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Extraction kinetics of lanthanum and cerium in bis(2-ethylhexyl) phosphate (HDEHP)–lactic acid complex system using Lewis cell

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Abstract: The kinetics of the bis(2-ethylhexyl) phosphate (HDEHP) extraction of lanthanum and cerium were investigated in a lactic acid complex system. The effects of stirring speed, specific interface area, temperature and concentration of different solution components on the extraction rate were studied using a constant interface cell device. When the stirring speed was 130−180 r/min, the extraction reaction rate was mainly controlled by the chemical reaction, and increased with increasing the specific interface and temperature. The extraction kinetics shows that the extraction reaction conforms to a pseudo-first-order reaction, and the mass transfer process occurs at the interface between the organic and liquid phases rather than in the bulk phase. The Gibbs free energy of the extraction reaction $\Delta G<0$, indicating that the reaction can proceed spontaneously, while the calculation of the apparent activation energy shows that HDEHP is more likely to combine with cerium during extraction.

Key words: lanthanum; cerium; mechanism; extraction kinetics; Lewis cell

1 Introduction

Rare earth metals play an irreplaceable role in many fields. Due to their similar properties, the separation and purification of single rare earths with high purity is a prerequisite for industrial application [1,2]. Fractional crystallization and precipitation, chemical vapor transmission, ion exchange, extraction resin chromatography, solvent extraction, liquid membranes, and redox reactions have achieved the separation of rare earth elements to certain extents [3−7]. Among them, solvent extraction accounts for most of global production of the single rare earth products due to its advantages of strong pertinence, high separation coefficient, and continuous production.

P204-HCl and P507-HCl systems are the most commonly used extraction systems for the separation and purification of light, medium, and heavy rare earths in industrial production [8,9]. For the phosphoric acid extractants, saponification pretreatment is required before the extraction of rare earth elements to improve their separation performance [10]. However, the accompanying production of large amounts of ammonia nitrogen wastewater places huge pressure on the environment and increases the follow-up treatment costs of enterprises. Reflecting the increased focus on environmental protection, new non-saponified extraction processes have become a research hotspot [11,12]. Among them, complexation has been proven to improve the separation effect of rare earths under non-saponified conditions. NISHIHAMA et al [13] used ethylenediaminetetraacetic acid (EDTA) as a complexing agent to significantly increase the separation coefficient of Y in rare earth metals. They found that when the pH of the aqueous solution was 7.5, the concentration of the complexing agent diethylenetriaminepentaacetic acid (DPTA) was 0.5 mol/L. The separation coefficient $\beta_{\mathrm{Y/Er}}$ of the extractant P204 for Y and Er under non-

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saponification conditions was equal to 10.8, which was significantly higher than that without the separation factor of the complexing agent. In addition, the use of organic carboxylic acid as a complexing agent to improve the separation coefficient of the extractant for rare earths has also attracted much attention [15,16]. CHANG [17] compared the effect of P204 on the rare earth metals La and Ce. The separation effect of Pr and Nd was tested under ideal conditions and was found to be significantly better than that of the saponified P204 system, with separation coefficients of $\beta_{\mathrm{Ce/La}}$=4.16, $\beta_{\mathrm{Pr/Ce}}$=2.07, and $\beta_{\mathrm{Nd/Pr}}$=1.59. Organic carboxylic acids such as lactic acid, tartaric acid, and maleic acid can also combine with rare earth ions in solution to form complexes [18,19]. In previous experimental studies, it was found that when lactic acid was used as a complexing agent, the separation coefficient of the phosphonic acid extractant bis(2-ethylhexyl) phosphate (HDEHP) for La and Ce was improved under non-saponified conditions.

Studying the extraction kinetics and thermodynamics can reveal the control model of the mass transfer mechanism and the extraction reaction rate, providing theoretical support for the selection of equipment in industrial production. At present, increasing attention has been paid to the kinetics of the extraction of metal ions by solvent extraction. The Lewis cell, single-droplet analysis, high-speed stirring, gas stirring, and supported liquid membrane systems are several approaches used to study the kinetics of the extraction process [20−23]. Among them, the Lewis cell and single-droplet analysis have the advantages of simple operation, low reagent consumption, and low equipment requirements, making them become the main methods used for laboratory research on kinetics. DONG et al [24] studied the kinetics of the extraction of Lu by HEH (EHP) using the Lewis cell. The results show that when the concentration of HEH (EHP) was 0.2−0.4 mol/L, the rate equation of the extraction reaction is $-\mathrm{d}[\mathrm{Lu}^{3+}]/\mathrm{d}t=10^{-1.82}[\mathrm{Lu}^{3+}]\times \mathrm{H_2A_2}^{0.60}$. TORKAMAN et al [25] studied the kinetics of the extraction of Sm^{3+} from the P204-Cyanex301 system via the single-droplet method, revealing that the extraction process is dominated by diffusion control, and deduced the extraction kinetics equation. ZHANG et al [26] studied the kinetics of La extraction in the P204-P350 system by the Lewis cell method, and found that the extraction reaction of La^{3+} in the HEDEHP-P350 system was controlled by both diffusion and chemical reactions. The extraction reaction occurred in the interfacial area between the aqueous and organic phases rather than in the bulk phase [26]. There are relatively few studies on the extraction kinetics of the complexing system. The addition of a complexing agent improves the extraction performance of the organic extractant, but its effect on the extraction rate also needs to be explored.

In a previous study, it was found that adding lactic acid as a complexing agent to the solution can significantly improve HDEHP extraction and the separation of La and Ce; however, research on the extraction reaction mechanism is lacking. Herein, the constant interface cell method is used to systematically study the effects of stirring rate, specific interface area, temperature and different solution components on the extraction rate. In addition, the approach reveals the mass transfer process in the extraction reaction, and clarifies the extraction reaction mechanism in the complexing system, which provided data support for the extraction and separation of La and Ce.

2 Experimental

2.1 Reagents and chemicals

HDEHP was provided by Sinopharm Chemical Reagent Co., Ltd. (purity >99%), lactic acid was provided by Aladdin Reagent Co. (purity >99%), and the sulfonated kerosene used to dilute the extractant was provided by Guangzhou Xiangyang Fusen Petrochemical Co. The rare earth oxides ($\mathrm{La_2O_3}$ and $\mathrm{CeCl_3}$) used were provided by Sinopharm Chemical Reagent Co., Ltd. (purity >99.9%), and all other reagents were of analytical grade.

An inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy) was used to analyze and determine the concentration of La^{3+} and Ce^{3+} in the raffinate after different extraction reaction time; a pH meter (PHSJ−3F) was used to determine the pH of the aqueous solution; the reagents were weighed using an electronic analytical balance (ME104); an electrically heated constant-temperature water bath (HH−80) was used to maintain the temperature required for the extraction reaction.

2.2 Procedure and kinetic studies

The rare earth oxide La_2O_3 was dissolved in a 3 mol/L hydrochloric acid solution. Then, the initial aqueous solutions of La^{3+} and Ce^{3+} with concentration of 0.1 mol/L were prepared. While maintaining the concentration of the complexing agent lactic acid at 0.5 mol/L, the pH of the solution was adjusted with dilute hydrochloric acid and ammonia. Sulfonated kerosene was used as a diluent to adjust the concentration of the extractant HDEHP to 0.3 mol/L.

The structural diagram of the constant interface cell device is shown in Fig. 1. Equal volume (50 mL) of the preheated aqueous phase and the extraction organic solution were respectively added to the extraction reaction device. When the two phases were in contact, the mass transfer process began. The stirring paddle was turned on and a stopwatch was started. During the experiment, without interrupting the stirring reaction mixture, a volumetric syringe was used to obtain 0.5 mL samples of the aqueous and organic phases at different reaction time to ensure that the organic/water ratio remained unchanged. The content of rare earth ions in the liquid-phase solution was determined, and all kinetic tests were carried out at (298±0.1) K (except for the temperature test) and standard atmospheric pressure.

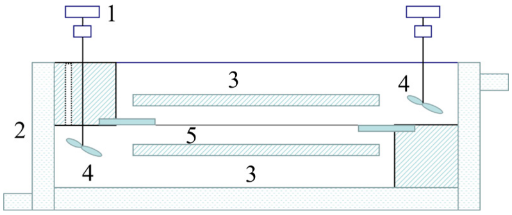

Fig. 1 Schematic diagram of constant interface pool device: 1—Stirrer; 2—Constant temperature water bath; 3—Flow deflector; 4—Stirring paddle; 5—Interface plate

2.3 Analysis of extraction kinetic data

Using the Danesi's method for data processing [27−29], it is assumed that the extraction reaction of RE^{3+} by the HDEHP-lactic acid complex system occurred as a first-order reversible reaction. Therefore, the mass transfer of RE^{3+} from the aqueous phase to the organic phase can be expressed as

$$RE_a^{3+} \underset{K_{oa}}{\overset{K_{ao}}{\rightleftarrows}} RE_o^{3+} \tag{1}$$

where the subscripts "a" and "o" represent the liquid-phase material and the organic phase, respectively, and K_{ao} and K_{oa} respectively represent the forward and reverse mass transfer coefficients of RE^{3+} from the liquid phase to the organic phase.

The extraction reaction rate can be expressed as

$$-\frac{d[RE]_{(o)}}{dt} = -\frac{dn_1}{Vdt} = \frac{Q}{V}\times(K_{oa}[RE]_{(o)} - K_{ao}[RE]_{(a)}) \tag{2}$$

where n_1 represents the molar amount of RE^{3+} in the organic phase at the time of extraction t, and Q and V represent the reaction boundary area (cm^2) and the volume of the aqueous or organic phase, respectively.

When the extraction is in equilibrium, $-\frac{d[RE]_{(o)}}{dt} = 0$.

Therefore,

$$K_{oa}[RE]^e_{(o)} = K_{ao}[RE]^e_{(a)},\quad K_{oa} = \frac{K_{ao}[RE]^e_{(a)}}{[RE]^e_{(o)}} \tag{3}$$

The relationship between the concentration of rare earth ions in the organic and water phases is such that:

$$[RE]^e_{(o)} = [RE]_{(a)} - [RE]^e_{(a)} \tag{4}$$

Substituting Eqs. (3) and (4) into Eq. (2),

$$\ln\left(1-\frac{[RE]_{(o)}}{[RE]^e_{(o)}}\right) = -\frac{Q}{V}\left(1+\frac{[RE]^e_{(o)}}{[RE]^e_{(a)}}\right)K_{ao}t \tag{5}$$

Considering that distribution coefficient K_d is defined as $K_d = \frac{[RE]^e_{(o)}}{[RE]^e_{(a)}}$, Eq. (5) can be rewritten as

$$\ln\left(1-\frac{[RE]_{(o)}}{[RE]^e_{(o)}}\right) = -\frac{Q}{V}(1+K_d)K_{ao}t \tag{6}$$

Let $-(V/Q)\times\ln(1-[RE]^e_{(o)}/[RE]^e_{(a)})=Y_t$ and $Y_t=(1+K_d)K_{ao}t$. Here, Y_t has a linear relationship with the extraction time t.

3 Results and discussion

3.1 Effect of stirring speed on extraction rate

The stirring speed is the most important factor affecting the extraction rate. At different stirring speeds, the control of the extraction reaction rate is typically divided into diffusion control, chemical reaction control, chemical reaction and diffusion mixing control. When the stirring speed is low, the extraction rate is generally proportional to the stirring speed and is mainly controlled by diffusion. As the stirring speed increases, the extraction rate may appear as a "flat area" due to the thinning of the viscous film and the stirring effect. Speed does not affect the extraction reaction rate, and the extraction reaction rate is mainly controlled by chemical control. When the stirring speed is further increased, the two-phase constant interface is destroyed and a turbulent zone appears. Therefore, the extraction reaction rate is mainly controlled by chemical reaction and diffusion [30]. The extraction of the rare earth elements La and Ce by the HDEHP-lactic acid system at different stirring speeds over the duration of the extraction reaction is shown in Fig. 2. The extraction rate (*E*) of the rare earths by the organic extractant increases with the stirring rate, reaching equilibrium after about 60 min.

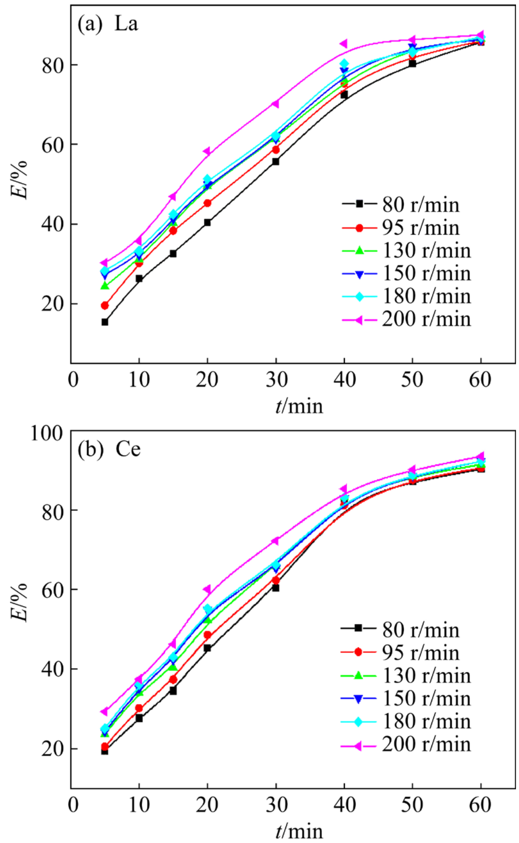

Fig. 2 Effect of stirring speed on extraction rate of La (a) and Ce (b) by HDEHP (Aqueous phase: La^{3+}=0.1 mol/L, Ce^{3+}=0.1 mol/L; $[C_3H_6O_3]$=0.5 mol/L; organic phase: [HDEHP]=0.3 mol/L; T=298.15 K)

The data are fitted according to Eq. (6), and the results are shown in Fig. 3. At the stirring speeds of 80−130 r/min, the extraction reaction rate increases linearly with the stirring speed, indicating that the extraction rate is mainly controlled by diffusion at this time. When the stirring speed is 130−180 r/min, a flat area appears where the stirring speed does not affect the extraction rate, indicating that the extraction rate is dominated by chemical diffusion. As the stirring speed continuously increases, the reaction enters the turbulent interface. In a follow-up study, the stirring rate was controlled at 150 r/min, so that the extraction reaction rate was controlled by the chemical reaction.

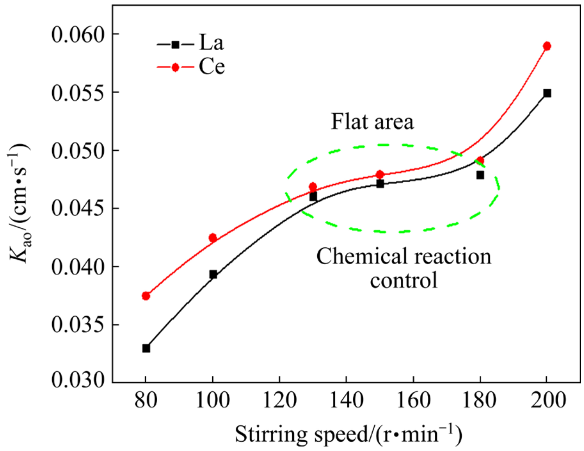

Fig. 3 Effect of stirring speed on extraction rate

3.2 Effect of specific interfacial area on extraction rate

The influence of the specific boundary area (extraction constant boundary area / phase volume, *Q*/*V*) on the extraction rate is an important basis for judging whether the extraction reaction occurred in the phase body or at the interface. If the extraction reaction rate is not affected by the change of the specific boundary area, the reaction took place inside the phase. However, if the extraction reaction rate is proportional to the specific boundary area and passes through the origin, the reaction occurred at the two-phase interface. However, if the extraction reaction rate is proportional to the specific boundary area but does not pass through the origin, the extraction reaction occurred at both the phase body and the interface [31,32].

Keeping the other test conditions unchanged, the position of the interface plate in the constant interface cell device was adjusted to change the specific boundary area of the extraction reaction (Fig. 4). The extraction rates of La and Ce in the HDEHP-lactic acid system have a linear relationship with the specific boundary area and neither pass through the origin, indicating that the extraction reaction occurred at the phase body and the interface at the same time.

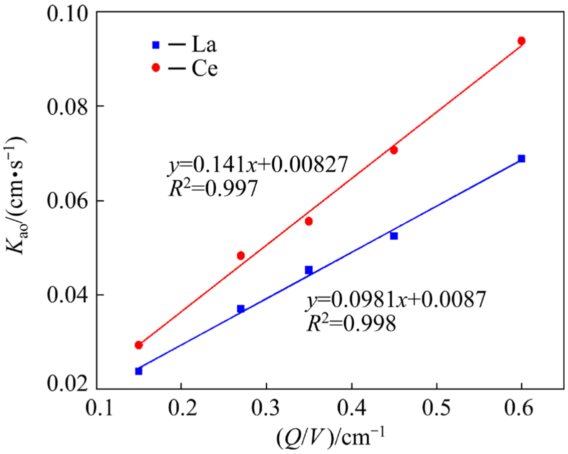

Fig. 4 Effect of specific interfacial area on extraction rate of La and Ce by HDEHP (Aqueous phase: La^{3+}=0.1 mol/L, Ce^{3+}=0.1 mol/L; $[C_3H_6O_3]$=0.5 mol/L; organic phase: [HDEHP]=0.3 mol/L; T=298.15 K)

3.3 Effect of temperature on extraction rate

The reaction temperature often greatly influences the rate of a chemical reaction. For both endothermic and exothermic chemical reactions, the change of temperature can significantly change the degree and rate of the reaction. In kinetic studies, the influence of temperature change on the diffusion rate is basically negligible compared to the chemical control process. It is generally believed that when the apparent activation energy of the extraction reaction E_a>42 kJ/mol, the extraction reaction is controlled by a chemical reaction. A diffusion-controlled extraction occurs when the apparent activation energy of the extraction reaction E_a<20.0 kJ/mol. However, when the apparent activation energy is such that 42.0> E_a >20.0 kJ/mol, the extraction process is controlled by both chemistry and diffusion [33].

The extraction reaction temperature was adjusted using a constant temperature water bath, and the effects of different temperatures on the extraction rates of La and Ce in the HDEHP-lactic acid system were studied. The linear relationship was fitted with Y_t–t, and the results are shown in Fig. 5. The higher the temperature of the extraction reaction is, the more favorably the extraction reaction proceeds.

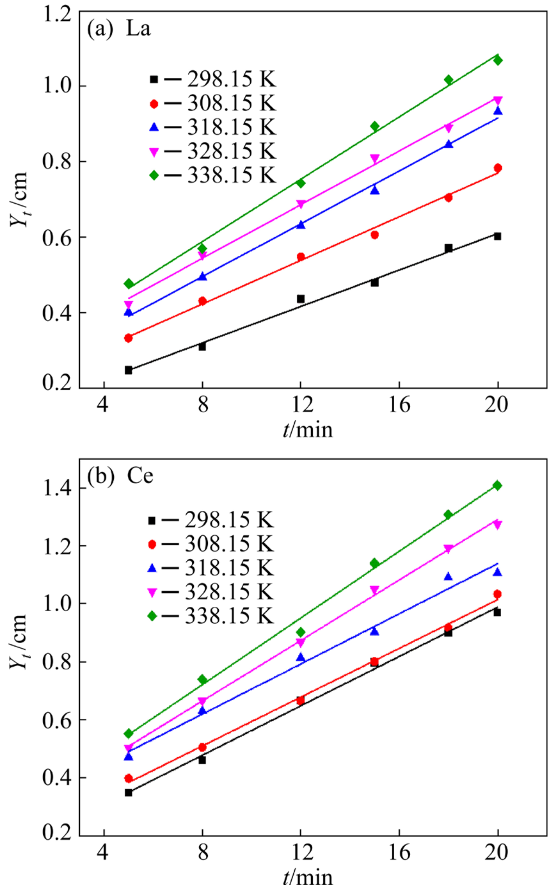

Fig. 5 Effect of temperature on extraction rate of La and Ce by HDEHP (Aqueous phase: La^{3+}=0.1 mol/L, Ce^{3+}= 0.1 mol/L; $[C_3H_6O_3]$=0.5 mol/L; organic phase: [HDEHP]=0.3 mol/L)

According to the Arrhenius equation, $1/T$ and $\lg K_{ao}$ are linearly related, allowing for fitting (Fig. 6).

$$\lg K_{ao} = -\frac{E_a}{RT} + \ln A \tag{7}$$

where E_a represents the activation energy of the extraction reaction, R and T respectively represent the gas molar constant and reaction temperature, and A is a constant.

The slope is equal to $-E_a/R$, and the apparent activation energies of the HDEHP–lactic acid extraction system to separate La and Ce were respectively 4.01 and 3.74 kJ/mol, both of which are below 20 kJ/mol. Combined with the influence of stirring speed on the extraction rate discussed in Section 3.1, the extraction process can be considered as being jointly controlled by chemical reaction and diffusion. The lower the apparent activation energy is, the more readily the reaction occurs. Therefore, the extraction of Ce by the extraction system is more likely to occur, conforming to the positive sequence law.

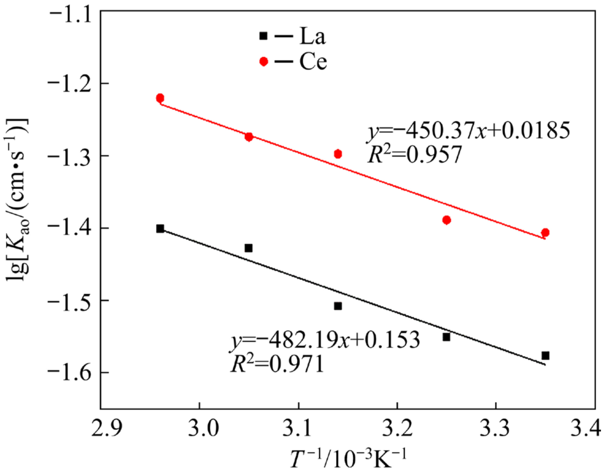

Fig. 6 Linear fit of relationship between $1/T$ and lg K_{ao}

According to the transition state theory, as shown in Eqs. (8) and (9), the enthalpy change ΔH, entropy change ΔS, and Gibbs free energy ΔG of the extraction of La and Ce in the complex system were calculated as [33]

$$\ln\frac{K_{ao}h}{kT}=\frac{-\Delta H}{RT}+\frac{-\Delta S}{R}+a\ln[\mathrm{La}^{3+}]+\cdots \tag{8}$$

$$\Delta G=\Delta H-T\Delta S \tag{9}$$

where k and h are respectively the Boltzmann's constant (6.63×10^{-23}) and Planck's constant (1.38×10^{-34}).

As is shown, $\ln[K_{ao}h/kT]$ has a linear relationship with $1/T$ (Fig. 7), and the changes in enthalpy ΔH and entropy ΔS can be calculated according to the slope and intercept. The calculated enthalpy change ΔH, entropy change ΔS, and Gibbs free energy ΔG are shown in Table 1. The Gibbs free energy of the extraction process is less than 0, indicating that the process occurs spontaneously, while the change in entropy is greater than 0, meaning that the disorder of the extraction reaction increases.

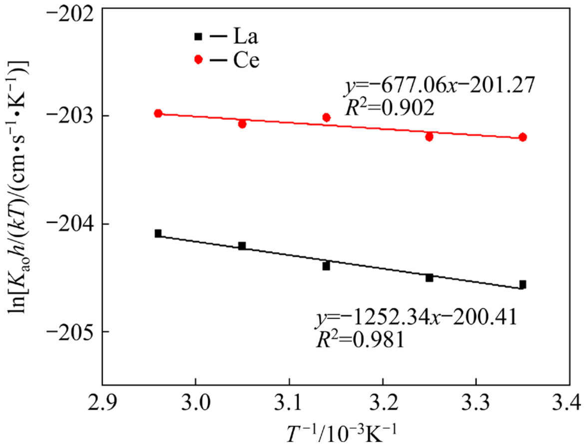

Fig. 7 $\ln(K_{ao}h/kT)-1/T$ relationship curve of La and Ce in organic-phase extraction

3.4 Effects of reactant concentration

The extraction reaction rate is generally affected by the components of the solution. Under non-saponification conditions, the components in the solution when the HDEHP–lactic acid complex system extracts rare earth RE^{3+} include: RE^{3+}, Cl^-, H^+, HDEHP, and $C_3H_6O_3$. The forward reaction rate equation of the system for the extraction of rare earth ions can be expressed as

$$R_0=-(\mathrm{d}[RE])/\mathrm{d}t=K[\mathrm{RE}^{3+}]^a[\mathrm{Cl}^-]^b[\mathrm{H}^+]^c[\mathrm{HDEHP}]^d[\mathrm{C_3H_6O_3}]^e \tag{10}$$

where K is the extraction reaction rate constant, and a, b, c, d, and e are the respective reaction stages of different solution components.

The natural logarithm was taken on both sides of Eq. (10) to obtain

$$\ln R_0=\ln K+a\ln[\mathrm{RE}^{3+}]+b\ln[\mathrm{Cl}^-]+c\ln[\mathrm{H}^+]+d\ln[\mathrm{HDEHP}]+e\ln[\mathrm{C_3H_6O_3}] \tag{11}$$

The reaction coefficients of different components in the solution have a linear relationship with $\ln R_0$, and the reaction order of each component can be respectively fitted and calculated by the controlled variable method (Fig. 8).

The fitting relationships discussed above are linear, indicating the possibility of the extraction

Table 1 Enthalpy change ΔH, entropy change ΔS, and Gibbs free energy ΔG during extraction process

Element	Fitting equation	R^2	ΔH/ (kJ·mol^{-1})	ΔS/ (J·mol^{-1}·K^{-1})	ΔG/ (kJ·mol^{-1})
La	$y=-1252.34x-200.41$	0.981	10.42	1666.21	−486.36
Ce	$y=-677.06x-201.27$	0.902	5.63	1673.36	−498.91

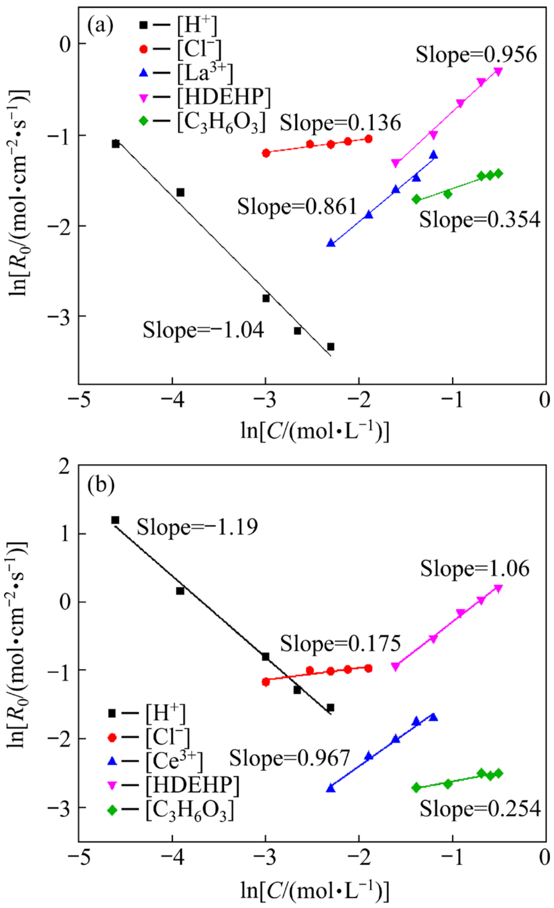

Fig. 8 Effect of reactant concentration on extraction rate: (a) La; (b) Ce

reaction being a first-order reversible reaction. The concentration of H^+ in aqueous solution relative to the extraction rate indicates a negative first-order reaction, and the coefficient c is close to −1. Relating the concentration of the extractant HDEHP and rare earth ions with the extraction rate indicates a first-order reaction. The coefficients a and d are both close to 1, the lactic acid complexing agent and Cl^- have a weak effect on the extraction rate, and the coefficients b and e approach to 0. According to the fitting results, the rate constant K for the extraction of La and Ce can be calculated as 1.05×10^{-2} and 1.74×10^{-2} $(\text{mol·L}^{-1})^{-1.217}$/s, respectively. Therefore, the extraction rate equations of La and Ce in the extraction system can be expressed as

$$R_{0,\text{La}}=\frac{-\text{d}[\text{La}^{3+}]}{\text{d}t}=1.05\times10^{-2}[\text{La}^{3+}]^{0.861}\cdot[\text{Cl}^-]^{0.136}[\text{H}^+]^{-1.04}[\text{HDEHP}]^{0.956}[\text{C}_3\text{H}_6\text{O}_3]^{0.354}$$

$$R_{0,\text{Ce}}=\frac{-\text{d}[\text{Ce}^{3+}]}{\text{d}t}=1.74\times10^{-2}[\text{Ce}^{3+}]^{0.967}\cdot[\text{Cl}^-]^{0.175}[\text{H}^+]^{-1.19}[\text{HDEHP}]^{1.06}[\text{C}_3\text{H}_6\text{O}_3]^{0.254}$$

3.5 Speculation on mass transfer mechanism of extraction reaction

As a phosphonic acid extractant, HDEHP generally exists as a dimer in non-polar organic solvents [34]. Assuming a complex system, the extraction of rare earth ions with an organic extractant can be divided into the following steps:

$$\text{H}_2\text{A}_{2(\text{o})}\overset{k_1}{\longleftrightarrow}2\text{HA}_{(\text{i})} \tag{12}$$

The extractant HDEHP is distributed from the organic phase at the extraction interface in the form of dimers. k_1 represents the dissociation constant of the extractant.

$$\text{HL}_{(\text{a})}\overset{k_2}{\longleftrightarrow}\text{L}^-_{(\text{a})}+\text{H}^+_{(\text{a})} \tag{13}$$

$$\text{RE}^{3+}_{(\text{a})}+2\text{L}^-_{(\text{a})}\underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}}\text{REL}^+_{2(\text{a})} \tag{14}$$

In the extraction reaction, the complex formed by the rare earth ion Re^{3+} and lactic acid mainly exists as ReL^{2+}, where k_2 is the dissociation constant of lactic acid.

$$\text{REL}^+_{2(\text{i})}+\text{HA}_{(\text{i})}\underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}}\text{REA}^{2+}_{(\text{i})}+\text{H}^+_{(\text{a})}+2\text{L}^-_{(\text{a})} \tag{15}$$

$$\text{REA}^{2+}_{(\text{i})}+\text{HA}_{(\text{i})}\underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}}\text{REA}^+_{2(\text{i})}+\text{H}^+_{(\text{a})} \tag{16}$$

$$\text{REA}^+_{2(\text{i})}+\text{HA}_{(\text{i})}\underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}}\text{REA}_{3(\text{i})}+\text{H}^+_{(\text{a})} \tag{17}$$

$$\text{REA}_{3(\text{i})}\underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}}\text{REA}_{3(\text{o})} \tag{18}$$

where the subscripts o, i, and a respectively represent the organic phase, extraction interface, and liquid-phase material. In the extraction reaction k_3, k_4, k_5, k_6, k_7 and k_{-3}, k_{-4}, k_{-5}, k_{-6}, k_{-7} represent the forward and reverse reaction rate constants of each reaction, respectively.

The rare earth ions undergoing complexation sequentially react with the extractant HA at the interface, and release H^+ and L^{2-} into the aqueous phase solution. The formed extract compound $\text{ReA}_{3(\text{i})}$ then diffuses from the interface into the organic phase. According to related studies, the slowest reaction stage in the extraction reaction controls the total extraction reaction rate. Assuming that Eq. (16) is the rate-determining step, the rate equation can be expressed as

$$R_0=k_5[\text{REA}^{2+}_{(\text{i})}][\text{HA}_{(\text{i})}] \tag{19}$$

$$\frac{\mathrm{d}[\mathrm{REA}_{(\mathrm{i})}^{2+}]}{\mathrm{d}t}=k_4[\mathrm{REL}_{2(\mathrm{i})}^{+}][\mathrm{HA}_{(\mathrm{i})}]- k_{-4}[\mathrm{REA}_{2(\mathrm{i})}^{+}][\mathrm{H}^{+}][\mathrm{L}_{(\mathrm{a})}^{-}]^2-k_5[\mathrm{REA}_{2(\mathrm{i})}^{+}][\mathrm{HA}_{(\mathrm{i})}] \tag{20}$$

The extraction process instantly reaches equilibrium:

$$\frac{\mathrm{d}[\mathrm{REA}_{2(\mathrm{i})}^{+}]}{\mathrm{d}t}=0 \tag{21}$$

$$[\mathrm{REA}_{(\mathrm{i})}^{2+}]=\frac{k_4[\mathrm{REL}_{2(\mathrm{i})}^{-}][\mathrm{HA}_{(\mathrm{i})}]}{k_{-4}[\mathrm{H}_{(\mathrm{a})}^{+}][\mathrm{L}_{(\mathrm{a})}^{-}]^2+k_5[\mathrm{HA}_{(\mathrm{i})}]} \tag{22}$$

Substituting Eq. (22) into Eq. (19),

$$R_0=k_5\frac{k_4[\mathrm{REL}_{2(\mathrm{i})}^{-}][\mathrm{HA}_{(\mathrm{i})}]^2}{k_{-4}[\mathrm{H}_{(\mathrm{a})}^{+}][\mathrm{L}_{(\mathrm{a})}^{-}]^2+k_5[\mathrm{HA}_{(\mathrm{i})}]}= \frac{k_5k_4K_1K_2[\mathrm{H_2A}_{2(\mathrm{o})}][\mathrm{RE}^{3+}]}{k_{-4}[\mathrm{H}_{(\mathrm{a})}^{+}][L_{(\mathrm{a})}^{-}]^2+k_5[\mathrm{HA}_{(\mathrm{i})}]} \tag{23}$$

In the extraction reaction process, $k_{-4}\gg k_5[\mathrm{HA}_{(\mathrm{i})}]$, and $K=(k_5k_4K_1K_2)/k_{-4}$, and the final extraction rate can thus be expressed as

$$R_0=K[\mathrm{RE}_{(\mathrm{a})}^{3+}][\mathrm{H_2A}_{2(\mathrm{O})}][\mathrm{H}_{(\mathrm{a})}^{+}]^{-1} \tag{24}$$

The rate equation calculated according Eq. (24) to the extraction mechanism is similar to the experimental extraction reaction rate, indicating that the extraction reaction is likely first-order. Based on the above study in the complex system, the mass transfer process of the extraction of rare earth ions by HDEHP is shown in Fig. 9.

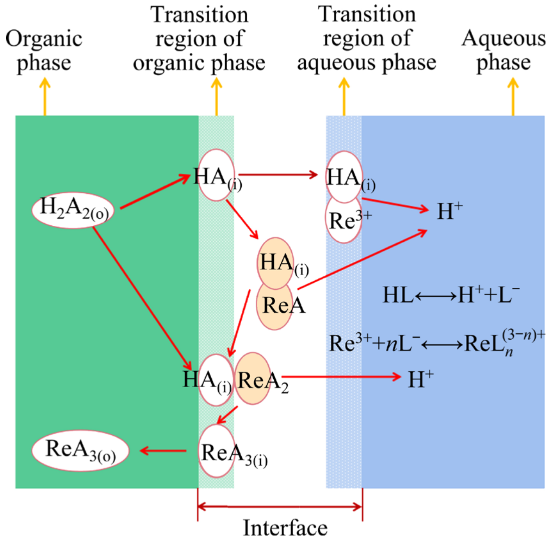

Fig. 9 Schematic diagram of mass transfer mechanism of HDEHP–lactic acid system for extraction of rare earths via complexation

4 Conclusions

(1) The effects of stirring speed, extraction reaction temperature, specific boundary area (*Q*/*V*), and other conditions on the extraction rate were studied. It is revealed that the forward extraction rate of the extraction reaction is mainly controlled by diffusion and chemical reaction mixing control, and the extraction reaction occurs at the interface between the organic and liquid phases rather than in the bulk phase.

(2) The data were analyzed based on the principle of a pseudo-first-order reaction. According to the influence of $[\mathrm{Re}^{3+}]$, $[\mathrm{Cl}^{-}]$, $[\mathrm{H}^{+}]$, [HDEHP], and $[\mathrm{C_3H_6O_3}]$ in the solution on the extraction rate, the rate equations of La and Ce extraction were obtained as follows:

$$R_{0,\mathrm{La}}=-\frac{\mathrm{d}[\mathrm{La}^{3+}]}{\mathrm{d}t}=1.05\times10^{-2}[\mathrm{La}^{3+}]^{0.861}\cdot[\mathrm{Cl}^{-}]^{0.136}[\mathrm{H}^{+}]^{-1.04}[\mathrm{HDEHP}]^{0.956}[\mathrm{C_3H_6O_3}]^{0.354}$$

$$R_{0,\mathrm{Ce}}=-\frac{\mathrm{d}[\mathrm{Ce}^{3+}]}{\mathrm{d}t}=1.74\times10^{-2}[\mathrm{Ce}^{3+}]^{0.967}\cdot[\mathrm{Cl}^{-}]^{0.175}[\mathrm{H}^{+}]^{-1.19}[\mathrm{HDEHP}]^{1.06}[\mathrm{C_3H_6O_3}]^{0.254}$$

(3) Combining the Arrhenius formula and the transition state theory, the enthalpy change, entropy change, Gibbs free energy, and apparent activation energy during the extraction reaction were calculated. Since ΔG is less than 0, the extraction reaction can occur spontaneously, with the reaction rate directly correlating with temperature.

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采用恒界面池法研究双(2-乙基己基)磷酸酯(HDEHP)−乳酸复合体系萃取镧和铈动力学

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摘 要：研究在乳酸络合体系中 HDEHP 萃取镧和铈的动力学。通过恒界面池装置分别研究不同搅拌速度、比界面积、温度和溶液组分浓度对萃取速率的影响。当搅拌速度为 130~180 r/min 时，萃取反应速率以化学反应控制为主，并且随着比界面和温度的升高，萃取速率变快。萃取动力学研究表明，萃取反应符合准一级反应，传质过程发生在有机相与液相界面而不是在相体内。萃取反应吉布斯自由能 $\Delta G<0$，能够自发进行反应，表观活化能的计算表明 HDEHP 在萃取中更易与铈结合。

关键词：镧；铈；机理；萃取动力学；恒界面池

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