Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.

This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright

Author's personal copy

Journal of Membrane Science 378 (2011) 520–530

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Stripping dispersion hollow fiber liquid membrane containing PC-88A as carrier and HCl for transport behavior of trivalent dysprosium

Liang Pei[a,c,*], Liming Wang[b,c], Wei Guo[b], Nan Zhao[c]

[a] Key Laboratory of Water Cycle and Related Land Surface Processes, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China
[b] School of Environment and Chemistry Engineering, Xi'an Polytechnic University, Xi'an 710048, China
[c] Faculty of Water Resources and Hydraulic Power, Xi'an University of Technology, Xi'an 710048, China

ARTICLE INFO

Article history:
Received 22 January 2011
Received in revised form 16 May 2011
Accepted 19 May 2011
Available online 12 June 2011

Keywords:
Stripping dispersion hollow fiber liquid membrane
2-Ethyl hexyl phosphoric acid-mono-2-ethyl hexyl ester
Dysprosium
Transport process
Kinetic equation

ABSTRACT

The transport of Dy^{3+} through stripping dispersion hollow fiber liquid membrane system (SDHFLM) containing dispersion phase with HCl solution as stripping solution and 2-ethyl hexyl phosphoric acid-mono-2-ethyl hexyl ester (PC-88A) dissolved in kerosene as membrane solution, has been studied. Many factors of the interface chemical reaction and composition of the liquid membrane including pH value, initial concentration of Dy^{3+}, different ionic strength of feed phase, volume ratio of membrane solution to stripping solution (O/W), HCl concentration, carrier concentration, different stripping agents of dispersion phase, hydrodynamic characteristic (flow rates, stability) and hollow fiber structure parameters (inner diameter of fibers, membrane thickness, porosity, etc.) on Dy^{3+} transport with SDHFLM were investigated. The advantages of SDHFLM compared to the traditional HFLM was investigated too. Experimental results indicated that the optimum transport conditions of Dy^{3+} were that HCl concentration was 4.00 mol/L, PC-88A concentration was 0.150 mol/L, O/W was 0.5 in the dispersion phase, and pH value was 5.00 in the feed phase. Ionic strength had no obvious effect on transport of Dy^{3+}. When initial Dy^{3+} concentration was 1.50×10^{-4} mol/L, the transport efficiency of Dy^{3+} was up to 95.4% in 170 min. The kinetic equation was developed in terms of the law of mass diffusion and the theory of interface chemistry. The results were in good agreement with the literature data.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Rare earth metals and their compounds have been widely used in all walks of life due to their spectrascopic physical and chemical characteristics. The property of the metal alloy can be improved by adding some rare earth metals or compounds in it. Therefore, rare earth elements are known as vitamin of metallurgical industry [1]. For example, plasticity, toughness, steel resistance, heat resistance, oxidation resistance and corrosion resistance can be enhanced when some rare earth elements are added in steel. Another example, rare earth metals can be used to make a fire alloy, permanent magnetic materials, superconducting materials, dyeing materials, luminescence materials and microelements fertilizer, etc. Therefore, rare earth metals have been also widely used in petrochemical, glass, ceramics, fluorescent materials, electronic material, medicine, agriculture department, a lot of modern science and technology field. In China, there are abundant rare earth resources. With the development of rare earth industry, the application of rare earth elements widely for transport and enrichment has become more and more necessary [2].

Liquid membrane technique is a novel transport method, which combines the characteristics of solvent extraction with solid membrane separation. It has several potential advantages compared to the conventional methods of solvent extraction technique. Liquid membrane transport of rare earth metals is characterized by a short process, high speed, great enrichment ratio, little reagent consuming and low cost, which has extensive industrial application prospect. In China, the studies about liquid membrane began in the early 1980s. Organic solvents of liquid membrane system for transport of rare earth metal are carried with kerosene or common sulfonated kerosene. The carrier used LA, P204 and P507, etc. The stripping phase used HCl and HNO_3, etc. Leaching mother liquor of rare earth can be grouped, purified and separated as required [3].

Konda used double stearic acid and organophosphate as carrier to study supported liquid membrane (SLM) system for transport

* Corresponding author at: Key Laboratory of Water Cycle and Related Land Surface Processes, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, 11A, Datun Road, Chaoyang District, Beijing 100101, China. Tel.: +86 1064889586; fax: +86 1064889586.
E-mail addresses: peiliang@igsnrr.ac.cn, pellys_0311@163.com, pellys38994327@qq.com (L. Pei).

0376-7388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2011.05.037

Author's personal copy

of rare earth samarium^{3+} and to establish a migration model [4]. Lee used polypropylene porous membrane as supported membrane and PC-88A as carrier to establish supported liquid membrane system for transport of rare earth europium^{3+} and established a mathematical model of migration process of Co^{2+} [5]. Kim [6] and others used composited supported liquid membrane to deal with La^{3+} in rare earth wastewater. In recent years, Yi et al. [7] and others studied on flat sandwich SLM system, tested the permeability coefficient of transport of La^{3+}, compared the differences of supported membrane with different materials in extraction, and investigated transport efficiency and stability of liquid membrane system.

SLM method has the virtue of simplicity of operation without using expensive surfactants. However, the contradiction between the decline of membrane stability caused by the membrane solution (organic solvent, extraction agents and modifiers) dissolved in aqueous phase and high transport flux is still not well solved [8]. As for SLM problems, some experts have turned to study new liquid membrane configuration in recent years. They want to maintain characteristics of membrane transport and at the same time to overcome the shortcomings of instability of supported liquid membrane. Therefore, hybrid liquid membrane and combination technique are proposed [9,10]. It combines solid membrane or various chemical processes with liquid membrane, which can effectively overcome the leakage of the carrier from membrane. In our previous works, dispersion supported liquid membrane (DSLM) for transport of rare earths has been studied and the transport results were very obvious [11–13]. In this work, based on DSLM of our previous works and pseudo-emulsion-based hollow fiber stripping dispersion (PEHFSD) techniques [14], the stripping dispersion hollow fiber liquid membrane system (SDHFLM) with HCl as stripping agent and 2-ethyl hexyl phosphoric acid-mono-2-ethyl hexyl ester (PC-88A) dissolved in kerosene as the mobile carrier was proposed. In SDHFLM process, a very thin organic film was developed within the internal surface of fibers, which was used for separation of the feed phase and stripping phase, due to the wetting affinity of the hydrophobic hollow fibers and dispersion phase. The solute was selectively transported from feed phase to the stripping phase across the liquid membrane film. SDHFLM not only has the advantages of non-equilibrium mass transfer and up-hill effect, but also avoids the disadvantages of traditional HFLM and emulsion liquid membrane, such as loss of mobile carrier, difficult operation of emulsification and de-emulsification steps, etc.

These advantages of SDHFLM are very attractive. More studies are needed for the application of SDHFLM in industry. For example, the behavior of transport of single cation and a new permeability coefficient equation should be studied, because of the diversity of transport behavior of ions in the two systems of traditional HFLM and SDHFLM. Secondly, some works about the separation of two or more rare earth metals are required in order to solve more practical separation problems [11]. Rare earth Dy^{3+} is playing an increasingly important role in high technology. $Dy^{3+}$is typical in heavy rare earths. In order to investigate the transport regularity of heavy rare earths by liquid membrane, we chose Dy^{3+} as the sample in experiment. A few of studies about transport of $Dy^{3+}$by liquid membrane has been done during the last decade [12,16], but the effect of transport was not good enough because of disadvantages above. In this work, we chose a novel liquid membrane system to transport Dy^{3+}in the experiment.

Currently, there were not some reports on the application of stripping dispersion hollow fiber liquid membrane system (SDHFLM) for transport of Dy^{3+}. It is mainly to study the transport feasibility of SDHFLM for Dy^{3+}. On the basis of membrane module design, parameter optimization, transport efficiency control and other aspects, the transport process of rare earth metals were studied. Finally, new methods and new system of SDHFLM for transport of rare earth metal have been established. The studies of this paper could provide more theoretical basis for the further investigations and the results are expected to achieve a breakthrough in industrial applications of the SDHFLM technique.

2. Experimental

2.1. Reagent

$Dy(CH_3COO)_3{\cdot}4H_2O$, Arsenazo III ($C_{22}H_{18}As_2O_{14}N_4S_2$), HCl, NaH_2PO_4, Na_2HPO_4, CH_3COONa, and CH_3COOH et al. used in the present work were of analytical grade. 2-Ethyl hexyl phosphoric acid-mono-2-ethyl hexyl ester (PC-88A) is a commercial extractant (purity > 95%) and used without any further purification. Kerosene was washed with concentrated sulfuric acid and distilled at 185–225 °C. All agents were from Beijing chemical reagent plant

2.2. Preparing of solutions

Dy^{3+} stock solution: it was prepared by dissolving $Dy(CH_3COO)_3{\cdot}4H_2O$ in 1.0 mol/L HCl, and analyzed by Arsenazo III ($C_{22}H_{18}As_2O_{14}N_4S_2$) as the chromogenic agent.

Dy^{3+} feed solution: a certain amount of the Dy^{3+} stock solution was diluted with 0.01 mol/L HCl solution to a given extent after adding a calculated amount of CH_3COONa and CH_3COOH or NaH_2PO_4 and Na_2HPO_4.

Arsenazo III ($C_{22}H_{18}As_2O_{14}N_4S_2$) stock solution: a stock solution of Arsenazo III was prepared by dissolving powder of Arsenazo III in deionized water.

Stripping solution: it was prepared with a required amount of HCl dissolved and diluted with deionized water to a known concentration.

Distilled kerosene: it was obtained by distilling at 185–225 °C the commercial kerosene washed with concentrated sulfuric acid.

PC-88A solution: it was prepared by diluting a calculated amount of extractant with kerosene.

2.3. Experimental material and process

All the experiments were the self-designed systems. The hollow fiber membrane were laboratory scale versions with two 0–1.0 L min^{-1} pumps and flowmeters, which makes it possible to evaluate the performance without having to prepare large amounts of feed, stripping and organic phases, and also to avoid the influence of non-ideal flow in the shell side of the component. Membrane component had a PVDF module of commercial product with a nominal porosity of 62%, a tortuosity of 2.22, effective component length of 20 cm, inner diameter of 8 mm of module with fiber number of 20. Inner diameter of fiber, outer diameter, thickness and effective membrane area of fiber were 0.9 mm, 1.2 mm, 0.3 mm and 188 cm^2, respectively. The hollow fiber membrane were from Tianjing University of Technology

Samples containing Dy^{3+} in the feed phase only were analyzed for ion concentration with a UV-1200 spectrophotometer using Arsenazo III as the chromogenic agent (under the detection wave lengths: 653 nm). The UV-1200 spectrophotometer is made in Shanghai China. The water purification systems is made in Jiangsu China.

The feed phase was prepared by dissolving a weighed amount of $Dy(CH_3COO)_3{\cdot}4H_2O$ in acetate buffer media in which the pH was adjusted. The organic phase was composed of PC-88A as carrier dissolved in kerosene and the stripping phase was 3.0 mol/L HCl aqueous solution. The hydrophobic fibers were prewetted with organic phase at least 48 h in order to make the pores of fibers fully filled with organic phase. In these experiments, there were two operation modes: (I) the stripping phase was pumped through the

Author's personal copy

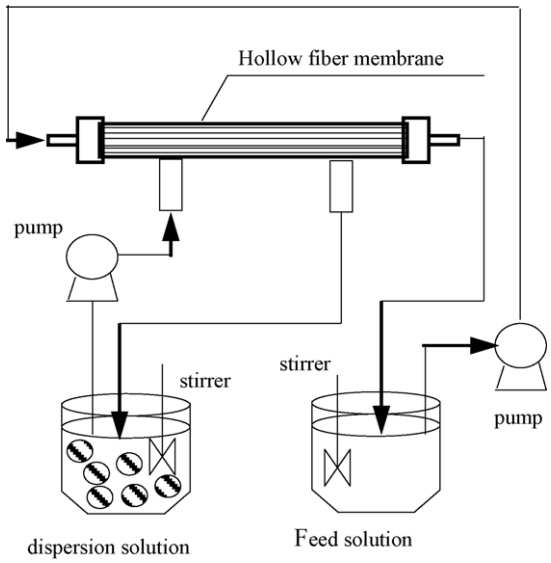

Fig. 1. Experimental installation of SDHFLM process.

shell side of the component and the feed phase through the tube side. (II) The feed phase pumped through the shell side and stripping phase through the tube side. Both fluids were transported in opposite direction and single path processes. In general, the usage of a stirrer can disperse a stripping solution in a membrane solution and form the droplets of the aqueous stripping solution in a continuous organic phase because of the weak surface-active of the extractant. It is called as the dispersion phase. In the experimental process, there is a constant supply of the membrane solution, i.e. the membrane solution of the dispersion phase, contacting the pores of HFLM. This constant supply of the membrane solution ensures a stable and continuous operation of the HFLM. In this way, the metal–carrier complex could diffuse to the interface between the stripping solution and the membrane solution in pores of HFLM. Therefore, the direct contact between the stripping solution and the membrane solution provides efficient mass transfer for stripping. Secondly, once removal of the target species is completed, the stirring for the stripping dispersion and pumps are stopped. The dispersion phase is thus allowed to suspend, resulting in separation of the dispersion phase into two phases: the membrane phase readily wetting the pores of support and the stripping supply containing concentrated metal ions. The concentrated stripping solution is the product of this process. Fig. 1 shows the experimental installation of the SDHFLM process.

In order to prevent the mobile carrier leakage from membrane pores, pressures of the both sides were controlled by the flow velocity to make a slightly positive pressure of the shell side to form a stable interface.

Based on our previous experiments, the stable concentration of Dy^{3+} profiles were developed after 20 min in both the feed phase and the dispersion phase, then the stable mass transfer performance was achieved and the similar results were also found when the dispersion phase flowed through the tube side. Initial stabilization time was set over 30 min in later experiments in order to get more reliable results.

3. Results and discussion

3.1. Principle and theory of the SDHFLM process

Fig. 2 shows the principle of SDHFLM process, in which concentration change and transport processes are depicted. The co-transport involves various equilibrium reactions, which are described as follows [13]:

(a) Dy^{3+} diffuses from the feed phase to the interface A.
(b) On the feed side interface of the SDHFLM, the extraction of Dy^{3+} from feed solution with carrier PC-88A [can be as $(HR)_2$] in kerosene can be expressed as [11]:

$$Dy_f^{3+} + 3(HR)_{2,org} \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} DyR_3 \cdot 3HR + 3H_f^+ \quad (1)$$

where f and org stand for feed phase and organic phase, respectively; $(HR)_2$ indicates that the PC-88A in kerosene mainly exists as a dimer; K_1, and K_{-1} stand for forward and backward reaction percentage constant at the interface between the feed phase and membrane phase.
(c) The metal-complex ($DyR_3{\cdot}3HR$) diffuses through the membrane A–B.
(d) At the stripping side interface of the SDHFLM, the $DyR_3{\cdot}3HR$ dissolved in membrane solution and the metal ion Dy^{3+} are stripped by stripping agent.
The stripping reaction on the other side of the SLM is written as follows:

$$DyR_3 \cdot 3HR + 3H_s^+ \underset{K_{-2}}{\overset{K_2}{\rightleftarrows}} Dy^{3+} + 3(HR)_{2,org} \quad (2)$$

where s represents the dispersion phase; K_2 and K_{-2} stand for forward and backward reaction efficiency constant at the interface between the membrane phase and dispersion phase.
(e) Carrier PC-88A returns from B to A.

In this mechanism the transport of Dy^{3+} across SDHFLM was described by considering diffusion coefficient of Dy^{3+}, because the complex reaction between the Dy^{3+} and PC-88A at the interfaces is much faster compared to the diffusion in the feed phase and membrane phase [13].

To formulate the model, the following assumptions were made:

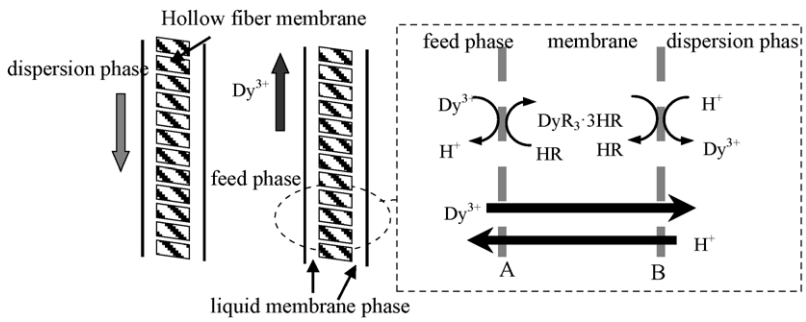

Fig. 2. Schematic principle and description of Dy^{3+} transport in SDHFLM.

Author's personal copy

(1) The Dy^{3+} diffuses in the organic medium only as the $DyR_3 \cdot 3HR$ complex.
(2) There is no net flow due to convection within the liquid membrane.
(3) The metal ions react only with PC-88A at the membrane interfaces.
(4) The PC-88A monomer and dimer are in equilibrium at all times throughout the organic phase.
(5) The solubility of PC-88A in the aqueous acid solution has been found to be negligible, therefore, its concentration in the SDHFLM is assumed to remain constant [15].

Then in this model, the transport of Dy^{3+} in the SDHFLM can be considered to include four sequential steps. If the diffusion process is described by the Fick's law, the transport flux of each step is given as follows [15–19]:

The flux of feed phase can be written as:

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

where J_f, D_f, d_f, c_f and c_{fi} stand for the transport flux in the feed phase, the diffusion coefficient of Dy^{3+} in the membrane and thickness of diffusion layer between the feed phase and the membrane phase, the concentration of Dy^{3+} in the feed phase, and the concentration of Dy^{3+} in the diffusion layer between the feed phase and membrane phase, respectively.

The extraction equilibrium constant K_{ex} in Eq. (1) can be expressed as:

$$K_{ex} = \frac{[H^+]^3 c^0_{mf}}{c_{fi}[(HR)_2]^3} = \frac{K_d[H^+]^3}{[(HR)_2]^3} = \frac{8K_d[H^+]^3}{[HR]^3} \tag{4}$$

where m stands for membrane phase and K_d indicates that the distribution ratio of Dy^{3+}.

The transport flux of diffusion layer between the feed phase and membrane phase can be written as:

$$J_{mf} = K_1 c_{fi} - K_{-1} c^0_{mf} \tag{5}$$

where J_{mf}, and c^0_{mf} indicate the transport flux and the concentration of Dy^{3+} in the diffusion layer between the feed phase and membrane phase.

$$J_m = \frac{D^0_m}{d_m}(c^0_{mf} - c^0_{ms}) \tag{6}$$

where J_m, c^0_{ms}, D^0_{mf} and d_m stand for the transport flux in the membrane, the concentration of Dy^{3+} in the diffusion layer between the dispersion phase and membrane phase, diffusion coefficient of Dy^{3+} in the membrane and thickness of the membrane, respectively.

In view of distinct character of different membranes, tortuosity and porosity of membrane impose an effect on the transport flux of membrane. The greater the porosity of membrane is, the higher the flux is, and the greater the tortuosity of membrane is, the lower the flux is. So considering correction coefficient, Eq. (6) can be rewritten as:

$$J_m = \frac{D^0_m \varepsilon}{d_m \tau}(c^0_{mf} - c^0_{ms}) \tag{7}$$

where τ and ε stand for tortuosity and porosity of membrane.

In homeostatic reaction system under ideal condition, all of these above individual transport fluxes can be taken for equality [12,15–19].

$$J_f = J_m = J_{mf} = J_s \tag{8}$$

where J_s stands for the transport flux in the dispersion phase.

After taking Eqs. (3), (4), (6), (7) and (8), following formula can be obtained:

$$J = \frac{1}{(d_f/D_f) + (8d_m\tau[H^+]^3/D^0_m\varepsilon K_{ex}[HR]^3)} c_f \tag{9}$$

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

$$J = P_C \cdot c_f = -\frac{V_f}{\varepsilon A}\left(\frac{dc_f}{dt}\right) \tag{10}$$

where V_f stands for the volume of the feed phase, A stands for the effective area of membrane, and J stands for the membrane flux.

P_C stands for the permeability coefficient, which can be defined as:

$$P_C = \frac{1}{(d_f/D_f) + (8d_m\tau[H^+]^3/D^0_m\varepsilon K_{ex}[HR]^3)} \tag{11}$$

The d_f/D_f and d_m/D^0_m can be defined as follows:

$$\delta_f = \frac{d_f}{D_f} \tag{12}$$

$$\delta_m = \frac{d_m}{D^0_m} \tag{13}$$

Eq. (11) can be simplified as:

$$\frac{1}{P_C} = \frac{8\delta_m\tau[H^+]^3}{\varepsilon K_{ex}[HR]^3} + \delta_f \tag{14}$$

In Eq. (14), ε, τ, and K_{ex} are all constants. As a result of extraction experiments, K_{ex} of 1.5×10^{-11} was obtained. The relationship between $1/P_C$ and $[H^+]^3$ are examined to be linear at the same concentration of PC-88A. So the diffusion coefficient of Dy^{3+} in the membrane and the thickness of diffusion layer between the feed phase and membrane phase can be obtained with the linear slope method. In the same way, the relationship between $1/P_C$ and $[HR]^3$ are examined to be linear at the same H^+ concentration in the feed phase.

Then, δ_f and δ_m can be obtained. From Eq. (14) combined with Eqs. (12) and (13), D^0_m and d_f values can also be obtained.

The transport efficiency of Dy^{3+} is obtained by determination of dc_f/dt.

Considering and integrating Eq. (10) as follows:

$$\ln \frac{c_t}{c_0} = -\frac{\varepsilon A}{V_f} P_C t \tag{15}$$

$$\eta = 1 - e^{-(\varepsilon A/V_f)P_C t} \quad \text{or} \quad \ln(1-\eta) = -\frac{\varepsilon A}{V_f} P_C t \tag{16}$$

$$\int_c^{c_t} \frac{dc_f}{c_f} \frac{-V_f}{\varepsilon A P_C(t^*)} = t - t_0 \tag{17}$$

where c_t and c_0 stand for the concentrations of Dy^{3+} in the feed phase at $t = 0$ and $t = t$ time, and t^* stands for average time, respectively. Eq. (15) demonstrates the value of P_C is the slope of line, which is obtained in different operation conditions.

Combining Eqs. (10)–(17), following formula can be obtained:

$$\eta = 1 - e^{(8\delta_m\tau V_f[H^+]^3/\varepsilon^2 K_{ex} A t[HR]^3) + (\delta_f V_f/\varepsilon A t)} \tag{18}$$

According to the Fick's second law, Eq. (18) can be also written as follows [13]:

$$J|t = \frac{D^0_m K_{ex}[(HR)_2]^3 c_f}{d_m[H^+]^3}\left(1 - \frac{d^2_m}{6D^0_m t}\right) \tag{19}$$

where η stands for transport efficiency of Dy^{3+} through SDHFLM, J stands for transport flux of Dy^{3+}, C_f stands for concentration of feed phase, t stands for time, D_f stands for the diffusion coefficient of

Author's personal copy

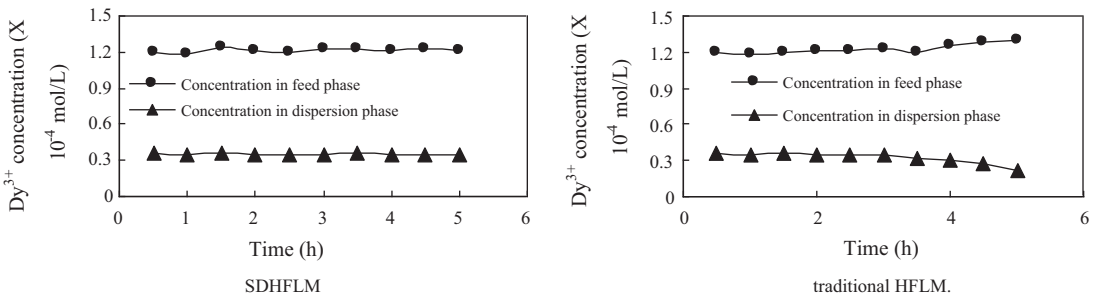

Fig. 3. The stability comparison between SDHFLM and traditional HFLM.

Dy^{3+} in the membrane, d_f stands for the thickness of diffusion layer between the feed phase and the membrane phase, D_m^0 stands for the coefficient of Dy^{3+} in the membrane, and d_m stands for thickness of the membrane, respectively.

3.2. Stability of SDHFLM

In order to define stability of SDHFLM compared with traditional HFLM, the tendency of Dy^{3+} concentration changes in feed phase and dispersion phase with time was studied under the fixed operating conditions lasting a long time.

In this experiment, two operation modes were investigated in mode 1: the dispersion phase was pumped through the shell side of the component and the feed phase through the tube side. The flow velocities of feed phase and dispersion phase were 0.02 m/s and 0.005 m/s. The flow velocities of two phases have been maintained in experiment.

The assumed experimental conditions chosen were in the certain pH value in the feed phase, which was adjusted to 4.80. Initial concentration of Dy^{3+} was 1.74×10^{-4} mol/L, volume ratio of membrane solution/stripping solution (O/W) was 0.3 in the feed phase, the HCl concentration was 3.00 mol/L and the PC-88A concentration was 0.200 mol/L of dispersion phase. The results are shown in Fig. 3(a) and (b). After 30 min, the tendency of Dy^{3+} concentration changes was stable, so we took a sample in 30 min in each transport experiment. We can find that after 3.5 h, the Dy^{3+} concentration and stability of dispersion phase decreased gradually under using traditional HFLM and the Dy^{3+} concentration in both feed phase and dispersion phase remained stable under using SDHFLM. This is because the carrier in traditional HFLM loses gradually and SDHFLM with dispersion phase can supply carrier to the membrane system. So we can draw the conclusion that stability of SDHFLM was better than traditional HFLM.

3.3. Effect of flow rates in both feed phase and dispersion phase

In order to study the mechanism of mass transfer in SDHFLM and determinate the dominated part of total mass transfer resistance, it is necessary to investigate the hydrodynamic characteristics of this system. The flow rates in both feed phase and dispersion phase plays a vital role in the transport of metal ion from the feed phase to the stripping phase. In traditional HFLM, the carrier could be washed away gradually by the high-speed flowing solution. In SDHFLM, dispersion solution could contribute to supply carrier to the membrane system under the condition of high-speed flowing. So the effect of the flow rates of the feed phase and dispersion phase on transport efficiency of Dy^{3+} was studied in this section. All the other parameters, such as pH value, initial concentration of Dy^{3+} in the feed phase, volume ratio of membrane solution/stripping solution (O/W) and PC-88A concentrations were adjusted to 4.80, 1.74×10^{-4} mol/L, 0.50 and 0.200 mol/L, respectively. The effect of the flow rates in both feed phase and dispersion phase on transport efficiency of Dy^{3+} is shown in Figs. 4 and 5.

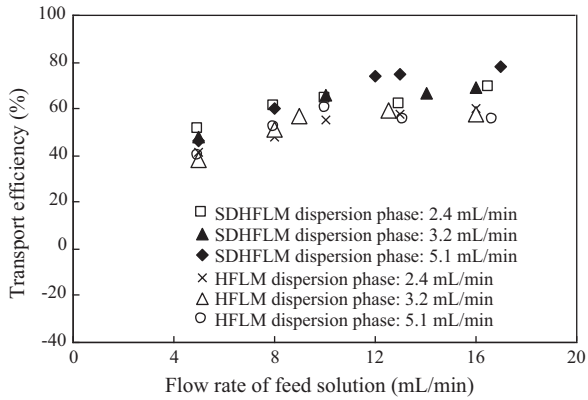

Fig. 4. The comparison between SDHFLM and traditional HFLM about flow rates effect on transport of Dy^{3+} in both two phases (I).

We can find that the carrier can be washed away gradually by the high-speed flowing solution in traditional HFLM, so the higher the flow rate is, the lower the transport efficiency is. In SDHFLM, dispersion solution can contribute to supply carrier to the membrane system under the condition of high-speed flowing, so the flow rate of solution in shell side have not obvious effect on the transport efficiency of Dy^{3+}. The flow rate of feed solution in tube side have a few effects on the transport efficiency of Dy^{3+}, because feed solution diffusion rate in boundary layer of tube side is an important rate control step in the whole transport processes [20,21]. In following experiments, flow rate of dispersion solution in shell side was kept approximately within 5.0 mL min^{-1} and flow rate of feed solution in tube side was confined to 10.0 mL min^{-1}.

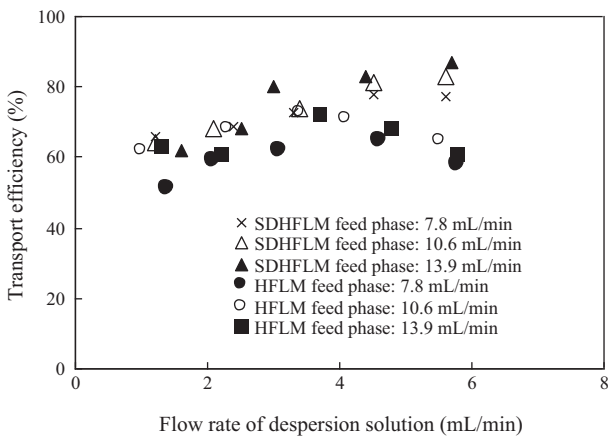

Fig. 5. The comparison between SDHFLM and traditional HFLM about flow rates effect on transport of Dy^{3+} in both two phases (II).

Author's personal copy

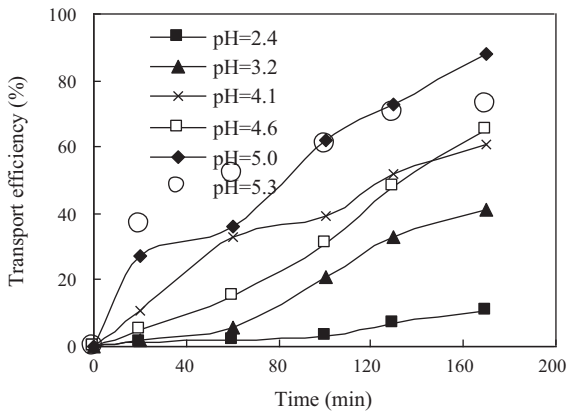

Fig. 6. Effect of pH of the feed phase.

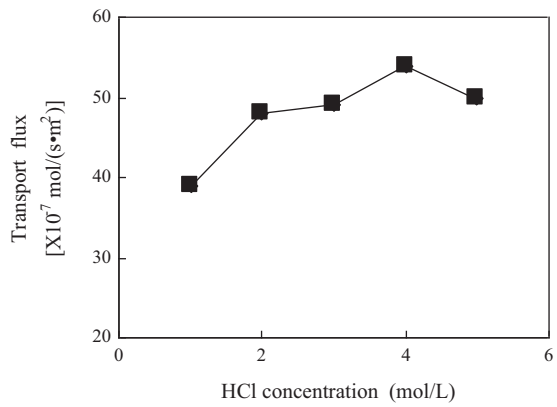

Fig. 7. Effect of HCl concentration.

3.4. pH effect in feed phase

Based on mechanism of mass transfer process, the concentration difference between feed phase and dispersion phase is the driving power of mass transfer process [11]. So in the feed phase the lower the H^+ concentration is, the stronger the driving power of mass transfer process will be. Stronger power will promote the transport flux of Dy^{3+}. Equally, the greater the pH value in the feed phase is, the higher the transport flux of Dy^{3+} is. The effect of pH in the feed phase on transport of Dy^{3+} was studied in the pH range of 2.40–5.30. Initial concentration of Dy^{3+} in the feed phase was 1.50×10^{-4} mol/L. HCl concentration solution was 4.00 mol/L, volume ratio of membrane solution to stripping solution (O/W) was 0.50, PC-88A concentration was 0.100 mol/L in the dispersion phase. The results are shown in Fig. 6. The Dy^{3+} transport efficiency increased when the pH in the feed phase increased from 2.40 to 5.30, and a maximum transport efficiency observed at pH 5.00 was 88.2% during 170 min. When pH value was higher than 5.0, hydroxy complex of Dy^{3+} was formed in the feed phase and the transport efficiency of Dy^{3+} decreased. Contrast to the previous cases, the literature [11,16] suggested the influence of pH on distribution coefficient of extraction process. It is large because the transport process is mainly governed by the driving power of mass transfer caused by the distribution equilibrium, when the renewal effect of the liquid membrane and the diffusion mobility of Dy^{3+} ions are determined under specific experimental conditions [12,17,18]. As far as our researching conditions were concerned, considering saving chemical agents as well as increasing transport rate, we chose pH of 5.00 as the optimum pH condition of the feed phase for the following experiments.

3.5. Effect of HCl concentration in dispersion phase

The stripping reaction in the dispersion phase plays a vital role in the transport of metal ion from the feed phase to the stripping phase. So the effect of the HCl concentration of the dispersion phase on transport flux of Dy^{3+} was studied in this section. Under the above subsection condition obtained, the effect of HCl concentration of dispersion phase on transport flux of Dy^{3+} is shown in Fig. 7. It indicates that, with the increasing of acid concentration in the dispersion phase, the transport flux of Dy^{3+} increased. It can be seen that the effective HCl concentration for transport were 3.00 mol/L, 4.00 mol/L and 5.00 mol/L, which gives a transport fluxes of Dy^{3+} were about 49.4×10^{-6} mol/(s m^2), 55.7×10^{-7} mol/(s m^2) and 50.4×10^{-7} mol/(s m^2).

The increasing of concentration of HCl solution from 1.00 mol/L to 2.00 mol/L had no significant effect on transport flux of Dy^{3+}, because the number of Dy^{3+} complex and the concentration of membrane solution which transport through the membrane per unit area of the membrane per unit time are definite. Considering controlling acidity as well as increasing transport flux, we chose 4.00 mol/L as the optimum HCl concentration of the dispersion phase for the following experiments.

3.6. Effect of the volume ratio (O/W) of dispersion phase

The effect of volume ratio of membrane solution to stripping solution (O/W) in the dispersion phase on transport of Dy^{3+} was studied. Under the above subsection condition obtained, the effect of volume ratio (O/W) of dispersion phase on transport of Dy^{3+} is shown in Fig. 8. The volume ratio increased from 0 to 2.00. It can be seen that the most effective volume ratio was 0.50, which gave rise to a transport flux of Dy^{3+} much higher than others.

This indicates the Dy^{3+} transport flux increases with the increasing of the volume ratio of the dispersion phase. When volume ratio in the dispersion phase increases, the droplets of the dispersion solution disperse obviously in the membrane phase and the chances of contacting between PC-88A and Dy^{3+} increase. In this way, the mixing between the membrane phase and dispersion phase provides an extra stripping surface and renewal percentage of liquid membrane, which leads to extremely stripping percentage for the target species from organic phase and life of liquid membrane. Increasing to an extent of the volume ratio, the flux become lower because of decreasing of H^+ of dispersion phase [11]. We chose 0.50 as the optimum volume ratio of membrane solution to stripping solution (O/W) in the dispersion phase for the following experiments.

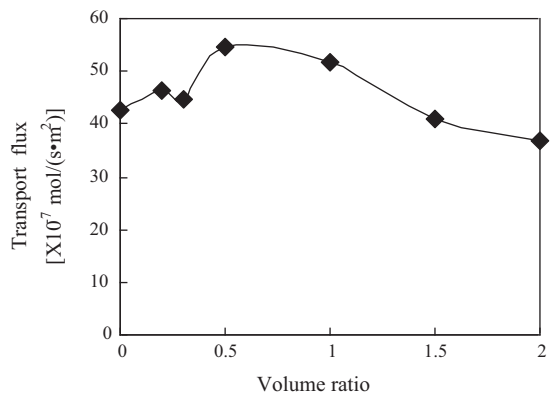

Fig. 8. Effect of volume ratio of membrane solution to HCl solution.

Author's personal copy

Table 1
Effect of initial Dy^{3+} concentration.

Time (min)	Transport efficiency (%)				
	5.00×10^{-5} mol/L	1.00×10^{-4} mol/L	1.20×10^{-4} mol/L	1.50×10^{-4} mol/L	2.00×10^{-4} mol/L
0	0	0	0	0	0
20	51.3	39.7	24.8	27.5	17.3
60	79.8	58.6	52.1	36.9	19.9
100	92.1	71.4	70.3	62.9	48.7
130	–	87.0	80.4	74.1	53.5
170	–	–	95.2	88.2	69.0

3.7. Effect of other stripping agents

The stripping agent at the membrane-dispersion side plays a vital role in transport of metal ions from feed phase to stripping phase. So the effects of different stripping agents in the dispersion phase on transport of Dy^{3+} were studied. Using hydrochloric acid (HCl), sulfate acid (H_2SO_4) and nitric acid (HNO_3) as the stripping agent respectively under the same acidity condition, it was found that hydrochloric acid is the most efficient stripping agent in this investigation.

3.8. Effect of initial Dy^{3+} concentration in feed phase

Effect of initial Dy^{3+} concentration on transport efficiency of Dy^{3+} was studied in the Dy^{3+} concentration range from 5.00×10^{-5} mol/L to 2.00×10^{-4} mol/L. The results obtained are presented in Table 1. With the increasing of initial Dy^{3+} concentration of the feed phase from 2.00×10^{-5} mol/L to 1.60×10^{-4} mol/L, the transport efficiency of Dy^{3+} decreased during the same time. This is because the PC-88A number is definite through the membrane when the interface between the feed phase and the membrane phase is definite. That is to say, the Dy^{3+} number transported is definite in this transport process [11]. When the Dy^{3+} concentrations were 5.00×10^{-5} mol/L, 1.00×10^{-5} mol/L, 1.20×10^{-5} mol/L, 1.50×10^{-4} mol/L and 2.00×10^{-4} mol/L, the transport efficiencies were up to 92.1%, 71.4%, 70.3%, 62.9 and 48.7% in 100 min, respectively.

3.9. Effect of carrier concentration

PC-88A concentration in the membrane phase and dispersion phase also plays a significant role in transport of Dy^{3+}. Effect of PC-88A concentration on transport efficiency of Dy^{3+} was studied in the PC-88A concentration range from 0.060 mol/L to 0.200 mol/L. Under the above subsection condition obtained, the results are shown in Fig. 9. With the increasing of concentration of carrier in the membrane phase from 0.060 mol/L to 0.200 mol/L, the Dy^{3+} transport efficiency increased, however, when PC-88A concentration increased to 0.200 mol/L from 0.150 mol/L, the increasing of transport efficiency of Dy^{3+} was not obvious. Within this concentration of PC-88A range from 0.060 mol/L to 0.200 mol/L, the availability of PC-88A at the feed–membrane–dispersion interfaces increased with the increasing of concentration of carrier. The chemical equilibrium moved toward left, vice versa, when concentration of PC-88A became low, the equilibrium moved toward the right [13]. The transport efficiency of Dy^{3+} was no longer increase with time with increasing of concentration of PC-88A to a significant extent [11]. When the PC-88A concentrations were 0.100 mol/L, 0.120 mol/L, 0.150 mol/L and 0.200 mol/L, the transport efficiencies were 88.2%, 91.8%, 95.4% and 96.1%, respectively. The PC-88A concentration is proportionate with Dy^{3+} concentration in membrane phase. When the concentration of PC-88A in the membrane phase becomes higher in comparison to Dy^{3+} concentration of feed phase, there are not Dy^{3+} to react on redundant PC-88A, so the increasing of transport efficiency of Dy^{3+} will become slow. This indicates that the number of PC-88A used to transport Dy^{3+} through the membrane per unit area of the membrane per unit time is definite, when the initial concentration of Dy^{3+}, the effect area of membrane and time are definite. 0.150 mol/L was chosen as the optimum concentration of carrier. Under the conditions, the transport efficiency of Dy^{3+} was 95.4% during 170 min.

3.10. Effect of ionic strength in feed phase

The effect of ionic strength of feed phase on transport efficiency of Dy^{3+} was studied in this section. The results indicate that the ionic strength had not obvious influence on the transport flux of Dy^{3+}, because the HCl effect surrounded by membrane solution is weak, which leads to the ignorable ionic strength of the dispersion phase. When the concentration of ions in the feed phase is low, the ionic strength of two phases is neglected. The operational condition, comparing to other technologies of liquid membrane, is further simplified [13].

3.11. The reuse of membrane solution

The reuse of membrane solution was studied under the optimal conditions. From Fig. 10, we can know the membrane solution in SDHFLM can be reused many times before the re-extraction with the strong acid after every experiment. Membrane solution in SDHFLM can be reused many times and the tendency of transport efficiency changes was stable with SDHFLM in 4 experiments. After 4 experiments, the Dy^{3+} transport efficiency decreased gradually.

3.12. The reuse of membrane module

The reuse of membrane module was studied under the optimal conditions. The membrane solution was reused only 3 experiments and we took new membrane solution or membrane solution after

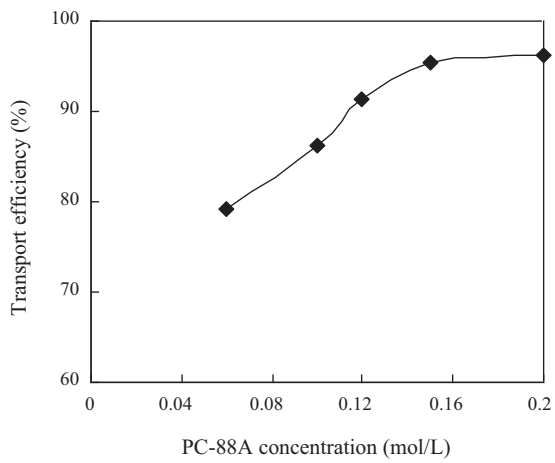

Fig. 9. Effect of carrier concentration.

Author's personal copy

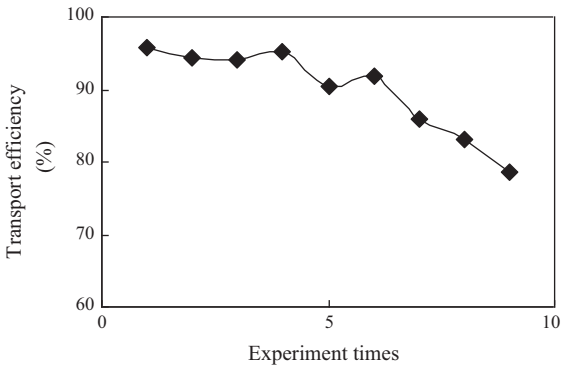

Fig. 10. Reuse of membrane solution.

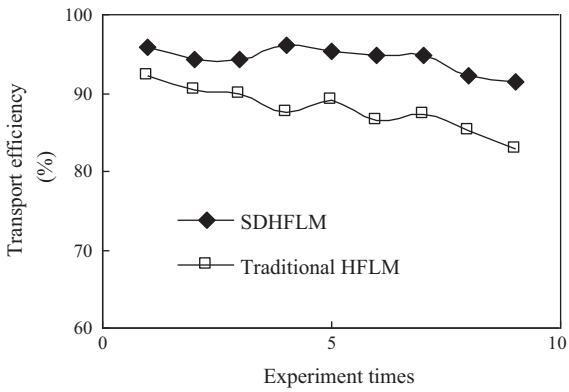

Fig. 11. Reuse effect of membrane module.

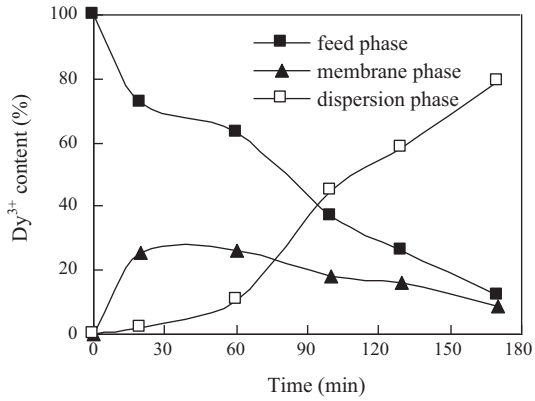

Fig. 12. Retention in membrane phase and effect of stripping.

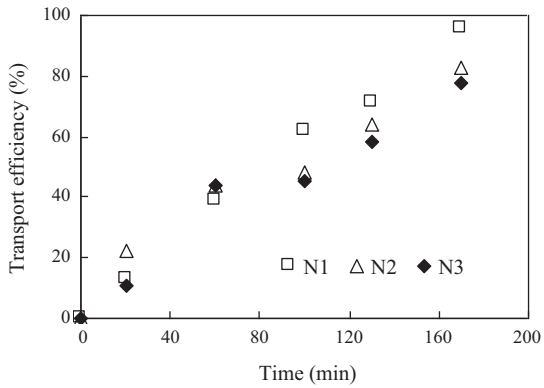

Fig. 13. Effect of thickness of membrane.

being purged by reversed extraction with the strong acid in the forth experiment. The results are shown in Fig. 11. Membrane module of SDHFLM with dispersion phase can be reused many times and the tendency of transport efficiency changes was stable with SDHFLM in 8 experiments, but under the condition of membrane module of traditional HFLM without dispersion phase, the tendency of transport efficiency changes was unstable and transport efficiency decreased gradually after three experiments. In this study, we can also draw the conclusion that stability of SDHFLM was better than traditional HFLM.

3.13. Retention in membrane phase and effect of stripping

The retention in membrane phase and effect of stripping was studied under the optimal conditions. According to the concentration of Dy^{3+} in both feed phase and stripping phase, the concentration of Dy^{3+} in membrane phase can be obtained, then the effect of stripping in dispersion phase and retention phenomenon of membrane phase can be obtained. The results are shown in Fig. 12. We can draw the conclusion that retention percentage of Dy^{3+} in membrane decreased gradually as time extended, because the stripping rate is faster than the complexing rate in transport process.

3.14. Effect of structure parameters of membrane module

In this study, hollow fiber structure parameters (inner diameter of fibers, membrane thickness, porosity, etc.) on the mass transfer performance of SDHFLM process on transport of Dy^{3+} were also studied. Six kinds of polyvinglidene fluoride (PVDF) hollow fibers were chosen and additional information about these modules are listed in Table 2.

The thickness of fiber could have an effect on the thickness of membrane phase in membrane module and transport rate of Dy^{3+} complex. The membrane modules N1, N2 and N3 were chosen to study the effect of thickness of fiber on transport of Dy^{3+} under the optimum transport conditions. The results are shown in Fig. 13. We can draw the conclusion that the thicker fiber, the lower transport efficiency of Dy^{3+}. The main reason might be that the thicker fiber, the lower transport rate of Dy^{3+} complex.

Table 2
Structure parameters of membrane and membrane module.

No	PVDF hollow fiber structure parameters				
	Effective length of module, L (m)	Porosity	Number of fiber	Inner diameter of fiber, d_i (mm)	Thickness of membrane, d_m (mm)
N1	0.20	62%	20	0.9	0.3
N2	0.20	62%	22	0.9	0.5
N3	0.20	62%	20	0.9	0.6
N4	0.20	62%	22	0.6	0.5
N5	0.20	62%	20	0.4	0.5
N6	0.20	21%	23	0.9	0.3

Author's personal copy

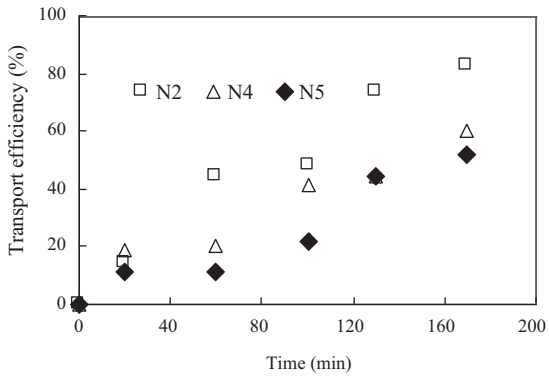

Fig. 14. Effect of inner diameter of fiber.

The inner diameter of fiber could have an effect on the liquid flowing state in membrane module system and transport efficiency of Dy^{3+}. The membrane modules N2, N4 and N5 were chosen to study the effect of inner diameter of fiber on transport of Dy^{3+} under the optimal transport conditions. The results are shown in Fig. 14. We can draw the conclusion that the larger inner diameter of fiber, the higher transport efficiency of Dy^{3+}. The main reason might be that the larger the inner diameter of fiber is, the more dispersion solution the membrane module system have. So more dispersion solution can make the stripping and complexing reaction more efficient.

The membrane porosity could play an important role in transport rate of Dy^{3+} complex. The membrane modules N1 and N6 were chosen to study the effect of membrane porosity on transport of Dy^{3+} under the optimal transport conditions. The results are shown in Fig. 15. We can draw the conclusion that the larger membrane porosity, the higher transport efficiency of Dy^{3+}. The main reason might be that the larger membrane porosity, the larger effective mass transport area of membrane.

4. Kinetic analysis

Based on the data of effect of pH in the feed phase, the relationship is developed between $1/P_C$ and $[H^+]^3$ (Eq. (14)). When concentration of carrier is definite, Fig. 16 can be obtained.

It indicates that the relationship between $1/P_C$ and $[H^+]^3$ is linear. The value of R^2 is 0.973, which is in good agreement with the theory from Eq. (14). The slope and intercept of the line are 1.61×10^{18} s/(m^2 mol) and 9.308×10^5 s/m. The thickness of diffusion layer d_f, which is obtained by diffusion coefficient of Dy^{3+} in the aqueous solution (5.0×10^{-10} m^2/s) determined using certain

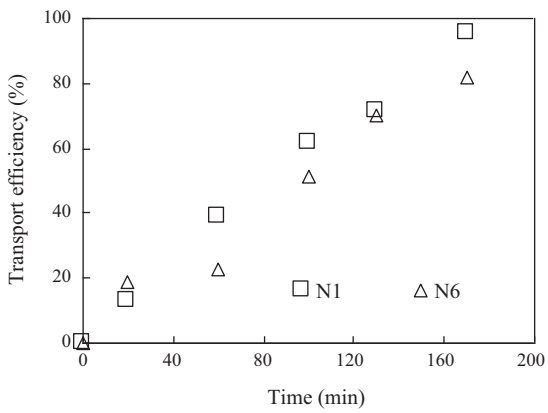

Fig. 15. Effect of membrane porosity.

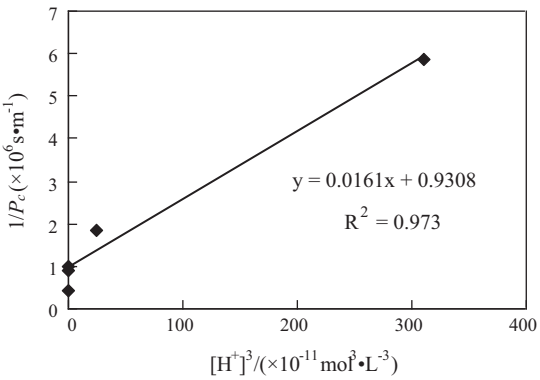

Fig. 16. Comparison between experimental and theoretical (I).

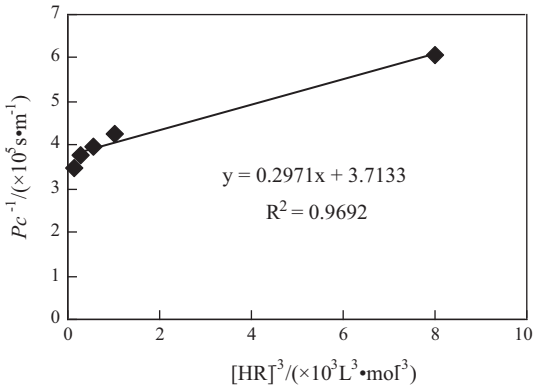

Fig. 17. Comparison between experimental and theoretical (II).

methods [22,23], is equal to $\Delta_f D_f = 4.65 \times 10^{-6}$ m = 4.65 μm. Then the diffusion coefficient D_m^0 in the membrane, obtained by Eqs. (13) and (14), is that $D_m^0 = d_m/\Delta_m = 3.56 \times 10^{-7}$ m^2/s.

The new kinetic equation is determined by using d_f and D_m^0 in the SDHFLM system. It can be written as

$$P_c = \frac{1}{9.308 \times 10^5 + 1.61 \times 10^{18}[H^+]^3} \tag{20}$$

And when H^+ concentration in the feed phase is determined, the effect of concentration of carrier on $1/P_C$ is studied. The results are shown in Fig. 17. It indicates that the relationship between $1/P_C$ and $[HR]^{-3}$ is linear. The value of R_2 is 0.9692, in good agreement with the Eq. (14). In the same way, another kinetic equation can be developed as below:

$$P_c = \frac{1}{3.713 \times 10^6 + 2.97 \times 10^4[HR]^{-3}} \tag{21}$$

5. Conclusions

It has been found that Dy^{3+} can be selectively transported from HCl media using a SDHFLM system with PC-88A over the rare earth metals. We can draw the following conclusions: Optimum transport conditions of Dy^{3+} in the SDHFLM system were that the concentration of HCl solution was 4.00 mol/L, volume ratio of membrane solution to stripping solution (O/W) was 0.50, the concentration of PC-88A was 0.150 mol/L in the dispersion phase, pH value was 5.00 in the feed phase. When initial concentration of Dy^{3+} was 1.50×10^{-4} mol/L, the transport effect of Dy^{3+} was very obvious in the optimum condition and the transport efficiency of Dy^{3+} was up to 95.4% during the transport time of 170 min.

The stability of SDHFLM was better than traditional HFLM. The flow rate of solution in shell side had not obvious effect on the trans-

Author's personal copy

port efficiency of Dy^{3+} and the flow rate of feed solution in tube side had a few effects on the transport efficiency of Dy^{3+}. Membrane solution in SDHFLM can be reused less than 4 times before the re-extraction with the strong acid after every experiment. Membrane module of SDHFLM with dispersion phase can be reused many times and the tendency of transport efficiency changes was stable with SDHFLM in 8 experiments. The retention percentage of Dy^{3+} in membrane decreased gradually as time extended.

The transport efficiency of Dy^{3+} increased, when thickness of membrane decreased, inner diameter of fiber increased and membrane porosity increased, respectively.

Based on the surface renewal theory, a mathematical model for the SDHFLM system was developed. The calculated overall permeability coefficients were in good agreement with experimental results and the literature data.

Acknowledgements

The authors are grateful for financial support of the National Natural Science Foundation of China for Young Scientists (41001131 and 51009126), the Action Plan for the Development of Western China of the Chinese Academy of Sciences (KZCX2-XB2-13), the Knowledge Innovation Program of the Chinese Academy of Sciences (KSCX2-YW-N-003) and Research Fund for Excellent Doctoral Thesis of Xi'an University of Technology (602-210805 and 602-210804).

Nomenclature

A	effective area of membrane (m^2)
c_f	concentration of metal ion in the feed phase (mol/L)
c_{fi}	concentration of metal ion in the diffusion layer in feed phase (mol/L)
c^0_{mf}	concentration of metal ion in the membrane near feed phase(mol/L)
c^0_{ms}	concentration of metal ion in the membrane near dispersion phase(mol/L)
$c_{f(0)}$	concentration of metal ion in the feed phase when time = 0 (mol/L)
$c_{f(t)}$	concentration of metal ion in the feed phase when time = t (mol/L)
d_f	thickness of diffusion layer between the feed phase and membrane phase (m)
d_i	inner diameter of fiber (mm)
d_m	thickness of the membrane (m)
D_f	diffusion coefficient of metal ion in the feed phase (m^2/s)
D^0_m	diffusion coefficient of metal ion in the membrane (m^2/s)
[HR]	concentration of carrier PC-88A (mol/L)
$(HR)_2$	extractant/carrier PC-88A
$[H^+]$	concentration of H^+ (mol/L)
J	membrane flux ($mol\,m^{-2}\,s^{-1}$)
K_1	forward reaction percentage constant at the left interface of the membrane
K_{-1}	backward reaction percentage constant at the left interface of the membrane
K_2	forward reaction percentage constant at the right interface of the membrane
K_{-2}	backward reaction percentage constant at the right interface of the membrane
K_{ex}	extraction equilibrium constant
K_d	distribution ratio of metal ion
L	effective length of module (m)
P_c	permeability coefficient of metal ion (m/s)
$DyR_3 \cdot 3HR$	dysprosium -carrier complex
V_f	volume of the feed phase (m^3)

Greek letter

ε	porosity of the membrane
τ	tortuosity of the membrane
η	transport efficiency of Dy^{3+} (%)
Δ_f	transport resistance due to diffusion by aqueous feed boundary layer (s/m)
Δ_m	transport resistance due to diffusion through the membrane (s/m)

Subscripts

f	feed phase
m	membrane phase
org	organic phase
s	dispersion phase

References

[1] J. Yu, S.T. Yao, S.J. Chi, Rare earth separation techniques in the development, J. Shenyang Univ. Technol. 21 (1999) 83–85.
[2] L. Pei, B.H. Yao, X.L. Fu, L.M. Wang, Transport and separation of Cerium(IV)in dispersion supported liquid membrane system, Chin. J. Proc. Eng. 8 (2008) 851–858.
[3] R.H. Zhang, D.X. Jiang, The extraction of rare earths from aqueous solution with emulsion liquid membrane, Membr. Sci. Technol. 5 (1985) 70–75.
[4] K. Konda, Mechanisms of samarium extraction with diisostearyphosphoric acid and its permeation through supported liquid membrane, J. Chem. Eng. Jpn. 28 (1995) 511–516.
[5] C.J. Lee, Extraction of trivalent europium via a supported liquid membrane containing PC-88A as a mobile carrier, Chem. Eng. J. 57 (1995) 253–260.
[6] J.K. Kim, J.S. Kim, Y.G. Shul, K.W. Lee, W.Z. Oh, Selective extraction of cesium ion with calyx[4]arene crown ether through thin sheet supported liquid membranes, J. Membr. Sci. 187 (2001) 3–11.
[7] T. Yi, C.H. Yan, D. Li, The flat extraction system of sandwich supported liquid membrane of transport of La^{3+}, J. Chin. Rare Earth Soc. 9 (1995) 197–200.
[8] D.S. He, M. Ma, H. Wang, Effect of kinetic synergist on transport of copper(II) through a liquid membrane containing P507 in kerosene, Can. J. Chem. 79 (2001) 1213–1219.
[9] S.X. Gu, Y.D. Yu, D.S. He, M. Ma, 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, Sep. Purif. Technol. 51 (2006) 277–284.
[10] D.S. He, S.X. Gu, M. Ma, Simultaneous removal and recovery of cadmium(II) and CN^- from simulated electroplating rinse wastewater by a strip dispersion hybrid liquid membrane (SDHLM) containing double carrier, J. Membr. Sci. 305 (2007) 36–47.
[11] L. Pei, B.H. Yao, C.J. Zhang, Transport of Tm(III) through dispersion supported liquid membrane containing PC-88A in kerosene as the carrier, Sep. Purif. Technol. 65 (2009) 220–227.
[12] L. Pei, B.H. Yao, X.L. Fu, Study on transport of Dy(III) by dispersion supported liquid membrane, J. Rare Earths 27 (2009) 447–456.
[13] L. Pei, B.H. Yao, L.M. Wang, N. Zhao, M. Liu, Transport of Tb^{3+} in dispersion supported liquid membrane system with carrier P507, Chin. J. Chem. 28 (2010) 839–846.
[14] J.V. Sonawane, A.K. Pabby, A.M. Sastre, Au(I) extraction by LIX-79/n-heptane using the pseudo-emulsion-based hollow-fiber strip dispersion (PEHFSD) technique, J. Membr. Sci. 300 (2007) 147–155.
[15] R.S. Juang, H.L. Huang, Mechanistic analysis of solvent extraction of heavy metals in membrane contactors, J. Membr. Sci. 213 (2003) 125–135.
[16] M.R. Yaftian, M. Burgard, C.B. Dieleman, D. Matt, Rare-earth metal-ion separation using a supported liquid membrane mediated by a narrow rim phosphorylated calix(IV) arene, J. Membr. Sci. 144 (1998) 57–64.
[17] A. Jyothi, G.N. Rao, Solvent extraction behaviour of lanthanum(III), cerium(III), europium(III), thorium(IV) and uranium(VI) with 3-phenyl-4-benzoyl-5-isoxazolone, Talanta 37 (1990) 431–433.
[18] M.I Kandah, J.L. Meunier, Removal of nickel ions from water by multi-walled carbon nanotubes, J. Hazard. Mater. 146 (2007) 283–288.
[19] Z.Q. Ren, W.D. Zhang, Y.M. Liu, Y.A. Dai, C.H. Cui, New liquid membrane technology for simultaneous extraction and stripping of copper(II) from wastewater, Chem. Eng. Sci. 62 (2007) 6090–6101.

Author's personal copy

[20] A.B. De Haan, P.V. Bartels, J. de Graauw, Extraction of metals from wastewater: modelling of mass transfer in a supported liquid membrane process, J. Membr. Sci. 45 (1989) 281–297.
[21] S.Y. Hu, J.M. Wieneek, Emulsion liquid membrane extraction of copper using a hollow fiber contactor, AIChE J. 44 (1998) 570–581.
[22] R. Chiarizia, A. Castagnola, P.R. Danesi, E.P. Horwitz, Mass transfer rate through solid supported liquid membranes: influence of carrier dimerization and feed metal concentration on membrane permeability, J. Membr. Sci. 14 (1983) 1–11.
[23] M.Z. Su, S.L. Du, D.X. Tang, Diffusion coefficient of Dy in Liquid Al, J. Chin. Rare Earth Soc. 6 (2) (1988) 81–83.