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Transfer and separation of Cd(II) chloride species from Fe(III) by a hybrid liquid membrane containing tri-*n*-octylamine–secondary octylalcohol–kerosene

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Abstract

In this study the separation of cadmium(II) from iron(III) has been successfully realized by a hybrid liquid membrane (HLM) containing tri-*n*-octylamine (TNOA, R_3N)–secondary octylalcohol (ROH)–kerosene. The effect of different variable on the separation has been carefully studied. The apparatus composed of three compartments, including a reservoir of organic solution, with double solid supports was used in this study. The experiments show that the transport of Cd(II) ions is coupled by the co-transport flow of protons and the nitric acid in the feed phase of the HLM system can apparently improve the separation efficiency of cadmium(II) from iron(III). The loss of TNOA in the membrane phase was determined. The experiments demonstrated that the HLM can automatically and continuously replenish the membrane supports pores by the membrane solution (organic phase).

Keywords: Hybrid liquid membrane; Cadmium ions; Iron ions; Separation; Tri-*n*-octylamine

1. Introduction

The presence of cadmium compound in the environment is seriously imperiling human health. Therefore, the removal of Cd(II) ions from wastewater is of great significance. Especially, the separation of Cd(II) from other metals is very valuable for environment protection and comprehensive utilization of natural resources. However, a great majority of natural mining waters or wastewater contain less than 1.0 g/l metal ions, thus, they are considered as very dilute streams unsuited to be treated by conventional liquid–liquid extraction processing [1–5].

The liquid membrane has been proposed as an alternative to liquid–liquid extraction technology for the selective separation and concentration of cadmium and other metal ions from dilute aqueous solutions [6–10]. Two configurations of liquid membrane are currently being used: emulsion liquid membrane (ELM) and supported liquid membrane (SLM) [11–13]. The supported liquid membrane possesses high specificity, low energy utilization, and other advantages. A great number of studies have been done for the application of SLM to the industry. But the defects of SLM are also discovered in operation. One disadvantage of SLM is its instability due mainly to loss of the membrane liquid into the aqueous phases on each side of the membrane [14–16]. In addition, the flux of solute through SLM is lower. The above disadvantages of SLM hamper potential applications of liquid membrane in industry.

For solving the above difficulties of application of liquid membrane in industry and devising the liquid membrane system of high efficiency, the new liquid membrane configurations have been reported [17]. For example, Ho and Lexington [18] firstly reported a combined supported liquid membrane/strip dispersion system. Kislik and Eyal [19] reported a hybrid liquid membrane (HLM). Guangiu et al. [20] reported the transport of Au(III) through double solid supported liquid membrane from the combination of bulk liquid membrane and supported liquid membrane. Similar systems have been described by other research groups such as Basu and Sirkar [21], Boyadzhiev [22], Teramoto [23], Kedem and Bromberg [24], Eyal and Bressler [25], and Schlosser [26]. In these literatures, the authors and their cooperators have discussed the transport mechanisms, researched the effect of different experimental conditions on

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the transport of solutes, and developed the theory of membrane transport. Their target of study is mainly single-cation transport by HLM. Since relatively few studies concerning the separation of two or more competitive solutes by the new type of liquid membrane are encountered in the actual literature, more work is required in this field in order to approach more practical separation problems. As a model system we have chosen the selective cadmium/iron cations transport by HLM containing tri-*n*-octylamine (TNOA, R_3N)–secondary octylalcohol (ROH)–kerosene. Because commercially available membrane modules may be used in the HLM and the lower loss of TNOA for HLM has been investigated in our work [27], the HLM is chosen as the liquid membrane configuration for the transport and separation of Cd(II) from Fe(III). In hydrometallurgy, the transport and separation of Cd(II) from Fe(III) is very significant to the comprehensive application of chloride leaching solution of smithsonite.

One of the main objectives of this study is to investigate the technical feasibility of separation of Cd(II) from Fe(III) ions by HLM. With this objective, the effect of different aqueous and organic phase variable on the separation should be carefully researched. Another objective is aimed at exploring the potential of hybrid techniques. For the purpose, an insight into the transport of ions in the given system is required. In this way, the combination of these experimental results allowed us to evaluate and forecast the potential of HLM in the industry. It is more valuable to hydrometallurgy and wastewater treatment than the traditional SLM and is expected to be an environmentally friendly and economical liquid waste management technology for the transfer of small amounts (50–1000 mg/l) of valuable or toxic metals [19].

2. Theoretical consideration of transport of ions

The membrane system consisted of three membranes in series contacted with an external feed solution containing Cd(II) ions, and a stripping solution at the opposite interface:

feed solution	polymeric support	R_3N and ROH in kerosene	polymeric support	stripping solution

The transport of ions across membrane is a result of a number of steps, comprising the extraction and strip reaction and diffusion steps.

In Fig. 1 the reactions and transport processes are depicted. The co-transport involves various (equilibrium) reactions, which are described below:

(a) Complexation of cadmium(II) by chloride ions in the feed solution:

$$Cd^{2+} + nCl^- \overset{\beta_n}{\longleftrightarrow} CdCl_n{}^{2-n} \tag{1}$$

This is a very fast reaction [27]. β_n is known as the *n*th overall formation constant [28]. The fraction, α_n, of cadmium(II) present as $CdCl_n{}^{2-n}$ is equal to

$$\alpha_n = \frac{\beta_n[Cl^-]^n}{1+\sum_{n=1}^{4}\beta_n[Cl^-]^n} \tag{2}$$

(b) Reaction of R_3N at the feed/membrane interface with HCl in the feed solution:

$$R_3N_{org} + HCl_{aq} \rightleftharpoons R_3NHCl_{org} \tag{3}$$

In the organic solution with modifier (ROH) no third phase formation was detected. Since the R_3NHCl formation is very fast this reaction is not rate limiting.

(c) The extraction reaction of cadmium(II) ions as $CdCl_4{}^{2-}$ is depicted by the following equation [29] at the feed/membrane interface:

$$2R_3NHCl_{org} + CdCl_{4aq}{}^{2-} = (R_3NH)_2CdCl_{4org} + 2Cl_{aq}{}^- \tag{4}$$

Because the time of extraction equilibrium in our shake test is very short, Eq. (4) is not rate limiting. The stoi-

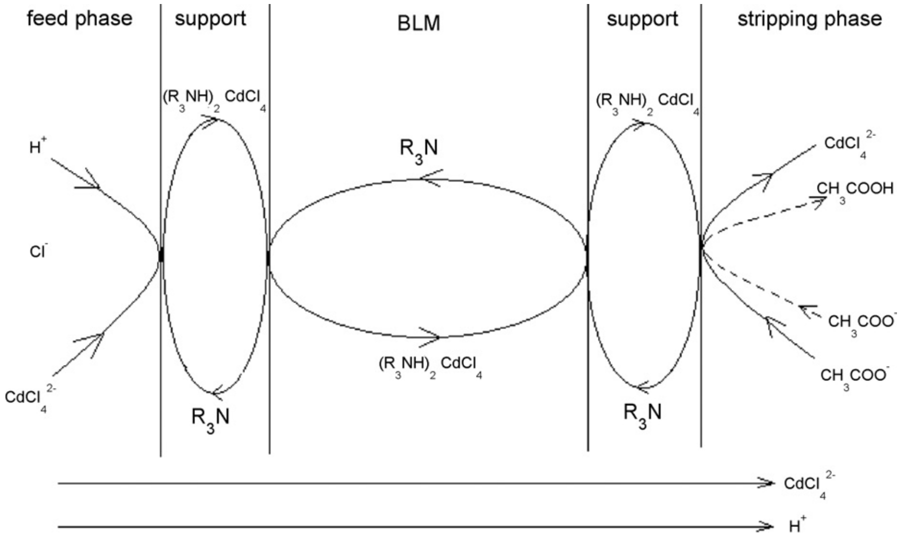

Fig. 1. Schematic representation of the transport mechanism of Cd(II) ions in a hybrid liquid membrane.

chiometric composition $(R_3NH)_2CdCl_4$ is verified in the literature [29].

It is convenient to define a distribution ratio, K_d, of Cd(II) ions at the interfaces:

$$K_d = \frac{[(R_3NH)_2CdCl_{4org}]}{[Cd^{2+}]_i} \tag{5}$$

where $[(R_3NH)_2CdCl_{4org}]$ and $[Cd^{2+}]_i$ denote the concentration of Cd(II) in the organic phase and in the feed phase, respectively.

(d) The stripping reaction:

$$(R_3NH)_2CdCl_{4org} + 2CH_3COO^- = 2R_3N_{org} + 2CH_3COOH_{aq} + CdCl_{4aq}{}^{2-} \tag{6}$$

$$2CH_3COOH_{aq} \Leftrightarrow 2H_{aq}{}^+ + 2CH_3COO_{aq}{}^- \tag{7}$$

$$H_2O \Leftrightarrow H^+ + OH^- \tag{8}$$

$$(R_3NH)_2CdCl_{4org} + 2OH_{aq}{}^- = 2R_3N_{org} + CdCl_{4aq}{}^{2-} + 2H_2O_{aq} \tag{9}$$

Thus the permeability coefficient can be expressed as

$$P = \frac{J}{[Cd^{2+}]} \tag{10}$$

where the flux of a species removed from the feed solution can be defined by the following formula:

$$J = -\frac{d[Cd^{2+}]}{dt}\frac{V}{Q} \tag{11}$$

where V denotes the aqueous feed volume and Q is the effective membrane area which was calculated by multiplying the geometrical area and the porosity of the polymer support. The effect of experimental conditions on the transport efficiency is indicated by the magnitude of P. The flux of Cd(II) through the membrane was calculated from the slope of the initial linear plot of Cd(II) concentration in the feed phase against time according Eq. (11).

For the convenience of discussion the separation factor is defined as [30]

$$\gamma_{HLM} = \frac{[Cd^{2+}]_s/[Cd^{2+}]_f}{[Fe^{3+}]_s/[Fe^{3+}]_f} \tag{12}$$

$$\gamma_{sx} = \frac{[Cd^{2+}]_{org,t}/[Fe^{3+}]_{org,t}}{[Cd^{2+}]_{f,0}/[Fe^{3+}]_{f,0}} \tag{13}$$

where γ_{HLM} and γ_{sx} are the separation factor for HLM and solvent extraction, respectively. The s and f stand for stripping phase and feed phase, respectively. In Eq. (13), t and 0 stand for time $t = t$ and $t = 0$, respectively. The org stands for organic phase.

3. Experimental

3.1. Materials

All the reagents such as $CdCl_2{\cdot}2.5H_2O$, NaCl, HCl, CH_3COONH_4, $ZnCI_2{\cdot}6H_2O$ and $FeCl_3{\cdot}6H_2O$ et al. used in the present work were of analytical grade. TNOA is a commercial extractant (purity > 95%) and used without any further purification except for balancing with 0.5 M HCl solutions before usage. Secondary octylalcohol (ROH) is chemical pure grade.

Cd(II) stock solution: a stock solution of Cd(II) was prepared by dissolving $CdCl_2{\cdot}2.5H_2O$ in deionized water, and 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 HCl and NaCl.

Fe(III) stock solution: a stock solution of Fe(III) was prepared by dissolving $FeCl_3{\cdot}6H_2O$ in deionized water, and analyzed by $K_2Cr_2O_7$ titration using sodium diphenylamine sulfonate as indicator.

Stripping solution: the required amount of CH_3COONH_4 was solved and diluted with deionized water to a known concentration.

Distilled kerosene: commercial kerosene was washed with concentrated sulfuric acid and distilled at 185–225 °C.

The solid support is a microporous polypropylene flat film having 51% porosity and a thickness of 0.02 mm.

3.2. Apparatus

The experiments were performed with a three-compartment cell as shown in Fig. 2, where one membrane (a) is placed between the feed and carrier solution, and another membrane (b) separates the carrier solution and stripping solution. The three compartments are made of plastic cylinders. The effective lengths of the feed and stripping compartments are 80 mm each, and an inner diameter of cylinders is 56 mm. The compartment for the organic solutions is 50 mm in length. The volumes of the feed and stripping solutions are 147 cm^3 each, while the volume of the organic solutions is 23 cm^3. The geometrical area of the membrane is 15.2 cm^2. The stirring speed of the feed and

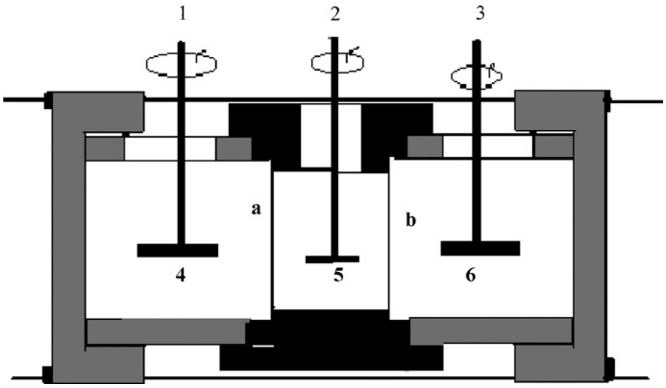

Fig. 2. Scheme of transport cell: (1), (2), (3) stirrer; (4) feed solution; (5) organic solution; (6) stripping solution; (a) and (b) membrane.

stripping solution was kept at 900 rpm except for experiments to investigate the influence of the stirring speed on the permeability coefficients. The stirring speed of the compartment of the organic solution was kept at 400 rpm in all the experiments except for a set of experiments where the stirring speed was varied.

In the experiments, the samples were taken out from the feed solution and stripping solution at scheduled time intervals and analyzed for an ion contents with a UV–visible spectrophotometer (492 nm for Cd, PAR (4-(2-pyridylazo)-resorcinol) used as developer). The content of ion in the solution containing two or more ions was determined by atomic absorption spectroscopy (228.8 nm for Cd, 213.7 nm for Zn, 248.3 nm for Fe). The fluxes and permeability coefficients obtained were reproducible within about ±10%. All the experiments were carried out at 30 ± 0.1 °C. The content of TNOA dissolved in feed and stripping solutions is analyzed by bromophenol blue-spectrophotometry [31]. The pH of the stripping solution was measured with a pH meter, and H^+ concentration of the feed solution was analyzed by acid–base titration using methyl orange as indicator.

3.3. *Extraction equilibrium*

An aqueous solution ($10\,cm^3$) containing 8.90×10^{-4} M Cd(II), 0.1 M HCl, and 0.4 M NaCl was shaken with an equal volume of the kerosene solution of 0.1 M TNOA + 10% (v/v) ROH for 10 min at room-temperature (Experiments indicates that the extraction equilibrium is reached after 10 min.). The metal concentration in the organic phase was calculated from the concentration differences of the aqueous phases before and after extractions.

4. Results and discussion

4.1. *Extraction separation of Cd(II) and Fe(III)*

Fig. 3 indicates that Cd(II) is almost completely extracted, whereas Fe(III) is partially extracted under experimental conditions. Therefore, it is very difficult to separate Cd(II) from Fe(III) in different concentration of HCl.

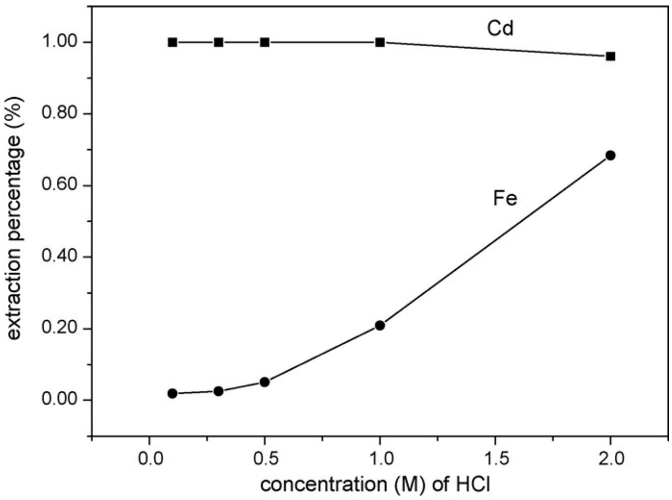

Fig. 3. Influence of HCl concentration on the extraction of Cd(II) and Fe(III).

4.1.1. *Effect of HNO_3 on the extraction of Cd(II) and Fe(III)*

In general, the extraction of Cd(II) and Fe(III) depends on their ability of coordination with anions and the exchanging ability of their complex anions for the anions of amine salt in the organic phase (see Eqs. (1) and (4)). According to the coordination chemistry the ability of coordination between Cd(III) and Cl^- is superior to the coordination between Fe(III) and Cl^-. Based on the difference of ion radius and ion polarization for Cd(II) and Fe(III), $CdCl_4^{2-}$ has a larger polarizability between Cd(II)-Cl^- than $FeCl_4^-$. In this way, the degree of covalent character for $CdCl_4^{2-}$ is superior to $FeCl_4^-$. This behavior brings about the larger solubility of $(R_3NH)_2CdCl_4$ in organic phase over $(R_3NH)FeCl_4$ and high extraction of cadmium(II) over Fe(III). Fig. 3 verifies the conclusion.

Table 1 indicates the influence of HNO_3 concentration in feed phase on the separation factor of Cd(II) and Fe(III) and the maximum separation factor (β_{sx}) when $[HNO_3] = 0.5$ M. According to solvent extraction, $CdCl_4^{2-}$ and $FeCl_4^-$ are probably extracted into organic phase or are probably escaped into feed phase from the organic phase because of the stripping of HNO_3 [32]. In other words, the addition of HNO_3 into the feed phase influences the exchanging ability of their complex anions for the anions of amine salt in the organic phase (see Eq. (4)) and depresses the extraction of Cd(II) and Fe(III).

At last, because the coordination compound of cadmium(II)-chloride ions possesses fine stability and the extraction of cadmium(II) is main over back extraction of cadmium(II) in the presence of HNO_3 cadmium(II) were priorly extracted into organic phase and HNO_3 in the feed solution is beneficial to the separation of Cd(II) from Fe(III) in the system. Fig. 4 indicates that the separation of Cd(II) from Fe(III) is well realized below 0.5 M Cl^- in the presence of 0.5 M HNO_3. However, the extraction percentage of Cd(II) comes down by comparison with the absence of HNO_3 in the feed phase.

4.1.2. *Effect of Br^- concentration on the extraction of Cd(II) and Fe(III)*

In the separation of Cd(II) from Fe(III) in order to maintain the higher extraction percentage for Cd(II) and to suppress the extraction of Fe(III) in the feed phase containing 0.5 M HNO_3

Table 1
Influence of HNO_3 concentration in feed phase on the separation factor of Cd^{2+} and Fe^{3+}[a]

HNO_3 concentration in feed phase (M)	Separation factor γ_{sx}
0.02	37.4
0.10	42.1
0.30	47.5
0.50	53.2

[a] Feed phase: 0.89 mmol/l Cd^{2+}, 1.79 mmol/l Fe^{3+}, 0.1 M KBr, 0.5 M NaCl and various concentration of HNO_3. Organic phase: 0.1 N TNOA, 10% (v/v) ROH, kerosene.

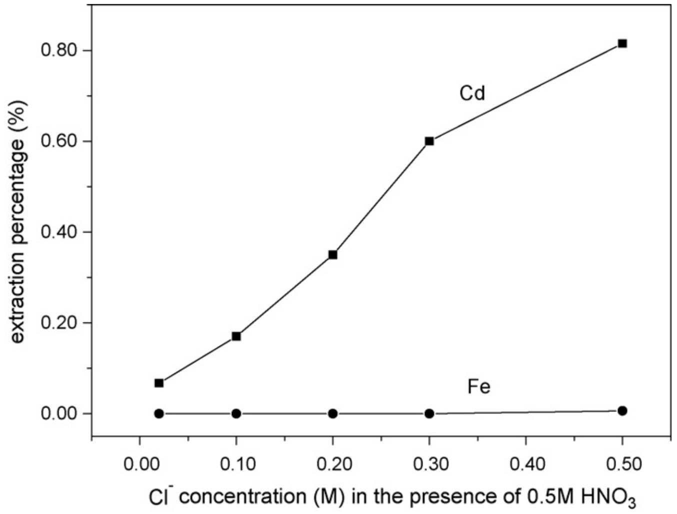

Fig. 4. Effect of NaCl concentration on the extraction of Cd(II) and Fe(III) in the presence of 0.5 mol/l HNO_3.

Table 2
Influence of Br^- concentration in feed phase on the separation factor of Cd^{2+} and Fe^{3+}[a]

Br^- concentration in feed phase (M)	Separation factor γ_{sx}
0.02	20.6
0.1	53.2
0.3	52.5
0.5	33.5

[a] Feed phase: 0.89 mmol/l Cd^{2+}, 1.79 mmol/l Fe^{3+}, 0.5 M HNO_3, 0.5 M NaCl and various concentration of Br^-. Organic phase: 0.1 M TNOA, 10% (v/v) ROH, kerosene.

we choose Br^- as a complex agent. Table 2 shows that the separation factor is the maximum in the feed phase containing 0.10 M Br^-. Fig. 5 indicates that the separation of Cd(II) from Fe(III) is complete in the presence of 0.10 M Br^-, considering the result of separation and reagent cost.

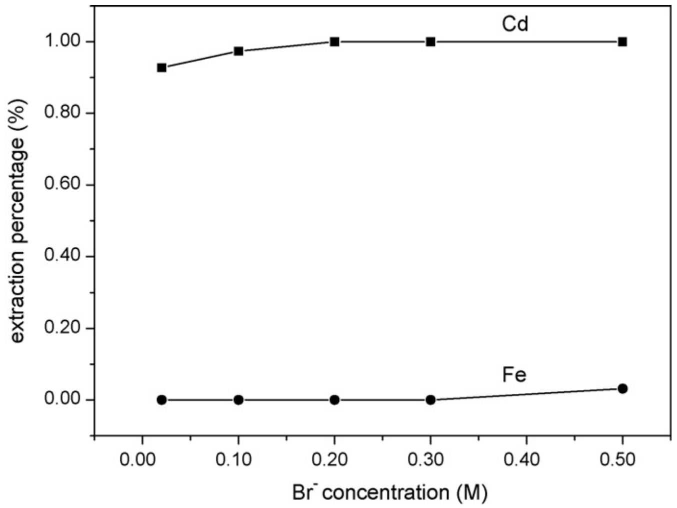

Fig. 5. Effect of KBr concentration on the extraction of Cd(II) and Fe(III) in the presence of 0.5 mol/l HNO_3.

4.2. Separation of Cd(II) and Fe(III) by hybrid liquid membrane

4.2.1. Evaluation of permeability coefficient

A ‘blank’ experiment of transport for Cd(II) and Fe(III) was finished in which the membrane contained no carrier. No detectable movement of Cd(II) and Fe(III) ions was found in the stripping solution. The line D in Fig. 6 almost overlaps the line C. They are nearly parallel to the X-axis. This is in a good agreement with the result of the blank experiment.

The straight line B in Fig. 6 shows a typical linear relationship of $\mathrm{Ln}([Cd^{2+}]_t/[Cd^{2+}]_0)$ versus time. In the extraction tests and membrane transport, no solid phase was detected in the organic solution. The straight line B in Fig. 6 indicates that the transport of cadmium(II) is induced by the carrier.

It is conceivable that in experiments of very long duration small amounts of Fe(III) would eventually be transported through the liquid membrane to strip side. In contact with a stripping solution at pH 6 approximately, would the Fe(III) ions precipitate in the pores of the solid membrane as colloidal iron hydroxide? Eventually this completes blocking the ion transfer process. In our experiments CH_3COONH_4 is a stripping agent. According to literature [33], the nth overall formation constant for Fe(III)-CH_3COO^- complex is $\log\beta_n = 3.2, 6.1, 8.3$ ($n = 1, 2, 3$, respectively). Consequently, the Fe(III) ions dose not precipitate as colloidal iron hydroxide because of the formation of Fe(III)-CH_3COO^- complex and the larger value of overall formation constant for the Fe(III)-CH_3COO^- complex.

4.2.2. Effect of stirring rate on transport of Cd(II)

The effect of the stirring rate of the feed phase on the flux of Cd(II) is given in Fig. 7(A). In the study we applied the same stirring rate to both the feed and the stripping solutions while maintaining a constant stirring rate of 400 rpm in the membrane

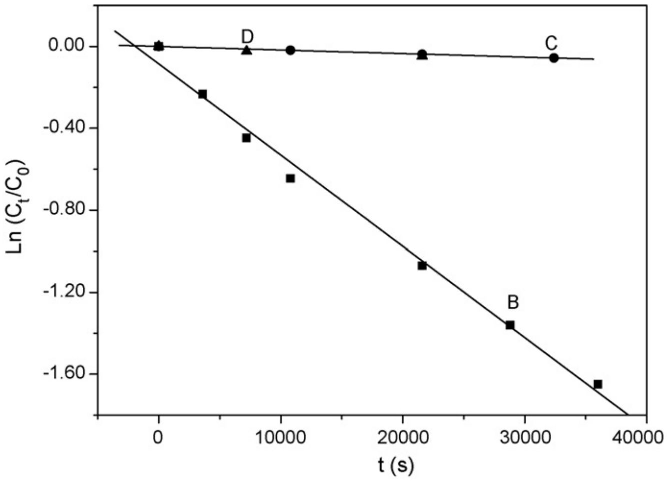

Fig. 6. $\mathrm{Ln}(C_t/C_0)$ vs. t for the transport of Cd(II) or Fe(III) through HLM. For line B (■): feed solution: 8.90×10^{-4} M Cd^{2+}, 0.1 M HCl, 0.4 M NaCl; stripping solution: 0.5 M CH_3COONH_4; membrane: 0.1 M TNOA, 10% (v/v) ROH, kerosene (pre-equilibrated with 0.5 M HCl before usage). For line C (●): membrane phase is pure kerosene. Feed and stripping phase is the same as line B. For line D (▲): feed phase: 1.79×10^{-3} mol/l Fe^{3+}, 0.1 M HCl, 0.4 M NaCl; stripping phase is the same as the line B; membrane: pure kerosene.

Table 3
The variation of H^+ concentration in feed and stripping solution[*]

Feed composition	H^+ concentration in feed phase (M)		pH in stripping phase	
	$t=0$	After 9 h	$t=0$	After 9 h
0.89 mmol/l Cd^{2+}, 0.422 M HNO_3, 0.5 M NaCl(a)	0.422	0.407	7.25	6.09
1.79 mmol/l Fe^{3+}, 0.5 M HNO_3, 1.0 M NaCl(a)	0.515	0.503	6.50	5.96
0.89 mmol/l Cd^{2+}, 1.79 mmol/l Fe^{3+}, 0.1 M KBr, 0.5 M NaCl, 0.5 M HNO_3(b)	0.535	0.521	6.63	6.26
0.89 mmol/l Cd^{2+}, 1.79 mmol/l Fe^{3+}, 0.1 M KBr, 0.5 M NaCl, 0.5 M HNO_3(c)	0.535	0.519	6.63	6.18
0.89 mmol/l Cd^{2+}, 1.79 mmol/l Fe^{3+}, 0.1 M KBr, 0.5 M NaCl, 0.5 M HNO_3(d)	0.535	0.512	6.63	6.01

Membrane: (a) 0.1 M TNOA, 10% (v/v) ROH, kerosene; (b) 0.04 M TNOA, 10% (v/v) ROH, kerosene; (c) 0.07 M TNOA, 10% (v/v) ROH, kerosene; (d) 0.12 M TNOA, 10% (v/v) ROH, kerosene.

[*] Stripping phase: 0.5 M CH_3COONH_4.

solutions. Fig. 7(A) shows that the flux increases with increasing stirring speed until a plateau is reached. We can then assume that the thickness of the aqueous diffusion film reaches a constant limiting value, d_a, when rpm > 900. The stirring rate of the stripping solution was found to have no influence on the flux because the rate of stripping at the interface between the membrane and stripping phase is fast.

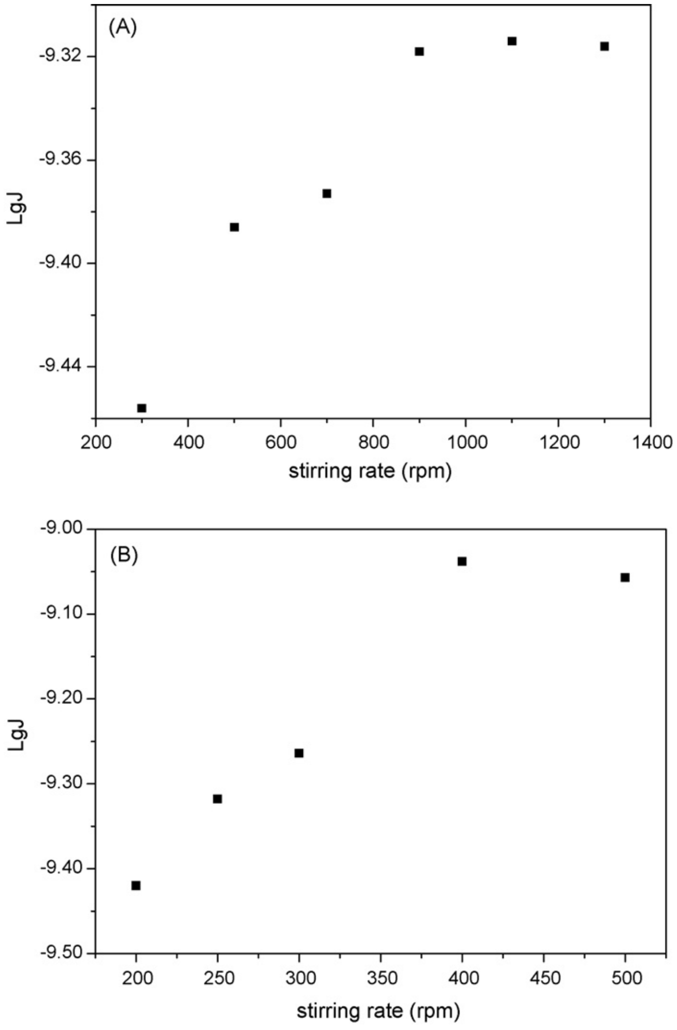

Fig. 7. (A) Effect of stirring rate of feed solution on permeation of Cd(II). Stirring rate of membrane phase: 400 rpm. (B) Effect of stirring rate of membrane phase on permeation of Cd(II). Stirring rate of feed and stripping phase: 900 rpm.

The dependence of flux on the stirring rate in the membrane phase is shown in Fig. 7(B). The experiments were carried out by changing the stirring speed of the membrane phase while maintaining a constant stirring rate of 900 rpm in the feed and stripping phase. Fig. 7(B) indicates that J is dependent on the stirring speed of the organic phase below 400 rpm. At higher stirring speeds (rpm > 400) J is independent of the rate of stirring. Increasing the stirring rate decreases the diffusion film thickness on both membrane a and b, to a minimum constant value. The chosen stirring rate were such that hydrodynamic complications (whirls, interface deformations, etc.) were still absent.

4.2.3. Description of coupled transport of Cd(II) and Fe(III) ions

Table 3 indicates the variation of the concentrations of H^+ in feed and stripping solution at $t=0$ and after the transport of 9 h for the feed solution containing only Fe^{3+} or Fe^{3+} and Cd^{2+}. The experiments for the two feed solutions show that protons were transported into the stripping phase from the feed phase. Meanwhile, the transport of Cd(II) or Fe(III) ions into the stripping phase from the feed phase was also observed. The result demonstrates that the transport of Cd(II) or Fe(III) ions is coupled by the co-transport flow of protons.

4.2.4. Effect of Cl^- concentration in feed phase on permeability coefficient

The permeability coefficients for Fe^{3+} and Cd^{2+} were separately determined under different concentration of CI^- ions. The data is collected in Table 4. Table 4 also shows that the separation of Cd(II) from Fe(III) is based on the difference of their

Table 4
Influence of Cl^- concentration in feed phase on permeability coefficient[a]

Cl^- concentration in feed phase (M)	Permeability coefficient (cm/s)	
	Cd^{2+}	Fe^{3+}
0.5	1.30×10^{-3}	2.66×10^{-6}
1.0	1.90×10^{-3}	1.73×10^{-5}
1.5	1.91×10^{-3}	1.78×10^{-5}

[a] Feed phase (Cd^{2+}): 0.89 mmol/l Cd^{2+}, 0.1 M KBr, 0.5 M HNO_3, and NaCl of different concentration. Feed phase (Fe^{3+}): 1.79 mmol/l Fe^{3+}, 0.1 M KBr, 0.5 M HNO_3, and NaCl of different concentration. Membrane for Cd^{2+} and Fe^{3+} is the same: 0.1 M TNOA, 10% (v/v) ROH, kerosene. Stripping phase: 0.5 M CH_3COONH_4.

Table 5
Influence of carrier concentration on the separation factor of Cd^{2+} and Fe^{3+}[a]

TNOA concentration (M)	Separation factor γ_{HLM}
0.04	17.4
0.07	113.7
0.10	245.2
0.12	284.1
0.16	158.0

[a] Feed phase: 8.9 mmol/l Cd^{2+}, 1.79 mmol Fe^{3+}, 0.1 M KBr, 0.5 M HNO_3, 0.5 M NaCl. Stripping phase: 0.5 M CH_3COONH_4. Membrane is the same as Table 3 except for TNOA concentration.

permeability coefficient. In this study Cd(II) species is quickly transported than Fe(III) species by the HLM containing TNOA.

4.2.5. *Effect of carrier concentration on the separation factor of Cd(II) and Fe(III)*

Table 5 indicates that the separation factor increase with the increase of carrier concentration up to 0.12 M and beyond 0.12 M the decrease of separation factor is observed. It is probably because the increase of viscosity in membrane results in the drop of transport rate when the concentration of carrier is 0.16 M.

4.2.6. *Analysis of the loss of TNOA in membrane phase*

Instability of supported liquid membrane is due to the loss of carrier and/or membrane solvent from the membrane phase. In this study the experimental results of the loss of TNOA in membrane phase are shown in Table 6. Table 6 indicates that the usage of two solid membranes in HLM can prevent the carrier from escaping from the membrane phase into the aqueous solutions and the loss of TNOA is very low in the HLM operation. Consequently, the experiments demonstrated that the HLM can automatically and continuously replenish the membrane supports pores by the membrane solution (organic phase) once the loss of membrane phase has started in operation. To some extent the above instability can be overcome by designing the hybrid liquid membrane. Certainly, the influence of the type of salt in aqueous solutions on the loss of carrier and solvent should be carefully investigated in late experiments.

4.2.7. *Comparison of separation of Cd(II) from the different feed phase containing Fe(III) and/or Zn(II)*

The data of Table 4 show that the transfer rate of Cd(II) and Fe(III) differs by 100 times at least. The different transfer rate arises from adding the HNO_3 into the feed phase of liquid membrane. As a consequence, the overall permeation rate is mainly controlled by the stability of TNOA-metal ion coordination compounds, their solubility in the organic phase, and the difference of stripping efficiency of HNO_3 for $CdCl_4^{2-}$ and $FeCl_4^{-}$. As an overall result, the membrane becomes more selective to Cd. Table 4 also allows one to predict that a good separation of Cd(II) from Fe(III) can be achieved. This prediction is well confirmed by the data reported in Table 7.

Table 6
Comparison of the uptake of TNOA into the feed phase and stripping phase[a]

Cl^- concentration (M)	TNOA concentration (mg/l)	
	In feed solution	In stripping solution
0.5	0.23	0.28
1.0	1.1	0.21
1.5	0.078	0.12

[a] Feed phase: 0.89 mmol/l Cd^{2+}, 1.79 mmol/l Fe^{3+}, 0.5 M HNO_3, 0.1 M Br and various concentration of NaCl. Stripping phase: 0.5 M CH_3COONH_4. Membrane is the same as Table 3.

Table 7
Comparison of separation of Cd^{2+} from Fe^{3+} after the transport of 25 h[a]

Content of metal ions in feed phase at $t = 0$ (mg/l)	Recovery of Cd^{2+} and Fe^{3+} in stripping phase (mg/l)
$[Cd^{2+}] = 100$ $[Fe^{3+}] = 100$	$[Cd^{2+}] = 100$ $[Fe^{3+}] = 0$
$[Cd^{2+}] = 100$ $[Fe^{3+}] = 500$	$[Cd^{2+}] = 100$ $[Fe^{3+}] = 0$
$[Cd^{2+}] = 100$ $[Fe^{3+}] = 100$	$[Cd^{2+}] = 100$ $[Fe^{3+}] = 0$
$[Zn^{2+}] = 100$	$[Zn^{2+}] = 4.88$

[a] Feed phase: 0.1 M KBr, 0.5 M HNO_3, 0.5 M NaCl and various concentration of metal ions. Stripping phase: 0.5 M CH_3COONH_4. Membrane is the same as Table 5.

5. Conclusion

In the present study the separation of Cd(II) species from Fe(III) by a hybrid liquid membrane containing tri-*n*-octylamine–secondary octylalcohol–kerosene has been successfully realized. The present work verifies that the transport of Cd(II) ions is coupled by the co-transport flow of protons and the presence of HNO_3 in the feed solution is beneficial to separation of Cd(II) from Fe(III) for HLM. The experiments demonstrated that the HLM can automatically and continuously replenish the membrane supports pores by the membrane solution (organic phase) and the separation of Cd(II) from Fe(III) for HLM is based on the difference of their permeability coefficients.

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