Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Simultaneous Transport and Separation of Cu(II) and Zn(II) in Cu-Zn-Co Sulfate Solution by Double Strip Dispersion Hybrid Liquid Membrane (SDHLM)

Xiaojian Luo[a]; Dingsheng He[a]; Ming Ma[a]
[a] Institute of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, P.R. China

To cite this Article Luo, Xiaojian , He, Dingsheng and Ma, Ming(2010) 'Simultaneous Transport and Separation of Cu(II) and Zn(II) in Cu-Zn-Co Sulfate Solution by Double Strip Dispersion Hybrid Liquid Membrane (SDHLM)', Separation Science and Technology, 45: 14, 2130 — 2140
To link to this Article: DOI: 10.1080/01496395.2010.504442
URL: http://dx.doi.org/10.1080/01496395.2010.504442

Separation Science and Technology, 45: 2130–2140, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.504442

Simultaneous Transport and Separation of Cu(II) and Zn(II) in Cu-Zn-Co Sulfate Solution by Double Strip Dispersion Hybrid Liquid Membrane (SDHLM)

Xiaojian Luo, Dingsheng He, and Ming Ma
Institute of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, P.R. China

A double strip dispersion hybrid liquid membrane (SDHLM) was successfully used in the simultaneous extraction and separation of Cu(II), Zn(II), and Co(II) from Cu-Zn-Co dilute feed phase. In the double SDHLM system, Acorga M5640-loaded membrane was placed between the 1st and the 2nd compartment, whereas the mono(2-ethylhexyl) 2-ethylhexyl phosphonate [HEH(EHP)]-loaded membrane was placed between the 1st and the 3rd compartment of the transport cell. The feed solution was filled in the central feed compartment(1st compartment) of the transport cell. The effect of the different experimental variables on separation was examined. The optimum separation conditions were summarized.

An analysis of mass transfer resistances in the double SDHLM system shows that the mass transfer resistance for the diffusion of Zn(II) ions in the microporous membrane phase is dominant and the mass transfer resistances for the diffusion of copper (II) ions in the aqueous boundary layer and in the microporous membrane phase are dominant in comparison with the overall mass transfer resistance. The experiments verify that the double strip dispersion hybrid liquid membrane (SDHLM) possesses the nonequlibrium mass transfer characteristic.

Keywords copper ions; mass transfer resistance; separation; strip dispersion hybrid liquid membrane; zinc ions

INTRODUCTION

There are two basic types of liquid membrane processes—emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs). The disadvantages of the ELMs is that the emulsion swells upon prolonged contact with the feed stream and membrane ruptures, resulting in a leakage of the contents in the aqueous droplets into the feed stream and a concomitant reduction of separation efficiency (1).

The facilitated transport of solutes through the supported liquid membranes (SLMs) was widely studied in the literature and attracts extensive attention in the separation and hydrometallurgy field (2–8). However, the instability of the supported liquid membranes (SLMs) due to the uptake of the carrier and the membrane solvent into an adjacent aqueous phase, limits the lifetime of SLMs. Thus far, in the industrial application of liquid membrane still there is a need for maximizing the stability of liquid membrane and resulting in the efficient removal and recovery of solutes from the aqueous feed solutions. In order to satisfy a need of the industry a novel liquid membrane configuration has been brought forward and developed.

A combined supported liquid membrane (SLM)/strip dispersion process was first reported for the removal and recovery of the target species from a feed solution (9–10). It is a new liquid membrane process. The reference (11–13) used the same liquid membrane configuration as the refs. (9,10)., incorporating the concepts of the supported liquid membrane and the emulsion liquid membrane, denoted the strip dispersion hybrid liquid membrane (SDHLM). This liquid membrane has several advantages—increased stability of membrane, reduced costs, increased simplicity of operation, and extremely efficient stripping of the target species from the organic phase to obtain a high concentration of the recovered target species in the aqueous strip solution (10–13). These advantages are very attractive, nevertheless more studies are necessary for the application of the SDHLM process in industry. Otherwise, scaling up for the new liquid membrane configuration will fail unless a complete understanding of the efficiency parameter is done and reported in such a way that a concise and global insight of the separation characteristics of a given system can be easily drawn.

We selected the simultaneous transport and separation of Cu(II) and Zn(II) in Cu-Zn-Co sulfate solution as our object of the study. In hydrometallurgy, the transport and separation of Cu(II) and Zn(II) in Cu-Zn-Co sulfate solution is very significant to the comprehensive utilization of the sulfate leaching solution of the flue dust. It seems that the current three-compartment separation system might be suitable for industrial use in a hydrometallurgical plant. We think that the three-compartment simultaneous

---

Received 22 July 2009; accepted 29 April 2010.

Address correspondence to Dingsheng He, Institute of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Changsha 410081, P.R. China. Fax: +86-731-8872531. E-mail: hedingsh@hunnu.edu.cn

separation system has the advantages of the high separation efficiency and the simplicity of operation. The industrial realization of three-compartment simultaneous separation will be allowed to consider the experimental study with a module containing two sets of hollow fibers or the other new devices.

For the industrial use of the process presented, the present study is first concerned with the technical feasibility of recovery and separation of Cu(II) and Zn(II) from Cu-Zn-Co sulfate solution by the SDHLM process. Another objective is to optimize the various operational parameters for the development of the SDHLM process in practical applications. Since relatively few studies concerning the simultaneous separation of two or more competitive solutes by the new liquid membrane process are encountered in the literature, more work is required in this field in order to approach more practical separation problems. At the end, we should discuss and analyze the transport mechanism in the SDHLM process.

THEORETICAL ANALYSIS

In this study SLM configuration employs a polypropylene microporus film as the liquid membrane support. The aqueous strip solution comprises an aqueous phase containing a stripping agent in solvent extraction, while the organic phase contains an extractant in an organic solvent.

The SDHLM operation is as follows (9). First, a feed solution containing one or more metal ions is passed on one side of the SLM embedded in a microporous support material. In the step the extraction takes place in the interface between the feed solution and the membrane. Meanwhile, the metal-carrier complex diffuses to the other side of the SLM and treated to remove the metal ions by the use of a strip dispersion phase. In general, the usage of a mixer can disperse an aqueous strip solution in an organic liquid and form the droplets of the aqueous strip solution in a continuous organic phase because of the weak surface activity of extractant. It is called the strip-dispersion phase. In the experimental process there is a constant supply of the organic membrane solution, i.e., the organic liquid of the strip-dispersion phase, contacting the pores of the SLM. This constant supply of the organic liquid ensures a stable and continuous operation of the SLM. In this way, the metal-carrier complex could diffuse to the interface between the aqueous strip solution and the organic liquid in the pores of the SLM. Therefore, the direct contact between the aqueous strip solution and the organic liquid provides an efficient mass transfer for stripping. Secondly, once removal of the target species is complete, the mixer for the strip dispersion is stopped. The strip-dispersion phase is allowed to stand, resulting in the separation of the strip-dispersion phase into two phases—the organic phase readily wetting the pores of support and the aqueous strip solution phase containing concentrated metal ions. The concentrated strip solution is the product of this process. Figure 1 is a schematic representation of the SDHLM process.

On the feed side interface of the SLM, the extraction of divalent metal cation (Zn^{2+}) from the aqueous solutions with HEH(EHP) (abbreviation: HR) in kerosene can be expressed as follows (14):

$$\mathrm{Zn_f^{2+}} + 2(\mathrm{HR})_{2,\mathrm{org}} \rightleftharpoons \mathrm{ZnR_2(HR)}_{2,\mathrm{org}} + 2\mathrm{H_f^+} \qquad (1)$$

Where *org* and *f* stand for the organic phase and the feed solution, respectively. The symbol $(HR)_2$ indicates that HEH(EHP) in low-polarity kerosene mainly exists as a dimer.

The stripping reaction on the other side of the SLM is written as follows:

$$\mathrm{ZnR_2(HR)}_{2,\mathrm{org}} + 2\mathrm{H_s^+} \rightleftharpoons \mathrm{Zn_s^{2+}} + 2(\mathrm{HR})_{2,\mathrm{org}} \qquad (2)$$

Where s represents the strip phase.

The extraction of copper(II) by Acorga M5640 extractant (abbreviation:HL) dissolved in kerosene can be described by the next reaction (15):

$$\mathrm{Cu_f^{2+}} + 2\mathrm{HL_{org}} \rightleftharpoons \mathrm{CuL}_{2,\mathrm{org}} + 2\mathrm{H_f^+} \qquad (3)$$

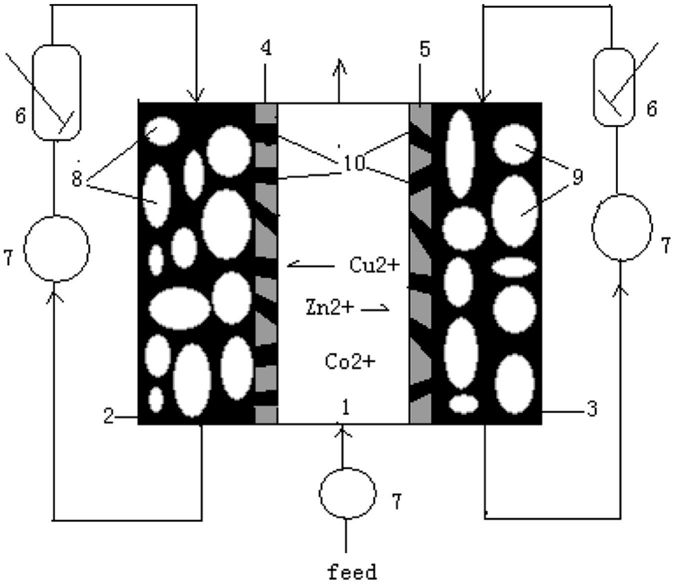

FIG. 1. Scheme of the strip dispersion hybrid liquid membrane used for performing transport experiments. 1. Feed phase compartment containing Cu^{2+}, Zn^{2+}, Co^{2+}, and SO_4^{2-}. 2. Compartment containing strip dispersion phase for extraction of Cu^{2+}. 3. Compartment containing strip dispersion phase for extraction of Zn^{2+}. 4. Supported liquid membrane for extraction of Cu^{2+}. 5. Supported liquid membrane for extraction of Zn^{2+}. 6. Mixer for mixture of organic solution and strip solution. 7. Pump for circulating flux. 8. Strip solution containing 3 M HCl. 9. Strip solution containing 2 M H_2SO_4. 10. Organic solution impregnated in support pores.

The stripping reaction on the other side of the SLM is written as follows:

$$\mathrm{CuL_{2org} + 2H_s^+ \rightleftharpoons Cu_s^{2+} + 2HL_{org}} \tag{4}$$

The flux of a species removed from the feed solution can be defined by the following formula (3):

$$\mathrm{J} = -\frac{\mathrm{V_f}}{\mathrm{A}}\frac{\mathrm{dC_f}}{\mathrm{dt}} \tag{5}$$

Where V_f is the volume of the feed solution treated, A is the effective area of the membrane, and C_f is the concentration of a species removed in the feed solution.

For discussing and describing the permeation of metal species through the SDHLM process, a new mass transfer coefficient, k, of the metal species removed from the feed solution can be defined by the following formula (3):

$$\mathrm{J} = \mathrm{k} \cdot \mathrm{C_f} \tag{6}$$

Integrating Eqs. (5)–(6), we have:

$$\mathrm{Ln}\frac{\mathrm{C_{f(t)}}}{\mathrm{C_f(o)}} = -\frac{\mathrm{A}}{\mathrm{V_f}}\mathrm{k} \cdot \mathrm{t} \tag{7}$$

$C_{f(t)}$ and $C_{f(o)}$ are the concentration of metal ions in the feed solution at time t = t and t = o, respectively. Equation (7) furnishes the value of k from the slope of plot of $\mathrm{Ln}(C_{f(t)}/C_{f(o)})$ versus t. Equation (7) quantitatively explains the coupled transport of metal species through the SDHLM system as a function of experimental variables. We can choose the experimental conditions based on k.

EXPERIMENTAL SECTION

Materials

All reagents ($CuSO_4 \cdot 5H_2O$, $Na_2SO_4 \cdot 10H_2O$, $CoSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, HCl, and H_2SO_4) used in the present work were of analytical grade. HEH(EHP) is a commercial extractant and used without any further purification. It is from the research institute of Shanghai Organic Chemistry. Dodecanol, supplied by the Hunan Chemical Reagent Corporation, was chemical pure grade. Acorga M5640 was a product from Avecia (England) and was used without further purification. The active substance of the reagent is 5-nonylsalicylaldoxime.

A stock solution of Cu(II) was prepared by dissolving $CuSO_4 \cdot 5H_2O$ in deionized water, and analyzed by $Na_2S_2O_3$ titration using starch as indicator.

Zn^{2+} stock solution: a stock solution of Zn^{2+} was prepared by dissolving $ZnSO_4 \cdot 7H_2O$ in deionized water and analyzed by EDTA titration using eriochrome black T as indicator.

Co^{2+} stock solution: a stock solution of Co^{2+} was prepared by dissolving $CoSO_4 \cdot 7H_2O$ in deionized water and analyzed by EDTA titration using eriochrome black T as indicator.

Zn^{2+} or Cu^{2+} feed solution: a known amount of the Zn^{2+} or Cu^{2+} stock solution was diluted with deionized water to a given extent after adding a calculated amount of $Na_2SO_4 \cdot 10H_2O$, respectively.

Mixed feed solution containing Zn^{2+}, Cu^{2+}, and Co^{2+}: a known amount of Zn^{2+}, Cu^{2+}, and Co^{2+} stock solution was diluted with deionized water to a given extent after adding a calculated amount of $Na_2SO_4 \cdot 10H_2O$.

Distilled kerosene: commercial kerosene was washed with concentrated sulfuric acid and distilled at 165–225°C.

HEH(EHP) kerosene solution: a calculated amount of extractant was diluted with kerosene.

M5640 kerosene solution: a calculated amount of extractant was diluted with kerosene.

Stripping solution was prepared taking the required amount of HCl or H_2SO_4 and diluting it with deionized water to a known volume, respectively. The membrane supports for SDHLM process was polypropylene Celgard 2500 (25 μm thickness, 45% porosity, 0.05×0.19 μm effective pore size, and the tortuosity is 2.40.) (18).

Flux Measurement

Flux of the SDHLM Process

The experiments were accomplished at 30 ± 0.1°C with a simple diffusion cell. The diffusion cell consists of a perspex half cell and two poly-tetrafluoroethylene half cells. The perspex half cell was placed between two poly-tetrafluoroethylene half cells. A M5640-loaded membrane was clampled between a poly-tetrafluoroethylene half cell and a perspex half cell, whereas a HEH(EHP)-loaded membrane was placed between another poly-tetrafluoroethylene half cell and the perspex half cell. Two membranes were used for simultaneous separation of Zn^{2+} and Cu^{2+} in Zn-Cu-Co sulfade solution (see Fig. 1). The effective area of the membrane was 22.6 cm^2. The aqueous feed solution (150 mL) consisted of 1.57×10^{-3} M Cu^{2+}, 1.53×10^{-3} M Zn^{2+}, 1.70×10^{-3} M Co^{2+}, and 0.167 M Na_2SO_4. It was poured into the Perspex half cell. The role of Na_2SO_4 is for maintaining the constant ionic strength in the feed solution. For the extraction of Zn^{2+}, the mixed strip dispersion system consisted of 110 mL organic solution containing 0.4 M HEH(EHP)and 0.24 M dodecanol and 10 mL 2 M H_2SO_4 strip solution except for the experiments of the different volume ratio and was placed into the polytetrafluoroethylene half cell. For the extraction of Cu^{2+}, the mixed strip dispersion system consisted of 100 mL organic solution containing 10% M5640 (w/v) and 20 mL 3 M HCl strip solution except for the experiments of the different volume ratio and was placed into another polytetrafluoroethylene half cell. The samples from the feed solution and the strip dispersion phase were taken at scheduled time intervals. The strip dispersion samples were allowed to stand until the phase separation occurred. Then, the aqueous phase from the strip dispersion samples was collected. The samples containing ions were analyzed for every ion content with atomic absorption spectroscopy(16). In these experiments, a pressure differential (ΔP) between the feed (P_a) and the organic solution(P_o) was required. We maintained a $\Delta P = P_a - P_o = 200$ Pa differential between the feed and the organic solution.

For the feed solution containing single ion (only Zn^{2+} or Cu^{2+}), the diffusion cell is the same as Fig. 1 and contains one membrane.

Determination of pH and H^+ Concentration in Solution

The pH in solution was determined by a Mettler Toledo Delta 320-S pH meter (Mettler Toledo Instruments (Shanghai) Co., Ltd.). The H^+ concentration in solution was analyzed by 0.1012 M NaOH titration using methyl orange as indicator.

RESULTS AND DISCUSSION

In the Feed Phase Containing Single Cation

Effect of Carrier Concentration on Transport

In order to investigate the effect of the carrier concentration on the transport, the different concentrations of the carrier were considered for Cu^{2+} or Zn^{2+}, respectively. Figure 2 shows that the mass transfer coefficient of Zn^{2+} increases with an increase of the carrier concentration (0.1–0.3 M) and the mass transfer coefficient of Cu^{2+} reaches a maximum when the concentration of M5640 is 10% (w/v). Then, the mass transfer coefficient of Cu^{2+} ion decreases when the concentration of M5640 continues increasing. According to reference (17), M5640 possesses surface activity and adsorbs at the interface. This adsorption of the carrier increases with an increase of the carrier concentration in the bulk phase and is beneficial to the interface extraction reaction. But the membrane viscosity increases with an increase of the carrier concentration in the bulk phase and this is not beneficial to the transport and diffusion of copper (II). Because of the influence of two opposite factors, in the later experiments the preferable concentration of M5640 is 10%. For Zn(II), the interface between the feed phase and the membrane is not saturated by the carrier (0.1–0.3 M). Therefore, the mass transfer coefficient of Zn(II) ions increases with an increase of the carrier concentration. When the concentration of HEH(EHP) is 0.4 M, the mass transfer coefficient of Zn(II) ions is of access to the mass transfer coefficient of Zn(II) ions at 0.3 M HEH(EHP). In the later experiments the concentration of HEH(EHP) is 0.4 M for maintaining a higher viscosity in the membrane. This is beneficial to the increase of membrane life.

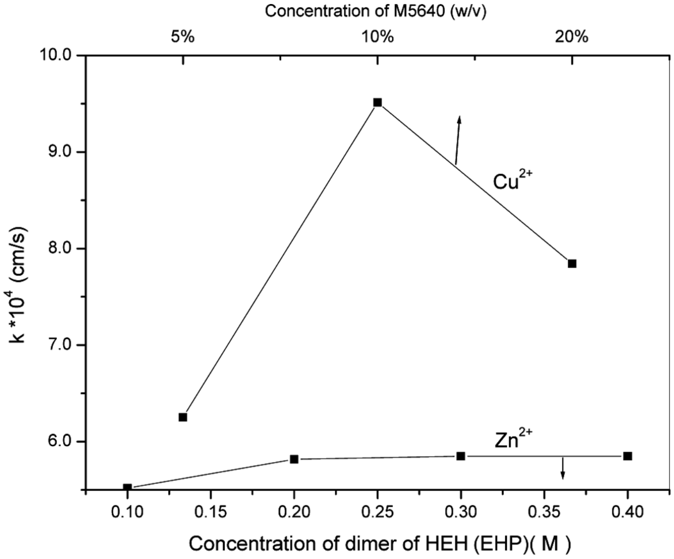

FIG. 2. Effect of carrier concentration on transport of ions. For Cu(II), feed phase: 1.57×10^{-3} M Cu^{2+}, 0.167 M Na_2SO_4, pH = 3.20, circulating flux = 9900 ml/h. strip dispersion system : 100 mL kerosene solution containing 5–20% M5640 (w/v) and 20 mL 3 M HCl strip solution; the circulating flux of strip dispersion system = 560 ml/h. For Zn(II), feed phase: 1.53×10^{-3} M Zn^{2+}, 0.167 M Na_2SO_4, pH = 4.33, circulating flux = 5600 ml/h. strip dispersion system: 110 mL kerosene solution containing dimer of HEH(EHP) of different concentration, 0.12 M dodecanol and 10 mL 2 M H_2SO_4 strip solution; The circulating flux of strip dispersion system = 560 ml/h.

Effect of Dodecanol in Membrane on Transport

Dodecanol is a modifier for the membrane stability. Figure 3 shows that dodecanol is benificial to the transport of Zn(II) ions, but dodecanol in membrane hinders the transport of Cu(II) ions. In the later experiments, the concentration of dodecanol in the membrane was 0.24 M for Zn(II) and no dodecanol was added in the membrane for Cu(II).

Effect of Volume Ratio (x) in the Strip Dispersion System on the Transport of Ion

For convenience of discussion, we define the volume ratio (x) for the strip dispersion system:

x = volume (ml) of the aqueous strip solution: volume (ml) of the organic solution

Figure 4 indicates that the mass transfer coefficient of zinc (II) ions increases with an increase of x up to x = 10:110 = 0.091 and beyond x = 10:110 the mass transfer coefficient decreases. For the transport of Cu(II), the mass transfer coefficient of Cu(II) increases with an increase of x up to x = 20:100 = 0.20 and beyond x = 20:100 the mass

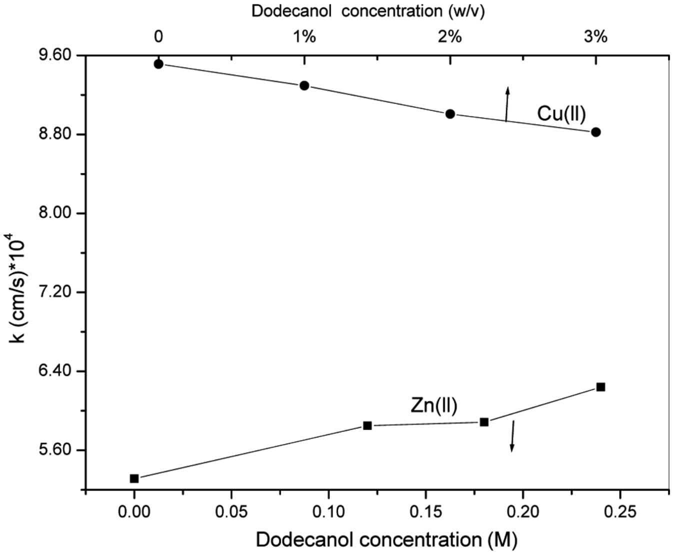

FIG. 3. Effect of dodecanol on the transport on Zn(II) and Cu(II) ion. For Cu(II), feed phase: 1.57×10^{-3} M Cu^{2+}, 0.167 M Na_2SO_4, pH = 3.20, circulating flux = 9900 ml/h. Strip dispersion system : 100 mL kerosene solution containing 10% M5640 (w/v), dodecanol of different concentration, and 20 mL 3 M HCl strip solution. The circulating flux of strip dispersion system = 560 ml/h. For Zn(II), feed phase: 1.53×10^{-3}M Zn^{2+}, 0.167 M Na_2SO_4, pH = 4.33, and circulating flux = 5600 ml/h. strip dispersion system : 110 mL kerosene solution containing 0.4 M dimer of HEH(EHP), dodecanol of different concentration and 10 mL 2 M H_2SO_4 strip solution. The circulating flux of strip dispersion system = 560 ml/h.

transfer coefficient decreases. When x increases, the droplets of the aqueous strip solution dispersed in the organic phase obviously increase and the membrane thins out. In this way, the mixing between the organic phase and the aqueous strip phase provides an extra mass transfer surface area, leading to the efficient stripping of the target species from the organic phase. This efficient stripping enhances the transport rate of zinc(II) or Cu(II) ions. Beyond x = 10:110 (for Zn^{2+} ions) and x = 20:100 (for Cu^{2+} ions), the excessive stripping solution is dispersed in the organic phase. Because of the lack of the high active surfactant in the organic phase, the excessive stripping solution accelerates the coalescence of the droplets of the aqueous strip solution in a continuous organic phase. Consequently, the membrane phase of the liquid membrane thickens out. The diminution of the mass transfer coefficient of Zn(II) and Cu(II) was observed. Figure 4 indicates that the optimum volume ratio for the transport of Zn^{2+} and Cu^{2+} is 10:110 and 20:100, respectively.

Effect of Circulating Flux of Feed Phase and Strip Dispersion Phase on the Transport of Zn(II) and Cu(II) Ion

Figure 5 indicates that the transport of Zn(II) or Cu(II) increases with an increase of the circulating flux of the feed phase. As seen, the increase of the circulating flux of the feed phase brings about a decrease of the thickness of the aqueous feed boundary layer. Then, the transport of Zn(II) and Cu(II) through the membrane is accelerated.

Figure 6 shows that the maximum of the mass transfer coefficient for Zn(II) is observed when the circulating flux of the strip dispersion phase is 560 ml/h. Based on the theoretical analysis of operation in SDHLM system, the mixer can disperse an aqueous strip solution (2 M H_2SO_4,

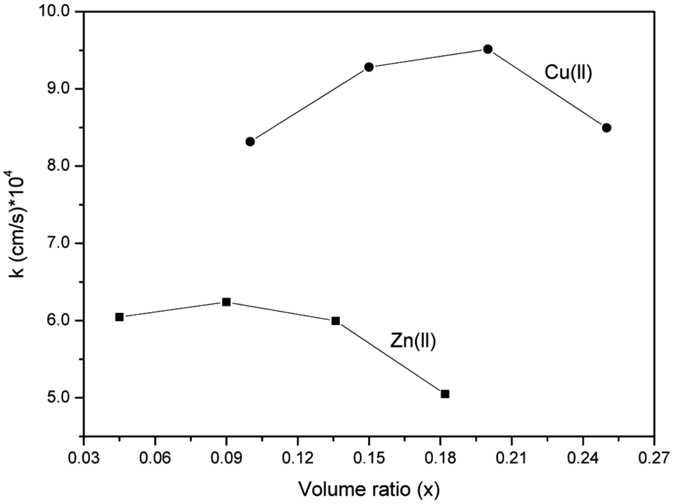

FIG. 4. Effect of volume ratio (x) on transport. For Cu(II), the other experimental conditions are the same as Fig. 3 except for 3 M HCl of different volume. For Zn(II), the other experimental conditions is the same as Fig. 3 except for 2 M H_2SO_4 of different volume. The concentration of dodecanol is 0.24 M.

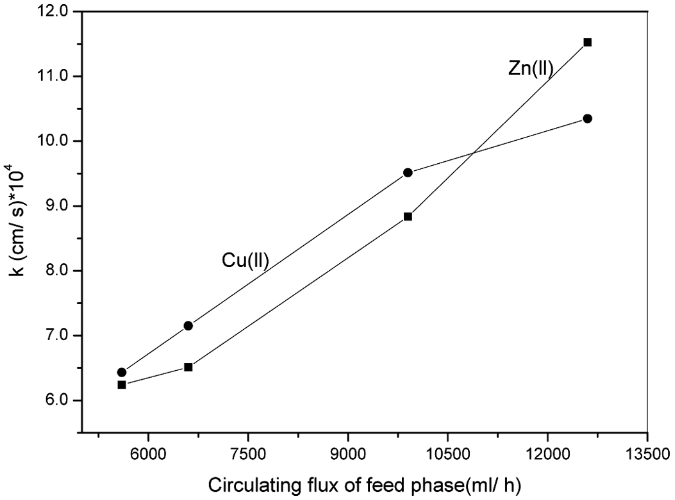

FIG. 5. Effect of circulating flux of the feed phase on transport. For Cu(II), the other experimental conditions are the same as Fig. 3 except for the circulating flux of feed phase. For Zn(II), the other experimental conditions are the same as Fig. 3 except for the circulating flux of feed phase. The concentration of dodecanol is 0.24 M.

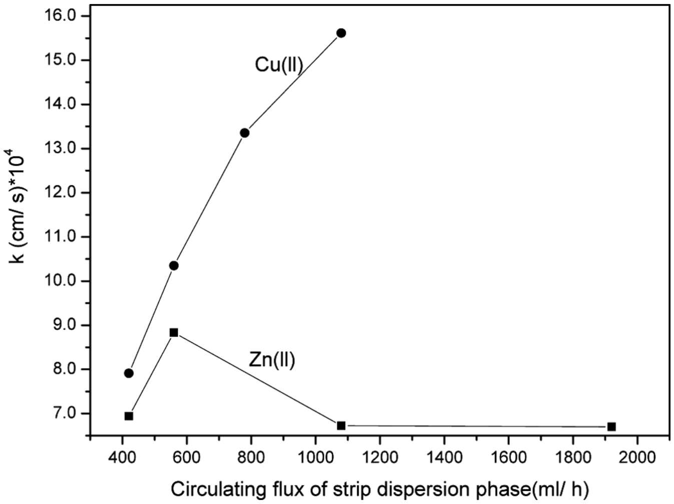

FIG. 6. Effect of circulating flux of strip dispersion phase on transport. For Cu(II), the circulating flux of feed phase is 12600 ml/h. The other experimental conditions are the same as Fig. 3 except for the circulating flux of strip dispersion phase. For Zn(II), the circulating flux of feed phase is 9900 ml/h. The concentration of dodecanol is 0.24 M. The other experimental conditions are the same as Fig. 3 except for the circulating flux of strip dispersion phase.

density is 1.12 g/cm^3.) in kerosene (Density is 0.8 g/cm^3) and form the droplets of the aqueous strip solution in the continuous organic phase because of the weak surface-active extractant. If the circulating flux of the strip dispersion phase is far beyond 560 ml/h, this brings about two results:

1. To form hydrodynamic complications in the stripping side of SLM (whirls, interface deformations, etc.).
2. To result in the collision and agglomerate between the droplets of the aqueous strip solution in a continuous organic phase because of the difference of the density between 2 M H_2SO_4 and kerosene.

The collision and agglomerate give rise to separation of the strip dispersion phase into two phases: the organic phase and the aqueous strip solution. This reduces the transport efficiency of the membrane because of the lack of the efficient mixing between the organic phase and the aqueous strip solution. For Zn(II), the excessive or lower circulating flux of the strip dispersion phase reduces the mass transfer coefficient of the ions. In the later experiments, the circulating flux of the strip-dispersion phase for Zn(II) ions is 560 ml/h. For Cu(II), the maximum of the mass transfer coefficient is not observed when the circulating flux of the strip-dispersion phase increases. In order to prevent the membrane from rupturing, the circulating flux beyond 1080 ml/h was not choosed. In the later experiments, 560, 780, and 1080 ml/h is selected as the circulating flux of the strip-dispersion phase for Cu(II) ions, respectively.

In the Feed Phase Containing Three Metal Ions

Effect of the Value of pH in the Feed Phase on Separation

Table 1 indicates that the value of k of copper (II) and zinc (II) increases with an increase of the value of pH in the feed phase. This shows the importance of protons in the feed phase. If the proton concentration in the feed phase decreases, reactions (1) and (3) shift forward. This is beneficial to the transport of copper (I) and zinc (II) ions through the membrane.

In the analysis of the overall mass transfer resistance we first consider the influence of the transfer of copper species. The overall mass transfer resistance through the SDHLM is related to all individual mass transfer resistances consisting of

1. the resistance due to Cu (II) species diffusion in the aqueous feed/membrane boundary layer,
2. the interfacial reaction resistance due to the complexation/extraction,
3. the membrane-phase diffusion resistance,
4. the interfacial resistance due to the decomplexation/stripping reaction, and
5. the strip-side resistance due to diffusion in the aqueous strip/membrane boundary layer (18,19).

This can be expressed as

$$\frac{1}{k}=\frac{1}{k_{fb}}+\frac{1}{K_f k_e}+\frac{1}{K_f k_m}+\frac{1}{K_f k_s}+\frac{1}{(K_f/K_s)k_{as}} \qquad (8)$$

$$k_{fb}=D_a/\delta_{fb} \qquad (9)$$

$$k_m=\frac{D_m}{\delta_m}\frac{\varepsilon}{\tau} \qquad (10)$$

$$k_e=D_a K_f/\delta_{fb} \qquad (11)$$

where the description of the symbols in Eqs. (8–11). is given in the section, List of Symbols. k is the overall mass transfer coefficient (18,19).

The mass transfer coefficient across the feed boundary layer (k_{fb}) was estimated to be 2.6×10^{-3} cm/s ($D_a=7.2\times10^{-6}$ cm^2/s (20); $\delta_{fb}=2.8\times10^{-3}$ cm (3,21)). Obviously, $k_{fb}=2.6\times10^{-3}$ cm/s, $k=10.39\times10^{-4}$ cm/s (see Table 1), this k_{fb} value is the same order of magnitude as the overall mass transfer coefficient. The mass transfer resistance for the aqueous feed/membrane boundary layer is not insignificant in comparison with the overall mass transfer resistance. The term $1/k_{fb}$ in Eq. (8) is not neglected while considering the overall mass transfer resistance.

The membrane mass transfer coefficient, k_m, was calculated from Eq. (10). For this calculation, a value of 6.89×10^{-10} m^2 s^{-1} (D_m), predicted by the Wilke-Chang equation (22), was taken for calculating the membrane mass transfer coefficient across the membrane (The tortuosity of Celgard

TABLE 1

Effect of pH in feed phase on separation of Cu^{2+}, Zn^{2+}, and Co^{2+} from dilute feed*

pH in feed	Ion in feed	Concn. of ions in feed (mg/L)		Extraction of ions in feed after 6 h (%)	k*10^4 (cm/s)	Separation factor β		Recovery of ions in 2 M H_2SO_4 after 6 h		Recovery of ions in 3 M HCl after 6 h	
		t = 0	t = 6 h			$\frac{Cu}{Zn}$	$\frac{Zn}{Cu}$	Concn. (mg/L)	(%)	Concn. (mg/L)	(%)
2.00	Cu^{2+}	100.0	2.1	97.9	10.39	528.6		14.4	0. 96	681.3	90.8
	Zn^{2+}	101.0	6.2	93.4	7.56		32.3	1371.0	90.5	3.8	0.50
	Co^{2+}	106.6	104.6	1.9				1.2	0.075	0.7	0.09
2.50	Cu^{2+}	101.0	1.2	98.8	12.16	559.1		35.9	2.37	683.3	90.2
	Zn^{2+}	100.5	5.1	94.9	8.16		9.1	1390.0	92.2	5.2	0.69
	Co^{2+}	106.6	102.8	3.6				1.4	0.09	0.7	0.09
3.00	Cu^{2+}	100.0	0.5	99.5	14.35	814.3		55.0	3.7	688.2	91.8
	Zn^{2+}	101.0	4.2	95.8	8.58		3.0	1406.3	92.8	7.1	0.94
	Co^{2+}	106.7	101.3	5.1				2.5	0.16	1.3	0.16

*Feed phase: 150 ml the feed solution of Cu^{2+}, Zn^{2+}, and Co^{2+}, 0.167 M Na_2SO_4, the circulating flux of feed phase = 12600 ml/h.

For Cu(II), strip dispersion system: 100 mL organic solution containing 10% M5640 (w/v) and 20 mL 3 M HCl strip solution. The circulating flux of strip dispersion system = 780 ml/h.

For Zn(II), strip dispersion system: 110 mL organic solution containing 0.4 M dimer of HEH(EHP), 0.24 M dodecanol, and 10 mL 2 M H_2SO_4 strip solution. The circulating flux of strip dispersion system = 560 ml/h.

The accumulation of metal ion-carrier coordination compound in membrane is not listed in Table 1. But the calculation of the accumulation of metal ion-carrier coordination compound in membrane is as follows: For Cu(II) in Table 1: Accumulation (%) = figure in column of 5-figure in column of 12; For Zn(II) in Table 1: Accumulation (%) = figure in column of 5-figure in column of 10.

2500 was 2.40 (18)). The calculated membrane mass transfer coefficient (k_m) was 5.17×10^{-4} cm/s.

In our optimum condition of extraction, K_f (for Cu) $\gg 1$. According to Eq. (11), we have $k_e > k_{fb} = 2.6 \times 10^{-3}$ cm/s. In this way, the mass transfer resistance for the interfacial reaction due to the complexation/extraction is insignificant in comparison with the overall mass transfer resistance (k). In other words, the term $1/K_f k_e$ in Eq. (8) is neglected while considering the overall mass transfer resistance.

Table 1 indicated that the accumulation of Cu(II) in the membrane is neglected for SDHLM ($\approx$8% for Cu). These experimental results show that the k_s and k_{as} are the same order of magnitude as k_e. If $k_s < k_e$ or $k_{as} < k_e$ the accumulation of Cu(II) in the membrane is not neglected for SDHLM. Therefore, the mass transfer coefficient in SDHLM was on the order of $k_e \approx k_s \approx k_{as} > k_{fb} > k_m < k$. According to the literature (3,19), K_f is much greater than K_s. However, in our optimum conditions of extraction, K_f (for Cu) $\gg 1$. In this way, the interfacial resistance due to the decomplexation/stripping reaction and the mass transfer resistance due to the aqueous strip solution are insignificant in comparison with the overall mass transfer resistance (k). In other words, the term $1/K_f k_s$ and $1/(K_f/K_s)k_{as}$ in Eq. (8) are neglected while considering the overall mass transfer resistance. Consequently, the terms of $1/k_{fb}$ and $1/K_f k_m$ in Eq. (8) are not neglected.

Then, it may be concluded that the overall mass transfer process of Cu(II) ions in SDHLM is simultaneously controlled by the diffusion in the aqueous boundary layer and the diffusion in the microporous membrane phase in this study. This conclusion indicates that the membrane, which is as thin as possible, is used in the operation because of reducing the membrane transfer resistance.

By the same method, we analyze the overall mass transfer resistance of Zn(II) ions in this study. According to references, $D_a = 7.2 \times 10^{-6}$ cm^2/s (20), $\delta_{fb} = 6.3 \times 10^{-3}$ cm (3,21). The mass transfer coefficient across the feed boundary layer (k_{fb}) was estimated to be 1.14×10^{-3} cm/s. Because $k_{fb} = 1.14 \times 10^{-3}$ cm/s $>$ the mass transfer coefficient of Zn(II) (the order of magnitude of 10^{-4}), the term $1/k_{fb}$ in Eq. (8) is neglected while considering the overall mass transfer resistance. D_m is the diffusivity coefficient of Zn-HEH(EHP) coordination compound in the membrane. $D_m = 2.69 \times 10^{-10}$ m^2 s^{-1} (23). The calculated membrane mass transfer coefficient (k_m) was 2.02×10^{-4} cm/s (from Eq. (10)). Table 1 indicates that the accumulation of Zn(II) in the membrane is neglected for SDHLM (<5% for Zn). Therefore, the mass transfer coefficient of Zn(II) in SDHLM was on the order of $k_e \approx k_s \approx k_{as} > k_{fb} > k_m \approx k$. Based on the above discussions, the terms, $1/k_{fb}$, $1/K_f k_e$, $1/K_f k_s$, and $1/(K_f/K_s)k_{as}$ in Eq. (8), are neglected while considering the overall mass transfer resistance. Because the value of k_m is the same order of magnitude as the mass transfer coefficient of Zn(II), the term of $1/K_f k_m$ in Eq. (8) is not neglected. Lastly, it may be concluded that the overall mass transfer process of Zn(II) ions in the SDHLM is controlled by the diffusion in the microporous membrane phase in this study.

The accumulation of Zn(II) and Cu(II) ions in the membrane (see Table 1) is obviously lower. This is attributed to the efficient mixing and large stripping area between the organic phase and the stripping solution in the SDHLM. This illustrates that in the transport process of SDHLM the extraction equilibrium limitation between the feed phase and the organic phase is eliminated because of the efficient stripping and the backdiffusion of the regenerated carrier. This characteristic is called nonequlibrium mass transfer, the most important feature of liquid membrane processes. It is very essential to enhance the membrane transport efficiency.

In the transport and separation of Cu(II), Zn(II), and Co(II) by the double SDHLM, the overall mass transfer processes of Cu(II) and Zn(II) ions are controlled by the different transport mechanism, respectively. Since relatively few studies on controlling the overall mass transfer process of two or more competitive solutes by the different transport mechanism, respectively, are encountered in the literature, this study is very significant for recognizing the characteristics of the transport and separation process of the more competitive solutes in the feed phase.

Effect of the Concentration of Cu^{2+} and Zn^{2+} Ions in Feed Phase on Separation

Table 2 indicates that the value of k of copper (II) decreases with an increase of zinc (II) concentration in the feed phase (see No. 1–2 in Table 2). Table 2 also shows that the value of k of Zn (II) decreases with an increase of copper (II) concentration in the feed phase (see No. 1–3 in Table 2). This is because of the competitive coordination between the Cu(II) or Zn(II) ions and the carrier molecule. Table 2 shows that the value of k of copper (II) is higher than the value of k of Zn (II). Tables 1–2 also show that the separation of Cu(II) and Zn(II) in Cu-Zn-Co sulfate solution is very successful by the double strip dispersion hybrid liquid membrane (SDHLM). The separation factor (β) in Tables 1–2 is computed based on the below Eqs. (12–13). (18).

For the M5640-loaded membrane:

$$\beta\left(\frac{Cu}{Zn}\right) = \frac{(Cu/Zn)_{strip}}{(Cu/Zn)_{feed}} \tag{12}$$

For the [HEH(EHP)]-loaded membrane:

$$\beta\left(\frac{Zn}{Cu}\right) = \frac{(Zn/Cu)_{strip}}{(Zn/Cu)_{feed}} \tag{13}$$

TABLE 2
Effect of ions concentration in feed solution on separation of Cu^{2+}, Zn^{2+}, and Co^{2+} from dilute feed*

		Concn. of ions in feed phase (mg/L)				Separation factor β		Recovery of ions in 2 M H_2SO_4 after 6 h		Recovery of ions in 3 M HCl after 6 h	
No	Ions in feed phase	t = 0	t = 6 h	Extraction percentage in feed after 6 h (%)	k*10^4 (cm/s)	$\frac{Cu}{Zn}$	$\frac{Zn}{Cu}$	Concn. (mg/l)	Percentage (%)	Concn. (mg/l)	Percentage (%)
1	Cu^{2+}	100.0	2.1	97.9	10.39	528.6		14.4	0.96	681.3	90.8
	Zn^{2+}	101.0	6.2	93.4	7.56		32.3	1371	90.5	3.8	0.50
	Co^{2+}	106.6	104.6	1.9				1.2	0.075	0.7	0.09
2	Cu^{2+}	100.0	2.2	97.8	10.27	1006.5		21.4	1.4	681.1	90.8
	Zn^{2+}	199.0	17.9	91.0	6.43		15.2	2645.4	88.6	5.5	0.37
	Co^{2+}	105.0	103.0	1.9				1.0	0.06	0.5	0.06
3	Cu^{2+}	211.0	5.1	97.6	9.98	633.8		29.7	0.94	1484.9	93.8
	Zn^{2+}	103.0	7.4	92.8	7.07		31.6	1358.9	88.0	3.4	0.44
	Co^{2+}	106.0	104.5	1.9				1.1	0.07	0.8	0.10
4	Cu^{2+}	216.0	6.9	96.8	9.45	743.7		26.7	0.8	1479.7	91.3
	Zn^{2+}	205.0	20.1	90.2	6.25		35.0	2718.4	88.4	5.8	0.38
	Co^{2+}	209.0	206.3	1.3				1.7	0.05	0.4	0.03

*Feed phase: 150 ml the feed solution of Cu^{2+}, Zn^{2+}, and Co^{2+}, 0.167 M Na_2SO_4, pH = 2.0 the circulating flux of feed phase = 12600 ml/h.

For Cu(II), strip dispersion system: 100 mL organic solution containing 10% M5640 (w/v), and 20 mL 3 M HCl strip solution, the circulating flux of strip dispersion system = 780 ml/h.

For Zn(II), strip dispersion system: 110 mL organic solution containing 0.4 M dimer of HEH(EHP), 0.24 M dodecanol and 10 mL 2 M H_2SO_4 strip solution, the circulating flux of strip dispersion system = 560 ml/h.

CONCLUSIONS

1. The experiments demonstrate that the double strip dispersion hybrid liquid membrane (SDHLM) could efficiently separate Cu(II) and Zn(II) in Cu(II)-Zn(II)-Co(II) sulfate solution.
2. The optimum separation conditions are as follows:
   Carrier concentration: 10% (w/v) M5640 for Cu(II), 0.4 M HEH(EHP) for Zn(II);
   Circulating flux of feed phase: 12600 ml/h;
   Circulating flux of strip dispersion phase: 1080 ml/h for Cu(II) and 560 ml/h for Zn(II);
   Volume ratio (x) in the strip dispersion system: x = 20:100 for Cu(II); x = 10:110 for Zn(II);
   The value of pH in the feed phase: 2–3;
   For Zn(II), the concentration of dodecanol in the membrane is 0.24 M. For Cu(II), no dodecanol is added in the membrane;
3. In this separation system the overall mass transfer process of Cu(II) and Zn(II) ions is controlled by the different transport mechanism, respectively. The experiments demonstrate that the mass transfer resistance of copper (II) ions in the SDHLM is simultaneously controlled by the diffusion in the aqueous boundary layer and the diffusion in the microporous membrane phase and that the mass transfer resistance of Zn(II) ions in the SDHLM is controlled by the diffusion in the microporous membrane phase in this study.

LIST OF SYMBOLS

J =flux ($mol \cdot m^{-2} \cdot s^{-1}$)
V =volume (L)
A =membrane area (m^2)
C =concentration ($mol \cdot L^{-1}$)
t =time (s)
k =the overall mass transfer coefficient
k_{fb} =the mass transfer coefficient for the aqueous feed/membrane boundary layer
k_e =the mass transfer coefficient due to the complexation/extraction reaction
k_m =the mass transfer coefficient for the membrane phase
k_s =the mass transfer coefficient due to the decomplexation/stripping reaction
k_{as} =the mass transfer coefficient for the aqueous strip/membrane boundary layer
K_f =the distribution coefficient of metal ion species between the organic membrane phase and the aqueous feed solution at the reaction equilibrium for the feed-side interface
K_s =the distribution coefficient of metal ion species between the organic membrane phase and the aqueous strip solution at the reaction equilibrium for the strip-side interface
D_a =the diffusivity coefficient of solute in the aqueous feed solution ($m^2 \cdot s^{-1}$)
δ_{fb} =the thickness of boundary layer between feed and membrane (μm)
D_m =the diffusivity coefficient of solute in the membrane ($m^2 \cdot s^{-1}$)
δ_m =the thickness of membrane (μm)
ε =the porosity of membrane
τ =the tortuosity
β =separation factor

Subscript

f =feed
s =stripping phase
m =membrane
fb =boundary layer of feed and membrane

REFERENCES

1. Sastre, A.M.; Kumar, A.; Shukla, J.P.; Singh, R.K. (1998) Improved techniques in liquid membrane separation: An overview. *Separation and Purification Methods*, 27 (2): 213.
2. Kemperman, A.J.B.; Bargeman, D.; Van Den Boomgaard, Th.; Strathmann, H. (1996) Stability of supported liquid membranes: State-of-the-art. *Sep. Sci. Technol.*, 31 (20): 2733.
3. Danesi, P.R. (1984–1985) Separation of metal species by supported liquid membranes. *Sep. Sci. Technol.*, 19 (11–12): 857.
4. Yang, X.J.; Fane, A.G. (1999) Performance and stability of supported liquid membranes using LIX984N for copper transport. *J. Membr. Sci.*, 156: 215.
5. Parhi, P.K.; Sarangi, K. (2008) Separation of copper, zinc, cobalt and nickel ions by supported liquid membrane technique using LIX 84I, TOPS-99 and Cyanex 272. *Separation and Purification Technology*, 59 (2): 169.
6. Gill, J.S.; Singh, H.; Gupta, C.K. (2000) Studies on supported liquid membrane for simultaneous separation of Fe(III), Cu(II) and Ni(II) from dilute feed. *Hydrometallurgy*, 55: 113.
7. Schlosser, S.; Rothová, I. (1994) New type of hollow-fibre pertractor. *Separat. Sci. Technol.*, 29: 765.
8. Schlosser, S.; Rothova, I.; Frianova, H. (1993) Hollow-fibre pertractor with bulk liquid membrane. *J. Membr. Sci.*, 80: 99.
9. Ho, W.S. W.; Lexington, K.Y. (2002) Combined supported liquid membrane/strip dispersion process for the removal and recovery of metals[P]. US Patent 6350419, Feb. 26, 2002.
10. Ho, W.S.W.; Poddar, T.K. (2001) New membrane technology for removal and recovery of chromium from waste waters. *Environ. Prog.*, 20 (1): 44.
11. Dingsheng, He; Shuxiang, Gu; Ming, Ma. (2007) Simultaneous removal and recovery of cadmium(II) and CN^- from electroplating rinse wastewater by a strip dispersion hybrid liquid membrane (SDHLM) containing double carrier. *J. Membr. Sci.*, 305: 36.
12. Shuxiang, Gu; Yuanda, Yu; Dingsheng, He; Ming, Ma. (2006) Comparison of transport and separation of Cd(II) between strip dispersion hybrid liquid membrane (SDHLM) and supported liquid membrane (SLM) using tri-n-octylamine as carrier. *Separation and Purification Technology*, 51: 277.
13. Dingsheng, He; Xiaojian, Luo; Chunming, Yang; Ming, Ma; Yan, Wan. (2006) Study of transport and separation of Zn(II) by combined supported liquid membrane/strip dispersion process containing D2EHPA in kerosene as carrier. *Desalination*, 194: 40.

14. Hu, S.Y.B.; Wiencek, J.M. (1998) Emulsion-liquid-membrane extraction of copper using a hollow-fiber contactor. *AIChE J.*, 44: 570.
15. Alguacil, F.J.; Alonso, M. (2005) Description of transport mechanism during the elimination of copper(II) from wastewaters using supported liquid membranes and Acorga M5640 as carrier. *Environ. Sci. Technol.*, 39: 2389.
16. The Ministry of Environmental Protection, P. R. China. (1982) *Standard Methods for the Examination of Water and Wastewater*, 1st Ed.; 84–92.
17. Szpakowska, M.; Nagy, O.B. (1993) Interface structure effects on coupled transport of Cu(II) ions through binary liquid membranes. *J. Membr. Sci.*, 297: 109.
18. Yang, X.J.; Fane, A.G.; Soldenhoff, K. (2003) Comparison of liquid membrane processes for metal separations: Permeability, stability, and selectivity. *Ind. Eng. Chem. Res.*, 42 (2): 392.
19. Ho, W.S.W.; Wang, B. (2002) Strontium removal by new alkyl phenylphosphonic acids in supported liquid membranes with strip dispersion. *Ind. Eng. Chem. Res.*, 41 (3): 381.
20. Kolthoff, I.M.; Lingane, J.J. (1952) *Polarography, Vol. 1*; Wiley Interscience: New York, p. 52.
21. Fernandez, L.; Aparicio, J.; Muhammed, M. (1986) Coupled zinc transport through a bis(2-ethylhexyl)-phosphoric acid solid-supported liquid membrane from aqueous perchlorate media. *J. Membr. Sci.*, 27: 77.
22. Wilke, C.R.; Chang, P. (1955) Correlation of diffusion coefficients in dilute solution. *AICHE. J.*, 1: 264.
23. Bing, T.; Xiangde, W.; Yinhua, W.; Bin, Z.; Xiujuan, Z. (1999) Mathematical model for the mass transfer mechanism of diffusion-reaction double controlled process in emulsion liquid membrane. *Technology of Water Treatment*, 25: 137.