrease in the flux.

Effect of Carrier Concentration

The transport experiments were run at five different N_{235} carrier concentrations: 0.02, 0.04, 0.06, 0.08, and 0.10 M. The experiments demonstrate that the flux of Cd(II) increases with an increase in concentration from 0.02 to 0.1 M carrier in the membrane.

It is quite obvious from Eqs. (5)–(7) that the flux is related to the carrier concentration. At a lower carrier concentration the interface between the feed solution and the membrane is not saturated by the carrier. Therefore, the flux increases with an increase of carrier concentration.

In addition, a “blank” experiment was performed in which the membrane contained no carrier. No detectable movement of Cd(II) ions through the liquid membrane was found in this experiment. It has been found that the transport of Cd(II) ions through a liquid membrane is fulfilled by N_{235} carrier.

Effect of Temperature on Transport of Cd(II) Ions through Bulk Liquid Membrane

The effect of temperature on the transport of Cd(II) ions through a liquid membrane containing N_{235} in xylene was examined at 283, 293, 303, 313, and 323 K. The experimental results are collected in Table 2 and Figs. 4–7. It is quite obvious that k_{1d} and k_{2a} increase with an increase in temperature. Table 2 also shows that t_{max} decreases with an increase of temperature. Figure 4 indicates the time dependence of the reduced concentration of Cd(II) trans-

TABLE 2
Effect of Temperature on Kinetic Parameters for Transport of Cd(II) through Liquid Membrane[a]

t (°C)	$k_{1d} \times 10^3$ (min^{-1})	$k_{2a} \times 10^3$ (min^{-1})	$k_{2m} \times 10^3$ (min^{-1})	t_{max} (min)	R_m^{max}	$J_a^{max} \times 10^3$ (h^{-1})	$J_d^{max} \times 10^3$ (h^{-1})
10	5.03 ± 0.05	6.54 ± 0.08	6.77 ± 0.07	173.85	0.321	2.098	−2.098
20	6.43 ± 0.05	7.40 ± 0.08	7.55 ± 0.09	144.85	0.342	2.533	−2.533
30	8.08 ± 0.08	8.73 ± 0.12	8.88 ± 0.13	119.04	0.354	3.088	−3.088
40	9.88 ± 0.14	10.67 ± 0.20	11.00 ± 0.28	97.37	0.354	3.775	−3.775
50	10.61 ± 0.09	12.44 ± 0.17	12.55 ± 0.21	86.95	0.339	4.218	−4.218

[a] k_{1d}, k_{2m}, and k_{2a} are calculated from Eqs. (8), (9), and (10), respectively.

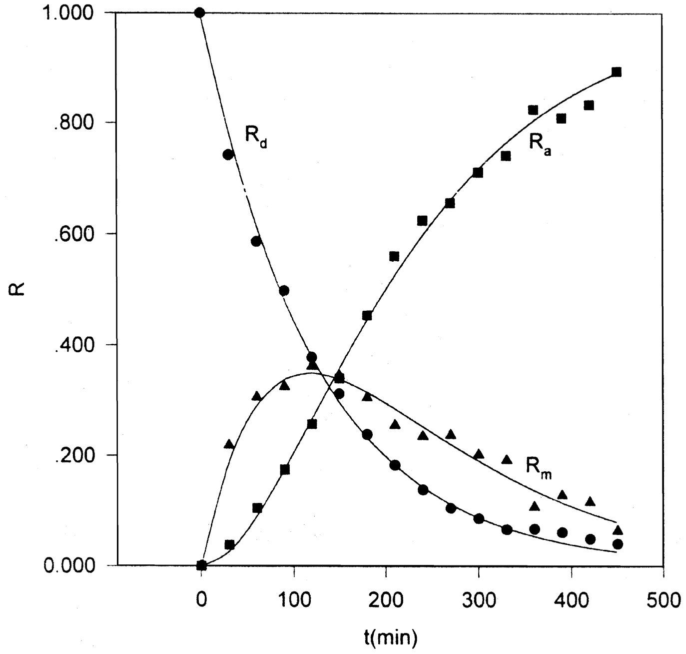

FIG. 4 Time dependence of R_d in the feed phase, R_m in the membrane phase, and R_a in the stripping phase. Membrane: 0.08 M N_{235}–xylene. Theoretical curves calculated from Eqs. (8), (9), and (10). $t = 30°C$.

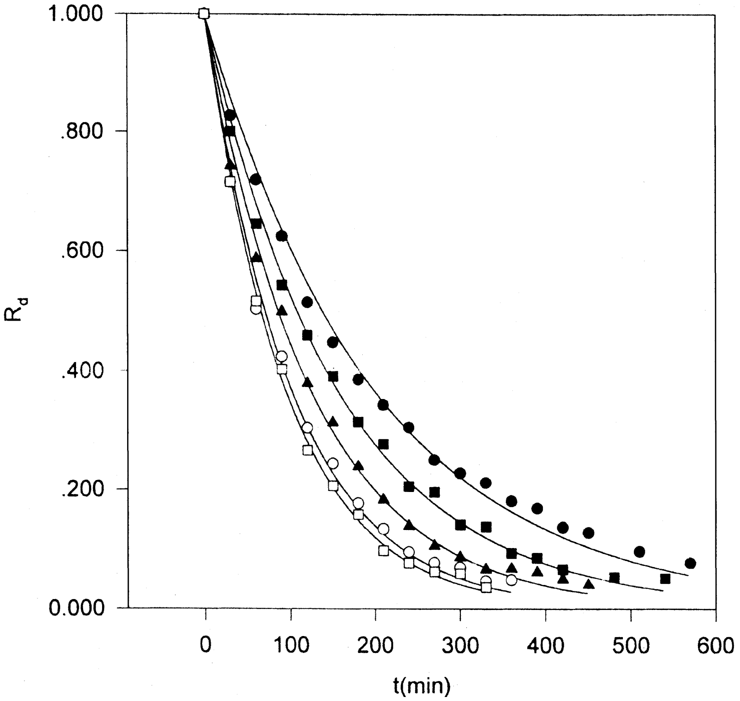

FIG. 5 Time evolution of R_d during coupled transport. Membrane: 0.08 M N_{235}–xylene. Theoretical curves calculated from Eq. (8). (•) $t = 10°C$, (■) $t = 20°C$, (▲) $t = 30°C$, (○) $t = 40°C$, (□) $t = 50°C$.

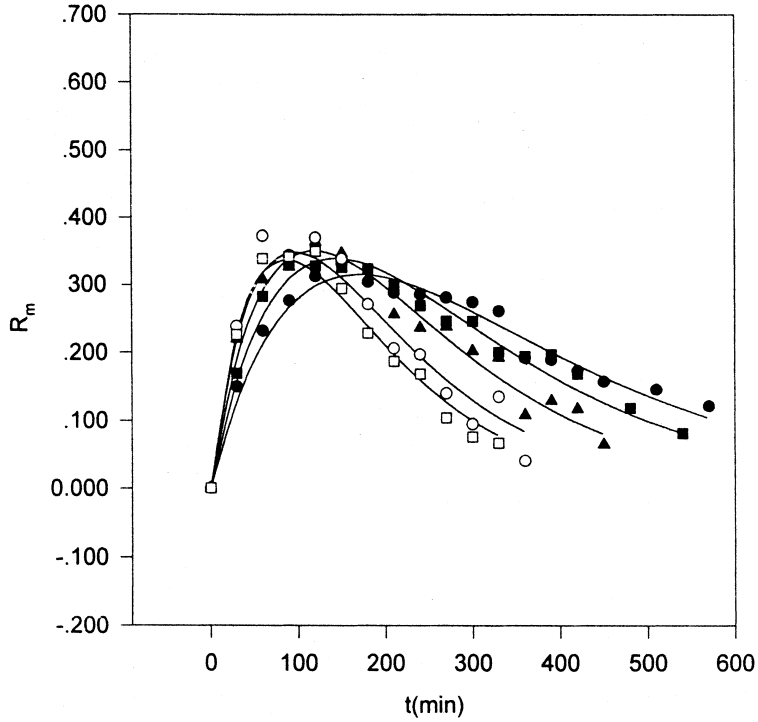

FIG. 6 Time evolution of R_m during coupled transport. Membrane: 0.08 M N_{235}–xylene. Theoretical curves calculated from Eq. (9). Symbols as in Fig. 5.

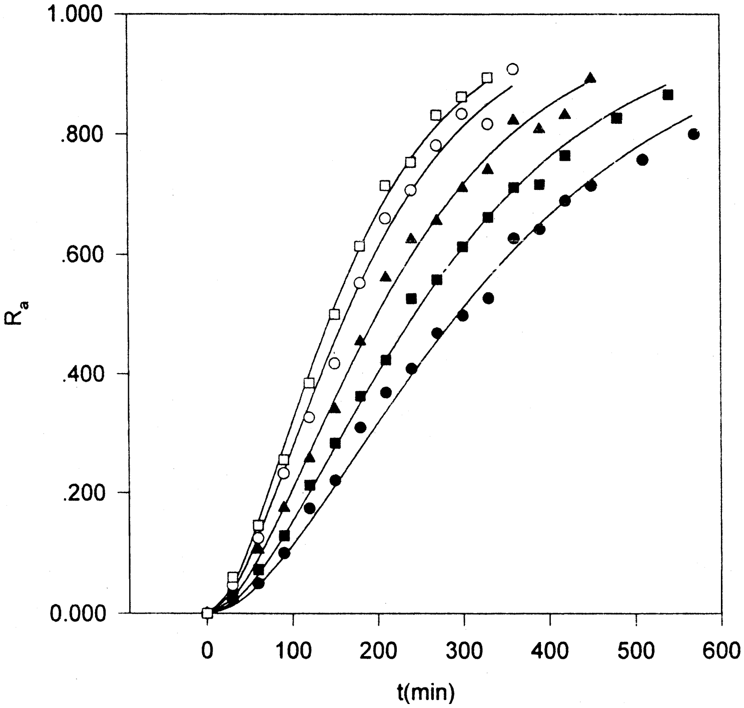

FIG. 7 Time evolution of R_a during coupled transport. Membrane: 0.08 M N_{235}–xylene. Theoretical curves calculated from Eq. (10). Symbols as in Fig. 5.

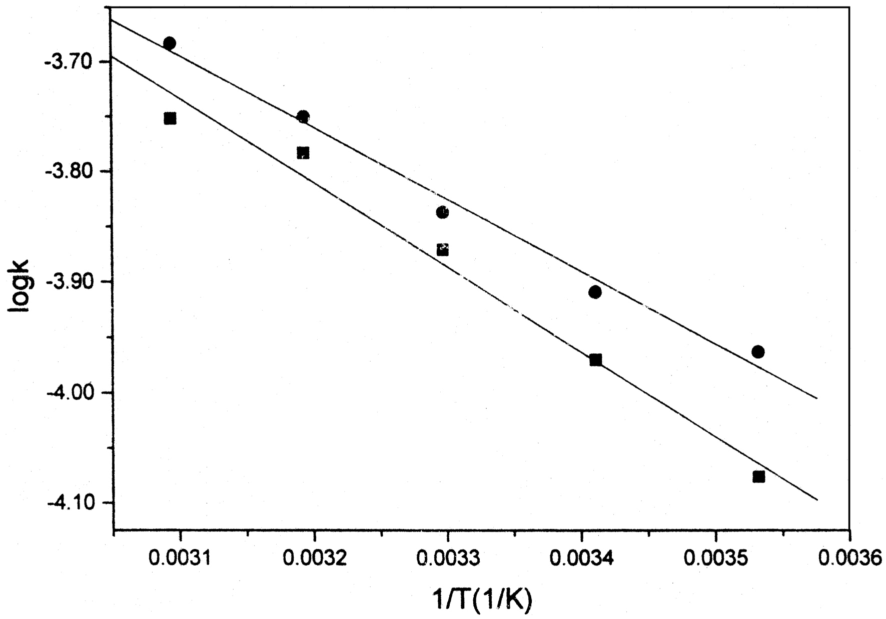

FIG. 8 Arrhenius plot of log k (k: s^{-1}) versus $1/T$ (1/K). (■) log k_1 ~ $1/T$, (•) log k_2 ~ $1/T$.

ported in the feed, membrane, and stripping phases, respectively. Good agreement between the theoretical curves and the experimental points is shown in Fig. 4. The results suggest that the transport of Cd(II) ions could be described by the kinetic laws of two consecutive irreversible first-order reactions (as shown above) in the present case, and that disregarding diffusion in the transport of Cd(II) ions is appropriate in this study. An Arrhenius—type plot is followed perfectly in Fig. 8. The activation energy values are 14.7 $kJ \cdot mol^{-1}$ for extraction and 12.4 $kJ \cdot mol^{-1}$ for stripping.

CONCLUSION

Cd(II) ions can be effectively transported through a liquid membrane containing N_{235} in xylene. The transport of Cd(II) ions is coupled by the cotransport flow of protons. The pseudofirst-order apparent rate constants, k_{1d} and k_{2a}, of the interfacial reactions of extraction and stripping were determined on the basis of a scheme implying two consecutive irreversible first-order reactions.

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