Tb(III) Transport in Dispersion Supported Liquid Membrane System with D2EHPA as Carrier in Kerosene

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Abstract The transport of Tb(III) in dispersion supported liquid membrane(DSLM) with polyvinylidene fluoride membrane(PVDF) as the support and dispersion solution including HCl solution as the stripping solution and Di(2-ethylhexyl) phosphoric acid(D2EHPA) dissolved in kerosene as the membrane solution, has been studied. The effects of pH value, initial concentration of Tb(III) and different ionic strength in the feed phase, volume ratio of membrane solution to stripping solution, concentration of HCl solution, concentration of carrier, different stripping agents in the dispersion phase on the transport of Tb(III) have also been investigated, respectively. As a result, the optimum transport conditions of Tb(III) were obtained, i.e., the concentration of HCl solution was 4.0 mol/L, the concentration of D2EHPA was 0.16 mol/L, and the volume ratio of membrane solution to stripping solution was 30:30 in the dispersion phase, and pH value was 4.5 in the feed phase. Ionic strength had no obvious effect on the transport of Tb(III). Under the optimum conditions, the transport percentage of Tb(III) was up to 96.1% during the transport time of 35 min when the initial concentration of Tb(III) was 1.0× 10⁻⁴ mol/L. The diffusion coefficient of Tb(III) in the membrane and the thickness of diffusion layer between feed phase and membrane phase were obtained and the values were 1.82×10⁻⁸ m²/s and 5.61 μm, respectively. The calculated results were in good agreement with the literature data.

Keywords Dispersion supported liquid membrane; Di(2-ethylhexyl) phosphoric acid; Terbium(III); Dispersion phase; Transport flux; Transport percentage
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1 Introduction

Sewages with nonbiodegradable and highly toxic heavy metal ions are generated in electrochemical, hydrometallurgy, and electroplating industry. By way of environmental resources recycling and conservation, the recovery and removal of these heavy metals have become stringent increasingly[1—3]. Recently, attention has been paid to rare earth metals which are applied in more and more technologies of our production and 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[2,3], reverse osmosis[4], adsorption[5], ion exchange[6], and solvent extraction[7,8] developed for these purposes have encountered various difficulties[1—3]. More efficient and low-cost removal and recovery methods are needed to develop to overcome these difficulties. Actually many liquid membrane(LM) techniques have attracted much attention due to their specific characteristics. LMs can carry out extraction and stripping processes simultaneously, and they show advantages of nonequilibrium mass transfer and up-hill effect, which means solute can move from low-to-high concentration solution[9—12]. The main types of liquid membrane systems include emulsion liquid membrane(ELM)[13], supported liquid membrane(SLM)[14], bulk liquid membrane(BLM), flowing liquid membrane(FLM)[15], electrostatic pseudo liquid membrane(EPLM)[10], supported emulsion liquid membrane(SELM)[16,17], hollow fiber contained liquid membrane(HFCLM)[18], and supported liquid membrane with stripping dispersion(SLM-SD)[19,20], and so on. The potential advantages of LM techniques, over tra-
ditional separation techniques and solid membranes techniques, are low capital and operating costs, low energy and extractant consumption, high concentration factors and high fluxes. However, LM techniques have not been adopted in large-scale industrial processes\cite{9,11,12,21-27}, primarily due to the lack of longtime stability, hard operations of emulsification and de-emulsification in ELM and SELM processes, and larger membrane resistance in BLM and HFCLM processes, and so on\cite{28}.

For the purpose of resolving these difficulties above mentioned in the conventional LM systems, a new liquid membrane technique, named dispersion supported liquid membrane(DSLM)\cite{29,30}, was established. The DSLM technique is based upon surface renewal, diffusion theory, and our previous work, which also integrates the advantages of fiber membrane extraction process, liquid film permeation process and most of other liquid membrane systems. This is a new liquid membrane process with several advantages: the increased stability of the membrane, reduced costs, the increased simplicity of operation, extremely efficient stripping of the target species from the organic phase to obtain high flux and a high concentration of the recovered target species\cite{30}.

Because of these attractive advantages, more studies are needed for the application of DSLM in industry. Otherwise, scaling-up for the new liquid membrane will fail unless there is a complete understanding of the efficiency parameters, reported in such a way that a concise and global insight of the separation characteristics of a given system, can be easily drawn. For example, the transport of single kind of cations 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 problems of separation\cite{30}.

The effects of various experimental parameters on the transport of rare earth Tb(III) ions were investigated. Although the metal ions’ transport by SLM containing the same carrier has been extensively studied, the researches about it by DSLM are still rare. The transport of Tb(III) through a DSLM consisting of polyvinylidene fluoride membrane(PVDF) as the support and dispersion solution including HCl solution as the stripping solution and Di(2-ethylhexyl)phosphoric acid(D2EHPA) dissolved in kerosene as the membrane solution, was studied. The effects of pH value, the initial concentration of Tb(III) and different ionic strengths in the feed phase, the volume ratio of membrane solution to stripping solution, the concentration of HCl solution, the concentration of D2EHPA, and different stripping agents in the dispersion phase on the transport of Tb(III) were also investigated, respectively. A kinetic equation for DSLM process was also developed in terms of the law of mass diffusion and the theory of interface chemistry.

2 Theoretical Analysis

2.1 DSLM Separation Process

PVDF was adopted as the liquid membrane support. The stripping solution comprises an aqueous phase containing a stripping agent in solvent extraction, while the membrane phase contains extractant in a membrane solvent. The transport process by DSLM includes two steps. Firstly, metal ions contained in the feed phase are passed to the one side of SLM embedded in a microporous support material. In this step the extraction takes place at the interface between feed phase and membrane phase. In the meanwhile, the metal is extracted and the metal-carrier complex diffuses to the other side of SLM to remove the metal ions by a dispersion phase. In general, stripping solution is dispersed under stirring into the membrane solution to form the droplets of the aqueous stripping solution in continuous organic phase, which is called dispersion phase. In the experimental process, there is a constant supply of membrane solution, i.e., the membrane solution of dispersion phase enters into the pores of SLM. This constant supply of membrane solution ensures a stable and continuous operation of SLM. Therefore, the direct contact between stripping solution and membrane solution provides efficient mass transfer for stripping. Secondly, once the removal of the target species is completed, the stirring for the stripping dispersion is stopped. The dispersion phase is thus allowed to suspend, resulting in separating dispersion phase into two phases: the membrane phase readily wetting the pores of support and the stripping solution containing concentrated metal ions. This process produces a concentrated stripping solution. Fig.1 is a
schematic principle of DSLM process.

Fig.1 Experimental installation of DSLM process

HR represents the carrier within the membrane, which is D2EHPA in this case; TbR₃(HR)₃ represents the organometallic compound, H⁺ is the hydrogen ion and Tb³⁺, the uncomplexed Tb(III); A and B are the boundaries of the membrane phase.

2.2 Principle and Theory of DSLM Process

Fig.2 is 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: Tb(III) diffuses from the feed phase to the interface A; On the feed side interface of DSLM, the extraction of Tb(III) from feed solution with carrier D2EHPA (monomer can be as HR) in kerosene can be expressed as [30,31]:

\[
K_1 \frac{K_{2}}{K_{-1}} \text{TbR}_3(\text{HR})_3 + 3\text{H}^+ \rightarrow \text{TbR}_3(\text{HR})_3 + 3(\text{HR})_{2,\text{org}} (1)
\]

where subscripts f and org stand for feed phase and organic phase respectively; (HR)₂ indicates that the D2EHPA in kerosene mainly exists as a dimer; \(K_1\) and \(K_{-1}\) stand for forward and backward reaction percentage constants at the interface between feed phase and membrane phase.

The metal-complex(TbR₃(HR)₃) diffuses through the membrane A-B; At the stripping side interface of DSLM, TbR₃(HR)₃ dissolved in membrane solution and the metal ion Tb(III) are stripped by stripping agent.

The stripping reaction on the other side of SLM is written as follows [30,31]:

\[
\text{TbR}_3(\text{HR})_3 + 3\text{H}^+ \rightarrow \text{Tb}^{3+} + 3(\text{HR})_{2,\text{org}} (2)
\]

where subscript s represents the dispersion phase; \(K_2\) and \(K_{-2}\) stand for forward and backward reaction percentage constants at the interface between membrane phase and dispersion phase.

Carrier D2EHPA returns from B to A.

In this mechanism the transport of Tb(III) across DSLM is described by considering only diffusion coefficient of Tb(III) because the complex reaction between Tb(III) and D2EHPA at the interfaces is much faster compared to the diffusion in the feed phase and dispersion phase [32–34].

To formulate the model, the following assumptions were made:

1. Tb(III) diffuses in the organic medium only in the form of TbR₃(HR)₃ complex; 2. There is no net flow due to convection within liquid membrane; 3. The metal ions react only with D2EHPA at membrane interfaces; 4. D2EHPA monomer and dimer are in equilibrium for all the time throughout the organic phase; 5. The solubility of D2EHPA in the aqueous acid solution has been found to be negligible, and therefore, its concentration in DSLM is assumed to remain constant [35].

In this mechanism the transport of Tb(III) across DSLM will be described by considering only diffusion coefficient of Tb(III) because the complex reaction between the Tb(III) and PC-88A at the interfaces is much faster compared to the diffusion in the feed phase and membrane phase [32–34]. Then in this model, the transport of Tb(III) in DSLM is considered to include four sequential steps. If the diffusion process can be 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:

\[
J_f = \frac{D_t}{d_f} (c_f - c_i) (3)
\]

where \(J_f\), \(D_t\), \(d_f\), \(c_f\) and \(c_i\) stand for the transport flux in feed phase, the diffusion coefficient of Tb(III) in membrane and the thickness of diffusion layer be-
between feed phase and membrane phase, the concentration of Tb(III) in feed phase, and the concentration of Tb(III) in diffusion layer between feed phase and membrane phase, respectively.

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

$$K_{ex} = \frac{[\text{HI}]^3 c_{mf}^0}{c_f} = \frac{K_d [\text{HI}]^3}{[\text{HR}]^3} = \frac{8 K_d [\text{HI}]^3}{[\text{HR}]^3}$$

(4)

where $m$ stands for membrane phase and $K_d$ indicates the distribution ratio of Tb(III).

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

$$J_{mf} = K_f c_f - K_m c_{mf}$$

(5)

where $J_{mf}$ and $c_{mf}^0$ indicate the transport flux and the concentration of Tb(III) in diffusion layer between feed phase and membrane phase.

$$J_m = \frac{D_m^0}{l} (c_{mf}^0 - c_{ms}^0)$$

(6)

where $J_m$, $c_{ms}^0$, $D_m^0$ and $l$ stand for the transport flux in membrane, the concentration of Tb(III) in diffusion layer between dispersion phase and membrane phase, diffusion coefficient of Tb(III) in membrane and the thickness of membrane, respectively.

In view of distinct characteristics of different membranes, the 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 in consideration of correction coefficient, Eq.6 can be rewritten as:

$$J_m = \frac{D_m^0}{l} (c_{mf}^0 - c_{ms}^0)$$

(7)

where $\tau$ and $\varepsilon$ stand for tortuosity and porosity of membrane.

In a homeostatic reaction system and under ideal conditions, all the above individual transport fluxes can be taken for equality[36–39]:

$$J_f = J_m = J_{mf} = J_s$$

(8)

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

After taking Eqs.3, 4, 6, 7, and 8 into account, the following formula can be obtained:

$$J = \frac{1}{d_f + \frac{d_m^0}{D_m^0} (c_{mf}^0 - c_{ms}^0)}$$

(9)

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

$$J = P c_J = \frac{V_f}{A} \left( \frac{dc_f}{dt} \right)$$

(10)

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

$P_c$ stands for the permeability coefficient, which can be defined as

$$P_c = \frac{1}{d_f + \frac{8 [\text{HI}]^3}{D_m^0 c_K [\text{HR}]^3}}$$

(11)

The $d_f/D_m^0$ and $d_m^0 c_K$ can be defined as follows:

$$\delta_f = \frac{d_f}{D_m^0}$$

(12)

$$\delta_m = \frac{1}{D_m^0}$$

(13)

Eq.(11) can be simplified as

$$\frac{l}{P_c} = \frac{8 \delta_m [\text{HI}]^3}{c_K [\text{HR}]^3} + \delta_f$$

(14)

In Eq.(14), $\varepsilon$, $\tau$, and $K_{ex}$ are all constants. As a result of extraction experiments, a $K_{ex}$ of $5.8 \times 10^{-11}$ was obtained. The relationship between $1/P_c$ and $[\text{HI}]^3$ was examined to be linear at the same concentration of PC-88A. So the Diffusion coefficient of Tb(III) in membrane and the thickness of diffusion layer between feed phase and membrane phase can be obtained with the linear slope method. In the same way, the relationship between $1/P_c$ and $[\text{HR}]^3$ was examined to be linear at the same H$^+$ concentration in feed phase.

Then, $\delta_f$ and $\delta_m$ can be obtained. From Eq.(14) combined with Eqs.12 and 13, $D_m^0$ and $d_f$ values can also be obtained.

The transport percentage of Tb(III) is obtained by the determination of $dc_f/dt$.

Considering and integrating Eq.(10) as follows:

$$\ln \frac{c_f}{c_0} = -\frac{\varepsilon A}{V_f} P_c g t$$

(15)

$$\int_{c_f}^{c_{f}} \frac{dc_f}{c_f - \frac{V_f}{A P_c g t}} = t - t_0$$

(16)

where $c_f$ and $c_0$ stand for the concentrations of Tb(III) in feed phase at $t=0$ and $t=t$, and $t^*$ stands for average time, respectively. Eq.(15) demonstrates the value of $P_c$ is the slope of line, which is obtained under different operation conditions.
3 Experimental

3.1 Reagent

All the reagents such as Tb(CH₃COO)₃·4H₂O, Arsenazo III(C₂₂H₁₈As₂O₁₄N₄S₂), HCl, NaH₂PO₄, Na₂HPO₄, CH₃COONa, and CH₃COOH et al. used in the present work were of analytical grade. Di(2-ethylhexyl) phosphoric acid(D2EHPA) 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.

3.2 Preparing of Solutions

Tb(III) stock solution: a stock solution of Tb(III) was prepared by dissolving Tb(CH₃COO)₃·4H₂O in 1 mol/L HCl, and analyzed by Arsenazo III(C₂₂H₁₈As₂O₁₄N₄S₂) as the chromogenic agent. Tb(III) feed solution: a certain amount of Tb(III) stock solution was diluted with 0.01 mol/L HCl solution to a given extent after adding a calculated amount of CH₃COONa and CH₃COOH or NaH₂PO₄ and Na₂HPO₄.

Arsenazo III(C₂₂H₁₈As₂O₁₄N₄S₂) stock solution: a stock solution of Arsenazo III was prepared by dissolving powder of Arsenazo III in deionized water.

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

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

D2EHPA solution: a calculated amount of extractant was diluted with kerosene.

3.3 Experimental Procedure and Determination

The Tb(III) measurements were performed as follows: the experiments were accomplished at (25±1) °C in a simple diffusion cell. The diffusion cell consisted of two-compartment perspex half-cells. Two half-cells were separated by the membrane. The membrane was impregnated with D2EHPA dissolved in kerosene and clamped between the two half-cells. The effective volume of each one is 80 mL. A microporous PVDF membrane was used as a solid support. It was a 65 μm thick film with a nominal porosity of 75% and a tortuosity of 1.67. The effective area was 12 cm². The feed phase(60 mL) consisted of Tb(III) and buffer solution, and was poured into the perspex half-cell. The mixed dispersion phase consisted of membrane solution containing the carrier D2EHPA and HCl stripping solution with different volume ratios was placed into another half-cell. Samples of the feed phase were taken at time intervals. The stirring of dispersion phase was allowed to stand until phase transport occurred. Then the Tb(III) sample from the dispersion phase was collected. Samples containing Tb(III) in the feed phase were only analyzed for ion concentration on a UV-1200 spectrophotometer with Arsenazo III as the chromogenic agent(under the detection wave lengths: 653 nm).

4 Results and Discussion

4.1 Effect of the 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 Tb(III) was studied. The assumed experimental conditions were chosen as in the certain pH value in the feed phase, which was adjusted to 3.8. Initial concentration of Tb(III) was 1.0×10⁻⁴ mol/L in the feed phase, the concentration of HCl solution was 4.0 mol/L and the concentration of D2EHPA was 0.16 mol/L in the dispersion phase. The effect of volume ratio of membrane solution to stripping solution in the dispersion phase on the transport of Tb(III) is shown in Fig.3. The volume ratios were increased from 0.2 to 5.0. It can be seen that the most effective volume ratio is 1.0, which gives rise to a transport flux of Tb(III) much higher than others.

Fig.3 Effect of volume ratio of membrane solution and HCl on transport of Tb(III)

This indicates the transport flux of Tb(III) increases with increasing the volume ratio of membrane solution to stripping solution in the dispersion phase. When the 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 D2EHPA and Tb(III)
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 the life of liquid membrane. Increasing to an extent of the volume ratio, the flux becomes lower because of decreasing of H⁺ in dispersion phase. We chose 1.0 as the optimum volume ratio of the membrane solution and the stripping solution in the dispersion phase during the following experiments.

4.2 Effect of Concentration of HCl Solution in the Dispersion Phase

The stripping reaction in the dispersion phase plays a vital role in the transport of metal ions from the feed phase to the stripping phase. Thus the effect of the concentration of HCl solution in the dispersion phase on transport flux of Tb(III) was studied. All the other parameters, such as pH value, initial concentration of Tb(III) in the feed phase kept constant, the volume ratio and the concentration of D2EHPA were adjusted to 3.8, 1.0×10⁻⁴ mol/L, 1.0 and 0.16 mol/L respectively. The effect of the concentration of HCl solution in the dispersion phase on the transport flux of Tb(III) is shown in Fig.4. It indicates that with increasing the acid concentration in the dispersion phase, the transport flux of Tb(III) increases. It can be seen that the effective concentration of HCl solution for transport is 4.0 mol/L, which gives rise to a transport flux of 22.01×10⁻⁷ mol/(s·m²) of Tb(III).

Increasing the concentration of HCl solution from 1.0 mol/L to 3.0 mol/L has no significant effect on the transport flux of Tb(III) because the concentration of Tb(III) complex and the concentration of membrane solution which transport through per unit area of the membrane per unit time are definite. However, at a condition of 5.0 mol/L of HCl solution, the transport flux is a little lower than 4.0 mol/L, because of higher acidity resulting in the receding of complexation ability of D2EHPA. Considering controlling acidity as well as increasing transport flux, we chose 4.0 mol/L as the optimum concentration of HCl solution in the dispersion phase during the following experiments.

4.3 Effect of pH in the Feed Phase

Based on the mechanism of mass transfer process, the concentration difference between feed phase and dispersion phase is the driving power of mass transfer process. So in 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 Tb(III). Equally, the greater the pH value in feed phase is, the higher the transport flux of Tb(III) is. The effect of pH in the feed phase on transport of Tb(III) was studied in a pH range of 1.0 to 5.0. Initial concentration of Tb(III) in the feed phase was 1.0×10⁻⁴ mol/L. Concentration of HCl solution was 4.0 mol/L, the volume ratio of the membrane solution to stripping solution was 1.0, the concentration of D2EHPA was 0.16 mol/L in the dispersion phase. The results are shown in Fig.5. The transport flux of Tb(III) increased when the pH in the feed phase increased from 1.0 to 4.5, and a maximum transport flux observed at pH 4.5 was 22.88×10⁻⁷ mol/(s·m²) during 35 min. Above the pH of 5.0 in the feed phase, the transport flux of Tb(III) was 22.95×10⁻⁷ mol/(s·m²) during 20 min because the feed phase emulsified. Against all the previous cases, the announcement of associated documents[30,36] put forward the influence of pH on the distribution coefficient of extraction process. The influence of pH 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 Tb(III) ions are determined under specific experimental conditions [37,38]. As far as our researching conditions are concerned, considering saving chemical agents as well as increasing transport flux, we chose a pH value of 4.5 as the optimum pH condition in the feed phase during the following experiments.

4.4 Effect of Initial Concentration of Tb(III) in the Feed Phase

Effect of the initial concentration of Tb(III) on transport percentage of Tb(III) was studied in a Tb(III) concentration range from $0.2 \times 10^{-4}$ mol/L to $1.5 \times 10^{-4}$ mol/L. The pH value in the feed phase was adjusted to 4.5, the volume ratio of membrane solution to stripping solution was adjusted to 1.0, the concentration of HCl solution was also adjusted to 4.0 mol/L in the dispersion phase, and the concentration of D2EHPA was 0.16 mol/L. The results obtained are presented in Fig.6. With the increasing of initial concentration of Tb(III) in the feed phase from $0.2 \times 10^{-4}$ mol/L to $1.5 \times 10^{-4}$ mol/L, the transport percentage of Tb(III) decreased. This is because the number of D2EHPA molecules is definite through the membrane when the interface between the feed phase and the membrane phase is definite. That is to say, the number of Tb(III) transported is definite in this transport process. When the Tb(III) concentration is $0.2 \times 10^{-4}$ mol/L, $0.5 \times 10^{-4}$ mol/L, $0.8 \times 10^{-4}$ mol/L, $1.0 \times 10^{-4}$ mol/L and $1.5 \times 10^{-4}$ mol/L, the transport percentage is up to 98.1%, 81.7%, 79.7%, 77.2% and 50.3% in 20 min, respectively.

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

4.5 Effect of Different Stripping Agents on Transport of Tb(III)

The stripping agent at the membrane-dispersion side plays a vital role in the transport of metal ions from feed phase to stripping phase. So the effects of different stripping agents in the dispersion phase on the transport of Tb(III) were studied. All the other parameters, such as pH value, initial concentration of Tb(III) in the feed phase kept constant, the volume ratio of membrane solution to stripping solution and the concentration of D2EHPA in the dispersion phase were adjusted to 4.5, $1.0 \times 10^{-4}$ mol/L, 1.0 and 0.16 mol/L respectively. The effects of different stripping agents in the dispersion phase on the transport percentage of Tb(III) are shown in Fig.7. With hydrochloric acid (HCl), sulphuric acid (H2SO4) and nitric acid (HNO3) 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. Choosing hydrochloric acid as the stripping agent, the transport rate of Tb(III) was more efficient, so hydrochloric acid was used as the optimum stripping agent.

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

a. Hydrochloric acid, 4 mol/L; b. Sulfuric acid, 2 mol/L; c. Nitric acid, 4 mol/L.

4.6 Effect of Concentration of D2EHPA on Transport of Tb(III)

D2EHPA concentration in the membrane phase and dispersion phase also plays a significant role in the transport of Tb(III). Effect of the concentration of D2EHPA on the transport flux of Tb(III) was studied in a D2EHPA concentration range from 0.036 mol/L to 0.23 mol/L. The pH value was adjusted to 4.5, the initial concentration of Tb(III) was $1.0 \times 10^{-4}$ mol/L in the feed phase, the volume ratio of membrane solution to stripping solution was adjusted to 1.0 and the concentration of HCl solution was also adjusted to 4.0 mol/L in the dispersion phase. The results are shown in Fig.8. With increasing the concentration of carrier in the membrane phase from 0.036 mol/L to 0.23 mol/L, the transport flux of Tb(III) increased, however, the increasing of transport flux of Tb(III) was not obvious when the concentration of D2EHPA increased to 0.23 mol/L from 0.10 mol/L. Within this concentration
range of D2EHPA from 0.036 mol/L to 0.23 mol/L in the dispersion phase, the availability of D2EHPA at the feed-membrane-dispersion interfaces increased with increasing the concentration of carrier. The chemical-reaction-balance went to the left. Similarly, when the concentration of D2EHPA became low, the balance shifted to the right. With the concentration of D2EHPA increased to a significant extent, the transport flux of Tb(III) would no longer increase with time. When the concentrations of D2EHPA were 0.10, 0.16 and 0.23 mol/L, the transport fluxes were $20.40 \times 10^{-7}$, $22.88 \times 10^{-7}$ and $22.97 \times 10^{-7}$ mol/(s·m²) respectively. The concentration of D2EHPA is proportionate to Tb(III) concentration in the membrane phase. When the concentration of D2EHPA in the membrane phase became higher in comparison to Tb(III) concentration in the feed phase, no Tb(III) reacted on redundant D2EHPA, so the increasing of transport flux of Tb(III) became slow. This indicates that the concentration of D2EHPA used to transport Tb(III) through per unit area of the membrane per unit time is definite when the initial concentration of Tb(III), the effect area of membrane and time are definite. A concentration of 0.16 mol/L of D2EHPA was chosen as the optimum concentration of carrier. Under the conditions, the transport percentage of Tb(III) was 96.1% in 35 min.

4.7 Effect of Ionic Strength in the Feed Phase

The effect of ionic strength in the feed phase on the transport flux of Tb(III) was studied. The results are shown in Fig.9. It indicates that the ionic strength has not influence on the transport flux of Tb(III) because the effect of HCl solution surrounded by membrane solution is weak, which leads to the ionic strength of the dispersion phase is ignorable. When the concentration of the metal ions in the feed phase is low, the ionic strength of the two phases is neglected. The operational conditions, compared to those of other technologies of liquid membrane, are further simplified.

5 Kinetic Analysis

Based on the data of the effect of pH in the feed phase, the relationship between $1/P_c$ and $[H^+]^3$ is developed [Eq.(14)]. When the concentration of carrier is definite, $P_c$ is definite, too(Fig.10).

6 Conclusions

Transport of Tb(III) through a dispersion supported liquid membrane with D2EHPA as the carrier, was studied with the following results.
Optimum transport conditions of Tb(III) in the DSLM system are that the concentration of HCl solution was 4.0 mol/L, the volume ratio of membrane solution to stripping solution was 1.0, the concentration of D2EHPA was 0.16 mol/L in the dispersion phase, and pH value was 4.5 in the feed phase. When the initial concentration of Tb(III) was $1.0 \times 10^{-4}$ mol/L, the transport effect of Tb(III) was very obvious under the optimum conditions and the transport percentage of Tb(III) was up to 96.1% during the transport time of 35 min.

A transient model was developed which considered the reaction between the Tb(III) and the extractant D2EHPA only at the aqueous-DSLM interfaces. The kinetic equation that describes the transport of Tb(III) in DSLM has been derived: $\frac{P_{\text{D}}}{P_{\text{M}}} = 1/(1.0208 \times 10^{4} + 2.68 \times 10^{14} [\text{H}^{+}]^{3})$. The equation has been developed and diffusion coefficient in the membrane and transport characteristics, such as the nature and diffusion layer between the feed phase and the membrane phase have been also obtained by linear slope method. They are $1.82 \times 10^{-8}$ m$^2$/s and 5.61 μm, respectively.

The results of the extraction of Tb(III) with respect to time produced by the model simulation coincide well with those obtained by experimentation. The application of this model to the extraction of other rare earth species is possible as long as the equilibrium and application of this model to the extraction of other rare earth species.

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