PAPER

Extraction and separation of Ce(III) and Pr(III) in the system containing two complexing agents with di-(2-ethylhexyl) phosphoric acid

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In order to develop a novel separation technology superior to the current extraction systems, the extraction behaviors of Ce(III) and Pr(III) from chloride medium with P204 in the presence of two complexing agents lactic acid (LA) and citric acid (H_3cit) have been reported. The distribution ratios increase with the increase of the equilibrium pH and the ratio of [H_3cit] : [LA] under certain conditions. The separation factors of Ce(III) and Pr(III) increase with the ratio of [H_3cit] : [LA] at fixed pH, and the maximum value is as high as 5.78 in this complexing system. The maximum saturated extraction capacity is 27.08 g L^{-1} which is close to that in the current saponified P507 extraction system. The equilibrium constants and thermodynamic functions, ΔG, ΔH and ΔS have been calculated. Lactic acid and citric acid can be effectively recycled and enriched, providing possibilities for dissolving minerals in the circular process. By comparison with the experimental results, this complexing extraction method could be regarded as an effective strategy for separating REs.

1. Introduction

From an industrial point of view, rare earth elements are important owing to their unique properties and wide range of applications in various fields such as electronics, magnetism, metallurgy, phosphors, catalysts, glass, laser and ceramic technology.[1,2] The separation of those elements has become important because of the high commercial value of rare earth elements in various important fields. During the last few years, solvent extraction is employed to separate the rare earth elements on an industrial scale, playing a main role in rare earths hydrometallurgy industry.[3,4] At present, P204 is a kind of typical organic phosphonic acid extractant, used for the light rare earths separation because of its higher acidity and lower cost, however, the needed high stripping acidity makes it restricted in the extraction process of middle and heavy rare earths.[5] Currently, saponification can enhance the extraction capacities of acidic extractants, but the resulting loss of ammonium ion to aqueous phase causes serious pollution, also, saponified acidic extractant is water in oil microemulsion systems in organic phase, especially, a high saponification extent will result in the emulsification and third phase during extraction.

Now, many researchers explored some new extractants,[6-8] extraction systems,[9-11] or extraction equipment,[12] superior to the current saponified extraction systems. It is considered that introducing additive like a water-soluble complexing agent into the aqueous phase is an effective method to improve the extraction characters of P204. Some literature surveys indicate that the selective extraction by adding EDTA, HEDTA and DTPA to the aqueous phase is an effective method for separating some adjacent rare earths.[13-16] In our earlier work, the organic acid, such as citric acid (H_3cit) or lactic acid (LA) was chosen as a complexing agent, and the effect of complexing agents on the extraction reveals that the complexing system could not only improve the extraction capacity of P204, but also heighten the selectivity among some adjacent rare earths.[17-20] Therefore, studies on the complexing agent H_3cit or LA promote us to investigate a new system for extracting and separating rare earths.

In the present study, the extraction behaviors of Ce(III) and Pr(III) with P204 in the presence of two complexing agents H_3cit and LA have been investigated. The purpose is to understand the influence of H_3cit and LA on the extraction and separation of Ce and Pr, provide fundamental information for complexing extraction systems, and offer a unique possibility for the separation between Ce and Pr.

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2. Experimental

2.1 Reagents and apparatus

P204 supplied by Tianjin Kermel Chemical Reagent Co. Ltd was used without further purification and dissolved in sulfonated kerosene to the required concentrations. The mixed stock

solutions of $RECl_3$ (RE^{3+} = La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+}) were prepared by dissolving their oxides (purity ≥ 99.9%) at an appropriate mass ratio with a certain proportion of LA, H_3cit and a small amount of hydrochloric acid and diluting to required volume with distilled water, and then standardized by titration using EDTA standard solution with xylenol orange as an indicator in hexamethylenetetramine buffer solution. Lactic acid (LA) and citric acid (H_3cit) were obtained from Sinopharm Chemical Reagent Co. Ltd. All other reagents were of analytical reagent grade.

The solution's pH was measured with a pH meter (model pHs-3C, ±0.01 pH unit). An Agilent 1100 model HPLC instrument was used to measure the concentrations of lactic acid and citric acid.

2.2 Solvent extraction experiments

Equal volumes (50 mL) of aqueous and organic solutions were mixed and shaken for 30 min with the help of a mechanical shaker at 293 ± 1 K (unless otherwise stated), and initial experiments showed that equilibrium was achieved within 30 min. After separating the phases, the organic phase loading rare earths was stripped with 6 mol L^{-1} HCl with an O/A volume ratio of 1 three times. In the extraction sections 3.1, 3.2 and 3.3, the concentration of rare earth ion in the aqueous phase was measured by EDTA titration, while in the temperature experience, the concentration of rare earth ion in the aqueous phase was determined by a Prodigy High Dispersion ICP Spectrometry, and these concentrations of rare earth ion in the organic phase were obtained by mass balance. Distribution ratio (D) is defined as the ratio of concentrations of metal ion in the organic and aqueous phases. The equilibrium pH (pH_{eq}) was measured using a pH meter.

2.3 A schematic flowsheet for the experiments

In our study, we choose the light rare earths (La–Nd) as an object, the separation of Ce/Pr is firstly studied, and then the separation processes of La/Ce and Pr/Nd are studied individually (not shown in this manuscript). In order to avoid the ammoniac nitrogen pollution at the source in the current saponified P507 or P204 extraction system, we propose the complexing extraction in the presence of lactic acid (LA) and citric acid (H_3cit), which are divided into three main sections: extraction and separation of rare earths; extraction of complexing agents; and recycling lactic acid and citric acid. The schematic flowsheet of this complexing extraction is shown in Fig. 1.

3. Results and discussion

3.1 Extraction of RE^{3+} in the P204–LA–H_3cit system

In our previous work, the optimal concentration of complexing agent lactic acid in the P204–LA extraction system is 0.60 mol L^{-1}.[19] In order to avoid the rare earth complex precipitation in the aqueous phase or the separation out of the extracted complexes in the organic phase, the ratio range of [H_3cit] : [LA] is chosen from 1 : 25 to 1 : 10.

In practical application, the effect of equilibrium pH is considered to be an important parameter, primarily because the acidity control of the aqueous phase is one of the key links in industrial processes. In general, lanthanide extraction by P204 is also pH dependent as the phase transfer mechanism relies on dissociation of three protons to accommodate a trivalent metal. It is thus obvious that the hydrogen ions released from acidic extractants in ion-exchange mechanism affect negatively the metal ion extraction due to the increase of acidity in aqueous phase.

Fig. 2 shows the effect of equilibrium pH (pH_{eq}) on the extraction of RE^{3+} when the initial concentrations of rare-earth chloride solution and extractant P204 are kept constant at 0.20 mol L^{-1} and 1.00 mol L^{-1}, respectively. In this figure, distribution ratios (D) are observed to increase with the increasing of pH_{eq}, also, it can be seen that the distribution ratios vary extensively enough at higher equilibrium pH. Therefore, the light rare earths could be separated from each other effectively at an appropriate acidic range.

Fig. 3 gives the effect of [H_3cit] : [LA] on the extraction of Ce and Pr under some constant conditions. It is evident that the distribution ratios D increase with [H_3cit] : [LA] increasing from 1 : 25 to 1 : 10. This can be taken as an indication that the complexing agents lactic acid and citric acid play a buffer role in this extraction system, that is, part of the hydrogen ions exchanged by RE^{3+} combine with the lactate and citrate anions, which slows down the effect of higher acidity in the raffinate on the distribution ratios.

3.2 Separation possibility between Ce and Pr

Based on the distribution ratios, we determine the separation factor (S.F.) which is defined as is the ratio of distribution ratios (D) of two metals measured under the same condition. In this section, mixed solutions of Ce/Pr are prepared, the total concentration is 0.20 mol L^{-1}, and the liquor with a composition of around, in mol L^{-1}, 0.15 Ce and 0.05 Pr. Table 1 gives the S.F. values between Ce and Pr in this system. It is interesting to note that the maximum S.F. value of Pr/Ce is larger enough than that in the current P507 system without complexing agents (1.8–2.2), and the S.F. value of Pr/Ce is as high as 5.78 at pH 2.5 and [H_3cit] : [LA] of 1 : 10, which indicates that the lighter lanthanides (La–Nd) can be separated between Ce and Pr firstly, and then La/Ce and Pr/Nd are separated individually. Therefore, the studied system has the potential application for separating the light rare earths, and provides useful information for developing more efficient separation processes.

3.3 Extraction capacity in the P204–LA–H_3cit system

In general, distribution ratio, separation factor and extraction capacity are three important extraction parameters. In this section, the mixture solution of Ce/Pr of 0.2 mol L^{-1} is prepared, and the concentrations of non-saponified P204 and lactic acid are 1.0 mol L^{-1} and 0.6 mol L^{-1}, respectively. Fig. 4 shows the changing relationship between extraction capacity and the complexing agents, and the extraction capacity increases with
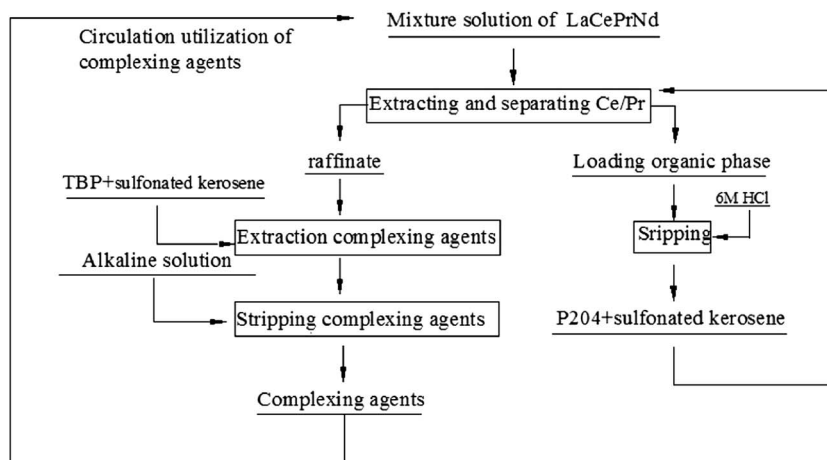
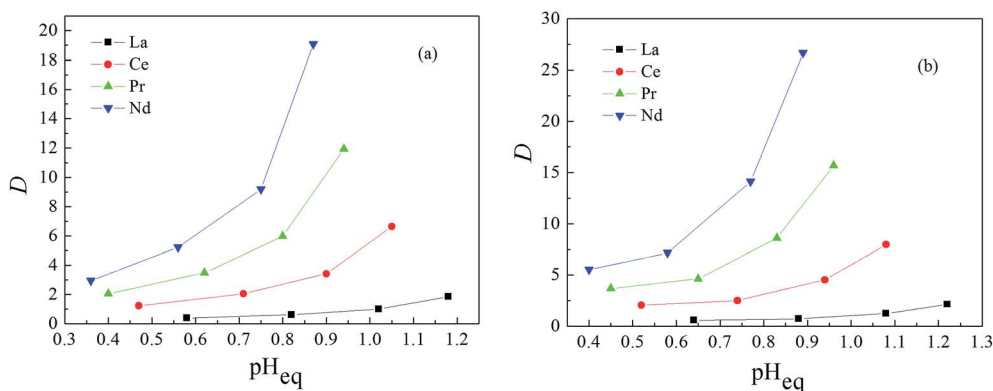Fig. 1 Schematic flowsheet of this complexing extraction system.

Fig. 2 Effect of pH_{eq} on the distribution ratios of RE(iii) with P204. (a) [LA] = 0.6 mol L^{-1}, [H_3cit] : [LA] = 1 : 25; (b) [LA] = 0.6 mol L^{-1}, [H_3cit] : [LA] = 1 : 15.

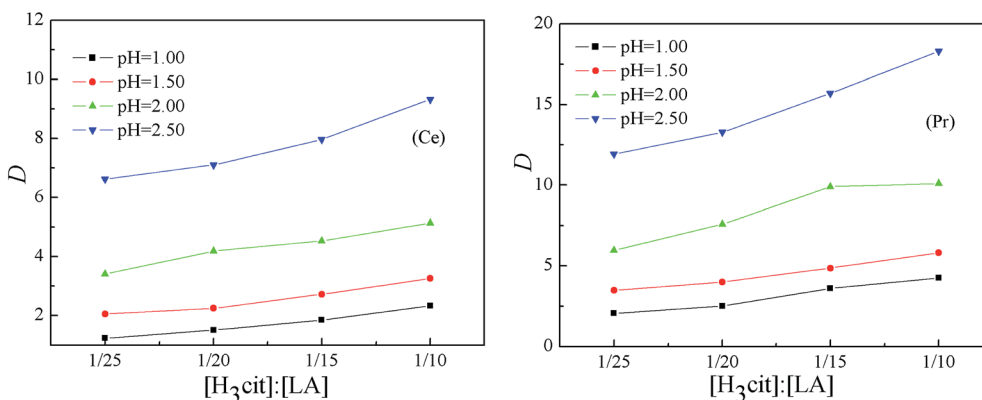

Fig. 3 Effect of the concentration ratio of [H_3cit] : [LA] on the distribution ratios of RE(iii) with P204. [RECl$_3$] = 0.2 mol L^{-1}, [LA] = 0.6 mol L^{-1}, [P204] = 1.0 mol L^{-1}.

the increasing of [H_3cit] : [LA], and the maximum value reaches up to 27.08 g L^{-1} which is larger than that in the P204–LA–system (24 g L^{-1}) under the same pH and lactic acid concentration.

3.4 Thermodynamic parameters measure and calculate

Temperature is another important parameter for practical application as it is obvious that only a small drop in the temperature of extraction may save a lot of energy. Based on the

Table 1 Separation factors (β) of Ce/Pr in the P204–RECl$_3$–LA–H$_3$cit system

pH	[LA] (mol L^{-1})	[H$_3$cit] : [LA]	D_{Ce}	D_{Pr}	$\beta_{Pr/Ce}$
2.00	0.60	1/10	1.5731	7.069	4.49
		1/15	1.4226	3.1439	2.21
		1/20	1.3683	2.6434	1.93
		1/25	1.2958	2.0514	1.58
2.50	0.60	1/10	2.6721	15.4484	5.78
		1/15	2.6053	6.0964	2.34
		1/20	2.2963	4.7674	2.08
		1/25	2.2702	4.0169	1.77
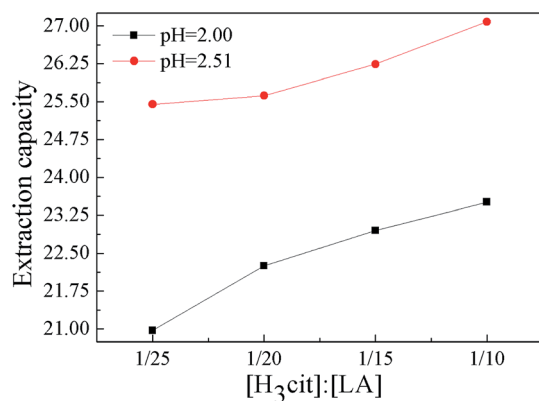
Fig. 4 Effect of the concentration ratio of [H$_3$cit] : [LA] on extraction capacity.

extraction mechanism in our previous studies, we conclude that the extraction mechanism is a cation exchange, and the extraction reaction in the complexing system is listed as: $RE_{(a)}^{3+}$ + $3H_2A_{2(o)}$ ↔ $REA_3 \cdot 3HA_{(o)}$ + $3H_{(a)}^+$, where, the following thermodynamic parameters are all established on the cation exchange reaction. Fig. 5 shows the effect of temperature on the extraction of Ce and Pr with P204 at fixed pH, fixed concentrations of P204 and complexing agents in different systems, the slopes shows that the temperature has little effect on the

extraction systems. The change of enthalpy of the reaction, ΔH, can be determined according to the following equation:

$$\log D = \frac{-\Delta H}{2.303RT} + C \quad (1)$$

where R is the gas constant and C is a constant. The change of Gibbs free energy, ΔG, and the change of entropy, ΔS of these systems at 293 K can be obtained:

$$\Delta G = -RT \ln K \quad (2)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (3)$$

ΔG, ΔH and ΔS can be obtained as shown in Table 2. The calculations of ΔH (>0 kJ mol^{-1}) indicate that the extraction processes are endothermic reactions, and ΔG values indicate that the extraction systems containing complexing agents are suitable to be carried at room temperature by comparing the ΔG values in different systems. The positive values of ΔS suggest the extraction system is more disordered, which is in accordance with the theory of increasing of entropy from the view of statistics.

3.5 Extracting and recycling lactic acid and citric acid

Recycling lactic acid and citric acid is the last section of the schematic flowsheet of this complexing extraction. Currently, the concept of "green chemistry" has been gained more and more attention, and more and more constraining environmental regulations have been adopted to limit the industrial pollution. In our previous studied results, these two complexing agents can be effectively recycled, more than 99% recovery is obtained, and the COD value (65.84 mg L^{-1}) in the raffinate meets the "Emission Standards of Pollutants from Rare Earths Industry" (COD ≤ 80 mg L^{-1}) from the Ministry of Environmental Protection, People's Republic of China (2006).[21] Fig. 6 shows the relationship between the enriched concentration and stripping stage, as can be seen, using the alkaline solution of pH = 13, the enriched concentrations of lactic acid and citric acid are up to 1.40 mol L^{-1} and 0.54 mol L^{-1} using a cross-flow
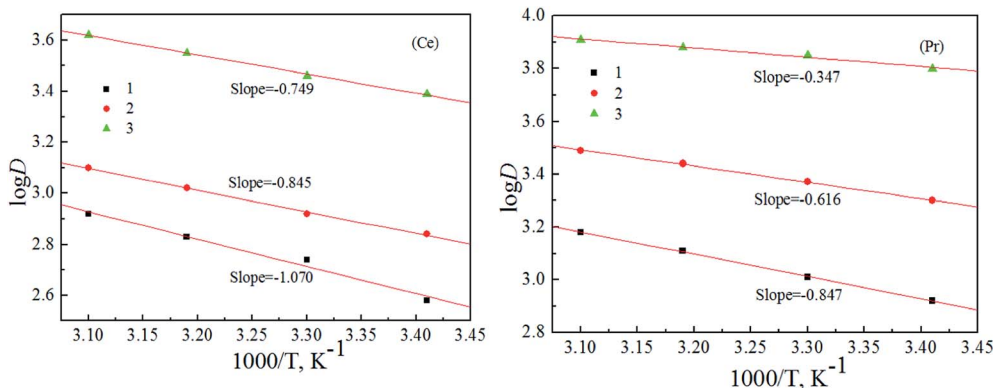

Fig. 5 Effect of temperature on the extraction of Ce and Pr with P204 in different systems. 1: P204–HCl system; 2: P204–HCl–LA system; 3: P204–HCl–LA–H$_3$cit system [RE^{3+}]$_{(a)}$ ≈ 5.0 × 10^{-3} mol L^{-1}, [P204] = 0.20 mol L^{-1}, pH ≈ 3.50, [LA] = 1.50 × 10^{-3} mol L^{-1}, [H$_3$cit] = [LA]/10.

Table 2 Thermodynamic parameters of RE(iii) with P204 in different systems

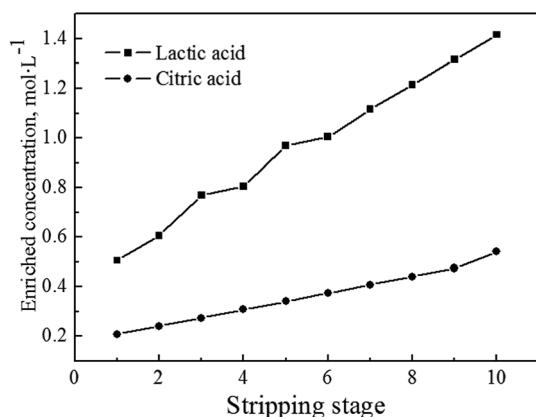|	Systems	log K	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Ce	P204–HCl–LA system	0.07	16.17	−0.39	56.52
	P204–HCl–LA–H$_3$cit system	0.202	14.34	−1.13	52.80
Pr	P204–HCl–LA system	0.152	11.79	−0.85	43.14
	P204–HCl–LA–H$_3$cit system	0.294	6.64	−1.65	28.29

Fig. 6 Relationship between the enriched concentrations of complexing agents and stages.

extraction with 10 extraction stages at a phase ratio $V_o/V_a = 5 : 1$ and $t = 50\,°C$, which will provide the probabilities for dissolving minerals in the circular process.

4. Conclusions

The extraction of Ce(iii) and Pr(iii) from chloride solution using two complexing agents lactic acid and citric acid has been performed. It is found that:

(1) The distribution ratios are observed to increase with equilibrium pH and the ratio of [H$_3$cit] : [LA], and the separation factor of Ce(iii) and Pr(iii) increases with the ratio of [H$_3$cit] : [LA], and the maximum value is 5.78.

(2) The effect of temperature on the extraction is studied, and the extraction process is an endothermic driven, and the thermodynamic functions, ΔG, ΔH and ΔS have been calculated.

(3) The enriched experiments show that lactic acid and citric acid can be effectively recycled and enriched, which provides the probabilities for dissolving minerals in the circular process.

Acknowledgements

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