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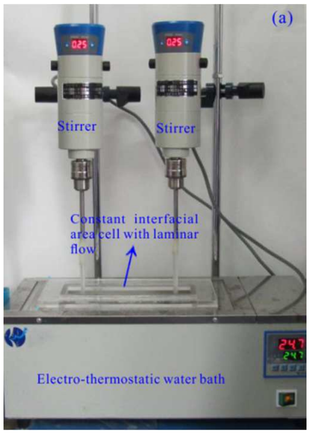
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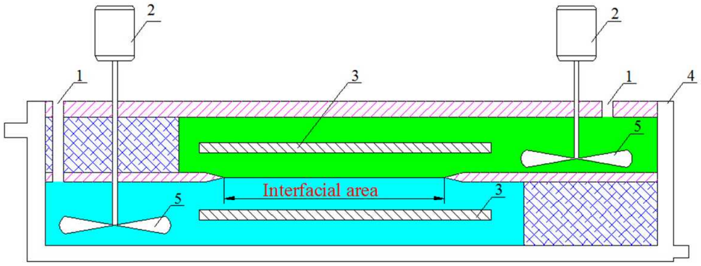
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The kinetics and mechanism of solvent extraction of Pr(III) from chloride medium in the presence of two complexing agents with di-(2-ethylhexyl) phosphoric acid

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Abstract: The extraction kinetic of Pr(III) from chloride medium containing two complexing agents lactic acid (HLac) and citric acid (H_3cit) with di-(2-ethylhexyl) phosphoric acid (D2EHPA, H_2A_2) has been investigated by constant interfacial area cell with lamina flow. The influence of stirring speed, temperature, specific interfacial area, extractant and hydrogen ion concentrations on the extraction rate has been studied. It is concluded that the extraction of Pr(III) takes place at the liquid–liquid interface, while the extraction regime belongs to diffusion-controlled kinetics process. The extraction rate equation and the rate-determining step have been obtained under the experimental conditions, and the extraction rate constant is calculated. The interfacial reaction model is proposed based on the kinetic steps.

Keywords: Pr(III); kinetics; H_2A_2; Lactic acid; Citric acid; Constant interfacial area cell

1. Introduction

Rare earths are important elements from an industrial point of view. They are extensively used in the astronavigation, luminescence, nuclear energy, and metallurgical industries.[1,2] Praseodymium (III) which is one of the most abundant rare earths, is of current interest, because it is used in the production of atomic batteries.[3,4] With the ever-increasing demand for high-purity rare earths and their compounds, the separation and purification of these elements recently have gained considerable importance.

Solvent extraction is employed to separate and purify rare earth elements on an industrial scale. Acidic organophosphorous extractants, such as di-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH/EHP), have been widely utilized in industry for the solvent extraction separation of rare earth elements (REEs). [5,6] However, these extractants have difficulties in the separating and purifying rare earths due to their similar chemical and physical properties, especially for the neighboring rare earth elements. Therefore, there is a growing interest in the development of new extractants and extraction systems for the separation of them as a group or from one another.

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Up to date, much effort has been devoted to explore some new extraction system superior to the current saponified D2EHPA or HEH/EHP system. One more effective method is to introduce complexing agents into the aqueous phase, such as EDTA, [7,8] DTPA, [9-11] 2-ethyl-2-hydroxy butyric acid, [12] acetic acid, [13] lactic acid [14] and citric acid [15]. These results show that complexing extraction has higher extraction efficiency and more pronounced separation selectivity. In our previous work, we have studied the extraction and separation of light rare earths using the complexing extraction system in the presence of two complexing agent lactic acid and citric acid with D2EHPA, and the results show that it could not only improve the extraction efficiency, but also heighten the selectivity among some adjacent rare earths.[16-18] However, until now, no information on the extraction kinetics of the complexing extraction system containing two complexing agents lactic acid and citric acid with D2EHPA extractant has been available.

Today, research into extraction kinetics, an important aspect for solvent extraction, has become a routine procedure, used together with thermodynamic studies to clarify the extraction mechanism and to optimize extraction processes. In general, there are three possibilities (diffusion, kinetic, or mixed) to control the extraction mass transfer rate. [19] Although the criteria that can be used to distinguish the extraction rate regime have been reported, it is necessary to associate different items of experimental information to fully describe the kinetics of extraction.

In the present work, the rate of interfacial mass transfer of Pr(III) from aqueous hydrochloric acid solution into sulfonated kerosene solution of the D2EHPA has been studied as function of the stirring speed of the phases, temperature, specific interface area, the concentration of the extractant and pH values. A model for the initial mass transfer rate has been elaborated. The reaction regime is deduced from the experimental results and the rate determining step determined.

2. Experimental

2.1. Reagents and apparatus

D2EHPA (H_2A_2) extractant and sulphonating kerosene are purchased from Luoyang ZhongDa Chemical Industry Co., Ltd (China). The extractant is used without further purification and dissolved in sulfonated kerosene to the required concentrations. The aqueous phase is prepared by dissolving Pr_6O_{11} (purity≥99.9%) with a certain proportion of lactic acid, citric acid and a small amount of HCl, and diluting to required volume with distilled water, and then analyzed by titration with a standard solution of EDTA at pH 5.5 using xylenol orange as an indicator. NaCl in all extraction experiments is used to keep the ionic strength constant. Lactic acid (HLac) and citric acid (H_3cit) are obtained from Sinopharm Chemical Reagent Co. Ltd (China). All other reagents are of analytical reagent grade.

A pHS-3C digital pH meter (Shanghai Rex Instruments Factory) is used for pH measurements. A Prodigy high dispersion inductively coupled plasma spectrometer (Leeman labs, America) is employed to measure Pr(III) concentration in the extraction process.

2.2. Experiments procedure

A constant interfacial area cell with laminar flow is made by our laboratory according to the literature [19] and employed as kinetics measurements. The schematic diagram of this constant interfacial area cell which is rectangular is shown in Fig. 1, mixing slurry is at opposite ends of the pool, fluids show reverse laminar flow under the action of guide plate. Therefore, the constant interfacial area cell can kept steady at a high stirring speed.

The interfacial area is 15 cm^2 unless otherwise stated. An aliquot of the aqueous phase (84 mL) followed by another aliquot of organic phase are added carefully to the cell chambers using a syringe, and stirring is started. Stirring speed for both phases in the majority of experiments is kept constant at 300 rpm unless otherwise stated. On starting the stirrer and after each 10 min interval, 0.2 mL of the aqueous phase is taken for analysis. The kinetic experiments are carried out at 298 K unless otherwise stated.

For the equilibrium experiments, equal volumes (20 mL each) of aqueous and organic phases are mixed and shaken for 30 min at 298±1 K.

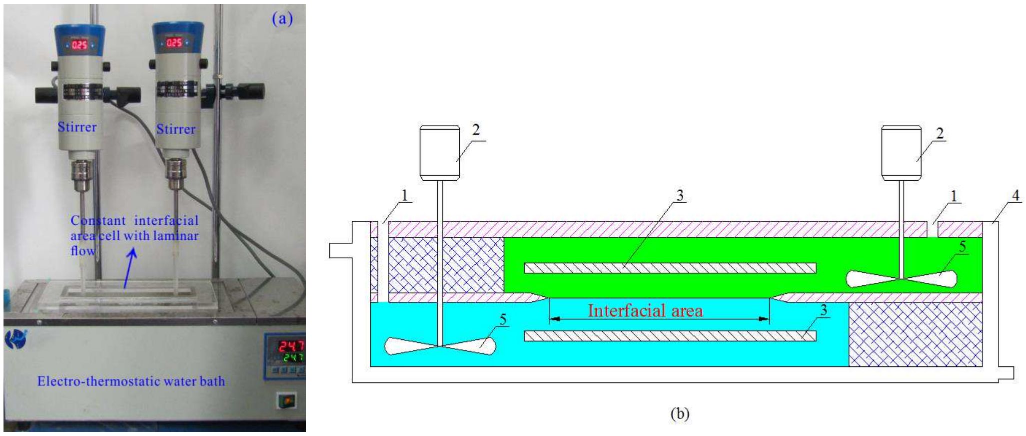

Fig. 1 Experimental devices of kinetics (a) and the structure of constant interfacial area cell with laminar flow (b). 1: sampling aperture; 2: motor; 3: guide plate; 4: electro-thermostatic water bath; 5: stirring paddle

2.3. Theoretical

It is assumed that the mass-transfer process could be formally treated as a pseudo-order reversible reaction with respect to Pr(III): [20]

$$\mathrm{Pr}_{(a)}^{3+} \underset{k_{oa}}{\overset{k_{ao}}{\rightleftarrows}} \mathrm{Pr}_{(o)}^{3+} \qquad (1)$$

where a, o, k_{ao} (cm·s^{-1}) and k_{oa} (cm·s^{-1}) represent the aqueous phase, organic phase, forward and backward mass transfer coefficient, respectively.

The change rate that the number of moles of Pr(III), n, enters into the organic phase, dn/dt, is given by the follow equation: [21]

$$-\frac{d[\mathrm{Pr}^{3+}]_{(o)}}{dt} = -\frac{dn}{Vdt} = \frac{Q}{V}(k_{oa}[\mathrm{Pr}^{3+}]_{(o)} - k_{ao}[\mathrm{Pr}^{3+}]_{(a)}) \qquad (2)$$

where t, V and Q represent time, either the aqueous or organic phase and the interfacial area, respectively.

Eq. (2) is equal to zero at equilibrium, the definition of the distribution ratio, k_d, is as follows:

$$k_\mathrm{d} = \frac{[\mathrm{Pr}^{3+}]^e{}_{(o)}}{[\mathrm{Pr}^{3+}]^e{}_{(a)}} = \frac{k_{ao}}{k_{oa}} \qquad (3)$$

According to the conservation of mass, and integrating Eq. (2), it follows that:

$$\ln(1 - \frac{[\mathrm{Pr}^{3+}]_{(o)}}{[\mathrm{Pr}^{3+}]^e_{(o)}}) = -\frac{Q}{V}(1 + k_\mathrm{d})k_{oa}t \qquad (4)$$

The slopes of the plots of $\ln\left\{1-([\mathrm{Pr}^{3+}]_{(o)} / [\mathrm{Pr}^{3+}]^e_{(o)})\right\}$ against t are used to evaluate k_{oa} and k_{ao}. All plots are straight lines in the present work, indicating that above assumption is reasonable.

The assumption is validated when the plot of $\ln\left\{1-([\mathrm{Pr}^{3+}]_{(o)} / [\mathrm{Pr}^{3+}]^e_{(o)})\right\}$ vs. t is constructed and the points at pH 2.5 and H_2A_2 concentration of 0.6 mol·L^{-1} are found to lie on straight line as show in Fig. 2, indicating that the mass transfer process could be treated as a pseudo-first-order reversible reaction.

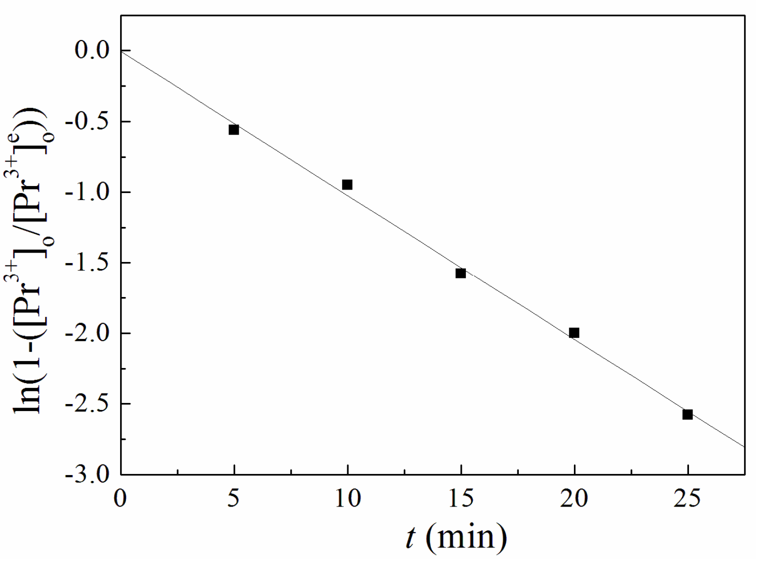

Fig. 2 Plots of $\ln\left\{1-([\mathrm{Pr}^{3+}]_{(o)}/[\mathrm{Pr}^{3+}]^{e}_{(o)})\right\}$ vs. *t* for this extraction system.

3. Results and discussion

3.1. Stoichiometry of the complex formation reactions for Pr(III)

The equilibrium equation corresponding to the extraction of Pr(III) from chloride medium in the presence of two complexing agents lactic acid and citric acid with D2EHPA in kerosene has been investigated based on the Eqs. (5) and (6).

$$\mathrm{Pr}^{3+}+\mathrm{x(HA)}_{(o)}+\mathrm{pL}^{-}=\mathrm{PrL_pA_{n\text{-}p}(HA)}_{\mathrm{x\text{-}n\text{+}p}(o)}+\mathrm{(n\text{-}p)H^+} \tag{5}$$

$$\log k_{\mathrm{d}}+\log Y=\log K+\mathrm{x}\log[\mathrm{HA}]_{(o)}+\mathrm{p}\log[\mathrm{L}^{-}]-(\mathrm{n}-\mathrm{p})\log[\mathrm{H}^{+}] \tag{6}$$

where *Y*, *K*, HA, and L^{-} represent complexing degree, equilibrium constant, one extractant and one complexing agent, respectively.

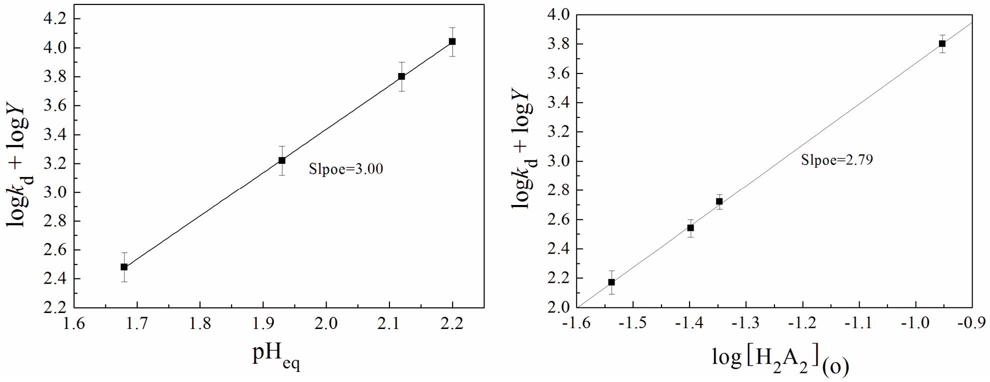

Fig. 3 Plots of the distribution ratio log k_{d} + log *Y* versus $\mathrm{pH_{eq}}$ and log k_{d} + log *Y* versus log $[\mathrm{H_2A_2}]$. $[\mathrm{PrCl_3}]_{(a)}\approx5.0\times10^{-3}$ mol·L^{-1}, [HLac]=1.50×10^{-3} mol·L^{-1}, $[\mathrm{H_3cit}]$=[LA]/10

As shown in Fig. 3, the plots of log k_d + log Y vs. pH_{eq} at fixed extractant and complexing agents concentrations give straight lines with the slope of about 3. Similarly, keeping the pH values and complexing agents concentrations as constant, the plots of log k_d + log Y vs. log [H_2A_2] are linear with slopes of about 3. According to the charge conservation in Eq. (5), p=0, this indicates that complexing agents do not enter into the organic phase. Thus, the equilibrium equation of extraction reaction for Pr(III) can be proposed as follows:

$$\mathrm{Pr}^{3+}_{(a)} + 3\mathrm{H_2A}_{2(o)} \underset{}{\overset{K_{ex}}{\rightleftarrows}} \mathrm{PrA_3}\cdot 3\mathrm{HA}_{(o)} + 3\mathrm{H}^{+}_{(a)} \quad (7)$$

where $\mathrm{PrA_3}\cdot 3\mathrm{HA}$ is the organic complex.

3.2. Extraction regime

In general, there are three possibilities to control the extraction mass transfer rate, including diffusion, kinetic or mixed controlled process. In fact, although criteria that can be used to distinguish the extraction rate regime have been reported, it is necessary to associate different items of experimental information to fully describe the kinetics of extraction.

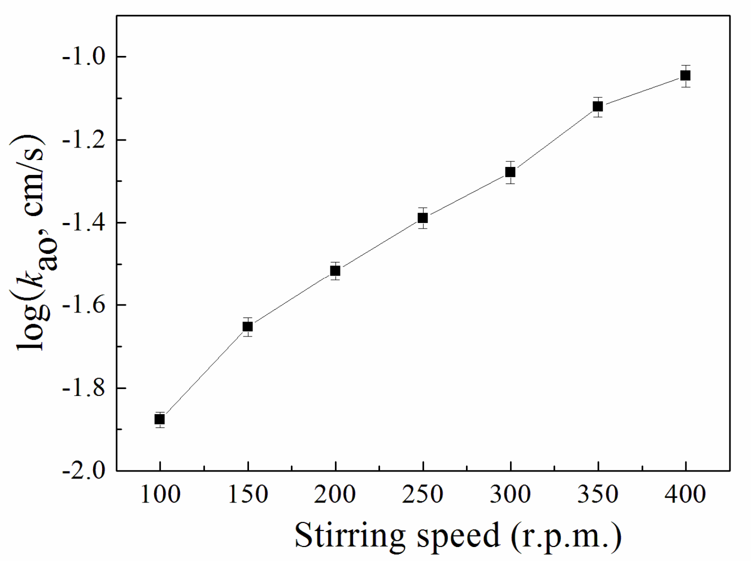

Fig. 4 Effect of stirring speed on mass transfer rate of Pr(III).
Aqueous phase: [$PrCl_3$]=0.10 mol·L^{-1}, pH=2.00; organic phase: [H_2A_2]=0.60 mol·L^{-1}, Q=15 cm^2, T=298K

For extraction kinetics, one criterion generally used to identify the extraction regime is independence of the extraction rate on the stirring speed in constant interfacial area cell. Fig. 4 shows the effect of the stirring speed on log k_{ao} for Pr(III) extraction with the H_2A_2 keeping the other conditions fixed. It shows an initial linear dependence in the range of 100-400 rpm, the possible reason might be that chemical reaction rate is faster than diffusion rate, so the effect of chemical reactions proceeds only to a small extend.

Another criterion that distinguishes between diffusion control and kinetic control is the experimental determination of the activation energy E_a of the extraction process. The effect of the temperature on the Pr(III) extraction rate is studied in the temperature range of 293 K to 318 K. The apparent activation energy (E_a) for the extraction is calculated from the slope of log k_{ao} vs. 1000/T, as shown in Fig. 5, and E_a is calculated as 10.76 kJ·mol^{-1} for Pr(III) extraction. In general, if the extraction rate is controlled by a chemical reaction, E_a is$>$40 kJ·mol^{-1}; if the rate is controlled by a diffusion process, E_a is$<$20 kJ·mol^{-1}; whilst E_a values value between 40 kJ·mol^{-1}and 20 kJ·mol^{-1}is expected for a mixed controlled regime.[22] The E_a of Pr(III) extraction in our experiments suggests a diffusion control regime in the temperature range of 293 K to 318K.

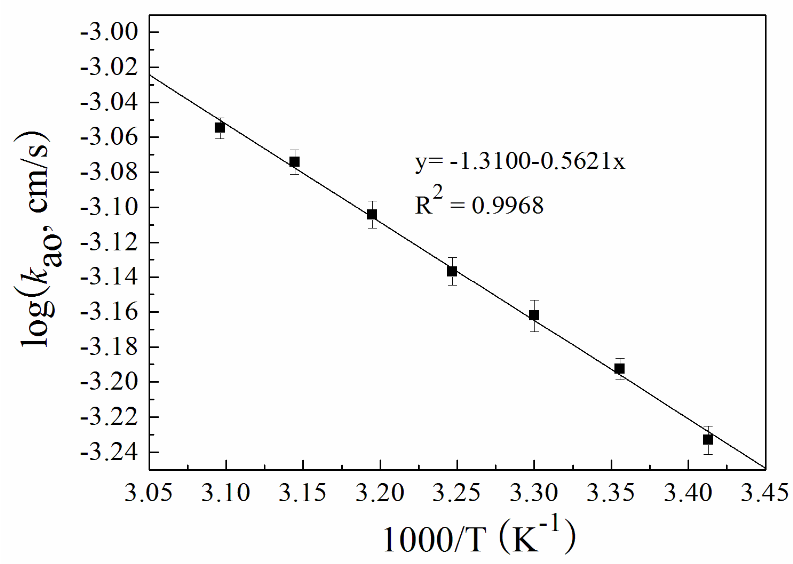

Fig. 5 Effect of temperature on the extraction rate of Pr(III).

Aqueous phase: [$PrCl_3$]=0.10 mol·L^{-1}, pH=2.00; organic phase: [H_2A_2]=0.60 mol·L^{-1}, Q=15 cm^2, 250 rpm

3.3. Reaction zone

The effect of specific interfacial area on the extraction rate also can be regarded as one of the important criteria to determine whether the chemical reaction that controlled the rate of extraction in a kinetic regime occurred in the bulk phase or at the interface. There are one problem to solve: whether the rate-controlling step occurs in the bulk phase or at the interface. If in the bulk phase, the initial rate will be independent of interfacial area. On the other hand, a reaction occurring at the interface will show a direct proportionality between the rate and the interfacial area.

The effect of the specific interfacial area Q/V (interfacial area/phase volume) on the extraction rate (k_{ao}) is studied, and it shows a linear relationship (Fig. 6), indicating that the reaction occurs in the interfacial zone for Pr(III) extraction with H_2A_2.

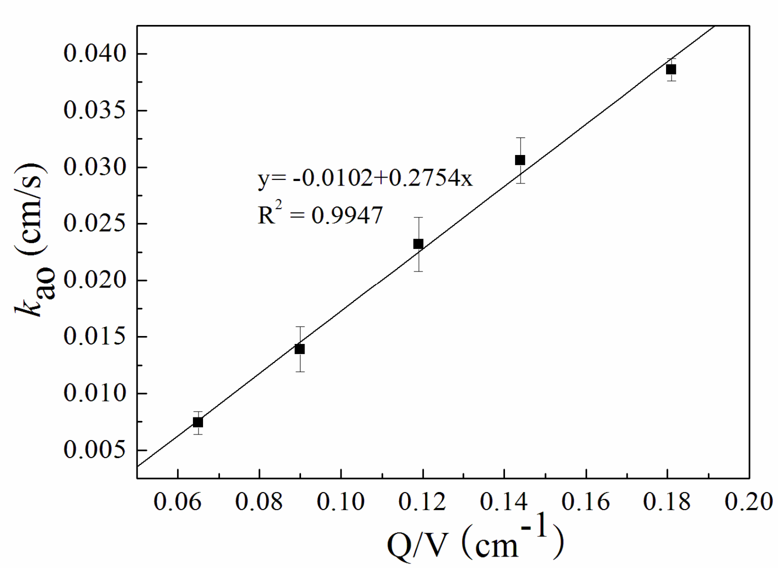

Fig. 6 The effect of the specific interfacial area Q/V on the extraction rate.
Aqueous phase: $[PrCl_3]$=0.10 mol·L^{-1}, pH=2.00; organic phase: $[H_2A_2]$=0.60 mol·L^{-1}, 250 rpm, T=298 K

3.4. Extraction rate equation for Pr(III)

The effect of pH (pH 1.75-2.50) and H_2A_2 concentration on the mass transfer rate of Pr(III) have been studied (Fig. 7). The information plotted logk_{ao} vs. pH yields straight line: y=-3.3434+0.9191x determines the 0.9191 slope, which is defensibly 1 and indicated that the reaction order with respect to hydrogen ion concentration is -1. The influence of extractant concentration on the extraction rate is investigated, too. A linear correlation between log k_{ao} and log $[H_2A_2]$ indicates that the order of extractant for Pr(III) extraction is 1.1274, that was 1.1274≈1.

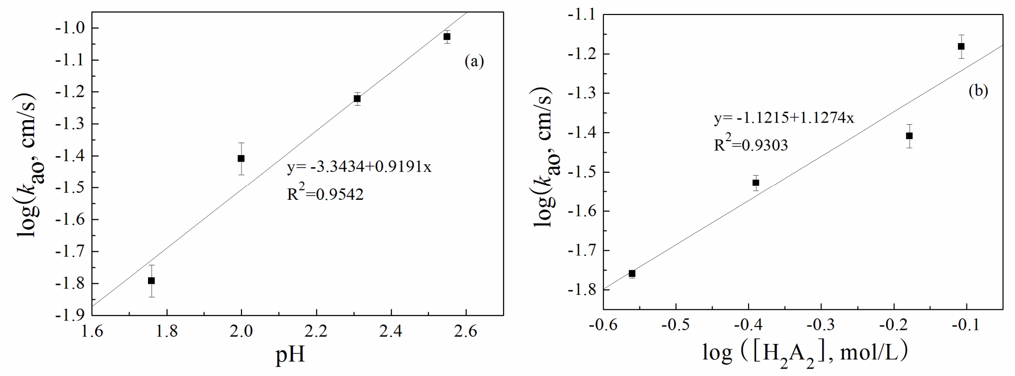

Fig. 7 Effects of pH value in the aqueous phase (a) and extractant concentration (b) on extraction rate.
$[PrCl_3]$=0.10 mol·L^{-1}, Q=15 cm^2, 300 rpm, T=298 K

According to the general kinetic equation for the formation of metal chelates, the extraction rate equation $R_\mathrm{f} = -d[\mathrm{Pr}^{3+}]/\mathrm{dt} = k_\mathrm{f}[\mathrm{Pr}^{3+}]^\mathrm{a}[\mathrm{HL}]^\mathrm{b}_{(\mathrm{o})}[\mathrm{H}^+]^\mathrm{c}$, moreover, using the values of the intercepts in Fig. 7, the extraction rate constant of the forward reaction, k_f is calculated to be $10^{-0.19}$. Accordingly, the rate equation for extraction at 298 K can be written as:

$$R_\mathrm{f} = -\frac{d[\mathrm{Pr}^{3+}]_{(o)}}{dt} = 10^{-0.19}[\mathrm{Pr}^{3+}]_{(a)}[\mathrm{H_2A_2}]_{(o)}[\mathrm{H}^+]^{-1}_{(a)} \qquad (8)$$

3.5. Mechanism and kinetic model for Pr(III)

From above, the chemical reaction for the extraction of Pr(III) by the H_2A_2 occurs at the liquid–liquid interface. Referring to the interfacial reaction model proposed by Danesi and Chiarizia, the mass-transfer process model of Pr(III) from the aqueous to the organic phase consists of the following steps (see Fig. 8), where, the complexing agents lactic acid and citric acid combine with hydrogen ions exchanged with Pr(III), and play a buffer role in the extraction, which slows down the effect of high acid on the extraction process. The following reactions will be considered.

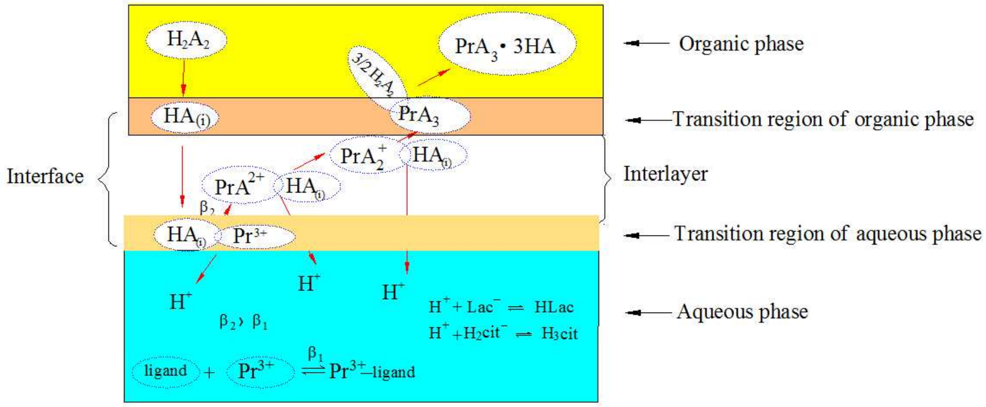

Fig. 8 The schematic description of mass-transfer process of Pr(III).
β_1 and β_2 are the complexing constant between Pr(III) and ligand, between Pr(III) and extractant, respectively.

$$\mathrm{H_2A_{2(o)}} \underset{}{\overset{K_1}{\rightleftarrows}} \mathrm{H_2A_{2(i)}} \overset{K_2}{\rightleftarrows} 2\mathrm{HA_{(i)}} \qquad (9)$$

$$\mathrm{Pr}^{3+}_{(a)} + \mathrm{HA}_{(i)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{PrA}^{2+}_{(i)} + \mathrm{H}^+_{(a)} \qquad (10)$$

$$\mathrm{PrA}^{2+}_{(i)} + \mathrm{HA}_{(i)} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{PrA}^{+}_{2(i)} + \mathrm{H}^+_{(a)} \qquad (11)$$

$$\mathrm{PrA}^{+}_{2(i)} + \mathrm{HA}_{(i)} \overset{K_{e1}}{\rightleftarrows} \mathrm{PrA}_{3(i)} + \mathrm{H}^+_{(a)} \qquad (12)$$

$$\mathrm{PrA}_{3(i)} + \frac{3}{2}\mathrm{H_2A_{2(o)}} \overset{K_{e2}}{\rightleftarrows} \mathrm{PrA_3 \cdot 3HA_{(o)}} \qquad (13)$$

where subscripts i, a and o represent the interface, aqueous and organic phases, respectively; k_1, k_2, k_{-1}

and k_{-2} are the forward and backward reaction constants, respectively; K_1 is the partition ratio of dimeric extractant between the organic phase and the interface, K_2 is the dissociation constant, respectively; K_{e1} and K_{e2} are the equilibrium constants.

Considering Eq. (11) as the rate-controlling steps, based on Eq. (9), one can write the following equations.

$$[\mathrm{HA}_{(i)}]^2 = K_2[\mathrm{H_2A_{2(i)}}] = K_2K_1[\mathrm{H_2A_{2(o)}}] \tag{14}$$

$$R_f = k_2[\mathrm{PrA}^{2+}_{(i)}][\mathrm{HA}_{(i)}] \tag{15}$$

$$\frac{d[\mathrm{PrA}^{2+}_{(i)}]}{dt} = k_1[\mathrm{Pr}^{3+}_{(a)}][\mathrm{HA}_{(i)}] - k_{-1}[\mathrm{PrA}^{2+}_{(i)}][\mathrm{H}^{+}_{(a)}] - k_2[\mathrm{PrA}^{2+}_{(i)}][\mathrm{HA}_{(i)}] \tag{16}$$

By assuming that an interfacial steady state is instantaneous, and then

$$\frac{d[\mathrm{PrA}^{2+}_{(i)}]}{dt} = 0$$

it follows that:

$$[\mathrm{PrA}^{2+}_{(i)}] = \frac{k_1[\mathrm{Pr}^{3+}_{(a)}][\mathrm{HA}_{(i)}]}{k_{-1}[\mathrm{H}^{+}_{(a)}] + k_2[\mathrm{HA}_{(i)}]} \tag{17}$$

When Eqs. (14) and (17) are substituted into Eq. (15), the following expression for the mass transfer rate is obtained:

$$R_f = k_2[\mathrm{PrA}^{2+}_{(i)}][\mathrm{HA}_{(i)}] = \frac{k_1k_2K_1K_2[\mathrm{Pr}^{3+}_{(a)}][\mathrm{H_2A_{2(o)}}]}{k_{-1}[\mathrm{H}^{+}_{(a)}] + k_2[\mathrm{HA}_{(i)}]} \tag{18}$$

Assuming that the rate of Pr^{3+} transfer from the aqueous to the organic phase is faster than the reverse rate, $k_{-1} \gg k_2[\mathrm{HA}_{(i)}]$, and Eq. (18) can be simplified as follows:

$$R_f = k_2[\mathrm{PrA}^{2+}_{(i)}][\mathrm{HA}_{(i)}] = k_f[\mathrm{Pr}^{3+}_{(a)}][\mathrm{H_2A_{2(o)}}][\mathrm{H}^{+}_{(a)}]^{-1} \tag{19}$$

where $k_1k_2K_1K_2 / k_{-1} = k_f$

The above mechanism is consistent with the rate Eq. (8) obtained from experimental results. The equations derived from interfacial-reaction models have been found to be in good agreement with the ones obtained from experimental data, confirming that the basic assumption and proposed model are reasonable. That means the chemical reaction is located at the liquid–liquid interface and the extraction rate is controlled by step Eq. (11) interfacial chemical reactions.

4. Conclusions

(1) Stoichiometry of the complex formation reactions for Pr(III) is determined to be $\mathrm{PrA_3 \cdot 3HA}$.

(2) The kinetics of extraction of Pr(III) from chloride medium in the presence of lactic acid and citric acid with the H_2A_2 is a diffusion- controlled process occurring at the interface.

(3) The dependence of the extraction rate on species concentration and the rate equations are deduced as follows:

$$R_{\mathrm{f}} = -\frac{d[\mathrm{Pr}^{3+}]_{(o)}}{dt} = 10^{-0.19}[\mathrm{Pr}^{3+}]_{(a)}[\mathrm{H_2A_2}]_{(o)}[\mathrm{H}^+]_{(a)}^{-1}$$

(4) The rate-determining step obtained by predictions derived from interfacial reaction models is

$$\mathrm{PrA}^{2+}_{\mathrm{(i)}} + \mathrm{HA}_{\mathrm{(i)}} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{PrA}^{+}_{2\mathrm{(i)}} + \mathrm{H}^{+}_{\mathrm{(a)}}$$

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