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## Modeling of Ce(IV) transport through a dispersion supported liquid membrane including P204 as the carrier

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### ABSTRACT

This paper presents a mathematical model for the transport of Ce(IV) from sulfate solutions through dispersion supported liquid membranes which contain 2-ethyl hexyl phosphoric acid-mono-2-ethyl hexyl ester (P204) as the carrier, dissolved in kerosene as the membrane solution. This process of facilitated transport, based on membrane technology, is a variation on the conventional technique of solvent extraction and may be described mathematically using Fick's second law. The equations for transport velocity are derived considering the diffusion of P204 and its metallic complexes through the liquid membrane. In this work, the system is considered to be in a transient state, and chemical reaction between Ce(IV) and the carrier takes place only at the solvent-aqueous interfaces. Modeling of concentration profiles is obtained for the Ce(IV) from which extraction velocities are predicted. The experimental and simulated Ce(IV) extractions showed similar tendencies for a high Ce(IV) concentration and acidity case. The model results indicate that the initial high concentration of Ce(IV) and acidity have detrimental effects on Ce(IV) extraction and stripping.

**Keywords:** Dispersion supported liquid membrane; Dispersion phase; Feed phase; P204; Cerium(IV)

### 1. Introduction

Industrial effluents containing highly toxic and nonbiodegradable heavy metal ions are generated in hydrometallurgy, electroplating, and electrochemical industry. For the purpose of environmental conservation and resources recycling, the removal and recovery of these heavy metals have become increasingly stringent [1–3]. Recently, people pay attention to rare earth metal which is applied in more and more technologies of 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 [1,2], reverse osmosis [4], adsorption [5], ion exchange [6], and solvent extraction [7,8] have been developed for these purposes but encounter various difficulties [1–3]. More efficient, low-cost removal and recovery methods are needed to overcome these difficulties.

Recently, many attentions have been paid to the liquid membrane (LM) techniques 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 transport effect, where solute can move from

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low-to-high concentration solution [9–12]. The main types of LM systems include emulsion liquid membrane (ELM) [13], supported liquid membrane (SLM) [11,12,14], bulk liquid membrane (BLM), flowing liquid membrane [15], electrostatic pseudo liquid membrane [10], supported emulsion liquid membrane (SELM) [16,17], hollow fiber contained liquid membrane (HFCLM) [18], supported liquid membrane with stripping dispersion (SLM-SD) [19,20], etc. The potential advantages of LM techniques over traditional separation techniques and solid membranes techniques are low capital and operating costs, low energy and extractant consumption, and high concentration factors and high fluxes. However, LM techniques have not been adopted for large-scale industrial processes [9,11,12,21–27], primarily due to the lack of long-term stability, hard to operate the emulsification and de-emulsification steps in ELM and SELM processes, and larger membrane resistance in BLM and HFCLM processes, etc. [28].

In order to overcome these above difficulties in the conventional LM systems, a new liquid membrane technique, namely dispersion supported liquid membrane (DSLM) [29], was proposed. 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 transport process, and most of other liquid membrane systems [12]. This is a new type of LM process with several advantages such as increased stability of the membrane, reduced costs, increased simplicity of operation, extremely efficient stripping of the target species from the organic phase by obtaining a high flux, and a higher concentration of the recovered target species in the stripping solution.

These advantages are very attractive; nevertheless, more studies are needed for the application of DSLM in industry. Otherwise, scaling-up for the new liquid membrane configuration will fail unless there is a complete understanding of the efficiency parameters, which is 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 behavior of transport of single cation and a new permeability coefficient equation should be studied because the diversity of transport behavior of ions is objectively present in the two systems of traditional SLM and DSLM.

Ce(IV) is a typical rare earth element. This metal can be used as glass additive, exhaust gas purifying catalyst, many sensitive materials, and so on. A few of research about transport of Ce(IV) by LM has been done during the last decade [30–35], and its separation from others elements is an interesting challenger; from

this we propose to study the Ce(IV) permeation through a novel liquid membrane system.

Mathematical modeling of the transport phenomena for the DSLM is equally important for the interpretation of laboratory results and to design and scale-up of the processes. Li et al. [36] presented a very simple model, where the extraction velocity is considered to be proportional to the concentration difference between the extraction and stripping phases. Later on Hochhauser and Cussler [37], Martin and Davies [38], Volk et al. [39] and Gladek et al. [40] adopted similar mathematical considerations. Their steady-state approach is, however, only valid when the extraction is far from equilibrium.

On the other hand, researchers in the area of DSLM have presented analytical solutions for the determination of the facilitation factor. Facilitated transport is a process by which a nonvolatile carrier facilitates or increases the transport of a solute across a liquid film and the facilitation factor may be defined as the ratio between the total flux of solute with facilitation and the total flux without it. In this direction, Smith [41] considered the uncomplexed carrier concentration to be constant within the liquid film, which is equivalent to having a large amount of the carrier in the organic phase relative to the amount of solute to be extracted. The differential equations that describe this process in steady state are linear and easy to solve. Their solution was first introduced by Donaldson [42] in 1984. Kreuzer [43] arrived at the same expression through a dimensional analysis whose solution was a function of the chemical reaction and the carrier concentration. Noble [44] and Elkamel et al. [45] derived another expression for the factor. However, this differs from each other by considering the mass transfer resistance. In the case of metal ion extraction, a facilitation factor is insignificant since the metal is insoluble and therefore cannot flow through the organic liquid membrane without forming a complex with the carrier.

The present work proposes a dynamic mathematical model that describes the transport of Ce(IV) through a LM composed of 2-ethyl hexyl phosphoric acid-mono-2-ethyl hexyl ester (P204) in kerosene. The Ce (IV)-(P204) reaction takes place only at the organic-aqueous interfaces and homogeneous equilibria are assumed in each of the three phases involved.

## 2. DSLM experimental procedure

The measurements of transport percentage for the DSLM were performed as follows: the experiments were accomplished with a simple diffusion cell. The

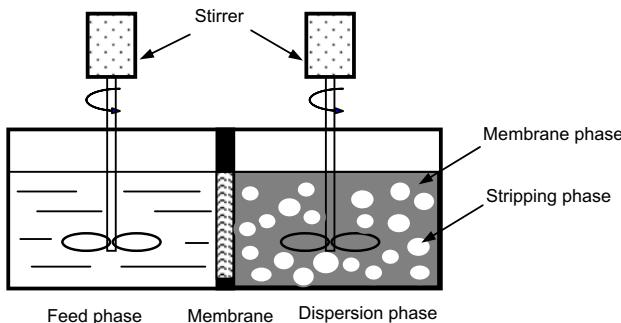


Fig. 1. Experimental installation of DSLM process.

diffusion cell consisted of two-compartment perspex half-cells. Two half-cells were separated by the membrane. The membrane was impregnated with P204 dissolved in kerosene and clamped between the two half-cells. The effective volume of each one is 140 ml. A polyvinylidene fluoride membrane was used as a solid support. It had a 65  $\mu\text{m}$  thick film with a nominal porosity of 75% and a tortuosity of 1.67. The effective area of support is 12  $\text{cm}^2$ . The feed phase (120 ml) consisted of  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ , and HCl solution, and was poured into a half-cell. All the reagents used in the present work were of analytical grade. The mixed dispersion phase consisted of the different volume ratios of the membrane solution containing the carrier P204; and HCl stripping solution was placed into another half-cell. Samples of the feed phase were taken at timed intervals. The stirring of dispersion phase was allowed to stand until phase separation occurred. Then the sample from the dispersion phase was collected at timed intervals. The stirring of dispersion phase was allowed to stand until phase transport occurred. Then the Ce(IV) sample from the dispersion phase was collected. Samples containing Ce(IV) in the feed phase only were analyzed for ion concentration with a UV-1200 spectrophotometer using Arsenazo III as the chromogenic agent (under the detection wave lengths: 531 nm). Fig. 1 shows the experimental setup of the DSLM process.

### 3. Transport velocity model

Figs. 2 and 3 show 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:

(a) Ce(IV) diffuses from the feed phase to the interface A.

(b) On the feed side interface of the DSLM, the extraction of Ce(IV) from feed solution with carrier P204 (can be as  $(\text{HR})_2$ ) in kerosene can be expressed as [46,47]:

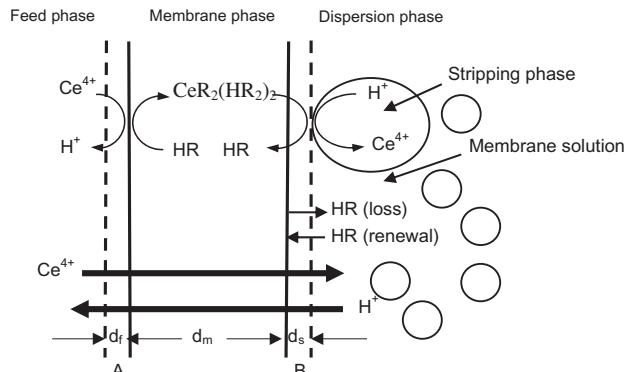


Fig. 2. Diagram of Ce(IV) transport through the dispersion supported liquid membrane. HR represents the carrier(P204) within the membrane,  $\text{CeR}_2(\text{HR}_2)_2$  represents the organometallic compound,  $\text{H}^+$  is the hydrogen ion and  $\text{Ce}^{4+}$ , the uncomplexed Ce(IV) (A and B are the boundaries of the membrane phase).

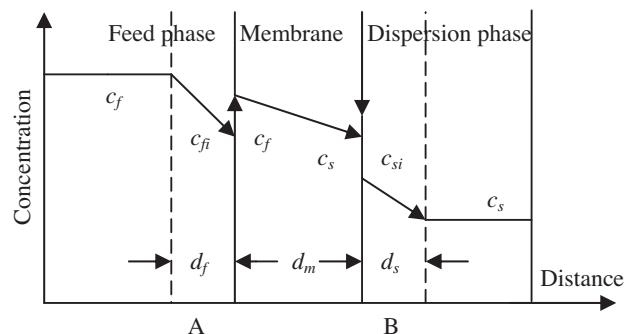
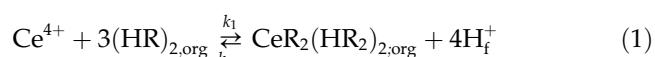


Fig. 3. Principle of DSLM process.

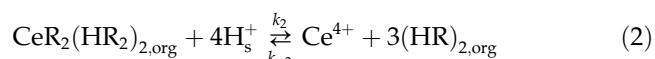


where f and org stand for feed phase and organic phase respectively;  $(\text{HR})_2$  indicates that the P204 in kerosene mainly exists as a dimeric form and then denoted as DR;  $k_1$ , and  $k_{-1}$  stand for forward and backward reaction rate constant at the interface between the feed phase and membrane phase.

(c) The metal-complex  $(\text{CeR}_2(\text{HR}_2)_{2,\text{org}})$  diffuses through the membrane A-B.

(d) At the stripping side interface of the DSLM, the  $\text{CeR}_2(\text{HR}_2)_{2,\text{org}}$  dissolved in membrane solution and the metal ions Ce(IV) are getting stripped by stripping agent.

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



where s represents the dispersion phase;  $k_2$  and  $k_{-2}$  stand for forward and backward reaction rate constant

at the interface between the membrane phase and dispersion phase.

(e) Carrier P204 returns from B to A.

In this mechanism, the transport of Ce(IV) across DSM will be described by considering only diffusion coefficient of Ce(IV), because the complex reaction between the Ce(IV) and P204 at the interfaces is much faster compared to the diffusion in the feed phase and membrane phase [48–50]. To formulate the model, the following assumptions were made:

- (1) The Ce(IV) diffuses in the organic medium as the  $\text{CeR}_2(\text{HR}_2)_2$  complex only.
- (2) There is no net flow due to convection within the LM.
- (3) The metal ions react only with P204 at the membrane interfaces.
- (4) The P204 monomer and dimer are in equilibrium at all times throughout the organic phase.
- (5) The solubility of P204 in the aqueous acid solution has been found to be negligible and, therefore, its concentration in the DSM is assumed to remain constant [51].

The diffusion of metal-complex( $\text{CeR}_2(\text{HR}_2)_2$ ) through the membrane may be described by Fick's second law:

$$\frac{\partial C_{\text{CeR}}}{\partial t} = D_{\text{CeR}} \frac{\partial^2 C_{\text{CeR}}}{\partial x^2} \quad (3)$$

where  $C_{\text{CeR}}$  stands for concentration of the Ce(IV)-(P204) complex in the organic solution;  $D_{\text{CeR}}$  stands for diffusivity of the Ce(IV)-(P204) complex;  $x$  stands for distance in the LM. The boundary conditions at each of the DSM-aqueous solution interfaces represent the equality of the free Ce(IV) mass transfer to or from the interfaces in the aqueous phase with the diffusion of the organometallic Ce(IV) complex into or out of the organic phase at each boundary:

$$D_{\text{CeR}} \frac{\partial C_{\text{CeR}}}{\partial x} \Big|_A = k(C_{\text{CeR}}^0 - C_{\text{CeR}}^A) \quad (4)$$

$$D_{\text{CeR}} \frac{\partial C_{\text{CeR}}}{\partial x} \Big|_B = k(C_{\text{CeR}}^B - C_{\text{CeR}}^0) \quad (5)$$

where  $k$  means mass transfer coefficient in the aqueous phase at boundary A or B;  $C_{\text{CeR}}^0$  stands for equivalent Ce(IV)-(P204) concentration corresponding to the bulk aqueous phase Ce(IV) concentration;  $C_{\text{CeR}}^A$  stands for interfacial Ce(IV)-(P204) concentration at interface A;  $C_{\text{CeR}}^B$  stands for interfacial Ce(IV)-(P204) concentration at interface B; and A, B stands for extraction and stripping boundaries, respectively. Given that the Ce(IV)-(P204) complex does not exist in the aqueous

phase, the mass transfer driving power of Ce(IV), as  $\text{Ce}^{4+}$ , must be estimated by transforming the aqueous phase concentrations to equivalent organic phase concentrations  $C_{\text{CeR}}^0$ , using the extraction equilibrium constant. Therefore, it is possible to calculate the equivalent Ce(IV)-(P204) concentration for the bulk aqueous free  $\text{Ce}^{4+}$  in the following manner:

Extraction equilibrium constant [52]:

$$K_{\text{EQ}} = \frac{[\text{H}^+]^4 [\text{CeR}_2(\text{HR}_2)_2]}{[\text{Ce}^{4+}]^3 [(\text{HR})_2]^3} \quad (6)$$

$$C_{\text{CeR}}^0 = [\text{CeR}_2(\text{HR}_2)_2]_{\text{bulk}} = K_{\text{EQ}} \frac{[\text{Ce}^{4+}]_{\text{bulk}} [(\text{HR})_2]^3}{[\text{H}^+]^4} \quad (7)$$

where  $[\text{Ce}^{4+}]_{\text{bulk}}$  stands for free Ce(IV) in the bulk aqueous solution;  $[\text{CeR}_2(\text{HR}_2)_2]_{\text{bulk}}$  stands for Ce (IV)-(P204) concentration in the organic phase in equilibrium with the bulk aqueous phase Ce(IV) concentration;  $[(\text{HR})_2]$  stands for P204 dimer concentration in the organic phase. On the other hand, in order to describe the P204 diffusion through the DSM, the different compounds which contain the extractant are in equilibrium and must be grouped together. Since the P204 dimer and the Ce(IV) complex contain two and six P204 molecules, respectively; the total P204 flux may be expressed as:

$$\frac{\partial C_{(\text{HR}, \text{DR}, \text{CeR})}}{\partial t} = D_{\text{HR}} \frac{\partial^2 C_{\text{HR}}}{\partial x^2} + 2D_{\text{DR}} \frac{\partial^2 C_{\text{DR}}}{\partial x^2} + 6D_{\text{CeR}} \frac{\partial^2 C_{\text{CeR}}}{\partial x^2} \quad (8)$$

where  $C_{(\text{HR}, \text{DR}, \text{CeR})}$  stands for P204 total =  $C_{\text{HR}} + C_{\text{DR}} + 6C_{\text{CeR}}$ ;  $C_{\text{HR}}$  stands for concentration of the P204 monomer;  $C_{\text{DR}}$  stands for concentration of the P204 dimer. Since no P204 enters the aqueous phases, in any form, its diffusion at both interfaces is considered to be negligible and the boundary conditions at A and B may be expressed as follows:

$$D_{\text{HR}} \frac{\partial C_{\text{HR}}}{\partial x} + 2D_{\text{DR}} \frac{\partial C_{\text{DR}}}{\partial x} + 6D_{\text{CeR}} \frac{\partial C_{\text{CeR}}}{\partial x} \Big|_{A,B} = 0 \quad (9)$$

The initial conditions reflect the uniformity of the P204 monomer and dimer concentrations, as well as the absence of Ce(IV), throughout the DSM:

Then for all  $x$ ,

$$C_{\text{CeR}} = 0 \quad (10)$$

$$C_{\text{HR}, \text{DR}} = [\text{PC} - 88A]^0 \quad (11)$$

where  $[\text{P204}]^0$  stands for initial concentration of P204.

To solve the model, aqueous solution mass balances and species distributions must be determined before solving the diffusion equations. Since, the extraction and stripping solutions contain an appreciable amount of sulfate, hydrogen, and hydroxide ions, much of the Ce(IV) is present as complexes with these ions. At each time, the free Ce(IV) concentration must be calculated in order to evaluate the boundary conditions from Eq. (7). Thereafter, the diffusion equations for Ce(IV) and total P2O4 are derived using the finite difference technique as proposed by Hoffman et al. [53]. The set of nonlinear algebraic equations formed by the diffusion equations and the boundary conditions are solved by a Newton–Raphson type method. Finally, Ce(IV) removal from the extraction phase and addition to the stripping phase are calculated using differential mass balances.

$$D_{CeR} \frac{\partial C_{CeR}}{\partial x} \Big|_{A,B} = \frac{V}{S} \frac{dC_{Ce}}{dt} \quad (12)$$

where  $S$  stands for area of the aqueous–organic interface;  $V$  stands for volume of the aqueous phase;  $C_{Ce}$  stands for total Ce(IV) concentration in the aqueous phase. According to the above-mentioned five assumptions, and  $S$ ,  $D$ , and  $V$  are certain, so the relationship between concentration and time is examined to be linear at the same  $H^+$  concentration in the feed phase.

#### 4. Results and discussion

##### 4.1. Effect of the volume ratio of membrane solution and stripping solution

The effect of volume ratio of membrane solution and stripping solution in the dispersion phase on transport of Ce(IV) is studied. The assumed experimental conditions chosen are in certain acidity in the feed phase, which is adjusted to 0.1 mol/L. Initial concentration of Ce(IV) is  $1.2 \times 10^{-4}$  mol/L in the feed phase, the concentration of HCl solution is 3.0 mol/L, and the concentration of P2O4 is 0.100 mol/L in the dispersion phase. The effect of volume ratio membrane solution and stripping solution in the dispersion phase on transport of Ce(IV) is shown in Fig. 4. The volume ratio is increased from 10:50 to 50:10. It can be seen that the most effective volume ratio is 50:10, which gives a transport percentage of Ce(IV) much higher than 10:50, but a little higher than 40:20.

Under 50:10 and 40:20 conditions, the transport percentages of Ce(IV) are above 90.3 and 91.9%, respectively. These transport percentages are near, but under volume ratio of 20:40 and 10:50 conditions

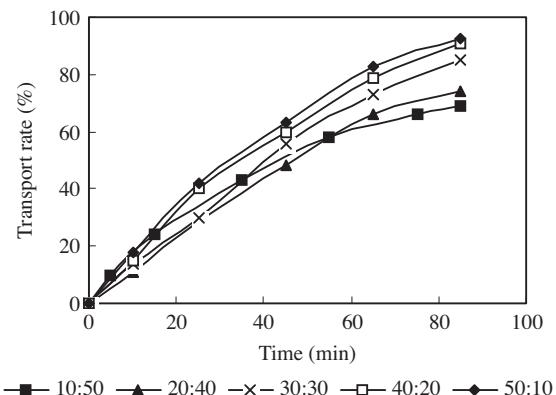


Fig. 4. Effect of volume ratio of membrane solution and stripping solution on transport of Ce(IV).

transport percentages are lower. It indicates that the transport flux of Ce(IV) increases with the increasing volume ratio in the dispersion phase. When volume ratio in the dispersion phase increases, the droplets of the dispersion solution disperse obviously in the membrane phase and the chances of contact between P2O4 and Ce(IV) increase. In this way, the mixing between the membrane phase and dispersion phase provides an extra stripping surface and renewal rate of LM, which leads to extremely stripping rate for the target species from organic phase and life of LM. Therefore, it enhances the transport percentage of Ce(IV). As far as our researching conditions are concerned, considering saving membrane solution as well as increasing transport percentage, we choose 40:20 as the optimum volume ratio of membrane solution and stripping solution in the dispersion phase for 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 ion from the feed phase to the stripping phase. So the effect of the concentration of HCl solution in the dispersion phase on transport percentage of Ce(IV) is studied in this section [53]. All the other parameters, such as acidity, initial concentration of Ce(IV) in the feed phase, volume ratio, and concentration of P2O4 are adjusted to 0.1,  $1.2 \times 10^{-4}$ , 40:20, and 0.100 mol/L, respectively. The effect of concentration of HCl solution in the dispersion phase on transport percentage of Ce(IV) is shown in Fig. 5. It indicates that, with the increasing of acid concentration in the dispersion phase, the transport percentage of Ce(IV) increases. It can be seen that the effective concentrations of HCl solution for transport is 6.0, 5.0, and 4.0 mol/L, which gives a transport percent-

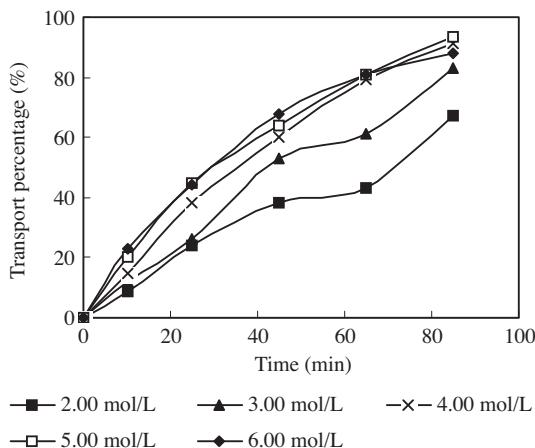


Fig. 5. Effect of concentration of HCl solution on transport of Ce(IV).

age of Ce(IV) about 86.2, 90.2, and 91.9%, respectively. The increase of concentration of HCl solution from 2.0 to 3.0 mol/L has no significant effect on transport percentage of Ce(IV), and it is less than 85%, because the number of Ce(IV) complex and the concentration of membrane solution which transport through the membrane per unit area of the membrane per unit time are definite. However, under the condition of 6.0 mol/L HCl solution, the transport percentage is little lower than 5.0 and 4.0 mol/L, because of higher acidity resulting in receding of complexation ability of P2O4. Considering controlling acidity as well as increasing transport percentage, we choose 4.0 mol/L as the optimum concentration of HCl solution in the dispersion phase during the following experiments.

#### 4.3. Effect of acidity 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 the feed phase, the lower the H<sup>+</sup> concentration is, the stronger the driving power of mass transfer process will be. Stronger power will promote the transport percentage of Ce(IV). Equally, the greater the acidity in the feed phase is, the lower the transport percentage of Ce(IV) is. The effect of acidity in the feed phase on transport of Ce(IV) is studied in the acidity range of 0.05 to 0.50 mol/L, which is adjusted with an HCl solution. Initial concentration of Ce(IV) in the feed phase is  $1.2 \times 10^{-4}$  mol/L. Concentration of HCl solution is 4.0 mol/L, volume ratio of membrane solution and stripping solution is 40:20, and concentration of P2O4 is 0.16 mol/L in the dispersion phase. The results are shown in the Fig. 6. The transport percentage of Ce(IV) increased when

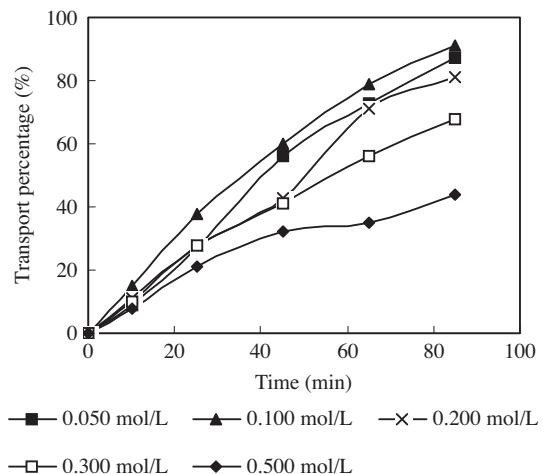


Fig. 6. Effect of acidity in the feed phase on transport of Ce(IV).

the acidity in the feed phase increased from 0.01 to 0.50 mol/L, and a maximum transport percentage observed at acidity of 0.1 mol/L is 90.2% during 85 min. Above the acidity of 0.1 mol/L in the feed phase, the transport percentage of Ce(IV) decreases to 50.2%. When acidity is less than 0.05 mol/L, the feed phase emulsifies, so the transport percentage of Ce(IV) decreases. Against all previous cases, announcement of associated documents [54] put forward that the influence of acidity on distribution coefficient of extraction process. It is large because the transport process is mainly governed by the driving power of mass transfer caused by the distribution equilibrium, when the renewal effect of the LM and the diffusion mobility of Ce(IV) ions are determined under specific experimental conditions [55,56]. As far as our researching conditions are concerned, considering saving chemical agents as well as increasing transport percentage, we choose acidity of 0.1 mol/L as the optimum acidity condition in the feed phase during the following experiments.

#### 4.4. Effect of concentration of P2O4 on transport of Ce(IV)

Concentration of P2O4 in the membrane phase and dispersion phase also plays a significant role in transport of Ce(IV). Effect of concentration of P2O4 on transport percentage of Ce(IV) is studied in the P2O4 concentration range from 0.036 to 0.23 mol/L. The acidity is adjusted to 0.1 mol/L, initial concentration of Ce(IV) is  $1.2 \times 10^{-4}$  mol/L in the feed phase, volume ratio of membrane solution and stripping solution is 40:20, and concentration of HCl solution is also adjusted to 4.0 mol/L in the dispersion phase. The results are shown in Fig. 7. With the

increasing of concentration of carrier in the membrane phase from 0.036 to 0.23 mol/L, the transport percentage of Ce(IV) increases, however, when concentration of P204 increases to 0.23 from 0.16 mol/L, the increasing of transport percentage of Ce(IV) is not obvious. Within the concentration of P204 range from 0.036 to 0.23 mol/L in the dispersion phase, the availability of P204 at the feed-membrane-dispersion interfaces increases with the increasing of concentration of carrier. The chemical reaction balances shift to the left. Similarly, when concentration of P204 becomes low, the balance shifts to the right. When concentration of P204 increases to a significant extent, the transport percentage of Ce(IV) will no longer increase with time. When the concentrations of P204 are 0.16 and 0.23 mol/L, the transport percentages are 93.5 and 95.1%, respectively. The concentration of P204 is proportionate with Ce(IV) concentration in membrane phase. When the concentration of P204 in the membrane phase becomes higher in comparison to Ce(IV) concentration in the feed phase, there is no Ce(IV) to react on redundant P204, so the increasing of transport percentage of Ce(IV) will become slow. This indicates that the number of P204 used to transport Ce(IV) through the membrane per unit area of the membrane per unit time are definite when the initial concentration of Ce(IV), the effect area of membrane, and time are definite. As far as our researching conditions are concerned, considering saving membrane solution and reagent as well as increasing transport percentage, we chose 0.16 mol/L as the optimum concentration of carrier in this study.

In Fig. 8, Ce(IV) extraction curves, both experimental and those predicted by the model, are presented as a function of time for a acidity run. In this case, the acidity of the feed phase was previously adjusted to

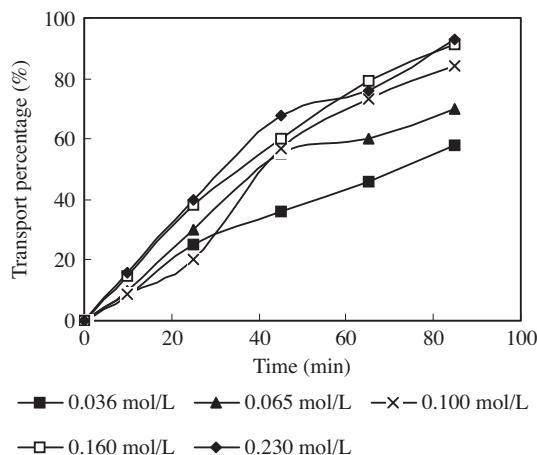


Fig. 7. Effect of concentration of P204 on transport of Ce(IV).

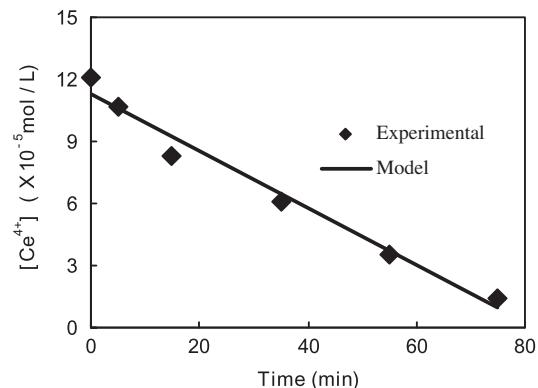


Fig. 8. Comparison between experimental and model.

0.1 mol/L, converting the P204 to its sodium salt. The acidity is accounted for in the program by eliminating the hydrogen ion balance, Eq. (11), in the extraction phase. As may be noted, the agreement between the experiment and the program results is quite good. The kinetics was also found to be close to the experimental value reported by Chiarizia et al. [57] and Su et al. [58] for this system.

#### 4.5. Long-term stability of LM

In order to define long-term stability of DSLM compared with traditional SLM, the tendency of Ce(IV) concentration changes in feed phase and dispersion phase with time was studied under the fixed operating condition lasting for a long time.

The assumed experimental conditions chosen were that the acidity was adjusted to 0.1 mol/L, initial concentration of Ce(IV) was  $1.2 \times 10^{-4}$  mol/L in the feed phase, volume ratio of membrane solution and stripping solution was adjusted to 40:20, concentration of HCl solution was also adjusted to 4.0 mol/L, and the P204 concentration was 0.16 mol/L in the dispersion phase.

The results are shown in the Figs. 9 and 10. After 80 min, the tendency of Ce(IV) concentration changes was stable, so we took a sample in 80 min in each experiment. We can find that after 9.0 h and 20 min, the Ce(IV) concentration and stability of dispersion phase decreased gradually using traditional SLM; and the Ce(IV) concentration in both feed phase and dispersion phase remained stable using DSLM. This is because the carrier in traditional SLM loses gradually and DSLM with dispersion phase can supply carrier to the membrane system. So we can draw the conclusion that stability of DSLM was better than traditional SLM.

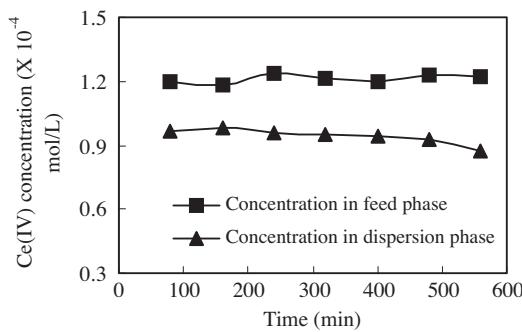


Fig. 9. The stability of DSLM.

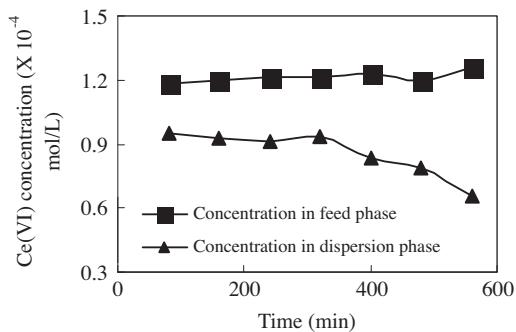


Fig. 10. The stability of traditional SLM.

## 5. Conclusions

Ce(IV) transport through a DSLM, containing P204 as the carrier, was studied and following conclusions were drawn: The LM with P204 in kerosene employed in the experiment permitted an adequate Ce(IV) extraction as long as the acidity of the feed solution was regulated below 0.1 mol/L. A transient model was developed which considers the reaction occurs between the Ce(IV) and the extractant P204 at the aqueous–DSLM interfaces only.

The results of Ce(IV) extraction with respect to time obtained by the model simulation is in agreement with those obtained by experimental values.

The application of this model for the extraction of other rare earth species is possible as long as the equilibrium and transport characteristics such as the nature and diffusivities of the complexes (monomer, dimer, organometallic complex, etc.) formed in the organic phase are known. In the future, the same methodology will be applicable to the systems which contain different rare earth species.

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