Separation of Eu$^{3+}$ Using a Novel Dispersion Combined Liquid Membrane with P507 in Kerosene as the Carrier

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Abstract The separation of Eu$^{3+}$ is studied with a dispersion combined liquid membrane (DCLM), in which polyvinylidene fluoride membrane (PVDF) is used as the liquid membrane support, dispersion solution containing HCl solution as the stripping solution, and 2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester (P507) dissolved in kerosene as the membrane solution. The effects of pH value, initial concentration of Eu$^{3+}$ 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 separation are investigated. The optimum condition for separation of Eu$^{3+}$ is that concentration of HCl solution is 4.0 mol·L$^{-1}$, concentration of carrier is 0.16 mol·L$^{-1}$, and volume ratio of membrane solution solution to stripping solution is 30:30 in the dispersion phase, and pH value is 4.2 in the feed phase. The ionic strength has no significant effect on separation of Eu$^{3+}$. Under the optimum condition, when the initial concentration of Eu$^{3+}$ is 0.8×10$^{-3}$ mol·L$^{-1}$, the separation percentage of Eu$^{3+}$ is 95.3% during the separation time of 130 min. The kinetic equation is developed in terms of the law of mass diffusion and the theory of interface chemistry. The diffusion coefficient of Eu$^{3+}$ in the membrane and the thickness of diffusion layer between feed phase and membrane phase are obtained and their values are 1.48×10$^{-5}$ m$^2$·s$^{-1}$ and 36.6 μm, respectively. The results obtained are in good agreement with literature data.

Keywords dispersion combined liquid membrane, 2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester, separation, europium$^{3+}$

1 INTRODUCTION

Liquid membranes (LMs) involve extraction and stripping processes simultaneously, and they have benefits of nonequilibrium mass transfer and uphill effect, where the solute can move from low to high concentration solution [1-4]. The main liquid membrane systems include emulsion liquid membrane (ELM) [5], supported liquid membrane (SLM) [6], bulk liquid membrane (BLM), flowing liquid membrane (FLM) [7], electrostatic pseudo liquid membrane (EPLM) [2], supported emulsion liquid membrane (SELM) [8, 9], hollow fiber liquid membrane (HFLM) [10], supported liquid membrane with stripping dispersion (SLM-SD) [11, 12], etc. The potential advantages of LM techniques, over traditional separation techniques and solid membrane 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 for large-scale industrial processes [13-19], primarily due to the lack of longitudinal stability, difficult operation and larger membrane resistance, etc [20]. For example, SLM will lose the carrier because of the turbulent shear force of liquid in both phases and concentration difference between organic phase and aqueous phase, and the operation of ELM involves the complexity of emulsification and de-emulsification techniques [10-12].

A new liquid membrane technique, named dispersion combined liquid membrane (DCLM), has been proposed [21]. The DCLM technique is based upon surface renewal and diffusion theory, with the advantages of fiber membrane extraction, liquid film permeation and most of other liquid membrane systems, resulting in more stable membrane, lower costs, simpler operation, extremely efficient stripping of target species from the organic phase with high flux, and high concentration of target species in the stripping solution. However, more studies are needed for the application of DCLM in industry [22, 23]. The scale-up for the new liquid membrane configuration requires 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 study on the separation of a single cation and a new permeability coefficient equation are needed, and more data for the separation of two or more competitive solutes are required for some applications, such as waste liquid of metallurgical industry.

The present study is concerned with the technical feasibility for separation of metal ions by DCLM. Eu$^{3+}$ is playing an increasingly important role in high technology. We choose DCLM to separate Eu$^{3+}$. The effects of various experimental parameters on separation of rare earth Eu$^{3+}$ ions are investigated. The separation of Eu$^{3+}$ is carried out with a DCLM, which consists of polyvinylidene fluoride membrane (PVDF) as
the support, dispersion solution concluding HCl solution as the stripping solution, and 2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester (P507) dissolved in kerosene as the membrane solution. Although the separation of metal ions by SLM containing the same carrier (P507) has been extensively studied, there is little research by DCLM. The effects of pH value, initial concentration of Eu$^{3+}$ and different ionic strength in the feed phase, volume ratio of membrane solution to stripping solution, concentration of HCl solution, concentration of P507, and different stripping agents in the dispersion phase on separation of Eu$^{3+}$ are investigated. The results with DCLM are compared to those with conventional SLM. A kinetic equation for DCLM process is derived from the law of mass diffusion and the theory of interface chemistry and tested.

2 EXPERIMENTAL

2.1 Reagent

All the reagents such as Eu(CH$_3$COO)$_3$·4H$_2$O, arsenazo III(C$_{22}$H$_{18}$As$_2$O$_{14}$N$_4$S$_2$), CH$_3$COONa, HCl, and CH$_3$COOH used in the present work were of analytical grade. 2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester (P507) is a commercial extractant (purity>95%) and used without any further purification. Kerosene was washed with concentrated sulfuric acid and distilled at 180–220°C.

2.2 Preparation of solutions

Eu$^{3+}$ stock solution was prepared by dissolving Eu(CH$_3$COO)$_3$·4H$_2$O in 1 mol·L$^{-1}$ HCl solution, and analyzed by arsenazo III as the chromogenic agent. For Eu$^{2+}$ feed solution, a certain amount of the Eu$^{3+}$ stock solution was diluted with 0.01 mol·L$^{-1}$ HCl solution after adding a calculated amount of CH$_3$COONa and CH$_3$COOH. Arsenazo III stock solution was prepared by dissolving the powder of arsenazo III in deionized water. To obtain the stripping solution, the required amount of HCl was solved and diluted with deionized water to a certain concentration. P507 solution was obtained by diluting a certain amount of extractant with kerosene.

2.3 Experimental procedure

The separation with the DCLM was determined as follows. The experiments were accomplished at (25±1)°C in a simple diffusion cell, which consists of two-compartment perspex half-cells, each with effective volume of 70 ml. The membrane impregnated with P507 dissolved in kerosene was clamped between the two half-cells. A microporous PVDF membrane was used as the solid support, the thickness of which is 65 μm, with nominal porosity of 75%, tortuosity of 1.67 and effective area of 10.5 cm$^2$. The feed phase (50 ml) consisted of Eu$^{3+}$ and buffer solution was poured into the perspex half-cell. The mixed dispersion phase consisted of certain volume ratio of the membrane solution containing the carrier P507 to HCl stripping solution was placed into another half-cell. The stability of the SLM was ensured by a modified SLM with stripping dispersion phase, where the aqueous stripping solution was dispersed in the organic membrane solution in a mixer. The stripping dispersion formed in the mixer went to the membrane module to provide a constant supply of the organic solution to the membrane pores. Samples of the feed phase were taken at intervals. The stirred dispersion phase were allowed to stand until the phase separation occurred, and then the Eu$^{3+}$ sample was collected from the dispersion phase. Samples containing Eu$^{3+}$ in the feed phase were analyzed for ion concentration with a UV-1200 spectrophotometer using arsenazo III as the chromogenic agent (under the detection wave length 652 nm). Fig. 1 is the experimental installation of the DCLM process.

![Figure 1 Experimental installation of DCLM process](image)

Figure 1  Experimental installation of DCLM process

1—feed pool; 2—PVDF membrane; 3—feed phase; 4—dispersion pool; 5—membrane solution; 6—stripping phase; 7—dispersion phase; 8—magnetic stirrer apparatus

2.4 Experimental principle and theoretical analysis

Figure 2 shows the principle of DCLM process, in which concentration change and separation processes are depicted, where subscripts m, f and s stand for membrane phase, feed solution, and dispersion phase, respectively. The co-separation involves following steps.

(a) Eu$^{3+}$ diffuses from the feed phase to interface A.

(b) In the membrane phase near interface A, the extraction of Eu$^{3+}$ from the feed solution with carrier P507 [such as (HR)$_2$] in kerosene can be expressed as [24, 25]:

\[
\text{Eu}^{3+} + 3(\text{HR})_{2,\text{org}} \xrightarrow{K_1} \text{EuR}_3(\text{HR})_{3,\text{org}} + 3\text{H}^+ 
\]

where $K_1$ and $K_{-1}$ are the reaction percentage constants of the reversible reaction at the interface between the feed phase and membrane phase.

(c) The metal-complex [EuR$_3$(HR)$_3$] diffuses through the membrane A-B.

(d) In the stripping side near interface B, EuR$_3$(HR)$_3$ dissolves in the membrane solution and
Eu\(^{3+}\) are stripped by stripping agent. At the drop interface, Eu\(^{3+}\) in the organic phase interchanges H\(^+\) in the stripping phase, then Eu\(^{3+}\) diffuses to the bulk of the stripping phase and the extractant is regenerated. The stripping reaction can be written as

\[
2 \text{EuR}_3(\text{HR})_3 + 3\text{H}^+ \xrightarrow{K_2} 3\text{EuR}_3(\text{HR}) + \text{3(HR)}_2,
\]

where \(K_1\) and \(K_2\) are the reaction rate constant of the reversible reaction at interface B.

e. Carrier P507 returns from interface B to interface A.

The equation for permeability coefficient can be defined as [26]

\[
P_c = \frac{1}{d_f + \frac{d_m}{D_f} + \frac{d_m}{D_m} + \frac{D_m}{D_m} \varepsilon K_{ex}[\text{HR}]}
\]

where \(d_f\) is the thickness of diffusion layer in the feed phase near the membrane surface A, \(D_f\) is the diffusion coefficient of Eu\(^{3+}\) in \(d_f\), \(d_m\) is the thickness of the membrane, \(D_m\) is the diffusion coefficient of Eu\(^{3+}\) in the membrane, \(\varepsilon\) and \(\tau\) stand for the tortuosity and porosity of membrane, respectively. The tortuosity and porosity affect the flux through the membrane. Higher porosity leads to higher flux, while larger tortuosity leads to lower flux.

We define

\[
\Delta_f = \frac{d_f}{D_f}
\]

\[
\Delta_m = \frac{d_m}{D_m}
\]

so that Eq. (1) is expressed as

\[
\frac{1}{P_c} = \frac{\Delta_m + \varepsilon K_{ex}[\text{HR}]}{P_c} + \Delta_f
\]

In Eq. (4), \(\varepsilon\), \(\tau\), and \(K_{ex}\) are constants. With extraction experiments, \(K_{ex}\) of 4.3\times10\(^{-10}\) was obtained [27]. Since the relationship between \(1/P_c\) and \([\text{H}^+]^3\) is linear at certain concentration of P507, and the relationship between \(1/P_c\) and \([\text{HR}]^3\) is also linear at the same H\(^+\) concentration in the feed phase, \(A_f\) and \(A_m\) can be obtained. Then the diffusion coefficient of Eu\(^{3+}\) in the membrane \(D_m^n\) and the thickness of diffusion layer \(d_f\) can be obtained.

In previous study, we obtained [26]

\[
\ln \frac{c_f(t)}{c_f(0)} = -\frac{A}{V_f} P_c \cdot t
\]

where \(c_f(0)\) and \(c_f(t)\) stand for the concentrations of Eu\(^{3+}\) in the feed phase at \(t=0\) and \(t=t\), respectively. The value of \(A P_c/V_f\) can be obtained from the slope of curve of \(\ln c_f(t)/c_f(0)\) vs. time \(t\).

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 separation of Eu\(^{3+}\) is shown in Fig. 3. The volume ratio is increased from 10 : 50 to 50 : 10. Volume ratio 50 : 10 is better.

![Figure 3](image-url)
At ratios of 50 : 10, 40 : 20 and 30 : 30, the separation percentage of Eu$^{3+}$ are 83.5%, 81.5% and 81% respectively. These separation percentages are satisfactory, so we choose the ratio 30 : 30 during the following experiments.

### 3.2 Effect of concentration of HCl solution in the dispersion phase

The effect of concentration of HCl solution in the dispersion phase on separation of Eu$^{3+}$ is shown in Fig. 4. As the acid concentration increases, the separation percentage increases. At the concentration of 5.0 and 4.0 mol·L$^{-1}$, the separation percentages of Eu$^{3+}$ are 82.5% and 81%, respectively. The increasing of concentration of HCl solution from 2.0 mol·L$^{-1}$ to 3.0 mol·L$^{-1}$ has no significant effect on separation percentage of Eu$^{3+}$, and it is less than 70%, because the number of Eu$^{3+}$ complex and the concentration of membrane solution which separation through the membrane per unit area of the membrane per unit time are definite. However, under the condition of 6.0 mol·L$^{-1}$ HCl solution, the separation percentage is a little lower than 5.0 mol·L$^{-1}$ and 4.0 mol·L$^{-1}$, due to higher concentration of HCl solution resulting in a large number of volatilization of HCl during a certain time. The concentration of HCl solution 4.0 mol·L$^{-1}$ in the dispersion phase can be chosen during the following experiments.

![Figure 4 Effect of concentration of HCl solution on separation of Eu$^{3+}$](image)

**Figure 4** Effect of concentration of HCl solution on separation of Eu$^{3+}$ (pH in feed phase: 4.0, initial concentration of Eu$^{3+}$: 1.0×10$^{-4}$ mol·L$^{-1}$, volume ratio of membrane solution to stripping solution in the dispersion phase: 30 : 30, concentration of P507: 0.16 mol·L$^{-1}$) concentration/mol·L$^{-1}$: ■ 2; ▲ 3; × 4; □ 5; ◆ 6

### 3.3 Effect of pH in the 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. 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 separation percentage of Eu$^{3+}$. Equally, the greater the pH value in the feed phase is, the higher the separation percentage of Eu$^{3+}$ is. The effect of pH in the feed phase on separation of Eu$^{3+}$ is studied in the pH range of 3.3 to 4.6, which is adjusted with an HAc-NaAc buffer solution. Initial concentration of Eu$^{3+}$ in the feed phase is 1.0×10$^{-4}$ mol·L$^{-1}$. The results shown in Fig. 5. The separation percentage of Eu$^{3+}$ increases when the pH in the feed phase increased from 3.3 to 4.6, and a maximum separation percentage observed at pH 4.2 is 90.8%. Above the pH of 4.2 in the feed phase, the separation percentage of Eu$^{3+}$ decreases to 86%. When pH value was higher than 4.6, hydroxy complex of Eu$^{3+}$ was formed in the feed phase and the separation percentage of Eu$^{3+}$ decreased. Contrast to the previous cases, the literature [28] suggested the influence of pH on distribution coefficient of extraction process. It is large because the separation 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 Eu$^{3+}$ ions are determined under specific experimental conditions [29, 30]. The pH of 4.2 as the optimum pH condition in the feed phase was chosen during the following experiments.

![Figure 5 Effect of pH in the feed phase on separation of Eu$^{3+}$](image)

**Figure 5** Effect of pH in the feed phase on separation of Eu$^{3+}$ (concentration of HCl solution in dispersion phase: 4.0 mol·L$^{-1}$, initial concentration of Eu$^{3+}$: 1.0×10$^{-4}$ mol·L$^{-1}$, volume ratio of membrane solution and stripping solution in the dispersion phase: 30 : 30, concentration of P507: 0.16 mol·L$^{-1}$) pH: ■ 3.3; ▲ 3.6; × 4.0; □ 4.2; ◆ 4.6

### 3.4 Effect of initial concentration of Eu$^{3+}$ in the feed phase

Effect of initial concentration of Eu$^{3+}$ on separation percentage of Eu$^{3+}$ is studied in the Eu$^{3+}$ concentration range from 0.16×10$^{-4}$ mol·L$^{-1}$ to 1.50×10$^{-4}$ mol·L$^{-1}$. The results obtained are presented in Fig. 6. With the increasing of initial concentration of Eu$^{3+}$ in the feed phase from 0.16×10$^{-4}$ mol·L$^{-1}$ to 1.50×10$^{-4}$ mol·L$^{-1}$, the separation percentage of Eu$^{3+}$ decreased during the same time. This is because the number of P507 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 Eu$^{3+}$ separated is definite in this separation process. When the Eu$^{3+}$ concentration is 0.8×10$^{-4}$ mol·L$^{-1}$, 1.0×10$^{-4}$ mol·L$^{-1}$, and 1.5×10$^{-4}$ mol·L$^{-1}$, the separation percentage is up to 95.3%, 90.8% and 73.1% in 130 min,
respectively. Further more, the separation percentage is up to 97.3% in 100 min, when initial concentration of Eu$^{3+}$ is adjusted to $0.16 \times 10^{-4}$ mol·L$^{-1}$, and after 100 min Eu$^{3+}$ is hardly determined, because the concentration of Eu$^{3+}$ is too low to determine, that is to say the Eu$^{3+}$ is exhausted in the feed phase and concentration of Eu$^{3+}$ is below the analytical determination limits.

3.5 Effect of different stripping agents on separation of Eu$^{3+}$

The effects of different stripping agents in the dispersion phase on separation of Eu$^{3+}$ are studied. The effect of different stripping agents in the dispersion phase on the separation percentage of Eu$^{3+}$ is shown in Fig. 7. Using hydrochloric acid (HCl) 4 mol·L$^{-1}$, sulphuric acid (H$_2$SO$_4$) 2 mol·L$^{-1}$ and nitric acid (HNO$_3$) 4 mol·L$^{-1}$ as the stripping agent respectively, it was found that hydrochloric acid is the most efficient stripping agent in this investigation. Under the conditions of hydrochloric acid solution, sulphuric acid solution and nitric acid solution, the separation percentage of Eu$^{3+}$ is up to 95.3%, 92% and 82% respectively. During the following experiment we have still chose the hydrochloric acid as the stripping agent.

3.6 Effect of concentration of P507 on separation of Eu$^{3+}$

Concentration of P507 in the membrane phase and dispersion phase also plays a significant role in separation of Eu$^{3+}$. Effect of concentration of P507 on separation percentage of Eu$^{3+}$ is studied in the P507 concentration range from $0.036 \text{ mol·L}^{-1}$ to $0.23 \text{ mol·L}^{-1}$. The results are shown in the Fig. 8. With the increasing of concentration of P507 in the membrane phase from $0.036 \text{ mol·L}^{-1}$ to $0.23 \text{ mol·L}^{-1}$, the separation percentage of Eu$^{3+}$ increases, however, when concentration of P507 increases to $0.23 \text{ mol·L}^{-1}$ from $0.16 \text{ mol·L}^{-1}$, the increasing of separation percentage of Eu$^{3+}$ is near. So $0.16 \text{ mol·L}^{-1}$ can be chosen as the optimum concentration of carrier.

3.7 Effect of ionic strength in the feed phase

Above experiments, we did not consider the influence of ionic strength. Under the optimum condition, the effect of ionic strength in the feed phase on separation percentage of Eu$^{3+}$ is studied in this section under the same concentration of Eu$^{3+}$ $0.8 \times 10^{-4}$ mol·L$^{-1}$. The reagent KNO$_3$ was used to adjust the ionic strength to 0.5, 1.0, 1.5 and 2.0 mol·L$^{-1}$ respectively. The results are shown in Fig. 9. It indicates that the ionic strength has not influence on the separation percentage of Eu$^{3+}$.

4 KINETIC ANALYSIS

Constructing based on the data of effect of pH in the feed phase, and the relationship developed between
When concentration of carrier is definite. It indicates that the relationship between \( P_c \) and \([H^+]^3\) [Eq. (4)], When concentration of carrier is definite.

The slope and intercept of the line are \( 2.3815 \times 10^{15} \) s·L\(^4\)·m\(^{-1}\)·mol\(^{-4}\) and \( 6.0998 \times 10^4 \) s·m\(^{-1}\). The thickness of diffusion layer \( d_f \), which is obtained by diffusion coefficient of Eu\(^{3+}\) in the aqueous solution \( (6.0 \times 10^{10} \text{ m}^2\cdot\text{s}^{-1}) \) [27, 31] is that \( d_f \triangleq \frac{D_f}{3.660 \times 10^5} \) m. Then the diffusion coefficient \( D_m \) in the membrane, obtained by Eqs. (3) and (4), is that \( D_m = \frac{D_f}{\Delta_m} = 1.48 \times 10^7 \) m\(^2\)·s\(^{-1}\).

The kinetic equation that describes the separation of Eu\(^{3+}\) in DCLM is derived: \( P_c = \frac{1}{6.0998 \times 10^4 + 2.3815 \times 10^{15} [H^+]^3} \) and \( P_c = \frac{1}{6.09 \times 10^5 + 18.791 [HR]^3} \).

These equations are developed and diffusion coefficient in the membrane and thickness of diffusion layer between the feed phase and the membrane phase are obtained by linear slope method. They are \( 1.48 \times 10^7 \) m\(^2\)·s\(^{-1}\) and 36.6 \( \mu \)m, respectively.

DCLM, owing to a large number of membrane solution is used in the dispersion phase, can supply the losing carrier of supported liquid membrane. As a result, the separation percentage of Eu\(^{3+}\) increases, the stability of membrane is enhanced, and the life span of the membrane is extended.

**NOMENCLATURE**

- \( A \): surface area of membrane
- \( c(t) \): concentration of metal ion in the feed phase when time = 0, mol·L\(^{-1}\)
- \( c(t) \): concentration of metal ion in the feed phase when time = \( t \), mol·L\(^{-1}\)
- \( D_f \): diffusion coefficient of the metal ion in feed phase, m\(^2\)·s\(^{-1}\)
- \( D_m \): diffusion coefficient of metal ion in the membrane, m\(^2\)·s\(^{-1}\)
- \( d_f \): thickness of diffusion layer between the feed phase and membrane phase, m
- \( d_m \): thickness of the membrane, m
- \([H^+]\): concentration of H\(^+\), mol·L\(^{-1}\)
- \([HR]\): concentration of carrier P507, mol·L\(^{-1}\)
- \( K_i \): forward reaction rate constant at the left interface of the membrane
- \( K_{-i} \): backward reaction rate constant at the left interface of the membrane
- \( K_{i} \): forward reaction rate constant at the right interface of the membrane
- \( K_{-i} \): backward reaction rate constant at the right interface of the membrane
- \( K_{ex} \): extraction equilibrium constant
- \( P_c \): permeability coefficient of metal ion, m·s\(^{-1}\)
- \( V_f \): volume of feed phase
- \( \Delta \): separation resistance due to diffusion by aqueous feed boundary layer, s·m\(^{-1}\)
\( A_{m} \) separation resistance due to diffusion through the membrane, \( s \ m^{-1} \)
\( \varepsilon \) porosity of the membrane
\( \tau \) tortuosity of the membrane

**Subscripts**

f feed phase

m membrane phase

s stripping phase

**REFERENCES**