

## Study on a Novel Disphase Supplying Supported Liquid Membrane for Transport Behavior of Divalent Nickel Ions\*

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**Abstract** A novel disphase supplying supported liquid membrane (DSSLM), containing supplying feed phase and supplying stripping phase for transport behavior of Ni(II), have been studied. The supplying supported feed phase included feed solution and di(2-ethylhexyl) phosphoric acid (HDEHP) as the carrier in kerosene, and supplying stripping phase included HDEHP as the carrier in kerosene and HCl as the stripping agent. The effects of volume ratio of membrane solution to feed solution (O/F), pH, initial concentration of Ni(II) and ionic strength in the feed solution, volume ratio of membrane solution to stripping solution (O/S), concentration of H<sub>2</sub>SO<sub>4</sub> solution, HDEHP concentration in the supplying stripping phase on transport of Ni(II), the advantages of DSSLM compared to the traditional supported liquid membrane (SLM), the system stability, the reuse of membrane solution and the retention of membrane phase were studied. Experimental results indicated that the optimum transport of Ni(II) was obtained when H<sub>2</sub>SO<sub>4</sub> concentration was 2.00 mol·L<sup>-1</sup>, HDEHP concentration was 0.120 mol·L<sup>-1</sup>, and O/S was 4 : 1 in the supplying stripping phase, O/F was 1 : 10 and pH was 5.20 in the supplying feed phase. The ionic strength in supplying feed phase had no obvious effect on transport of Ni(II). When initial Ni(II) concentration was 2.00×10<sup>-4</sup> mol/L, the transport percentage of Ni(II) was up to 93.1 % in 250 min. The kinetic equation was deduced in terms of the law of mass diffusion and the interface chemistry.

**Keywords** disphase supplying supported liquid membrane, organic phosphonic acid, supplying feed phase, supplying stripping phase, nickel ion

### 1 INTRODUCTION

The removal of toxic heavy metals such as cadmium, nickel, copper, platinum, chromium, silver, gold, mercury and zinc from aqueous environment have received considerable attention in recent years due to their toxicity and carcinogenicity which may cause damage to various systems of the human body. They also can be readily adsorbed by marine animals and enter directly the human food chains, thus presenting a high health risk to consumers [1]. Nickel ions are non-biodegradable toxic heavy metals and may cause dermatitis and allergic sensitization [2, 3]. According to the World Health Organization, nickel in effluents from the electroplating process wastewater in US is 4.1 mg·L<sup>-1</sup>, while that in drinking water should be less than 0.1 mg·L<sup>-1</sup> [4]. The major sources of nickel contamination to water come from aerospace, petrochemical, electroplating, batteries manufacturing, mine, metal material and many other industries. It is necessary to remove and recover these highly toxic and nonbiodegradable heavy metals in order to meet increasingly stringent environmental quality standards and promote the recycling and reuse of heavy metal resources [5]. The conventional methods for these purposes included adsorption, filtration, chemical precipitation, reverse osmosis, absorption (typically by

ion-exchange), solvent extraction, liquid membrane, biological systems, evaporation *etc.* Amongst these methods, chemical precipitation is usually frowned upon because it produces a sludge which must be land filled, the metal value is not recovered, it is highly costly and a semi-continuous process only. Biological systems are typically unstable and have slow kinetics. Sorbents can have high selectivity, capacity and absorption rate but can only work in semi-continuous operations in which the sorbent must be periodically regenerated [6-8]. Evaporation, reverse osmosis and electrodialysis exhibit no selectivity whereas precipitation, solvent extraction and ion exchange are not often used for the recovery of low-concentration metal ions, because of high operating costs in contrast to the value of materials recovered [9]. So it is necessary to develop more efficient and cost-effective removal and recovery methods.

Many scientists paid more and more attentions to liquid membrane (LM) techniques in recent years due to the special characteristics. The potential advantage of LM techniques, over traditional transport techniques and solid membrane techniques, are low operating costs, low energy and extractant consumption, and high recovery percentage [9, 10]. LMs can carry out simultaneous extraction and stripping processes in the same stage, and it has benefits of nonequilibrium mass transfer and the up-hill effect, by which

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solute can be transferred from low-to-high concentration solution. The main type of liquid membrane systems include emulsion liquid membrane (ELM) and supported liquid membrane (SLM). However, LM techniques have not been adopted for large-scale industrial process. One disadvantage of ELM is that the emulsion swells upon prolonged contact with the feed stream, causing a reduction of the stripping reagent concentration in the aqueous droplets, and reduced stripping efficiency. The second disadvantage is membrane rupture, resulting in leakage of the contents of aqueous droplets into the feed stream and concomitant reduction of transport efficiency. SLM is not used on a large scale in industry. The major reason for this is stability or lifetime of membrane, which is due to the loss of carrier or membrane solvent from the membrane phase that has some effects on selectivity of the membrane and transport percentage of elements [10].

More and more novel liquid membrane configurations have been studied in order to overcome these difficulties. Such as supported emulsion liquid membrane (SELM) and hollow fiber liquid membrane (HFLM) [5] *etc.* In our previous work, one-phase supplying supported liquid membrane named dispersion supported liquid membrane (DSL) has been studied for transport of rare earths and the transport results were very obvious [10, 11]. In this paper, a new liquid membrane technique, named disphase supplying supported liquid membrane (DSSL), was investigated for the removal and recovery of target species from a feed solution. The new liquid membrane process is featured with supplying the carriers to supported liquid

membrane to make up the carrier loss, in addition to high transport percentage and other advantages over DSLM and traditional SLM. As a model system, Ni(II) ions transport through DSSLM with HDEHP as mobile carrier is investigated.

## 2 THEORETICAL

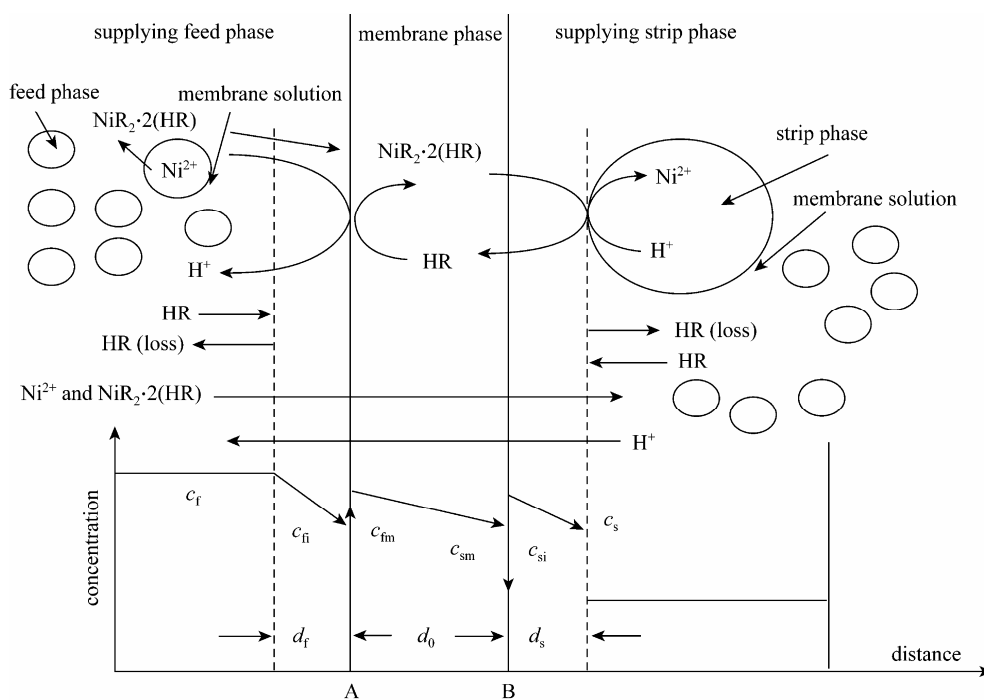
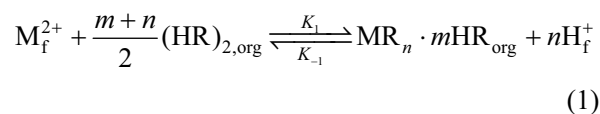
Figure 1 is the principle of DSSLM, in which transport processes and concentration changes are depicted.

The DSSLM system consists of three phases: (1) the supplying feed phase containing metals ions and membrane solution, (2) the membrane phase, which is supported by polyvinylidene fluoride membrane (PVDF), impregnated with an organic solution containing carrier and solvent, and serves as uniform barrier between two phases, (3) supplying stripping phase containing membrane solution and stripping solvent.

In this paper we proposed a mechanism for the transport of the metal ions through the DSSLM. The following steps are necessary:

(a) The diffusion of divalent metal ions from the supplying feed phase to the interface of feed-membrane phase.

(b) On the feed side interface of the DSSLM, extraction of the divalent metal ions from aqueous solutions with carriers can be expressed as

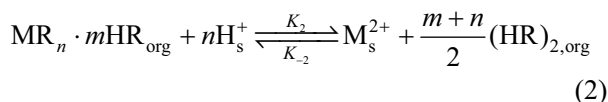


**Figure 1** Diagram of Ni(II) transport in disphase supplying supported liquid membrane. HR represents the carrier within the membrane, which in this case is HDEHP. NiR<sub>2</sub>·2(HR) represents the organometallic compound, H<sup>+</sup> is the hydrogen ion (A and B are the boundaries of the membrane phase)

where f,  $M_f^{2+}$  and org stand for supplying feed phase, divalent metal ions, and organic phase,  $(HR)_2$  denotes the dimeric form of active carriers such as HDEHP.

(c) The metal-complex diffuses through the membrane A-B.

(d) At the other side interface of the membrane, the metal-complex is dissolved membrane solution and the metal ions are stripped by stripping solvent. The chemical reaction can be written as



where s stands for supplying stripping phase.  $K_1$ ,  $K_{-1}$ ,  $K_2$ ,  $K_{-2}$  are the pseudo-first-order rate constants of the forward and backward reactions of two interfaces.

(e) Carrier HDEHP returns from B to A [11-15].

In this mechanism the transport of Ni(II) across DSSLM is described by considering only diffusional parameters, because the complex reaction between the Ni(II) and HDEHP in the interfaces is faster compared to the diffusion in the aqueous and membrane phase [4,16]. Then in this model, the transport of Ni(II) in the DSSLM process can be considered as four sequential steps. If the diffusion process is described by the Fick's law, the transfer flux of each step can be written as follows.

(a) The transport rate of Ni(II) through the liquid film at feed side of membrane:

$$J_f = \frac{D_f}{d_f} (c_f - c_{fi}) \quad (3)$$

where  $D_f$ ,  $d_f$ ,  $c_f$  and  $c_{fi}$  stand for diffusion coefficient and diffusion layer thickness, and the concentration of Ni(II) in supplying feed phase, and that in aqueous and membrane interface.

(b) The rate of Ni(II) transferred through membrane:

$$J_{oi} = K_1 c_{fi} - K_{-1} \bar{c}_f \quad (4)$$

where  $\bar{c}_f$  indicates that the concentration of Ni(II) in the membrane phase.

(c) The rate of Ni(II) transferred through diffusion layer between the feed phase and membrane:

$$J_0 = \frac{D_0}{d_0} (\bar{c}_f - \bar{c}_s) \quad (5)$$

where  $V_s$ ,  $D_0$  and  $d_0$  stand for the concentration of Ni(II), diffusion coefficient and thickness in membrane phase.

(d) The rate of Ni(II) transferred through diffusion layer between the stripping phase and membrane [17]:

$$J_{os} = K_2 \bar{c}_s \frac{V_0}{V_s} \quad (6)$$

where  $V_s$  and  $V_0$  stand for volume of stripping phase in supplying stripping phase and membrane phase.

Then, at steady state, all of these individual

transport fluxes are equal [4, 18-22]. By combining Eqs. (1) to (6), we get

$$J = \frac{K_d c_f}{K_d \frac{d_f}{D_f} + \frac{d_0}{D_0} + \frac{1}{K_2} \frac{V_s}{V_0} + (K_{-1})^{-1}} \quad (7)$$

with the equilibrium constant being  $K_d = K_1 / K_{-1}$ .

Equation (7) can also be written as

$$J = P_c c_f \quad (8)$$

where  $c_f$  stands for the concentration of supplying feed phase, and  $P_c$  stands for the permeability coefficient:

$$P_c = \frac{K_d}{K_d \frac{d_f}{D_f} + \frac{d_0}{D_0} + \frac{1}{K_2} \frac{V_s}{V_0}} \quad (9)$$

Equation (10) is attainable by rate constant and Eq. (1):

$$K_{ex} = \frac{[H^+]^n [MR_n \cdot mHR]}{[M^{2+}] [(HR)_2]^{m+n}} = \frac{K_d \cdot [H^+]^n}{[(HR)_2]^{m+n}} \quad (10)$$

Combining Eqs. (9) and (10) leads to

$$\frac{1}{P_c} = \frac{d_f}{D_f} + \left( \frac{d_0}{D_0} + \frac{V_s}{K_2 V_0} \right) \frac{1}{K_{ex}} \frac{[H]^n}{[(HR)_2]^{m+n}} \quad (11)$$

The rate of stripping is very fast in the DSSLM, so  $1/K_2$  can be ignored. So we can simplify Eq. (11) to

$$\frac{1}{P_c} = \Delta_f + \Delta_0 \frac{1}{K_{ex}} \frac{[H^+]^n}{[(HR)_2]^{m+n}} \quad (12)$$

where  $\Delta_f$  and  $\Delta_0$  are defined as

$$\Delta_f = \frac{d_f}{D_f} \quad (13)$$

$$\Delta_0 = \frac{d_0}{D_0} \quad (14)$$

The relationship between  $1/P_c$  and  $[H^+]^n$  was examined to be linear at the same carrier concentration. So the diffusion coefficient of Ni(II) in the membrane and the thickness of diffusion layer between the supplying feed phase and membrane phase can be obtained with the linear slope method. In the same way, the relationship between  $1/P_c$  and  $[(HR)_2]^{-2}$  were examined to be linear at the same  $H^+$  concentration in the supplying feed phase.

Based on the definition of permeability coefficient, transport flux of membrane can also be written as

$$J = -\frac{V_f}{A} \left( \frac{dc_f}{dt} \right) = P_c c_f \quad (15)$$

where  $V_f$  stands for the volume of supplying feed phase and  $A$  stands for effective area of membrane.

By integrating Eq. (15), we obtain the following linear relation:

$$\ln \frac{c_{f(t)}}{c_{f(0)}} = -\frac{A}{V_f} P_c t \quad (16)$$

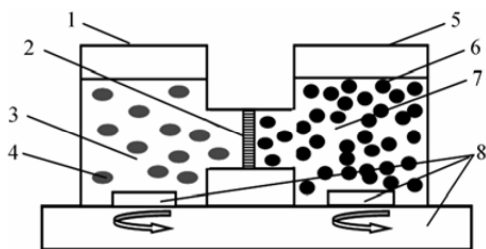
where  $c_{f(0)}$  and  $c_{f(t)}$  stand for the concentrations of Ni(II) in the supplying feed phase at  $t=0$  and a latter time instant, respectively. The value of  $P_c$  can be evaluated from the linear slope of  $\ln(c_{f(t)}/c_{f(0)})$  versus  $t$  under specified operation conditions.

### 3 EXPERIMENTAL

#### 3.1 Reagents and instruments

All the reagents such as Ni(II) nitrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ], anhydrous acetic acid and sodium acetate (HAc-NaAc) and 4-(2-pyridyl)resorcinol (PAR) used in the present work were of analytical grade. All chemical reagents are dissolved by deionized water. Di(2-ethylhexyl) phosphoric acid (HDEHP) is a commercial extractant (purity >95%, Bada Chemical Industry Co., Japan) and used without any further purification. Kerosene was washed with concentrated sulfuric acid and distilled at 185–225 °C.

All the experiments are conducted using 110 ml cells with effective volume of 0 ml for both feed solution and stripping solution. Two cells are separated by the PVDF film (Shanghai Yadong Peucine Co., Shanghai) as support, which has a porosity of 75%, thickness of 65  $\mu\text{m}$ , pore size of 0.30  $\mu\text{m}$  and refractive index of 1.67. The effective area is 10.5  $\text{cm}^2$ . The film was pre-wetted with organic phase at least 48 h in order to make the pores of film fully filled with membrane solution. The stability of membrane was represented by the determination of Ni(II) transport percentage and changes of carrier amount in membrane during experiments time. The JJ-1 accurate electronic stirrers (Danyang Glass Factory, Jintan, Jiangsu Province) were taken to stir two cells at 800  $\text{r}\cdot\text{min}^{-1}$ . The UV-1200 Spectrophotometer (Longnike Factory, Shanghai) was used to determine the optical absorbance.



**Figure 2** Experimental installation of DSSLM process  
1—supplying feed pool; 2—PVDF membrane; 3—supplying feed phase; 4—membrane solution in supplying feed phase; 5—supplying stripping pool; 6—membrane solution in supplying stripping phase; 7—stripping phase; 3+4—supplying feed phase; 6+7—supplying stripping phase; 8—magnetic stirrers

#### 3.2 Experimental procedure

The supplying feed phase is an aqueous solution

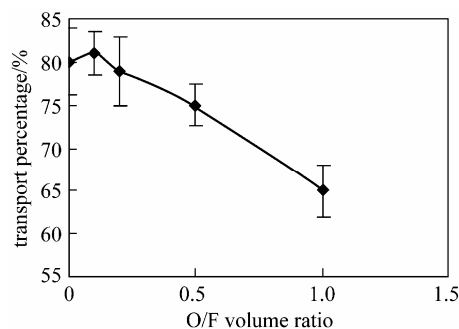
that contains Ni(II) and membrane solution. The metal solution was prepared by dissolving the required amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . The supplying stripping phase was the mixture containing  $\text{H}_2\text{SO}_4$  and membrane solution. The latter was disphasic, with  $\text{H}_2\text{SO}_4$  as the inner phase and the membrane solution as the outer phase. The membrane solution was prepared by dissolving of HDEHP in kerosene. The PVDF film as support was pre-wetted with the required amount of membrane solution more than 5 h in order to make the pores filled with carrier. The experiments were performed in the pH range of 3.0–5.6 to investigate the effect of pH of supplying feed phase on transport, the hydrogen ion concentration of supplying stripping phase, the volume ratio of membrane solution to  $\text{H}_2\text{SO}_4$  solution and concentration of Ni(II) of supplying feed phase. The pH of supplying feed phase in each experimental run was kept constant using buffer solutions ( $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ CH}_3\text{COONa}$  and  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ CH}_3\text{COOH}$  or  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaH}_2\text{PO}_4$  and  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{HPO}_4$ ).

The Ni(II) concentration was analyzed by UV spectrophotometry (493 nm) with 4-(2-pyridyl)resorcinol (PAR) as the developer. And a digital precision ionometer model PHS-3C with a glass electrode was used for pH measurements (accuracy  $\pm 0.01$ ).

### 4 RESULTS AND DISCUSSION

#### 4.1 Effect of the volume ratio of membrane solution to feed solution(O/F)

The effect of volume ratio of membrane solution to feed solution (O/F) was studied in this section. All other parameters such as pH, concentration of Ni(II) in supplying feed phase, concentration of  $\text{H}_2\text{SO}_4$  solution and the volume ratio of membrane solution to  $\text{H}_2\text{SO}_4$  solution (O/S) in supplying stripping phase were kept constant at 4.8,  $2.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ , 2.0  $\text{mol}\cdot\text{L}^{-1}$  and 3.0. The effect of volume ratio of membrane solution to feed solution (O/F) in the supplying feed phase on transport of Ni(II) was shown in Fig. 3. It indicates that the transport percentage of Ni(II)

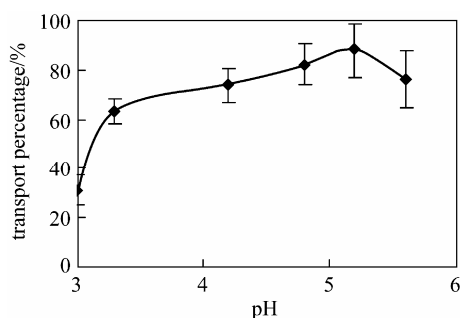


**Figure 3** Effect of volume ratio of membrane solution to feed solution on transport of Ni(II) (pH in the supplying feed phase: 4.80, initial concentration of Ni(II):  $2.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ , O/S: 3.0, concentration of  $\text{H}_2\text{SO}_4$  in the supplying stripping phase:  $2.00 \text{ mol}\cdot\text{L}^{-1}$ , HDEHP concentration:  $0.120 \text{ mol}\cdot\text{L}^{-1}$ )

decreased with the increasing of the volume ratio from O/F 0.1 to 1.0. When the volume ratio of O/F was 0.1, the transport percentage of Ni(II) was 82.3% in 250 min. Considering saving chemical agents as well as increasing transport percentage, we chose  $0.1 \text{ mol}\cdot\text{L}^{-1}$  as the volume ratio for the subsequent experiments.

#### 4.2 Effect of pH in the supplying feed phase

The effect of pH on permeation and transport of Ni(II) was studied in the range from 3.0 to 5.6, which was adjusted with an acetic acid/acetate sodium buffer solution. The results shown in Fig. 4 suggest that the percentage recovery of Ni(II) increased as pH of feed solution increased from 3.0 to 5.2, and a maximum percentage was observed at pH of 5.2. Above pH of 5.2 in the feed solution, the percentage of Ni(II) decreased.



**Figure 4** Effect of pH in the supplying feed phase on transport of Ni(II) (initial concentration of Ni(II):  $2.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ , O/F: 0.1, O/S: 3.0, concentration of  $\text{H}_2\text{SO}_4$  in the supplying stripping phase:  $2.00 \text{ mol}\cdot\text{L}^{-1}$ , HDEHP concentration:  $0.120 \text{ mol}\cdot\text{L}^{-1}$ )

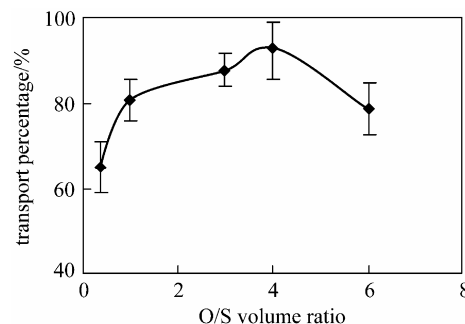
#### 4.3 Effect of initial concentration of Ni(II) in the supplying stripping phase

Effect of Ni(II) concentration on percentage and transport factor Ni(II) was studied in the range of  $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  to  $4.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ . Other experimental conditions were: pH of supplying feed phase was adjusted to 5.2. The O/F was adjusted to 0.1. The O/S was adjusted to 3 and  $\text{H}_2\text{SO}_4$  was adjusted to  $2.0 \text{ mol}\cdot\text{L}^{-1}$  in the supplying stripping phase. The results

obtained are presented in Table 1. With increasing of Ni(II) concentration in the supplying feed phase from  $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  to  $2.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ , the percentage of Ni(II) increased, then decreased as the initial concentration of Ni(II) increased further. Within this concentration range of Ni(II) in the supplying feed phase, the availability of Ni(II) at the feed-membrane interface increased with increasing of Ni(II) concentration. But when the Ni(II) concentration in the feed solution become higher in comparison to HDEHP concentration in membrane phase, the percentage of Ni(II) decreased. This indicates that the number of moles transported through the membrane per unit area of the membrane per unit time are determined when the concentration of HDEHP, since the effective area of membrane and time are fixed.

#### 4.4 Effect of the volume ratio of membrane solution to $\text{H}_2\text{SO}_4$ solution (O/S)

The effect of volume ratio of membrane solution to  $\text{H}_2\text{SO}_4$  solution (O/S) in the supplying stripping phase on transport percentage of Ni(II) was shown in Fig. 5. It indicates that the percentage recovery of Ni(II) increased with an increasing of the volume ratio. When volume ratio of O/S increased, the droplets of the stripping solution dispersed in the membrane



**Figure 5** Effect of volume ratio of membrane solution to  $\text{H}_2\text{SO}_4$  solution on transport of Ni(II) (pH in the supplying feed phase: 5.20, initial concentration of Ni(II):  $2.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ , O/F: 0.1, concentration of  $\text{H}_2\text{SO}_4$  in the supplying stripping phase:  $2.00 \text{ mol}\cdot\text{L}^{-1}$ , HDEHP concentration:  $0.120 \text{ mol}\cdot\text{L}^{-1}$ )

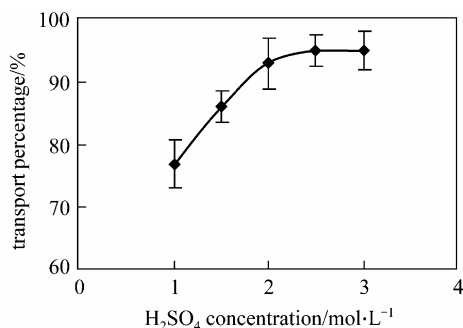
**Table 1** Effect of initial concentrations of Ni(II) on transport of Ni(II) (pH in the supplying feed phase: 5.20, O/F: 0.1, O/S: 3.0, concentration of  $\text{H}_2\text{SO}_4$  in the supplying stripping phase:  $2.00 \text{ mol}\cdot\text{L}^{-1}$ , HDEHP concentration:  $0.120 \text{ mol}\cdot\text{L}^{-1}$ )

Time /min	Transport percentage/%				
	$1.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$	$1.50 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$	$2.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$	$3.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$	$4.00 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$
0	0	0	0	0	0
60	48.4	30.1	24.6	16.4	11.5
100	73.6	51.1	36.1	31.3	17.3
130	91.5	67.9	50.2	42.9	32.9
200	—	89.3	73.1	54.5	43.5
250	—	—	88.7	68.9	55.6

phase increased obviously [4]. In this way, the membrane phase and supplying stripping phase provide an extra stripping surface and promotes renewal rate of liquid membrane, which lead to extremely stripping rate for the supplying feed phase from membrane phase and extension of liquid membrane lifetime. Therefore, it enhances the transport percentage of Ni(II).

#### 4.5 Effect of the concentration of H<sub>2</sub>SO<sub>4</sub> in the supplying stripping phase

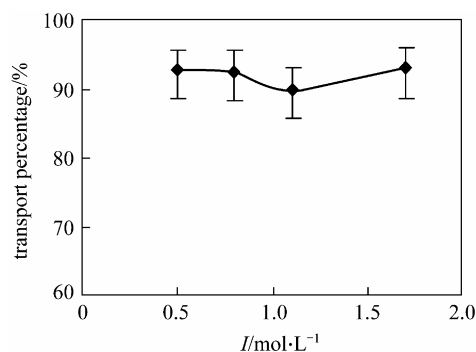
The stripping reaction at the membrane-stripping side plays a vital role in the transfer of metal ions from supplying feed phase to supplying stripping phase. So the effect of concentration of H<sub>2</sub>SO<sub>4</sub> was studied in this paper. Fig. 6 indicated that the percentage of Ni(II) increased with the increasing of acid concentration. Further increasing of concentration of H<sub>2</sub>SO<sub>4</sub> from 2.0 mol·L<sup>-1</sup> to 3.0 mol·L<sup>-1</sup> had no significant effect on the percentage of Ni(II), because the number of complex of Ni(II) and HDEHP which transported through the membrane per unit area of the membrane per unit time were determined when the concentration of HDEHP, the concentration of Ni(II) in the supplying feed phase and the effect area of membrane and time were determined. So 2.0 mol·L<sup>-1</sup> can be chose as the optimum concentration of H<sub>2</sub>SO<sub>4</sub> in the supplying stripping phase.



**Figure 6** Effect of concentrations of H<sub>2</sub>SO<sub>4</sub> in supplying strip phase on transport of Ni(II) (pH in the supplying feed phase: 5.20, initial concentration of Ni(II): 2.00×10<sup>-4</sup> mol·L<sup>-1</sup>, O/F: 0.1, O/S: 4.0, HDEHP concentration: 0.120 mol·L<sup>-1</sup>)

#### 4.6 Effect of ionic strengths in the supplying feed phase

Effect of ionic strengths in the supplying feed phase on percentage of Ni(II) was shown in Fig. 7. It indicated that the ionic strengths had not effect on transport of Ni(II), because the mixture of supplying feed phase containing H<sub>2</sub>SO<sub>4</sub> and membrane solution was not only a phase. It was disphasic, H<sub>2</sub>SO<sub>4</sub> was the inner phase and the membrane was the outer phase, which lead to the ionic strengths of supplying stripping phase are ignorable. So when the concentration of ions in the supplying feed phase is low, the ionic strengths of two phase can be neglected. The operational conditions,

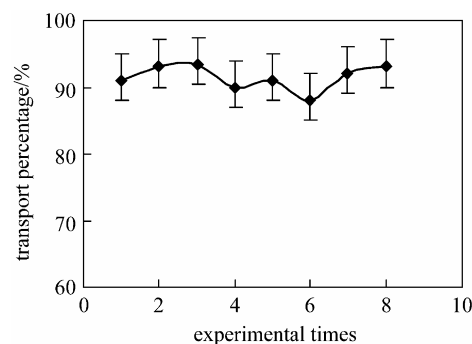


**Figure 7** Effect of ionic strengths on transport of Ni(II) (pH in the supplying feed phase: 5.20, O/F: 0.10, initial concentration of Ni(II): 2.00×10<sup>-4</sup> mol·L<sup>-1</sup>, O/S: 4.0, concentration of H<sub>2</sub>SO<sub>4</sub> in the supplying stripping phase: 2.00 mol·L<sup>-1</sup>, HDEHP concentration: 0.120 mol·L<sup>-1</sup>)

comparing to other techniques of liquid membrane, is further simplified.

#### 4.7 The reuse of membrane solution

From Fig. 8, we can know that the membrane solution in DSSLM can be reused many times before the re-extraction with the strong acid after every experiment. Membrane solution in DSSLM can be reused many times and the tendency of recovery percentage change was stable with DSSLM in 3 experiments. After 3 experiments, the Ni(II) recovery decreased gradually.

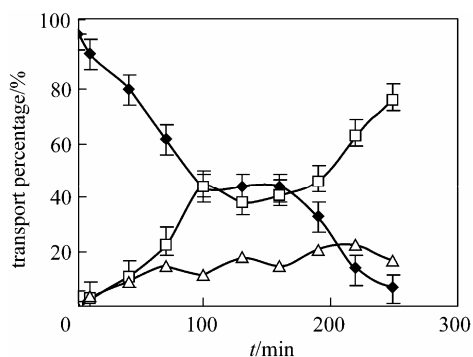


**Figure 8** The reuse of membrane solution (pH in the supplying feed phase: 5.20, O/F: 0.10, initial concentration of Ni(II): 2.00×10<sup>-4</sup> mol·L<sup>-1</sup>, O/S: 4.0, concentration of H<sub>2</sub>SO<sub>4</sub> in the supplying stripping phase: 2.00 mol·L<sup>-1</sup>, HDEHP concentration: 0.120 mol·L<sup>-1</sup>)

#### 4.8 Retention of Ni(II) in the membrane

The retention in membrane and effect of stripping was studied. According to the concentration of both supplying feed phase and stripping phase, the concentration of Ni(II) in membrane phase can be obtained, then the effect of stripping in supplying stripping phase and retention phenomenon of membrane

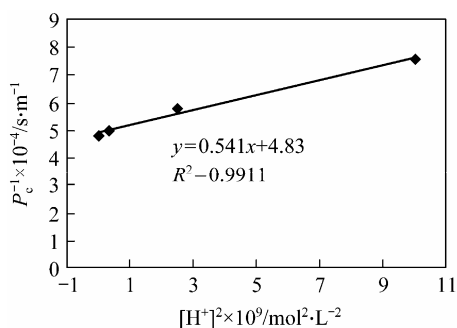
can be obtained as shown in Fig. 9.



**Figure 9 Retention in membrane phase and effect of stripping** (pH in the supplying feed phase: 5.20, O/F: 0.10, initial concentration of Ni(II):  $2.00 \times 10^{-4}$  mol·L<sup>-1</sup>, O/S: 4.0, concentration of H<sub>2</sub>SO<sub>4</sub> in the supplying stripping phase: 2.00 mol·L<sup>-1</sup>, HDEHP concentration: 0.120 mol·L<sup>-1</sup>)  
 ◆ supplying feed phase; □ supplying strip phase; △ membrane phase

## 5 KINETIC ANALYSIS

Based on the data of the effect of pH in the supplying feed phase, the relationship between  $1/P_c$  and  $[H^+]^2$  was developed. When concentration of mobile carrier was specified,  $P_c$  was decided, too. The results were shown in Fig. 10.



**Figure 10 Relationship between  $[H^+]^2$  and  $P_c$**  (H<sub>2</sub>SO<sub>4</sub> concentration in supplying strip phase: 2.0 mol·L<sup>-1</sup>, O/F: 0.1, O/S: 3.0, concentration of Ni(II) in the supplying feed phase:  $2.0 \times 10^{-4}$  mol·L<sup>-1</sup>, HDEHP concentration: 0.120 mol·L<sup>-1</sup>)

It indicated that the relationship between  $1/P_c$  and  $[H^+]^2$  was linear at certain pH. The value of  $R^2$  was 0.9911, which was a good agreement with the theoretical Eq. (12). The slope and intercept were  $5.41 \times 10^{12}$  s·L<sup>-2</sup>·m<sup>-1</sup>·mol<sup>2</sup> and  $4.83 \times 10^4$  s·m<sup>-1</sup>. The thickness of diffusional layer  $d_f$ , which was calculated by using diffusional coefficient of Ni(II) in the aqueous solution that was  $5.99 \times 10^{-10}$  m<sup>2</sup>·s<sup>-1</sup> [23], was  $2.08 \times 10^{-5}$  m.  $K_1$  as determined by extraction experiment was  $2.7 \times 10^{-8}$ . Then  $D_0$  of diffusional coefficient in the membrane, obtained via Eqs. (13) and (14), was  $1.28 \times 10^{-8}$  m<sup>2</sup>·s<sup>-1</sup>.

The new kinetic equation was determined by  $d_f$

and  $D_0$  in the DSSLM system. It can be written as

$$P_c = \frac{1}{4.83 \times 10^4 + 5.41 \times 10^{12} [H^+]^2} \quad (17)$$

## 6 CONCLUSIONS

The transport of Ni(II) with DSSLM technique using HDEHP as mobile carrier was studied. Following conclusions were drawn from the above studies.

(1) The optimum conditions for transport Ni(II) were that the concentration of sulfuric acid was 2.0 mol·L<sup>-1</sup>, O/F was 0.1, HDEHP concentration was 0.120 mol·L<sup>-1</sup> and O/S was 4.0 in the supplying stripping phase, initial concentration of Ni(II) was  $2.0 \times 10^{-4}$  mol·L<sup>-1</sup> and pH was 5.2 in the supplying feed phase. When transport time was 250 min, the transport percentage was 93.1% in optimum conditions.

(2) A modal was established to describe the reaction and transport of metal ions in the DSSLM. The new kinetic equation was deduced. The diffusion coefficient in the membrane phase and thickness of diffusion layer in the supplying feed phase were obtained by linear slope method. They were  $1.28 \times 10^{-8}$  m<sup>2</sup>·s<sup>-1</sup> and  $2.08 \times 10^{-5}$  m, respectively.

(3) In the DSSLM, owing to the large volume of membrane solution is used, it makes up the losing carrier in the supported liquid membrane. As a result, the transport percentage of Ni(II) was increased, the stability of membrane was enhanced, and the lifetime of the membrane was extended.

## NOMENCLATURE

$A$	effective area of membrane, m <sup>2</sup>
$c_f$	concentration of metal ion in the supplying feed phase, mol·L <sup>-1</sup>
$c_{fi}$	concentration of metal ion in the diffusion layer between the supplying feed phase and membrane phase, mol·L <sup>-1</sup>
$c_{f(0)}$	concentration of metal ion in the supplying feed phase when time = 0, mol·L <sup>-1</sup>
$c_{f(t)}$	concentration of metal ion in the supplying feed phase when time = $t$ , mol·L <sup>-1</sup>
$\bar{c}_s, \bar{c}_f$	concentration of metal ion in the membrane phase, mol·L <sup>-1</sup>
$D_f$	diffusion coefficient of the metal ion in supplying feed phase, m <sup>2</sup> ·s <sup>-1</sup>
$D_0$	diffusion coefficient of metal ion in the membrane, m <sup>2</sup> ·s <sup>-1</sup>
$d_f$	thickness of diffusion layer between the supplying feed phase and membrane phase, m
$d_m$	thickness of the membrane, m
$[H^+]$	concentration of H <sup>+</sup> , mol·L <sup>-1</sup>
(HR) <sub>2</sub>	carrier HDEHP
$[(HR)_2]$	concentration of carrier HDEHP, mol·L <sup>-1</sup>
$J$	membrane flux, m <sup>3</sup> ·m <sup>-2</sup> ·s <sup>-1</sup>
$K_1$	forward reaction rate constant at the left interface of the membrane
$K_{-1}$	backward reaction rate constant at the left interface of the membrane
$K_2$	forward reaction rate constant at the right interface of the membrane
$K_{-2}$	backward reaction rate constant at the right interface of the membrane

$P_c$	permeability coefficient of metal ion, $\text{m}\cdot\text{s}^{-1}$
$V_f$	volume of the supplying feed phase, $\text{m}^3$
$A_f$	transport resistance due to diffusion by aqueous feed boundary layer, $\text{s}\cdot\text{m}^{-1}$
$A_0$	transport resistance due to diffusion through the membrane, $\text{s}\cdot\text{m}^{-1}$
$\varepsilon$	porosity of the membrane
$\tau$	tortuosity of the membrane

### Subscripts

f	supplying feed phase
m	membrane phase
org	organic phase
s	supplying stripping phase

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