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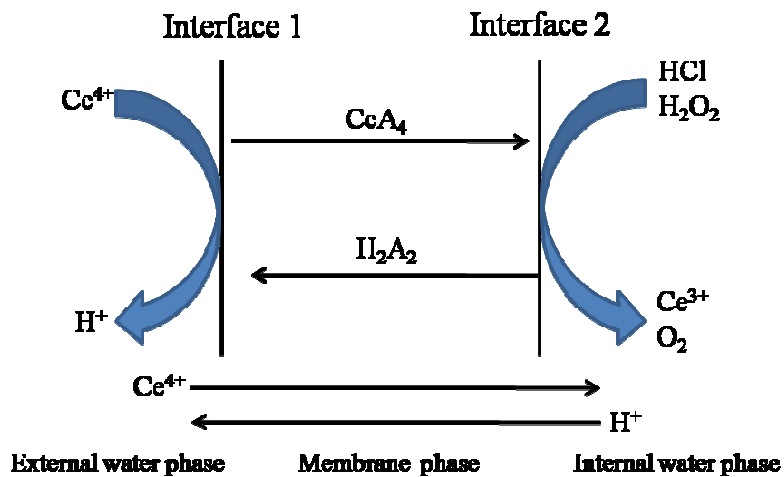
The graphical abstract shows the possible scheme for Ce(IV) extraction mechanism by ELM

using D2EHPA as extractant.

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Extraction of Ce(IV) from Sulfuric Acid Solution by Emulsion Liquid Membrane using D2EHPA as Carrier

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Abstract: In order to provide a potential application for extracting Ce(IV), the extraction of Ce(IV) from sulfuric acid solution by emulsion liquid membrane using D2EHPA as carrier was investigated. An ELM system was made up of sulfonated kerosene as diluent, Span 80 as surfactant, liquid paraffin as intensifier and hydrochloric acid containing hydrogen peroxide as inner aqueous solution. The influences of various parameters on the extraction of Ce(IV) have been investigated. The optimum conditions for Ce(IV) extraction can be summarized as the D2EHPA concentration 12% (v/v), Span 80 concentration 2%-3% (v/v), liquid paraffin concentration 2%-4% (v/v), hydrochloric acid concentration in the internal phase 4-5 mol/l, hydrogen peroxide concentration 0.02 mol/l, volume ratio of membrane phase to internal phase (R_{oi}) 1.5, acidity in external phase 0.4-0.5 mol/l, volume ratio of external phase to membrane phase (R_{we}) 2, extraction time 15 min and stirring speed 250 rpm. Then, the separation experiments of Ce(IV) from RE(III) under optimum conditions were carried out showing the system in extremely selective for Ce(IV). The mechanism of extraction of Ce(IV) has also been discussed. A demulsification process was conducted with the loss within 3%. The results reveal that the ELM method is a clean and frugal process for the extraction of Ce(IV) from sulfuric acid solution.

1 Introduction

The cerium, one of most abundant of the light rare earths, is widely used in industry mainly in the form of ceria (CeO_2) as a material for ceramic, catalyst, polishing powder and so on.[1,2] Solvent extraction is an important method to separate and purify cerium element, and is widely used in industrial production because of its simplicity, speed, and applicability in the extraction and separation of Res.[3,4] The most commonly used extractants are organophosphorus acids that belong to a compound formation class, such as di-(2-ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid-2-ethylhexyl ester (HEHEHP).[5] The conventional solvent extraction method possess many deficiencies, such as complex multi-stage extraction operation, larger volumes of solvent and associated equipment, high energy consumption, and higher investment costs.[6] Therefore, the investigation for more efficient extraction technique has attracted much attention, which has important significance in the development of rare earth industry. Liquid membrane technology is gaining importance and is emerging as an attractive and promising technology for the concentration and separation of metal ions from aqueous solutions.[7]

There are several different types of liquid membrane, such as bulk (BLM), supported (SLM), emulsion (ELM) liquid membranes, polymer inclusion membranes (PIMs) and hollow fiber liquid membrane (HFSLM).[8,9] BLMs consist of an aqueous feed and stripping phase separated by an immiscible membrane phase. BLMs are often used to study the transport properties of novel carriers, but a small membrane surface area of BLMs makes them technologically not very attractive.[10] SLMs have essentially the same configuration as BLMs, but now the organic phase is contained in the pores of a macroporous polymer sheet.[9] SLMs are very useful for laboratory research and development purposes, but the surface area to volume ratio of flat sheets is too low for industrial applications.[11] Of the SLMs, a HFSLM is the most promising. It possesses several advantages such as simultaneous one-step extraction and stripping, high selectivity, large surface area, high mass transfer rate, low extractant and energy consumption.[12] Despite its advantages, the application on a larger scale is still very limited due to the insufficient membrane stability,[13] and the surface active effects can lead to fouling and variable geometry leads to difficulty in modeling.[7] The PIMs are composed of polymers, plasticizers, and ion carriers, have gained considerable attention since the higher selectivity to the target metal ion, less carrier consumption, and extraction and stripping in one integrated process, however, the selection of suitable polymer for PIMs is one of the important factors for membrane separation.[14]

The emulsion liquid membrane (ELM), a separation technique proposed by Li, [15] has been regarded as an emerging energy-efficient technology combining the characteristics of solid membrane separation and solvent extraction. The main advantages of ELM method are: high interfacial area for mass transfer because of the small size of the aqueous phase droplets, high diffusion rate of the target ion through the membrane, simultaneous performance of extraction and stripping in single one-step, capability of treating a variety of elements and compounds in industrial setting at a greater speed and with a high degree of effectiveness, also with volume requirements.[16] Compared with HFSLM, the HFSLM requires a much smaller inventory of solvent and carrier since the volume ratios of

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the two aqueous phases to the membrane are large, but the large volume ratios are a disadvantage in that very hydrophobic membrane solvents and carriers are required to maintain membrane integrity and operate the system. [7]

The ELM contains three-phases as membrane phase, internal phase and external phase. The liquid membrane consists of a diluent, a surfactant and a carrier reagent (extractant) to separat solute by chemical reaction. The external continuous phase and internal phase are separated by liquid membrane. The selective component is transported through the liquid membrane from the external phase and concentrated in the internal phase.[17] After extraction, the loaded emulsion is separated from the feed solution, demulsification yields a membrane phase that can be recycled.[6] The extraction mechanism involved in liquid membrane transport is essentially the same as that in solvent extraction. It has been reported that various ions are successfully extracted by ELM.[18-23] Few papers were presented on the extraction of lanthanides by ELM.[24-26] Teramoto et al. [27] and Tang and Wai [28] explored the extraction and transport of trivalent lanthanides by liquid membrane system.

The transport of Ce(IV) with membrane system has been reported before,[29-31] but there is a lack of study for Ce(IV) extraction from sulfuric acid solution by ELM.

In this paper, the extraction of Ce(IV) from sulfuric acid solution by ELM was investigated. The D2EHPA was chosen as the extractant. The various parameters influencing the extraction of Ce(IV) had been investigated. The aim is to provide the potential application for extracting Ce(IV) by a clean and frugal separation method, and replace the existing system.

2 Experimental

2.1 Reagents and apparatus

Liquid paraffin with specific gravity of 0.835-0.890 was supplied by Tianjin Bodi Chemical Industry Co., Ltd. Span80 ($C_{24}H_{44}O_6$), hydrogen peroxide (H_2O_2), cerium (IV) sulphate ($Ce(SO_4)_2 \cdot 4H_2O$) etc. of analytical grade were supplied by Shenyang Guoyao Group Chemical Reagent Co., Ltd. Sulfuric acid (A.R. 98%), hydrochloric acid (A.R. 37.5%) were supplied by Shenyang Lab Science and Trade Co., Ltd. n-dodecane,D2EHPA and sulfonated kerosene were supplied by Shanghai Laiyashi Chemical Industry Co., Ltd. All solutions were prepared using deionised water with resistivities >18.23MΩ·cm^{-1}.

The FJ200-SH digital high speed dispersion homogenizer (Shanghai Specimen Model Factory) was used to prepare the liquid membrane solution. The DW-3 speed control magnetic stirrer (Gongyi Yuhua Instruments Co., Ltd.) was used to carry out the extraction experiments.

2.2 Experimental

2.2.1 Membrane preparation

Using sulfonated kerosene as membrane diluent, Span80 as surfactant, D2EHPA as carrier and liquid paraffin as liquid membrane intensifier, an organic solution was prepared by mixing a certain volume fraction of sulfonated kerosene, Span80, D2EHPA and liquid paraffin in a 250 mL beaker at stirring speed of 1000 rpm by means of a dispersion homogenizer. Then the hydrochloric acid aqueous solution with hydrogen peroxide as reductant was added dropwise to the stirred membrane solution until the desired volume ratio of membrane solution to stripping solution was obtained. The solution is stirred continuously for 20 min at stirring speed of 5000 rpm to obtain a stable W_1/O type ELM.

2.2.2 Feed solution preparation

The stock solution of Ce(IV) was prepared by treating the sulphuric acid and cerium (IV) sulphate in stoichiometric amounts to volumetric flask and then adding water to get the desired concentrations of cerium and acid.

2.2.3 Extraction

All experiments were performed at a constant temperature of 25±0.2°C. The prepared emulsion was added into specific volume of external aqueous solution. The contents were stirred by a speed control magnetic stirrer at speed of 250rpm for 15min to make the W_1/O/W_2 double emulsions. The stirred solution was allowed to separate to emulsion (W_1/O) and external aqueous solution (W_2) by gravity in a 125 ml separatory funnel. After two-phase separation, the concentration of Ce(IV) in external aqueous phase was analyzed. The concentration in the internal aqueous phase was obtained by mass balance. The emulsion was recovered and subsequently broken into its constituent organic and internal aqueous cerium concentrated solution.

To determine the important variables governing the extraction of Ce(IV), extractant concentration, surfactant concentration, intensifier concentration, hydrochloric acid and hydrogen peroxide concentrations of stripping solution, volume ratio of membrane phase to internal phase (R_{oi}), volume ratio of external phase to membrane phase (R_{we}), acidity in feed solution, extraction time and stirring speed were varied to observe their effects on Ce(IV) extraction. The separation of Ce(IV) from RE(III) was also investigated.

2.2.4 Demulsification of emulsion

After the extraction experiment, the loaded emulsion was broken using 45 kHz KQ-700VDE Dual-frequency NC Ultrasonic Processor (Kunshan Ultrasonic Instrument Co., Ltd) into internal Ce(IV) concentrated phase and organic phase. The internal phase was separated and centrifuged. The Ce(IV) concentration was determined.

2.3 Analyses methods

The chemical structure of D2EHPA complex with Ce(IV) was detected by the Nicolet-380 fourier transform infrared spectrometer (Thermo Electron Corporation). The viscosities of the emulsions were measured by DV2TLVTJ0 viscometer (Brookfield).

The average sizes of emulsions were measured by means of BT-9300H laser particle size analyzer (Dandong Bettersize Instruments Co., Ltd.) within few minutes after preparation. The globule size of emulsion was measured through diluting the sample with deionized water, and the internal droplet size of emulsion were measured through diluting the sample with *n*-dodecane. The average diameters of the emulsion liquid globule and droplet were represented by the sauter mean diameter ($d_{32} = \sum n_i d_i^3 / \sum n_i d_i^2$), representing a surface average value). Additionally, a BT-1600 particle image analysis system with an optical microscope (Dandong Bettersize Instruments Co., Ltd.) was used to view the morphology of emulsion and assess the average thickness of membrane.

The concentration of D2EHPA was determined by titration with standard NaOH solution using phenolphthalein and bromophenol blue as indicators. The acidity was determined by neutralization titration with standard NaOH solution using mixed indicators of methyl red and bromocresol green after masking the metal ions by Ca-EDTA solution. The concentration of RE(III) was determined by titration with standard EDTA solution with xylenol orange as the indicator. The concentration of Ce(IV) was determined by titration with standard $[(NH_4)_2Fe(SO_4)_2]$ solution using sodium diphenylamine sulfonate as indicator.

The extraction efficiency η was obtained by Eq.(1).

$$\eta = (C_0 - C_t) / C_0 \times 100\% \qquad (1)$$

where C_0 is Ce(IV) concentration in external aqueous phase before extraction, mol/l; C_t is Ce(IV) concentration in external aqueous phase after extraction, mol/l.

3 Results and discussion

3.1 Extraction mechanism in ELM system

D2EHPA is supposed to be present as a dimeric species such as H_2A_2 in non-polar diluent of sulfonated kerosene due to the role of the intermolecular hydrogen bond, [32] and the chemical structure of D2EHPA is shown in Fig. 1. Solvent extraction studies on rare earths by D2EHPA suggested that the extraction of Ce(IV) from aqueous acid medium with D2EHPA via a cation-exchange mechanism.[33] The FTIR spectra of D2EHPA complex with Ce(IV) are presented in Fig.2. The adsorption peaks at 2316cm^{-1}, 1685cm^{-1}, 1233 cm^{-1} and 1035cm^{-1} are due to the stretching modes of P-OH bonds, the dimeric peak of hydrogen bonds, the P=O bonds and the stretching modes of P-O-C bonds, respectively.[34] The band at 2316cm^{-1} nearly disappears after extraction, proving the extraction mechanism involving cation-exchange that Ce(IV) replaces the hydrogen atom in P-OH bonds. The band at 1685 cm^{-1} also disappears, indicating that the intermolecular hydrogen bonds in D2EHPA are eliminated. The shift of P=O stretching vibration from 1233 cm^{-1} to about 1283 cm^{-1} in the Ce(IV) loaded D2EHPA reveals strong interaction between Ce(IV) and P=O. The peak at 1035 cm^{-1} has no obvious variation indicating that there is no chemical bond between Ce(IV) and P-O-C. The extraction reaction between Ce(IV) and D2EHPA in ELM system is the same as solvent extraction. According to the results, the saturated extraction mechanism of Ce(IV) by ELM using D2EHPA as carrier in sulfuric acid medium(pH<1) can be expected as Eq.(2) .[3]

$$nCe(IV)_{(a)} + 2nH_2A_{2\,(o)} \leftrightarrows (CeA_4)_{n(o)} + 4nH(I)_{(a)} \qquad (2)$$
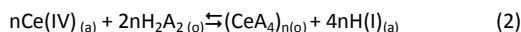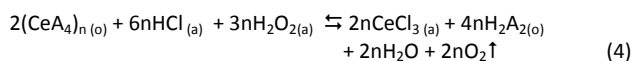
where the subscripts '(a)' and '(o)' represent species present in the aqueous and the organic phases, respectively. Because of the strong stability of extracted complex, it is hard to reverse extract Ce(IV) directly.

It is known that the hydrogen peroxide can be used as an oxidant, and also can be used as reductant. The standard electrode potentials in hydrochloric acid condition are as follows: [35,36]

Ce(IV) + e $\leftrightarrows$ Ce(III) $E^0_{(Ce(IV)/\,Ce(III))} = 1.28V$

$O_2 + 2H(I) + 2e \leftrightarrows H_2O_2$ $E^0_{(O2/H2O2)} = 0.693V$

$E^0 = \quad E^0_{(Ce(IV)/\quad Ce(III))} \quad -E^0_{(O2/H2O2)}=1.28-0.693=0.587>0$
(3)

From Eq.(3), the oxidizing ability of Ce(IV) in acid solution is stronger than hydrogen peroxide, so the Ce(IV) can oxidize hydrogen peroxide. It can be concluded that using hydrogen peroxide as reductant to reduce Ce(IV) is feasible in thermodynamics, and will not bring any impurity ions to the solution. Therefore, the internal aqueous phase is hydrochloric acid containing a certain amount of hydrogen peroxide. The hydrogen peroxide can reduce Ce(IV) to Ce(III) firstly, then the Ce(III) can be stripped with hydrochloric acid as the following equilibrium shown in Eq.(4).

$$2(CeA_4)_{n\,(o)} + 6nHCl_{(a)} + 3nH_2O_{2(a)} \leftrightarrows 2nCeCl_{3\,(a)} + 4nH_2A_{2(o)} + 2nH_2O + 2nO_2\uparrow \qquad (4)$$

It is concluded that both the equilibrium reactions take place in ELM system can be described as Fig.3:
(a) Transport of Ce(IV) ion from the bulk of the external phase to the interface1 with D2EHPA based membrane.
(b) Formation of the extracted complex at the external phase–liquid membrane interface.
(c) Diffusion of the extracted complex from the membrane phase to interface2.
(d) Stripping of the metal ion from the extracted complex by the internal phase stripping solution (HCl-H_2O_2) and enrichment of the Ce(III) ions in the internal phase droplets.

As discussed above, the extraction of Ce(IV) by ELM is a reverse transfer process that the Ce(IV) and H(I) transfer from high concentration region to low concentration region. The Ce(IV) transfers from external phase to internal phase, while the H(I) transfers from internal phase to external phase.
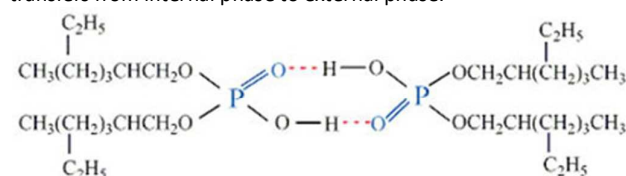

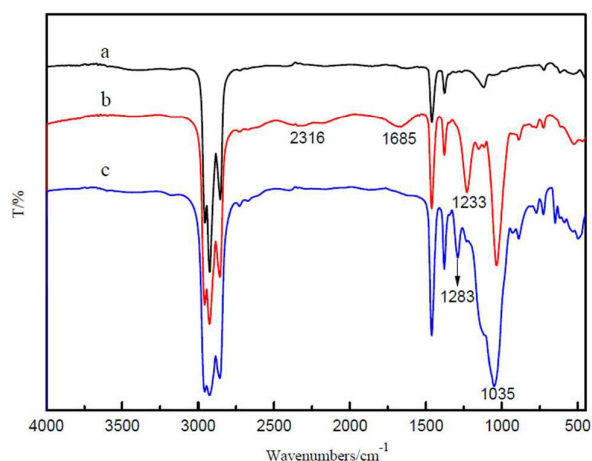Fig. 1. The chemical structure of D2EHPA in sulfonated kerosene.

Fig. 2. FTIR spectra of D2EHPA-Ce(IV)complex (a: sulfonated kerosene, b: sulfonated kerosene+12%D2EHPA (v/v) , c: sulfonated kerosene+12%D2EHPA (v/v)+Ce(IV)).
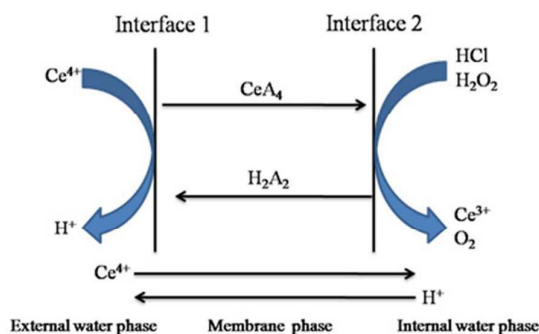
Fig. 3. Possible scheme for Ce(IV) extraction mechanism by ELM using D2EHPA as extractant.

3.2 Emulsion characterization

Liquid membranes were prepared by emulsifying an aqueous solution of strip phase (HCl-H$_2$O$_2$) with an organic phase (D2EHPA, Span80 and liquid paraffin in sulfonated kerosene) as discussed in Section 2. Studies carried out with varying emulsifier speed (1000–7000 rpm) indicates that the stable emulsion was obtained only when the emulsifier speed was higher than 2000 rpm. Therefore, an emulsifier speed of 5000 rpm was selected for the preparation of emulsion for all subsequent studies. The ELM was allowed to stand and kept under observation for any physical change to see the stability of ELM with respect to time. The photographs of the emulsion at different time are presented in Fig. 4. It is found that the ELM ia a milky emulsion, and is stable up to 2 h. The emulsion becoms unstable 6h later, and separates into two phases of organic phase and strip phase after 12h.

For further observation of emulsion, the typical photograph of the emulsion is presented in Fig.5. As shown, the clear and stable W$_1$/O type globules uniformly distribute in the emulsion, and the sauter mean diameter of globules is 47.26 μm. There are many droplets in the globules with the average diameter of 1.2 μm. The average thickness is estimated about 5 μm. Table 1 shows the

effects of different component of D2EHPA, Span 80 and liquid praffin on the viscosity . It shows that with the increase of various component, the viscosity of th emulsion increases. Based on these, the emulsion prepared can be applied for all subsequent experiments in the present study which included extraction of Ce(IV) under varying experimental conditions.

3.3 Effect of emulsion composition variables

3.3.1 Effect of D2EHPA concentration

As Eq. (2), the extraction of Ce(IV) is positively influenced by the concentration of D2EHPA. ELM extraction studies were carried out by preparing emulsions containing various D2EHPA concentrations in the range of 8%-16 % (v/v) and the results are presented in Fig. 6. The extraction efficiency is found to increase with the increase in the concentration of extractant from 8% to 16% (v/v). The viscosities of emulsions with various D2EHPA concentrations are shown in Table 1. It is also measured that the emulsion containing 8% D2EHPA has the globule size d_{32} =39.01 μm while the emulsion containing 16% D2EHPA has the globule size d_{32} =54.57 μm. Sengupta et al.[37] has found the similar tendency. Besides, the inner droplet size d_{32} is found as 1.20μm at 8% D2EHPA and 1.09μm at 16% D2EHPA with a slight decline.

Table 1 Viscosities at 10s^{-1}

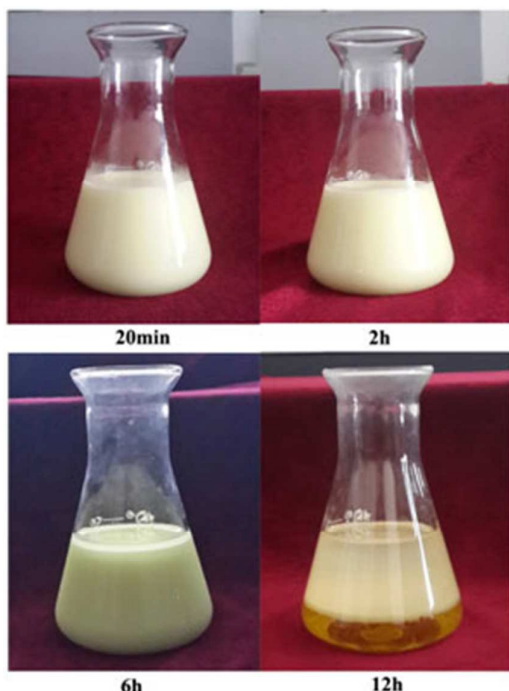| D2EHPA (%v/v)	Viscosity (cp)	Span 80 (%v/v)	Viscosity (cp)	liquid paraffin (%v/v)	Viscosity (cp)
8	20.40	1	12.00	0	24.00
10	23.70	2	24.60	2	28.50
12	24.60	3	33.10	3	29.70
14	27.90	4	45.32	4	31.32
16	31.20	8	86.70	6	33.90

mol/l; R_{oi}:1.5) .

Fig. 4. Photographs of emulsion at different time(experimental conditions: D2EHPA concentration 12% (v/v); Span 80 concentration : 2% (v/v); liquid paraffin concentration: 2% (v/v); hydrochloric acid concentration in internal phase: 5 mol/l; hydrogen peroxide concentration in internal phase:0.02
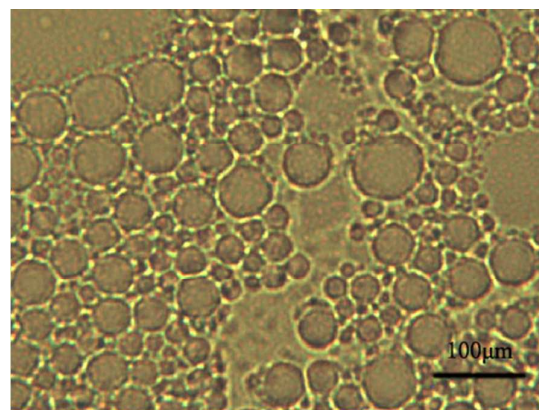

Fig. 5. Photograph of emulsion.

The higher concentration of carrier at the interface between external phase and emulsion promotes the transport of solute and the complex of Ce(IV) and D2EHPA. Increasing the amount of carrier to 12% (v/v), the extraction efficiency of Ce(IV) is over 95%. With further increase in the carrier concentration, the extraction efficiency shows no obvious change, which may be attributed to an increase in the viscosity leading to larger globules.[38] The literature shows that increase in emulsion viscosity with increasing carrier concentration will limit the extraction rate by affecting the

dispersion behaviour of the emulsion.[20] Chiha et al.[39] investigated that increasing the concentration of carrier leads to a decrease of the stability of the emulsion because the larger globules can aggregate quickly. Besides, the increase of the concentration of carrier will promote the permeation swelling, which diluted the stripping solution. Swelling effect is more serious when D2EHPA concentration is increased. [40] Higher concentration of carrier will also increase the cost. Therefore, the best value of the carrier concentration is found to be 12% (v/v).
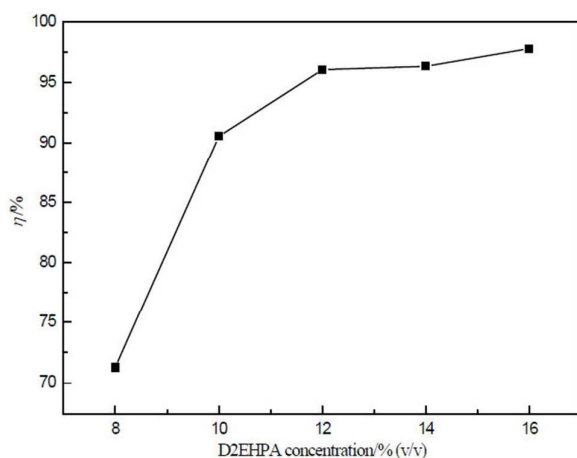

Fig. 6. Effect of D2EHPA concentration on the extraction of Ce(IV)(experimental conditions: Span 80 concentration : 2% (v/v); liquid paraffin concentration: 2% (v/v); hydrochloric acid concentration in internal phase: 5 mol/l; hydrogen peroxide concentration in internal phase:0.02 mol/l; R_{oi}:1.5; Ce(IV) concentration in external phase:0.01mol/l; acidity in external phase:0.5 mol/l; R_{we}:2; extraction time:15min; stirring speed:250rpm).

3.3.2 Effect of surfactant concentration

The effect of various Span 80 concentrations in the range of of 1%-8 %(v/v) was investigated as shown in Fig.7. It was observed that the extraction efficiency increases with the increase of surfactant concentration up to 3% (v/v) and decreases thereafter. The surfactant is expected to play a role as an emulsifier for the liquid membrane and act as a protective barrier between the external phase and the internal phase, preventing the leakage of

emulsion.[38] At lower surfactant concentrations (less than 2%), emulsion breaks easily and the extraction efficiency is poor, which is because the coverage of membrane interface is incomplete at low surfactant concentration. The increase of surfactant concentration lowers the membrane's surface tension and yields smaller globules, leading to a higher contact area.[41,42] At higher surfactant concentration (beyond 3%), the membrane stability increases, while the extraction efficiency decreases. This can be attributed to that the increase of the emulsion viscosity resulting from the increasing surfactant concentration as shown in Table 1 leads to the augmentation of mass transfer resistance due to presence of excessive surfactant at aqueous–organic phase interface,[16,43] resulting in less transfer of Ce(IV) molecules to internal phase. Similar phenomenon was observed previously.[39] Therefore, Span 80 concentration ranging from 2%-3%(v/v) was found to be optimum value with the extraction efficiency greater than 96%.
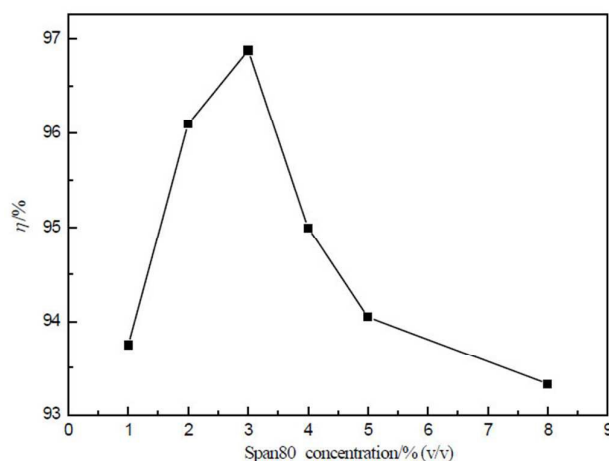

Fig. 7. Effect of Span80 concentration on the extraction of Ce(IV)(experimental conditions: D2EHPA concentration 12%(v/v); liquid paraffin concentration: 2% (v/v); hydrochloric acid concentration in internal phase: 5mol/l; hydrogen peroxide concentration in internal phase:0.02mol/l; R_{oi}:1.5; Ce(IV) concentration in external phase:0.01 mol/l; acidity in external phase:0.5 mol/l; R_{we}:2; extraction time:15 min; stirring speed:250 rpm).
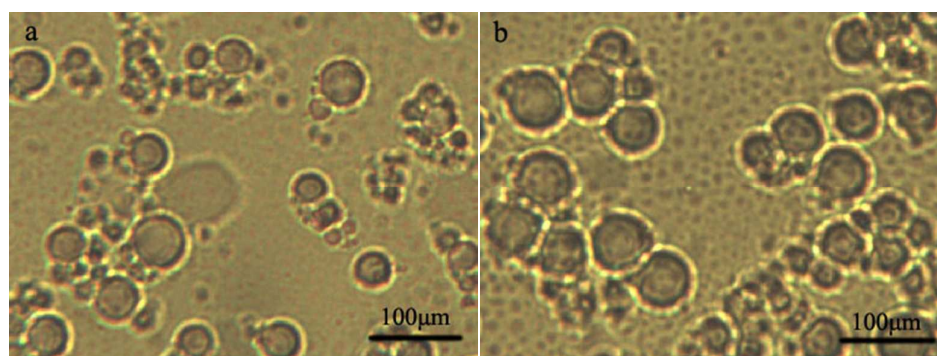

Fig. 8. Photographs of emulsions at different liquid paraffins: (a) 2% (v/v) and (b) 6% (v/v).

3.3.3 Effect of liquid paraffin concentration

The liquid paraffin was added as a membrane intensifier for the liquid membrane and it promoted the mechanical strength and stability of membrane. The photographs of emulsions at different

liquid paraffins are given in Fig.8. As shown, the higher liquid paraffin concentration corresponds to the thicker membrane of the globule. When the content of membrane intensifier is too low, the liquid membrane is very thin, resulting in the poor stability; when

the content is excessively high, the thickness of the membrane increases leading to the increase of diffusion and mass transfer resistance, resulting in the lower mass transfer velocity and extraction efficiency.

The effect of the liquid paraffin concentration on the extraction of Ce(IV) by ELM is shown in Fig.9. It is found that the extraction efficiency higher than 96% is obtained in the range of 2%-4% (v/v), of which is considered to be the optimum concentration.
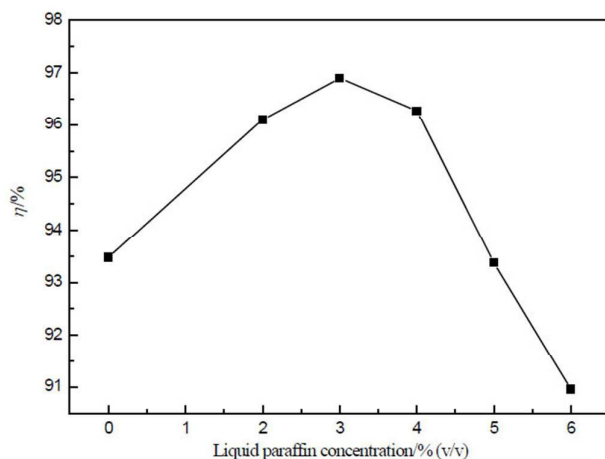

Fig. 9. Effect of liquid paraffin concentration on the extraction of Ce(IV) (experimental conditions: D2EHPA concentration 12% (v/v); Span 80 concentration : 2% (v/v); hydrochloric acid concentration in internal phase: 5 mol/l; hydrogen peroxide concentration in internal phase:0.02mol/l; R_{oi}: 1.5; Ce(IV) concentration in external phase:0.01 mol/l; acidity in external phase: 0.5 mol/l; R_{we}: 2; extraction time: 15 min; stirring speed:250 rpm).

3.3.4 Effect of hydrochloric acid concentration in the internal phase

The most commonly used stripping agent for reverse extraction of rare earth is acid, such as sulfuric acid, nitric acid and hydrochloric acid. The sulfuric acid and nitric acid have certain causticity and oxidizability at high concentration, which will damage the stability of liquid membrane and bring more difficulty to reduce Ce(IV). Therefore, the hydrochloric acid was used as perfect stripping acid solution. The capacity to trap and concentrate the solute in the stripping solution is determined by the concentration of acid solution in the internal phase. The effect of hydrochloric acid concentration of the internal phase on Ce(IV) extraction by ELM is shown in Fig.10. It is observed that the yield of Ce(IV) extraction increases with the increase of hydrochloric acid concentration, reaching 97% at 4-5 mol/l. This can be attributed to that higher hydrochloric acid concentration will lead to more dissociation of Ce-D2EHPA complex at the interface between the membrane and the stripping phase. Consequently, the driving force for transport of the Ce-D2EHPA complex is larger owing to the larger difference in Ce-D2EHPA complex concentration across the membrane. Thereafter, the extraction efficiency drops with further increase of acid concentration. This possibly because that higher acid concentration will damage the membrane, leading to the leaching of internal phase. Consequently, the concentration of hydrochloric acid in the stripping solution was 4-5 mol/l for effective extraction of Ce(IV).
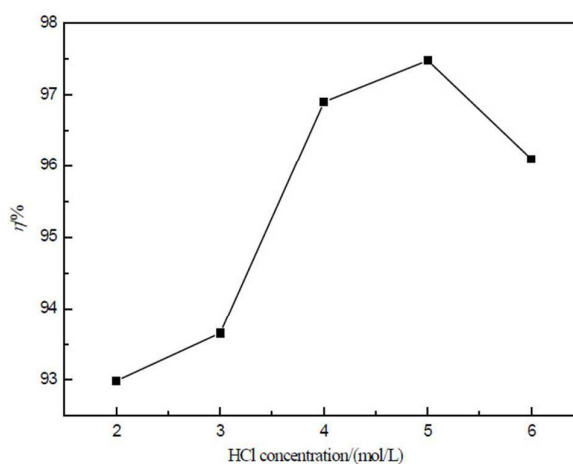

Fig. 10. Effect of HCl concentration in the internal phase on the extraction of Ce(IV) (experimental conditions: D2EHPA concentration 12%(v/v); Span 80 concentration : 2% (v/v); liquid paraffin concentration: 2% (v/v); hydrogen peroxide concentration in internal phase:0.02mol/l; R_{oi}:1.5; Ce(IV) concentration in external phase:0.01mol/l; acidity in external phase:0.5 mol/l; R_{we}:2; extraction time:15min; stirring speed:250rpm).

3.3.5 Effect of hydrogen peroxide concentration

Because it is difficult to strip Ce(IV) directly with hydrochloric acid, the hydrogen peroxide is important in the stripping process. The effect of hydrogen peroxide concentration on Ce(IV) extraction was studied. The obtained results are presented in Fig.11.
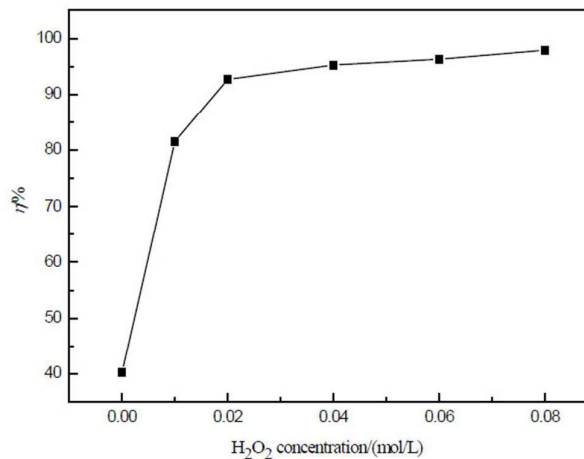

Fig. 11. Effect of H_2O_2 concentration in the internal phase on the extraction of Ce(IV) (experimental conditions: D2EHPA concentration 12% (v/v); Span 80 concentration: 2% (v/v); liquid paraffin concentration: 2% (v/v); hydrochloric acid concentration in internal phase: 5 mol/l; R_{oi}:1.5;Ce(IV) concentration in external phase:0.01mol/l; acidity in external phase: 0.5 mol/l; R_{we}: 2; extraction time:15 min; stirring speed: 250 rpm).

It can be seen that the extraction efficiency is extremely low in the absence of the hydrogen peroxide in stripping solution, and increase with the increase in the concentration of hydrogen peroxide. With the hydrogen peroxide concentration higher than 0.02mol/l, the extraction efficiency increases slowly. The addition amount of hydrogen peroxide should be controlled reasonably. When the amount added is too little, Ce(IV) can't be reduced and stripped completely, and is accumulated in organic phase, resulting in the decrease of extracting ability. However, excess amount of

hydrogen peroxide will lead to the entrainment of redundant hydrogen peroxide in organic phase and affect the extraction efficiency afterward. So the hydrogen peroxide concentration of 0.02 mol/l is selected to be the most appropriate value.

3.3.6 Effect of volume ratio of membrane phase to internal phase (R_{oi})

Volume ratio of membrane phase to internal phase (R_{oi}) plays an important role in determining the effectiveness of ELM system. The effect of R_{oi} on the extraction of Ce(IV) by ELM was investigated, and the obtained results are shown in Fig.12. At low R_{oi}, the volume of membrane solution is not enough for enclosing all the stripping solution,[44] leading to the low extraction efficiency. With increase of R_{oi} from 0.5 to 1.5, the transport rate and extraction efficiency of Ce(IV) increases. This can be attributed to the fact that an increase in the membrane phase volume fraction increases the thickness of the membrane phase resulting in enhanced mass transfer.[38] The extraction of Ce(IV) reaches 96% at R_{oi} of 1.5. Beyond the R_{oi} of 1.5, further increase in R_{oi} decreases both the rate and efficiency of extraction. This may be due to that at high R_{oi}, membrane thickness and viscosity of the emulsion phase is high due to the relatively high organic content. In addition, high R_{oi} also means less stripping agents are available for solute stripping. Thus, the R_{oi} of 1.5 is selected as the best volume ratio.
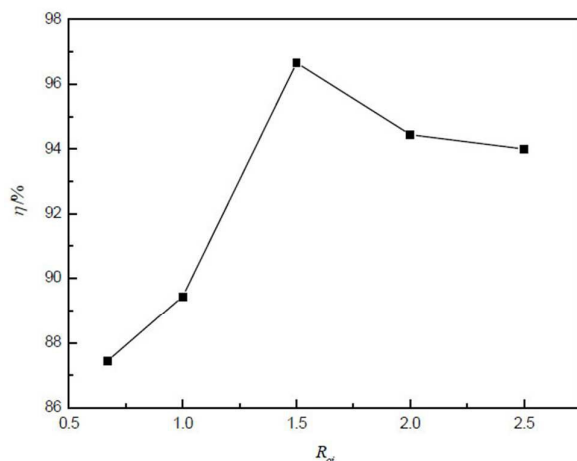

Fig. 12. Effect of volume ratio of membrane phase to internal phase(R_{oi}) on the extraction of Ce(IV) (experimental conditions: D2EHPA concentration 12% (v/v); Span 80 concentration: 2% (v/v); liquid paraffin concentration: 2% (v/v); hydrochloric acid concentration in internal phase: 5 mol/l; hydrogen peroxide concentration in internal phase: 0.02 mol/l; Ce(IV) concentration in external phase:0.01 mol/l; acidity in external phase:0.5 mol/l; R_{we}:2; extraction time: 15 min; stirring speed: 250 rpm).

3.4 Effect of extraction process variables
3.4.1 Effect of acidity in external phase

The acidity in the external phase determines the existing form of cerium element, and also affects the migration and extraction efficiency of Ce(IV). In order to explore the significant role being played by acidity in the external phase during the transport of Ce(IV) in ELM system, the studies were performed with various sulfuric acid concentrations in the acidity range of 0.2–1 mol/l and the obtained results are shown in Fig.13. It can be seen from this figure that the extraction efficiency is strongly dependent on the acidity in the external phase solution. The transport of Ce(IV) from external phase to internal phase is mainly driven by the difference in H^{+} concentration between the external and the internal phases.

Theoretically, the greater it is for the H^{+} concentration difference between the external phase and the internal phase, the easier the extraction.[3] However, the extraction efficiency is extremely low at lower acidity, which can be attributed to that the Ce(IV) is easy to reduce and hydrolyze in lower acidity leading to the loss of Ce(IV). Afterward, the Ce(IV) extraction efficiency decreases with the increase of acidity from 0.35 to 1 mol/l. Maximum extraction is achieved at acidity around 0.4 mol/l. At higher acidity in the external phase, the properties of the surfactant are reduced,[45] which leads to a destabilization of the emulsion and a diminution in the extraction efficiency. Thus, acidity in external phase between 0.4-0.5mol/l is chosen as the best range.
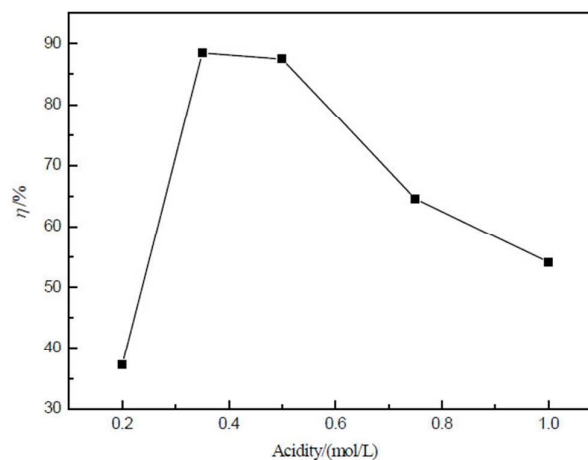

Fig. 13. Effect of acidity in external phase on the extraction of Ce(IV) (experimental conditions: D2EHPA concentration 12% (v/v); Span 80 concentration: 2% (v/v); liquid paraffin concentration: 2% (v/v); hydrochloric acid concentration in internal phase: 5mol/l; hydrogen peroxide concentration in internal phase:0.02mol/l; Ce(IV) concentration in external phase:0.01 mol/l; R_{oi}:1.5; R_{we}:3; extraction time:15 min; stirring speed: 250 rpm).

3.4.2 Effect of volume ratio of external phase to membrane phase (R_{we})

The volume ratio of the external phase to membrane phase (R_{we}) controls interfacial mass transfer and plays an important role in determining the efficiency of ELM. The effect of the R_{we} on Ce(IV) extraction efficiency was studied and the results are shown in Fig.14. The figure shows that the extraction efficiency decreases gradually in the range of R_{we} from 1.5 to 6 and reaches 96% at R_{we} lower than 2. The change of Ce(IV) concentration (C_{Ce}) in the external phase with time can be expressed as follows:[46,47]

$$-V_F \frac{dC_{Ce}}{dt} = AJ_{Ce} \tag{5}$$

$$-\frac{dC_{Ce}}{dt} = (V_E/V_F)(6/d)J_{Ce} = (1/R_{we})(6/d)J_{Ce} \tag{6}$$

where V_F is the volume of feed phase, V_E is the total volume of emulsion droplets, A is the total surface area of emulsion droplets and d is their average diameter. Taking account of area $A=V_E(6/d)$, and J_{Ce} is the transfer rate of Ce(IV) per unit surface area of emulsion droplets.

It is evident from Eq. (6) that the Ce(IV) extraction efficiency is affected by the volume ratio of external phase to membrane phase and by emulsion droplet diameter.[46] The increase of R_{we}

corresponds to the decrease of the amount of emulsion in the external phase, leading to the decrease in amount of available globules and interfacial surface area per unit volume of external phase and weakening the transfer efficiency of Ce(IV). Considering the cost, the volume ratio of external phase to membrane phase (R_{we}) of 2 is selected as the best treatment ratio.
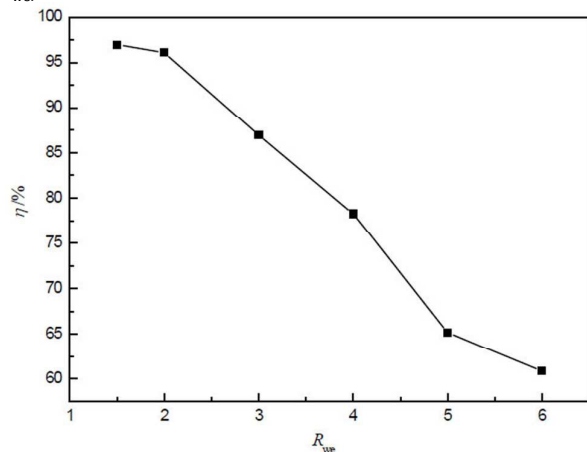

Fig. 14. Effect of volume ratio of external phase to membrane phase (R_{we}) on the extraction of Ce(IV) (experimental conditions: D2EHPA concentration 12% (v/v); Span 80 concentration: 2% (v/v); liquid paraffin concentration: 2% (v/v); hydrochloric acid concentration in internal phase: 5 mol/l; hydrogen peroxide concentration in internal phase:0.02 mol/l; Ce(IV) concentration in external phase:0.01 mol/l; R_{oi}:1.5; acidity in external phase: 0.5 mol/l; extraction time:15 min; stirring speed: 250 rpm).

3.4.3 Effect of extraction time

The effect of extraction time (5–25 min) on the extraction efficiency has been studied as shown in Fig.15. It shows that when the extraction efficiency increases by increasing the extraction time from 5 to 15 min, the Ce(IV) extraction increases from 86 to 97%, then when the extraction time increases from 15 to 25 min, the extraction of Ce(IV) has a little decrease. This may because that some membrane droplets begin to break for a long period of stirring. Therefore, the extraction time of 15 min is selected.
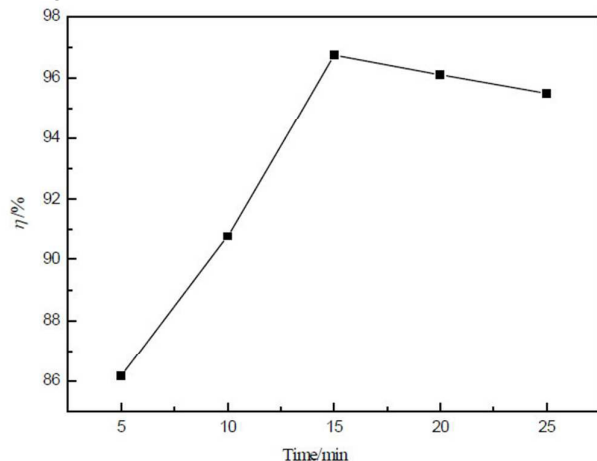

Fig. 15. Effect of extraction time on the extraction of Ce(IV) (experimental conditions: D2EHPA concentration 12% (v/v); Span 80 concentration : 2% (v/v); liquid paraffin concentration: 2% (v/v); hydrochloric acid concentration in internal phase: 5 mol/l; hydrogen peroxide concentration in internal phase:0.02 mol/l; Ce(IV) concentration in external phase:0.01 mol/l; R_{oi}:1.5; R_{we}:2; acidity in external phase: 0.5 mol/l; stirring speed: 250 rpm).

3.4.4 Effect of stirring speed

The stirring speed is a key factor in the rate of mass transfer through ELM.[38] In order to investigate the effect of the stirring speed on extraction, the external solution and emulsion were mixed at stirring speeds ranging from 100 to 350 rpm. The obtained results are shown in Fig.16. It is observed that increasing the stirring speed from 100 to 250 rpm increases the efficiency of extraction. This may be due to that the bigger globules may disintegrate to form smaller globules with the increase in stirring speed, thereby resulting in an increase in interfacial area and the mass transfer coefficient.[48] However, further increase in the stirring speed from 250 to 350 rpm results in a decrease in the extent of extraction. This is attributed to that the higher stirring speed affects the stability of the emulsion and makes the emulsion unstable. In addition, an increase in shear on the emulsion phase induces breakage of fragile emulsion droplets near the tip of the impeller.[49] Thus, there is a trade-off between decrease in external mass transfer resistance and stability of emulsion. 250 rpm is recommended as the most appropriate stirring speed.
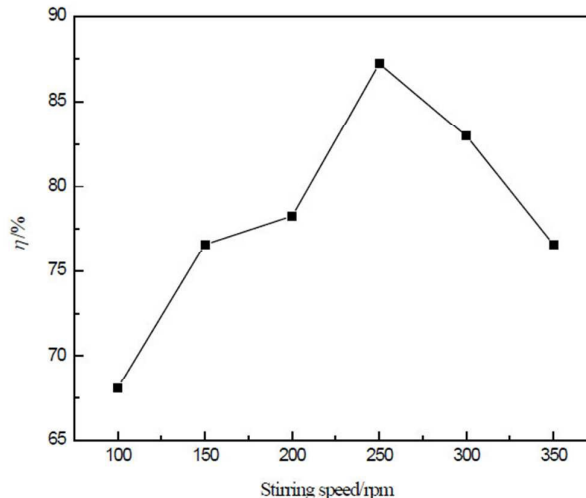

Fig. 16. Effect of stirring speed on the extraction of Ce(IV) (experimental conditions: D2EHPA concentration 12% (v/v); Span 80 concentration: 2% (v/v); liquid paraffin concentration: 2% (v/v); hydrochloric acid concentration in internal phase: 5 mol/l; hydrogen peroxide concentration in internal phase:0.02 mol/l; Ce(IV) concentration in external phase:0.01 mol/l; R_{oi}:1.5; R_{we}:4; acidity in external phase:0.5 mol/l; extraction time: 15 min).

3.5 The separation of Ce(IV)/RE(III)

The parameters that affect the extraction extent of ELM process were experimentally investigated. The optimum conditions for Ce(IV) extraction can be summarized as the D2EHPA concentration 12% (v/v), Span80 concentration 2%-3% (v/v), liquid paraffin concentration 2%-4% (v/v), hydrochloric acid concentration in the internal phase 4-5 mol/l, hydrogen peroxide concentration 0.02 mol/l, volume ratio of membrane phase to internal phase (R_{oi}) 1.5, acidity in external phase 0.4-0.5mol/l, volume ratio of external phase to membrane phase (R_{we}) 2, extraction time 15min and stirring speed 250 rpm. Under experimentally determined conditions, the extraction of Ce(IV) was conducted and the obtained extraction efficiency of Ce(IV) is over 98%.

It is known that the RE(III) such as La(III), Pr(III), Nd(III) and Sm(III) is often accompanied with Ce(IV) in solution. Under the optimum experimental determined conditions, the separation of Ce(IV) from

other RE(III) were investigated.

The separation factor $\beta_{Ce/RE}$ is calculated as follows:

$$\beta_{Ce/RE} = \frac{(C_{Ce}/C_{RE})_{strip}}{(C_{Ce}/C_{RE})_{feed,o}} = \frac{\eta_{Ce}}{\eta_{RE}} \tag{7}$$

where C_{Ce} and C_{RE} are the concentrations of Ce(IV) and RE(III) in the stripping and initial feed phases, mol/l. The extraction of Ce(IV) and RE(III) are given in Table 2. Clearly, the system in extremely selective for Ce(IV), and the separation factors are relatively high.

Table 2 Separation factors of Ce(IV) over RE(III) for various feed mixtures in the optimum conditions.

Initial concentration in the feed solution(mol/l)	Extraction efficiency (%)		$\beta_{Ce/RE}$
	Ce(IV)	RE(III)	
Ce 0.01+La 0.01	98.25	0.56	175.45
Ce 0.01+Pr 0.01	97.78	0.89	109.87
Ce 0.01+Nd 0.01	98.54	0.75	131.39
Ce 0.01+Sm 0.01	98.80	0.45	219.56

Presently, many such membrane separations for metals have been reported. Table 3 shows some previous studies on metals separation using different emulsion compositions. As shown, Span 80 and kerosene are most widely used for surfactant and diluents. The use of extractant and internal phase depend on the kinds of metals to be extracted. For rare earth metals, sulfuric acid is most used as an internal phase.

3.6 Demulsification

The Ce(IV) loaded emulsion obtained after extraction and separation is required to be demulsified in order to recover the metal ion and quantify the extraction experiments.

The stripping efficiency is calculated by Eq.(8):

$$Stripping efficiency(\%) = \frac{C_{in}V_{in}}{(C_{exo}V_{exo} - C_{ex}V_{ex})} \times 100 \tag{8}$$

where C_{in} is the final concentration of Ce(IV) in the internal phase, mol/l; C_{exo} is the initial concentration of Ce(IV) in the external phase, mol/l; C_{ex} is the final concentration of Ce(IV) in the external phase, mol/l; V_{in} is the final volume of the internal phase, ml; V_{exo} is the initial volume of the external phase, ml; V_{ex} is the final volume of the external phase, ml.

For the experiment, five tests have been carried out. The results are illustrated in Fig. 17. The satisfactory mass balance is obtained and the loss between the external phase and the recovery from the internal phase is within 3%.
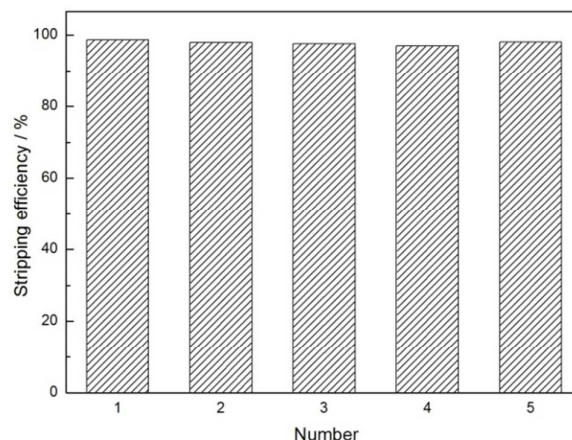

Fig. 17. The stripping efficiency after demulsification (experimental conditions: optimum conditions).

Table 3 Compositions and conditions of ELM on metals extraction and separation.

Solute	Surfactant	Extractant	Internal phase	Diluent	Reference
Nickel and cobalt	ECA 4360J	8-HQ	EDTA	Kerosene	6
Chromium,cobalt,nickel, copper and zinc	Span 80	TBP	$(NH_4)_2CO_3$	Kerosene	48
Cadmium,zinc, cobalt and nickel	Span 80	Triotylamine	NH_3 Na_2CO_3 $(NH_4)_2CO_3$ CH_3COONH_4	Kerosene	16
Rare earth metals	$2C_{18}\Delta^9GE$	$^tOct[4]CH_2COOH$	H_2SO_4	Toluene	50
Rare earth metals	Span 80, $2C_{18}\Delta^9GEC_2QA$	PC88A	H_2SO_4	n-Heptane	51
Rare earth metals	$2C_{18}\Delta^9GE$ $2C_{18}\Delta^9GEC_2QA$	PC88A	H_2SO_4	n-Heptane	52
Rare earth metals	$2C_{18}\Delta^9GE$	$^tOct[1]CH_2COOH$ $^tOct[4]CH_2COOH$ $^tOct[6]CH_2COOH$	H_2SO_4	Toluene	53
Lead, cadmium	ECA5025	D2EHPA	HCl, H_2SO_4	Tetradecane	54
Zinc,copper	Span80	D2EHPA	H_2SO_4	Iso-dodecane	55
Cobalt, nickel	Span80	TOPO	NH_3	Kerosene	56
Cobalt, nickel	ECA4360J	Alamine300	NH_4OH	Kerosene	57
Platinum, Palladium	Span80 PX100	TLA,TOMAC,TBP,TOPO,TIBPS	HCl	n-Heptane	58
Trace elements: Cd,Co,Cu,Fe,Mn,Ni,Pb,Zn	Span80	D2EHPA,PC88A	HCl+ H_2SO_4	Kerosene	59

4 Conclusions

In this study, the extraction of Ce(IV) from sulfuric acid solution by emulsion liquid membrane comprising of D2EHPA dissolved in sulfonated kerosene as carrier containing Span80 as the emulsifier

was investigated. The hydrochloric acid containing hydrogen peroxide was used as stripping solution. The obtained results can be concluded as follows:

1. The stable W_1/O type liquid membranes were prepared at an emulsifier speed of 5000 rpm for 20 min, and could be applied for all subsequent experiments

2. The optimum conditions for Ce(IV) extraction can be summarized as the D2EHPA concentration 12% (v/v), Span 80 concentration 2%-3% (v/v), liquid paraffin concentration 2%-4% (v/v), hydrochloric acid concentration in the internal phase 4-5 mol/l, hydrogen peroxide concentration 0.02 mol/l, volume ratio of membrane phase to internal phase (R_{oi}) 1.5, acidity in external phase 0.4-0.5 mol/l, volume ratio of external phase to membrane phase (R_{we}) 2, extraction time 15 min and stirring speed 250 rpm. The results demonstrate that the D2EHPA concentration, hydrogen peroxide concentration, acidity in external phase, R_{we} and stirring speed play a vital role amongst the parameters studied.

3. Under the optimum operating parameters, extraction efficiency of Ce(IV) is over 98%. The separation of Ce(IV) from RE(III) is realized showing that the system is extremely selective for Ce(IV).

4. The results obtained show the validity of the ELM method and represent an interesting advanced process for the extraction of Ce(IV) from sulfuric acid solution.

Acknowledgements

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