

La(III) Transport in Dispersion Supported Liquid Membrane Including PC-88A as the Carrier and HCl Solution as the Stripping Solution

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Abstract: The transport of La(III) through a dispersion supported liquid membrane with polyvinylidene fluoride membrane as the liquid membrane support and dispersion solution including HCl solution as the stripping solution and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) in kerosene as the membrane solution, was studied. As a result, the optimum transport conditions of La(III) were obtained as that concentration of HCl solution was 4.0 mol/L, concentration of PC-88A 0.16 mol/L, and volume ratio of membrane to stripping solution 30:30 in the dispersion phase, and pH value 4.0 in the feed phase. Ionic strength had no obvious effect on the transport of La(III). Under the optimum conditions, when initial concentration of La(III) was 0.8×10^{-4} mol/L, the transport rate was up to 96.3% during the transport time of 125 min. The kinetic equation was developed based on the law of mass diffusion and theory of interface chemistry. The diffusion coefficient of La(III) in the membrane and the thickness of diffusion layer between feed and membrane phases were obtained as 3.20×10^{-7} m²/s and 3.22×10^{-5} m, respectively. The calculated results were in good agreement with experimental results.

Key words: liquid separation; dispersion supported liquid membrane; 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester; lanthanum(III)

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1 INTRODUCTION

Industrial effluents containing highly toxic and non-biodegradable heavy metal ions are produced in hydrometallurgy, electroplating, and electrochemical industry. For the purpose of environmental protection and resources recycling, the removal and recovery of these heavy metals have been become increasingly necessary^[1-3]. Recently, people paid attention to rare earth metals which are widely applied in industrial productions and human life. It is also necessary to develop a method for the separation and recovery of rare earth metals. Several conventional methods, such as chemical precipitation^[1,2], reverse osmosis^[4], adsorption^[5], ion exchange^[6], and solvent extraction^[7,8] have been developed for these purposes, but various difficulties are encountered^[1-3]. More efficient and low-cost removal and recovery methods are needed to overcome these difficulties.

Recently, many attentions were been attracted to liquid membrane (LM) techniques due to their specific characteristics. LMs technology can carry out extraction and stripping processes simultaneously, and have benefits of non-equilibrium mass transfer and up-hill effect, where solute can be moved from low-to-high

concentration solution^[9-12]. The main types of liquid membrane systems include electrostatic pseudo liquid membrane (EPLM)^[10], emulsion liquid membrane (ELM)^[13], supported liquid membrane (SLM)^[14], bulk liquid membrane (BLM), flowing liquid membrane (FLM)^[15], supported emulsion liquid membrane (SELM)^[16,17], hollow fiber contained liquid membrane (HFCLM)^[18], and supported liquid membrane with stripping dispersion (SLMSD)^[19,20]. The potential advantages of LM techniques over traditional separation techniques and solid membrane techniques are lower capital and operational costs, lower energy and extractant consumption, and higher concentration factors and fluxes. However, LM techniques have not been adopted to large-scale industrial processes yet^[9,11,12,21-27], primarily due to the lack of longtime stability, difficulty in operation of the emulsification and de-emulsification steps in ELM and SELM processes, and membrane resistance in BLM and HFCLM processes, etc.^[28]

In order to overcome the above difficulties in conventional LM systems, a new liquid membrane technique, named as combined supported liquid membrane^[29], was proposed in this study, which was called as dispersion supported liquid membrane

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(DSLMS). The DSLM technique is based upon surface renewal and diffusion theory. In our previous work, the advantages of fiber membrane extraction process, liquid film permeation process and most of other liquid membrane systems were integrated. This is a new liquid membrane process with several advantages: increased stability of the membrane, reduced cost, increased simplicity of operation, extremely efficient stripping of the metal ions from the organic phase to obtain high flux and high concentration of the metal ions in the stripping solution.

These advantages are very attractive, nevertheless, more studies are needed for the application of DSLM in industry. Otherwise, scaling-up for the new liquid membrane configuration will fail, unless there is a complete understanding of the efficiency related parameters reported in such a way that a concise and global insight into the separation characteristics of a given system can be easily drawn. For example, the behavior of transport of single cation and a new permeability coefficient equation should be studied because the diversity of transport behavior of ions is objectively present in the two systems of traditional SLM and DSLM. Secondly, more work concerning the separation of two or more competitive solutes is required in order to solve more practical separation problems.

This present study is concerned with the technical feasibility of transport of metal ions by DSLM. Although the transport of metal ions by SLM containing the same carrier (PC-88A) was extensively studied, there was little research result about the transport of rare earths by DSLM. The transport of La(III) in DSLM consisting of polyvinylidene fluoride membrane (PVDF) as the support and dispersion solution including HCl solution as the stripping solution and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) in kerosene as the membrane solution was studied. The effects of pH value, initial concentration of La(III) and ionic strength in the feed phase, volume ratio of membrane to stripping solution, concentration of HCl solution, concentration of PC-88A, and different stripping agents in the dispersion phase on the transport of La(III) were also investigated, respectively. A kinetic equation for DSLM process derived from the law of mass diffusion and the theory of interface chemistry was developed.

2 EXPERIMENTAL

2.1 Reagents

All the reagents, such as LaCl_3 , Arsenazo III

($\text{C}_{22}\text{H}_{18}\text{As}_2\text{O}_{14}\text{N}_4\text{S}_2$), HCl, NaH_2PO_4 , Na_2HPO_4 , CH_3COONa and CH_3COOH , used in the present work are of analytical grade. 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) was a commercial extractant (purity>95%) and used without any further purification. Kerosene was washed with concentrated sulfuric acid and distilled at 185~225 °C.

2.2 Preparation of Solutions

La(III) stock solution. A stock solution of La(III) was prepared by dissolving LaCl_3 in 1 mol/L HCl solution, and analyzed by Arsenazo III ($\text{C}_{22}\text{H}_{18}\text{As}_2\text{O}_{14}\text{N}_4\text{S}_2$) as the chromogenic agent.

La(III) feed solution. A known amount of the La(III) stock solution was diluted with 0.01 mol/L HCl solution to a given extent after adding calculated amounts of CH_3COONa and CH_3COOH or NaH_2PO_4 and Na_2HPO_4 .

Arsenazo III ($\text{C}_{22}\text{H}_{18}\text{As}_2\text{O}_{14}\text{N}_4\text{S}_2$) stock solution. A stock solution of Arsenazo III was prepared by dissolving powder of Arsenazo III in deionized water.

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

Distilled kerosene. Commercial kerosene was washed with concentrated sulfuric acid solution and distilled at 185~225 °C.

PC-88A solution. A calculated amount of PC-88A was dissolved in kerosene.

2.3 Experimental Procedure

The measurement of transport rate of La(III) in DSLM was performed as follows: the experiments were carried out at $(25\pm 1)^\circ\text{C}$ with a simple diffusion cell. Fig.1 shows the experimental installation of DSLM process. The setup consisted of two-compartment perspex half-cells. Two half-cells were separated by the membrane. The membrane was impregnated with PC-88A dissolved in kerosene and clamped between the two half-cells. The effective volume of each one was 80 mL. A microporous PVDF membrane was used as a solid support. It had a 65 μm thick film with a nominal porosity of 75% and a tortuosity of 1.67. The effective area of the membrane is 12 cm^2 . The feed phase (60 mL) consisted of La(III) and buffer solution, and was poured into the perspex half-cell. The mixed dispersion phase consisting of different volume ratios of the membrane solution containing the carrier PC-88A and HCl stripping solution was placed into another half-cell. The stability of the SLM was ensured by a modified SLM with stripping dispersion, where the aqueous stripping solution was dispersed in the organic membrane solution in a mixer. The stripping dispersion formed

was calculated from the mixer to the membrane module to provide a constant supply of the organic solution to the membrane pores. Samples of the feed phase were taken in timed intervals. The stirring of dispersion phase was allowed to stand until phase transport occurred. Then the La(III) sample from the dispersion phase was collected. Samples containing La(III) in the feed phase were only analyzed for ion concentration with a UV-1200 spectrophotometer using Arsenazo III as the chromogenic agent ($\lambda_{\max}=653$ nm).

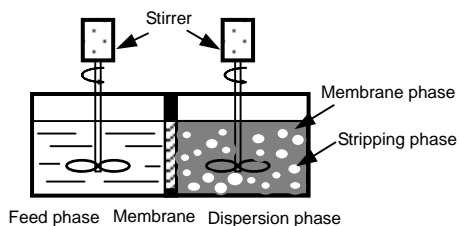


Fig.1 Experimental installation of DSLM process

2.4 Principle and Theoretical Analysis

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

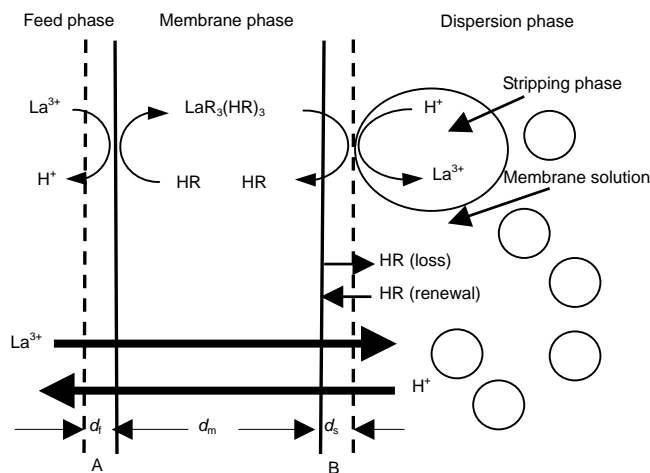
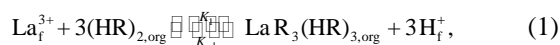


Fig.2 The principle of DSLM process

(1) La(III) diffuses from the feed phase to the interface A.

(2) On the feed side interface of the membrane, the extraction of La(III) from feed solution with carrier PC-88A (denoted as HR) in kerosene can be expressed as^[30,31],



where subscripts org and f stand for organic phase and feed solution, respectively, $(\text{HR})_2$ denotes that the PC-88A in kerosene mainly exists as a dimer, K_1 and

K_{-1} stand for forward and backward reaction rate constants at the interface between feed and membrane phases.

(3) The complex $[\text{LaR}_3(\text{HR})_3]$ diffuses through the membrane.

(4) At the stripping side interface of the DSLM, $\text{LaR}_3(\text{HR})_3$ dissolved in membrane solution and the metal ion La(III) are stripped by stripping agent.

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



where subscript s represents the stripping phase, and K_2 and K_{-2} stand for forward and backward reaction rate constants at the interface between the membrane and stripping phases.

(5) PC-88A returns to the interface A.

In this mechanism the transport of La(III) through a DSLM is described by considering only diffusion process of La(III), because the complex reaction between La(III) and PC-88A at the interface is much faster compared with the diffusion in the feed phase and membrane phase^[32-34]. Then in this model, the transport of La(III) in the DSLM 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 is given as follows^[28,35].

The flux of feed phase can be written as:

$$J_f = \frac{D_f}{d_f} (C_f - C_{fi}), \quad (3)$$

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 La(III) in the membrane and thickness of diffusion layer between feed and membrane phases, the concentration of La(III) in the feed phase, and the concentration of La(III) in the diffusion layer between the feed and membrane phases, respectively.

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

$$K_{\text{ex}} = \frac{[\text{H}^+]^3 C_{\text{mf}}^0}{C_{\text{fi}} [(\text{HR})_2]^3} = \frac{K_d [\text{H}^+]^3}{[(\text{HR})_2]^3}, \quad (4)$$

where K_d reflects the distribution ratio of La(III).

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

$$J_{\text{mf}} = K_1 C_{\text{fi}} - K_{-1} C_{\text{mf}}^0, \quad (5)$$

where J_{mf} and C_{mf}^0 denote the transport flux and concentration of La(III) in the diffusion layer between the feed and membrane phases.

$$J_m = \frac{D_m^0}{d_m} (C_{mf}^0 - C_{ms}^0), \quad (6)$$

where J_m , C_{ms}^0 , D_m^0 and d_m stand for the transport flux in the membrane, the concentration of La(III) in the diffusion layer between the dispersion and membrane phases, diffusion coefficient of La(III) in the membrane, and thickness of the membrane, respectively.

In view of different materials of membrane with distinct characters, such as tortuosity and porosity of membrane, they have 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:

$$J_m = \frac{D_m^0 \varepsilon}{d_m \tau} (C_{mf}^0 - C_{ms}^0), \quad (7)$$

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

In a homeostatic reaction system in ideal condition, these above individual transport fluxes can be taken for equality^[36-39]:

$$J_f = J_m = J_{mf} = J_s, \quad (8)$$

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

Combining Eqs.(3)~(8), the following formula can be obtained:

$$J = \frac{1}{\frac{d_f}{D_f} + \frac{d_m \tau [H^+]^3}{D_m^0 \varepsilon K_{ex} [(HR)_2]^3}} C_f. \quad (9)$$

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

$$J = P_c C_f = -\frac{V_f}{A} \frac{dC_f}{dt}, \quad (10)$$

where V_f stands for the volume of feed phase, A the effective area of membrane, and P_c the permeability coefficient, which can be defined as:

$$P_c = \frac{1}{\frac{d_f}{D_f} + \frac{d_m \tau [H^+]^3}{D_m^0 \varepsilon K_{ex} [(HR)_2]^3}}. \quad (11)$$

The d_f/D_f and d_m/D_m^0 are defined as follows:

$$\Delta_f = d_f/D_f, \quad (12)$$

$$\Delta_m = d_m/D_m^0. \quad (13)$$

Thus, Eq.(11) can be simplified as:

$$P_c^{-1} = \frac{\Delta_m \tau [H^+]^3}{\varepsilon K_{ex} [(HR)_2]^3} + \Delta_f. \quad (14)$$

In Eq.(14), ε , τ , and K_{ex} are all constants. From the result of extraction experiments, K_{ex} at 2.2×10^{-10} is obtained. The relationship between P_c^{-1} and $[H^+]^3$ is examined to be linear at a certain concentration of PC-88A. So the diffusion coefficient of La(III) in the membrane and the thickness of diffusion layer between feed and membrane phases can be obtained by a linear slope method. In the same way, the relationship between P_c^{-1} and $[(HR)_2]^{-3}$ are examined to be linear at a certain H^+ concentration in the feed phase. Then, Δ_f , Δ_m can be obtained. Combined with Eqs.(12) and (13), D_m^0 and D_f can also be obtained.

The following equation can be obtained by integrating Eq.(10):

$$\ln \frac{C_t}{C_0} = -\frac{A}{V_f} P_c t, \quad (15)$$

where C_0 and C_t stand for the concentrations of La(III) in the feed phase at $t=0$ and $t=t$, respectively. Eq.(15) implies that the value of AP_c/V_f is the slope of linear relationship between $\ln C_t/C_0$ and t , which can be obtained under different conditions.

3 RESULTS AND DISCUSSION

3.1 Effect of Volume Ratio of Membrane Solution to Stripping Solution

The effect of volume ratio of membrane solution to stripping solution in the dispersion phase on transport of La(III) was studied. The assumed experimental conditions chosen are in the certain pH value in the feed phase, which was adjusted to 3.6, and initial concentration of La(III) was 1.0×10^{-4} mol/L in the feed phase, the concentration of HCl solution 4.0 mol/L and

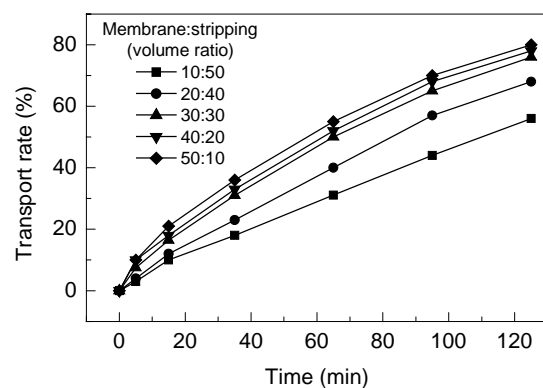


Fig.3 Effect of volume ratio of membrane solution to stripping solution on transport rate of La(III)

the concentration of PC-88A 0.16 mol/L in the dispersion phase. The volume ratio was increased from 10:50 to 50:10. It can be seen from Fig.3 that the most effective volume ratio is 50:10, which gives a transport rate of La(III) much higher than that at 10:50, but a little higher than those at 40:20 and 30:30.

When the volume ratios are 50:10, 40:20 and 30:30 respectively, the corresponding transport rates of La(III) are above 78.7%, 77.4% and 76.1% respectively. These transport rates are near, but under the volume ratios of 20:40 and 10:50, the transport rates are lower. It is indicated that the transport rate of La(III) increases with increasing of the volume ratio in the dispersion phase. When the volume ratio increases, the droplets of dispersion solution are dispersed obviously in the membrane phase, and the contacting chances between PC-88A and La(III) increase. In this way, the mixing between the membrane and dispersion phases provides an extra stripping surface and renewal rate of liquid membrane, which leads to extreme stripping rate for the target species from organic phase and life of liquid membrane. Therefore the transport rate of La(III) is enhanced. Therefore, the volume ratio of 30:30 as the optimum volume ratio of membrane solution to stripping solution in the dispersion phase can be chosen in the following experiments.

3.2 Effect of Concentration of HCl Solution in the Dispersion Phase

The stripping reaction in the dispersion phase plays a vital role in transport of metal ion from the feed phase to the stripping phase. So the effect of concentration of HCl solution in the dispersion phase on the transport rate of La(III) was studied in this section. The other parameters, such as pH value, initial concentration of La(III) in the feed phase, volume ratio and concentration of PC-88A, were adjusted to 3.6, 1.0×10^{-4} mol/L, 30:30 and 0.16 mol/L, respectively. The effect of concentration of HCl solution in the dispersion phase on the transport rate of La(III) is shown in Fig.4.

It can be seen from Fig.4 that with increasing of HCl concentration in the dispersion phase, the transport rate of La(III) increases. The effective concentrations of HCl solution for the transport are 6.0, 5.0 and 4.0 mol/L, leading to the transport rates of La(III) at about 74.8%, 77.8% and 76.1%, respectively. The increase of concentration of HCl solution from 2.0 to 3.0 mol/L has no significant effect on the transport rate of La(III), and it is less than 60%, because the number of La(III) complex and the concentration of membrane solution which transport through the membrane per unit area of

the membrane per unit time are definite. However, under the condition of 6.0 mol/L HCl solution, the transport rate is a little lower than 5.0 and 4.0 mol/L, due to higher acidity resulting in receding of complexation ability of PC-88A. Thus, the concentration of HCl solution at 4.0 mol/L as the optimum concentration of HCl solution in the dispersion phase can be chosen in the following experiments.

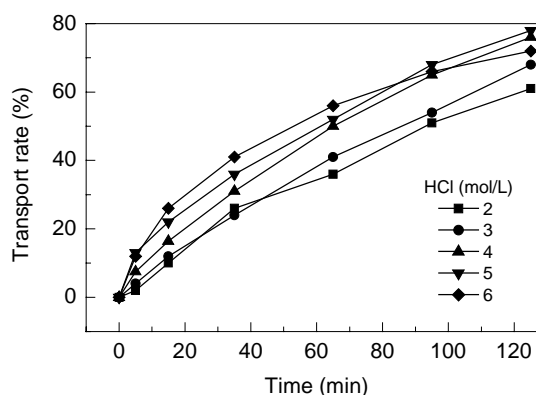


Fig.4 Effect of concentration of HCl solution on transport rate of La(III)

3.3 Effect of pH in the Feed Phase

Based on the mechanism of mass transfer process, the H^+ concentration difference between feed and dispersion phases is the driving power of mass transfer. So in the feed phase the lower the H^+ concentration is, the stronger the driving power of mass transfer will be. Stronger power will promote the transport rate of La(III). Furthermore, the greater the pH value in the feed phase is, the higher the transport rate of La(III) is. The effect of pH in the feed phase on the transport of La(III) was studied in the pH range from 3.0 to 4.3, which was adjusted with an HAc–NaAc buffer solution at different pH values under the above conditions. The results are shown in Fig.5.

As shown in Fig.5, the transport rate of La(III) increases when the pH value in the feed phase increases from 3.0 to 4.3, and a maximum transport rate observed at pH 4.0 is 81.2% for 125 min. Above the pH value of 4.3 in the feed phase, the transport rate of La(III) does not change. When the pH value is higher than 4.3, hydroxy complex of La(III) forms in the feed phase, and the transport rate of La(III) decreases. In contrast to the previous cases, Yaftian et al.^[40] suggested that the pH value influenced the distribution coefficient of extraction process. It is largely because the transport process is mainly governed by the driving power of mass transfer caused by the distribution equilibrium, when the renewal effect of liquid membrane and the

diffusion mobility of La(III) ions are determined under specific experimental conditions^[41,42]. As far as our research conditions are concerned, for the sakes of saving chemical agents and increasing transport rate, the pH value at 4.0 is chosen as the optimum pH condition in the feed phase in the following experiments.

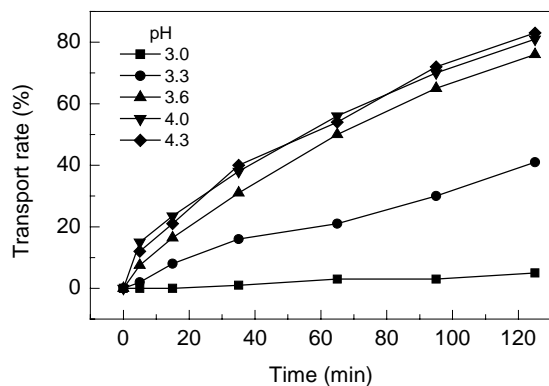


Fig.5 Effect of pH in the feed phase on transport rate of La(III)

3.4 Effect of Initial Concentration of La(III) in the Feed Phase

Under the above conditions, the effect of initial concentration of La(III) on the transport rate of La(III) was studied in the range from 0.5×10^{-4} to 2.0×10^{-4} mol/L. The obtained results are shown in Fig.6. With increasing of initial concentration of La(III) in the feed phase from 0.5×10^{-4} to 2.0×10^{-4} mol/L, the transport rate of La(III) decreases. This is because the number of PC-88A is definite on the membrane when the interface between the feed and membrane phases is determinate. That is to say, the number of La(III) transported is definite in transport process under the certain condition. When initial concentration of La(III) is 0.8×10^{-4} mol/L, the transport effect of La(III) is very obvious and the transport rate of La(III) up to 96.3% for 125 min. When the La(III) concentration is 1.5×10^{-4} and 2.0×10^{-4} mol/L,

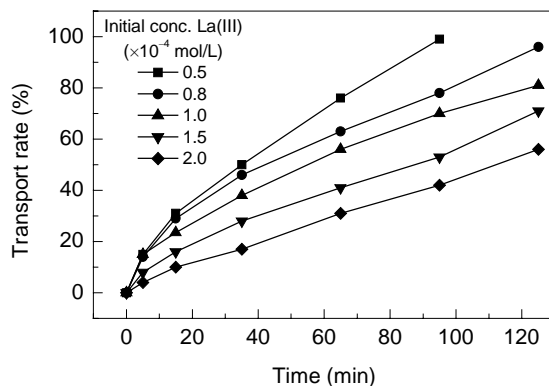


Fig.6 Effect of initial concentrations of La(III) on transport rate of La(III)

the transport rate up to 72% and 56% in 125 min, respectively. Furthermore, the transport rate is up to 99.2% in 95 min, when the initial concentration of La(III) is adjusted to 0.5×10^{-4} mol/L, and after 95 min La(III) is hardly determined.

3.5 Effect of Different Stripping Agents on Transport of La(III)

The stripping agent in the dispersion phase plays a vital role in transport of metal ions from the feed phase to stripping phase. So the effects of different stripping agents in the dispersion phase on the transport of La(III) were studied. All the other parameters, such as pH value, initial concentration of La(III) in the feed phase, volume ratio of membrane solution to stripping solution and concentration of PC-88A in the dispersion phase were adjusted to 4.0, 0.8×10^{-4} mol/L, 30:30 and 0.16 mol/L respectively. The effects of different stripping agents in the dispersion phase on the transport rate of La(III) are shown in Fig.7. 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 can be seen that hydrochloric acid is the most efficient stripping agent in this case. Choosing hydrochloric acid as the stripping agent, the transport rate of La(III) can be more efficient, so hydrochloric acid can be used as the optimum stripping agent in the following experiments.

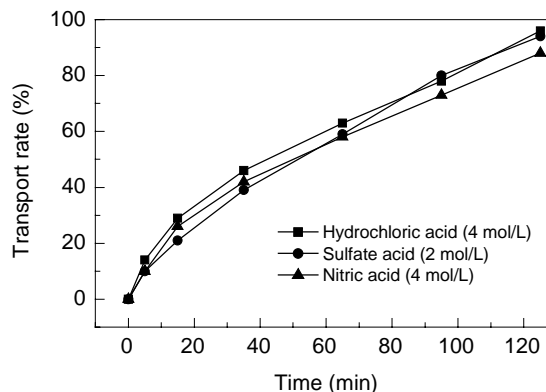


Fig.7 Effect of different stripping agents on transport of La(III)

3.6 Effect of Concentration of PC-88A on Transport of La(III)

Concentration of PC-88A in the membrane phase and dispersion phase also plays a significant role in the transport of La(III). The effect of concentration of PC-88A on the transport rate of La(III) was studied in the PC-88A concentration range from 0.036 to 0.23 mol/L. The results are shown in Fig.8. With increasing of concentration of the carrier in the membrane phase from 0.036 to 0.23 mol/L, the transport rate of La(III)

increases. When the concentration of PC-88A increases to 0.23 from 0.10 mol/L, however, the increase of transport rate of La(III) is not obvious. Within the concentration range of PC-88A from 0.036 mol/L to 0.23 mol/L in the dispersion phase, the availability of PC-88A at the feed-membrane-dispersion interfaces increased with increasing of concentration of the carrier. The chemical equilibrium moved towards left vice versa, when concentration of PC-88A became low, the equilibrium moved towards the right. The transport rate of La(III) no longer increased with time with increasing of concentration of PC-88A to a significant extent. When the concentration of PC-88A was 0.16 and 0.23 mol/L, the transport rate was 96.3% and 96.8% respectively.

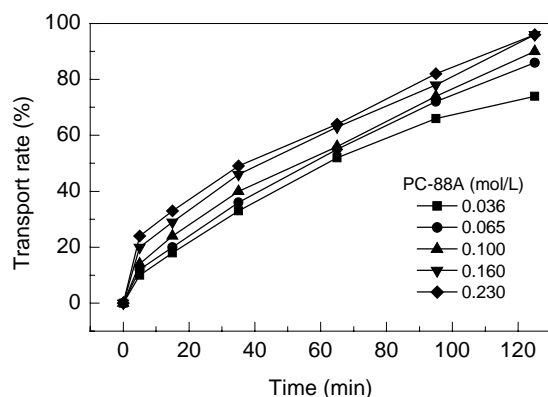


Fig.8 Effect of concentration of PC-88A on transport of La(III)

The concentration of PC-88A is proportionate with La(III) concentration in the membrane phase. When the concentration of PC-88A in the membrane phase becomes higher in comparison with La(III) concentration in the feed phase, there is not La(III) to react on redundant PC-88A, so the increase of transport rate of La(III) will become slow. This indicates that the number of PC-88A used to assist the transport of La(III) through the membrane per unit area of the membrane per unit time is definite, when the initial concentration of La(III) is given, the effective area of membrane and time are definite. For the sakes of saving membrane solution and reagent as well as increasing transport rate, 0.16 mol/L was chosen as the optimum concentration of carrier in this study.

3.7 Effect of Ionic Strength in the Feed Phase

Under the optimum condition, the effect of ionic strength in the feed phase on the transport rate of La(III) was studied. The experimental results are shown in Fig.9. It is indicated that the ionic strength has no influence on the transport rate of La(III).

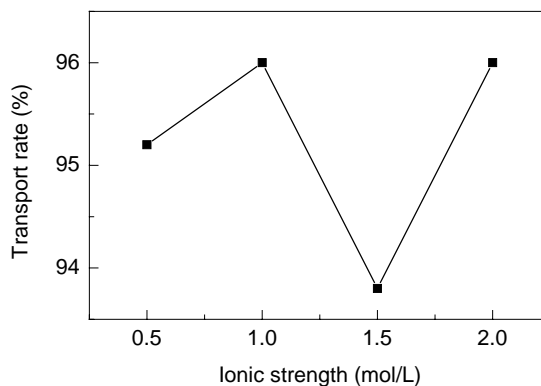


Fig.9 Effect of ionic strengths on transport of La(III)

4 KINETIC ANALYSIS

Based on the data of effect of pH value in the feed phase and the relationship between P_c^{-1} and $[H^+]^3$ [Eq.(14)] developed, when the concentration of carrier is definite, Fig.10 can be obtained. It can be seen that the relationship between P_c^{-1} and $[H^+]^3$ is examined to be linear. The correlated coefficient value of R^2 is 0.9980, showing good agreement with the theory from Eq.(14). The slope and intercept of the line are $5.03 \times 10^{14} \text{ s} \cdot \text{L}^4 / (\text{m} \cdot \text{mol}^4)$ and $6.18 \times 10^4 \text{ s/m}$. The thickness of diffusion layer d_f which is obtained by diffusion coefficient of La(III) in the aqueous solution ($5.2 \times 10^{-10} \text{ m}^2/\text{s}$) determined using certain methods^[43] is that $d_f = \Delta_r D_f = 3.22 \times 10^{-5} \text{ m}$. Then the diffusion coefficient D_m^0 in the membrane, obtained by Eqs.(13) and (14), is that $D_m^0 = d_m / \Delta_m = 3.20 \times 10^{-7} \text{ m}^2/\text{s}$.

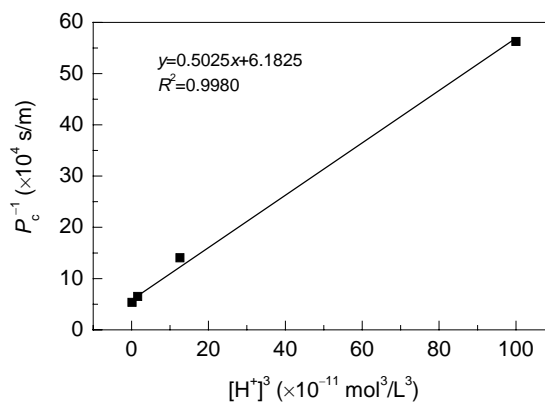


Fig.10 Comparison between experiment and theory (I)

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

$$P_c = \frac{1}{6.18 \times 10^4 + 5.03 \times 10^{14} [H^+]^3} \quad (16)$$

When H^+ concentration in the feed phase was determined, the effect of concentration of carrier on P_c^{-1}

was studied. The results are shown in Fig.11. It is indicated that the relationship between P_c^{-1} and $[(HR)_2]^{-3}$ are examined to be linear. The value of R^2 is 0.9965, which is in good agreement with the Eq.(14). In the same way, another kinetic equation can be developed as follows:

$$P_c = \frac{1}{4.35 \times 10^4 + 1.67[(HR)_2]^{-3}} \quad (17)$$

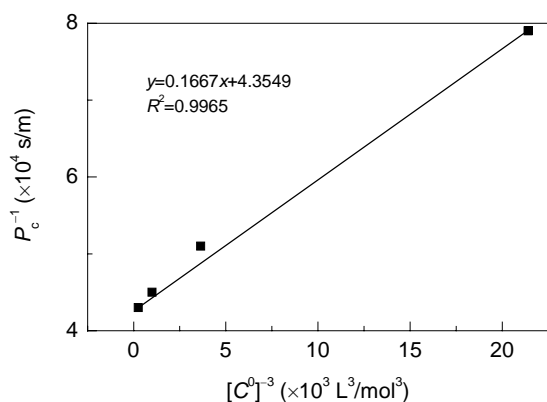


Fig.11 Comparison between experiment and theory (II)

5 CONCLUSIONS

The transport of La(III) through a dispersion supported liquid membrane (DSLMM) was studied. The effects of pH value, initial concentration of La(III) and ionic strength in the feed phase, volume ratio of membrane solution to stripping solution, concentration of HCl solution, concentration of PC-88A, and different stripping agents in the dispersion phase on the transport of La(III) have also been investigated. Some conclusions are drawn as follows:

The optimum transport conditions of La(III) in the DSLMM system are that the concentration of HCl solution was 4.0 mol/L, volume ratio of membrane solution to stripping solution 30:30, concentration of PC-88A in the dispersion phase 0.16 mol/L, and pH value in the feed phase 4.0. When initial concentration of La(III) was 0.8×10^{-4} mol/L, the transport effect of La(III) was very obvious under the optimum conditions and the transport rate up to 96.3% during the transport time of 125 min.

The kinetic equation describing the transport of La(III) in DSLMM was derived as: $P_c = 1/(6.18 \times 10^4 + 5.03 \times 10^{14} [H^+]^3)$, and when the initial concentration of La(III) was changed to 0.8×10^{-4} mol/L from 1.0×10^{-4} mol/L, $P_c = 1/(4.35 \times 10^4 + 1.67[(HR)_2]^{-3})$. These equations were developed and diffusion coefficient in the membrane and thickness of diffusion layer between the feed and membrane phases were obtained by a linear slope

method, which were determined as 3.20×10^{-7} m²/s and 32.2 μm, respectively.

NOMENCLATURE:

A	Effective area of membrane (m ²)
C_f	Concentration of metal ion in the feed phase (mol/L)
$C_{f(0)}$	Concentration of metal ion in the feed phase when $t=0$ (mol/L)
$C_{f(t)}$	Concentration of metal ion in the feed phase when $t=t$ (mol/L)
C_{fi}	Concentration of metal ion in the diffusion layer between the feed and membrane phases (mol/L)
C_{mf}^0, C_{ms}^0	Concentration of metal ion in the membrane (mol/L)
d_f	Thickness of diffusion layer between the feed and membrane phases (m)
d_m	Thickness of the membrane (m)
D_f	Diffusion coefficient of metal ion in the feed phase (m ² /s)
D_m^0	Diffusion coefficient of metal ion in the membrane (m ² /s)
$[H^+]$	Concentration of H ⁺ (mol/L)
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
K_d	Distribution ratio of metal ion
K_{ex}	Extraction equilibrium constant
P_c	Permeability coefficient of metal ion (m/s)
t	Time (min)
V_f	Volume of feed phase (m ³)
Δ_r	Transport resistance due to diffusion by aqueous feed boundary layer (s/m)
Δ_m	Transport resistance due to diffusion through the membrane (s/m)
ε	Porosity of the membrane
τ	Tortuosity of the membrane
Subscripts	
f	Feed phase
m	Membrane phase
org	Organic phase
s	Stripping phase

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