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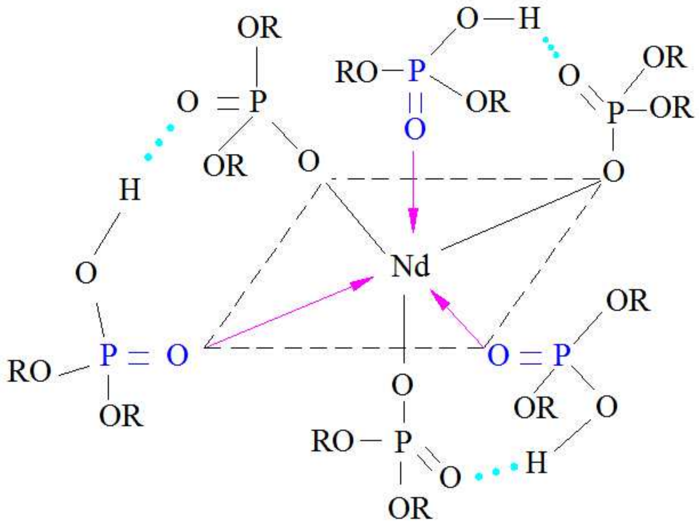

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Study on the aqueous solution behavior and extraction mechanism of Nd(III) in the presence of a complexing agent lactic acid with di-(2-ethylhexyl) phosphoric acid

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Abstract: The aqueous solution behavior and extraction mechanism of single Nd(III) from chloride medium with di-(2-ethylhexyl) phosphoric acid (D2EHPA, H_2A_2) in the presence of a complexing agent lactic acid (HLac) have been reported. The analyses of FT-IR and UV of aqueous solution indicate that there is a coordination mechanism between Nd^{3+} and Lac^- in the form of the carboxyl oxygen bridge bidentate ligand. Cation extraction mechanism has been studied using the method of slope analysis and saturation loading capacities, and also confirmed by FT-IR and NMR. The equilibrium constants and thermodynamic functions have been calculated. The separation factors of La/Ce, Ce/Pr and Pr/Nd are 3.24, 2.04 and 1.58, indicating that this system is beneficial for separating light rare earths. The results could provide some reference value for complexing extraction system.

Keywords: Nd(III); aqueous solution behavior; extraction mechanism; D2EHPA; lactic acid

1. Introduction

Lanthanide elements have gained a great attention in the last few decades, owing to their unique properties and wide range of applications, especially in metallurgy, ceramic industry, and nuclear fuel control. [1-3] Neodymium (Nd), which is one of the most abundant rare earths, is of current interest, because it is the basis of the most common solid-state lasers.[1,4] In industrial practices, Nd(III) has been applied extensively as a catalyst, additive, and permanent-magnet material. [5]

Solvent extraction is employed to separate the rare earth elements on an industrial scale, playing a main role in the production of neodymium compounds in the hydrometallurgical flowsheets. [6,7] Acidic organophosphorous extractants, such as di-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH/EHP), are widely used for this purpose. In the solvent extraction of metals with acidic extractants, the acid liberated during the process adversely affects the metal extraction. To overcome this problem, the use of the acidic extractants saponified with NaOH or

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$NH_3 \cdot H_2O$ is tried.[8] Partial saponification is preferred to avoid gel formation and the solubility of the saponified extractant in the aqueous phase,[9] but it will face major environmental problems in the coming decades with ammonia–nitrogen waste-water disposal. Therefore, there is a growing interest in the development of new extractants or extraction systems for the extraction and separation of rare earths as a group or individual ions.

Modification of the aqueous phase species by adding a water-soluble complexing agent is known to be one of the effective methods for improving the extraction and separation ability of the metals.[10] The most general water-soluble complexing agents employed in the extraction system are amino polyacetates, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Some literature surveys indicate that the extraction method including EDTA and DTPA has succeeded in enhancing the selectivity in rare earth metal separation.[10-13] While there are also some other complexing agents like 2-ethyl-2-hydroxy butyric acid,[14] acetic acid,[15] lactic acid,[16] citric acid.[17] These processes essentially exploit the different complexing abilities of lanthanides and actinides towards the extractant and the aqueous complexing agents for efficient separation. In our earlier work, the organic acid, such as citric acid (H_3Cit) or lactic acid (HLac) is chosen as a complexing agent, and the effect of complexing agents on the extracting and separating light rare earths reveals that the complexing system could not only improve the extraction capacity of D2EHPA, but also heighten the selectivity among some adjacent rare earths.[18-20]

If a new extraction system would be applied to the industrial practices, it is necessary to understand the basic aqueous solution behavior and extraction mechanism. As part of our continuing interest in the extraction process, the aqueous solution behavior and extraction mechanism of Nd(III) with non-saponification D2EHPA in the presence of complexing agent (HLac) has been investigated. The purpose is to understand the influence of HLac on the extraction and provide fundamental information for complexing extraction systems.

2. Experimental

2.1. Reagents and apparatus

D2EHPA extractant and sulfonated kerosene are purchased from Luoyang ZhongDa Chemical Industry Co., Ltd. The extractant is used without further purification and dissolved in sulfonated kerosene to the required concentrations. The aqueous phase is prepared by dissolving Nd_2O_3 (purity≥99.9%) with a

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certain proportion of HLac 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. The rare earth concentrations in the extraction mechanism and temperature experiments are measured by a Prodigy high dispersion inductively coupled plasma spectrometer (Leeman labs, America). The ionic strength of the aqueous phase is maintained constant by the addition of NaCl. Lactic acid (HLac) is obtained from Sinopharm Chemical Reagent Co. Ltd. All other reagents are of analytical reagent grade.

A pHS-3C digital pH meter (Shanghai Rex Instruments Factory) is used for pH measurements. UV-vis spectroscopy is analyzed by spectrophotometry using an Optizen 2120 spectrophotometer (Mecasys Co. Ltd, Korea). IR spectra are measured with an Affinity-1 FT-IR spectrometer. ^{1}H and ^{31}P NMR spectra are obtained in $CDCl_3$ with an AVANEC-600 NMR spectrometer (Bruker, Fällanden, Switzerland).

2.2. Experiments procedure

For the analysis of aqueous solution experiments: some different concentrations of lactic acid solutions are added into the $NdCl_3$ solution (0.05 $mol\cdot L^{-1}$), and a solution of NaCl (0.75 $mol\cdot L^{-1}$) is used to keep the ionic strength constant, and then the pH value is adjusted to be 2.5 by adding a small amount of HCl and NaOH solution. These solutions keep 30 min at room temperature after constant volume 50 mL, and then begin to conduct the measurements of FT-IR and UV-Vis in the quartz microplate.

For the extraction experiments: equal volumes (50 mL) of aqueous and organic solutions are mixed and shaken for 30 min at 298 ± 1 K (except for the temperature experiments), which is determined in preliminary experiments to be sufficient to attain equilibrium. After separating the phases, the organic phase is collected for the subsequent stripping and recycling experiments, and the aqueous phase samples are then analyzed for Nd(III) concentration. All the concentrations in the aqueous phase are obtained from three replicate measurements. The distribution ratio D is defined as follows:

$$D = \frac{C_i - C_a}{C_a} \tag{1}$$

where C_i and C_a represent initial and final concentrations of Nd^{3+} in the aqueous phase, respectively.

3. Results and discussion

3.1. UV analysis of the Nd-HLac aqueous solution

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Fig. 1 shows the UV absorption spectroscopy of Nd-HLac aqueous solution at the different HLac concentrations. As can be seen that, with increase in HLac concentration, the ultraviolet absorption peak has different levels of red shift, and the absorbance (A) increases as a whole, indicating that there is a coordination effect between Nd^{3+} and Lac^{-}. This may be explained that the electron cloud around the oxygen in the HLac molecular geometry shifts to the empty orbitals of Nd^{3+} after forming the coordination bond between Nd^{3+} and oxygen in the carboxylate radical, which prompts to increase the conjugate system, the π electron cloud density around Nd^{3+} and the delocalization degree of the conjugated π electron are both increased, the π-π* transition can be extremely reduced, so ultraviolet absorption enhances and the wavelength (λ) has the effect of "red shift". In addition, the absorbance begins to stabilize when the ratio of $[NdCl_3]$:[HLac] exceeds 3, which indicates that formation of complexes is basically stable.

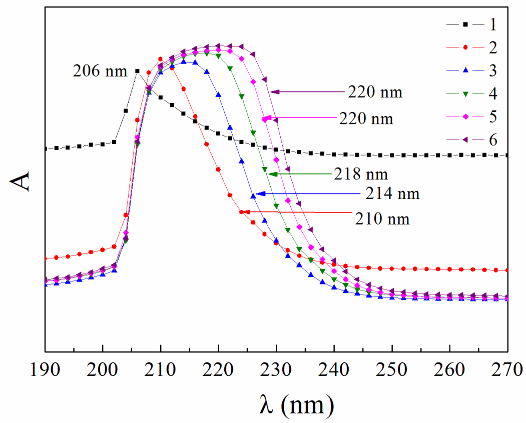

Fig. 1 UV absorption spectroscopy of Nd-HLac solution:
1: $[NdCl_3]$:[HLac]=5:1; 2: $[NdCl_3]$:[HLac]=1:1; 3: $[NdCl_3]$:[HLac]=1:2;
4: $[NdCl_3]$:[HLac]=1:3; 5: $[NdCl_3]$:[HLac]=1:4; 6: $[NdCl_3]$:[HLac]=1:5

The UV analysis of Nd-HLac solution shows that there is a coordination mechanism between Nd^{3+} and Lac^{-}, but the composition of complexes is not clear. In general, molar ratio is the usual method to determine the compositions of complexes. Fig. 2 shows the curves of Nd-Lac complexes determined by the molar ratio method at the maximum absorption wavelength 220 nm. As can be seen that, the molar ratio of $[Lac^{-}]$:$[Nd^{3+}]$ is in the range of 1-2, indicating that the combination between Nd^{3+} and Lac^{-} is 1:1 and 1:2, namely $Nd(Lac)^{2+}$ and $Nd(Lac)_2^{+}$ according to the principle of molar ratio method. Meantime, the relationship between distribution fraction and pH value for Nd^{3+}-Lac^{-} ligand complexes is calculated, and shown in Fig. 3. It is found that the main species are $Nd(Lac)^{2+}$ and $Nd(Lac)_2^{+}$ when the pH in the solution is 2.5 based on the pK_a of HLac and the stability

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constants of the complex between Nd and Lac$^-$, which is in accordance with the results analyzed by UV method.

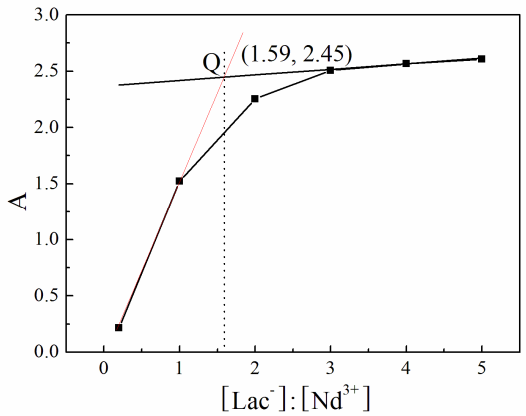

Fig. 2 The complex composition determined by the molar ratio method: $[NdCl_3]$=0.05 mol·L^{-1}, pH=2.50

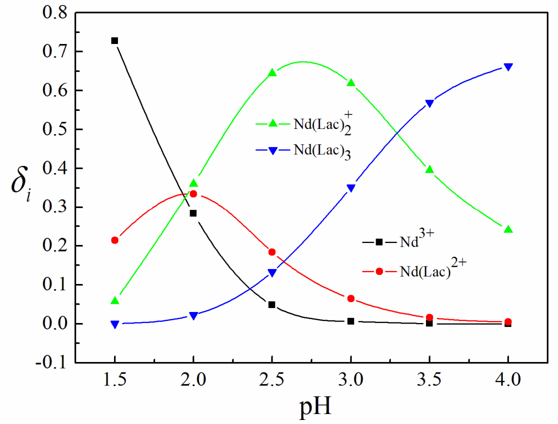

Fig. 3 Relationship between distribution coefficient and pH value for Nd^{3+}-Lac^- ligant complexes

3.2. FT-IR analysis of the Nd-HLac aqueous solution

In order to further confirm the coordination mechanism of Nd^{3+}-Lac^- complex, the infrared spectrum of HLac and $NdCl_3$-HLac solution are shown in Fig. 4. It is found that there are double peaks which are symmetric (v_s=1464 cm^{-1}) and asymmetric stretching vibration (v_{as}=1583 cm^{-1}) of COO^- in the $NdCl_3$-HLac solution while a single peak in the HLac solution, indicating that there is a coordination mechanism between $Nd^{3+}$and Lac^-. Deacon et al. considers that the coordination mechanism between metal ion and ligand is confirmed by comparison of the values ($\Delta v = v_{as} - v_s$) of metal-carboxylic acid complex and sodium carboxylate.[21] In general, if the coordination mechanism is in the form of chelate or bridging, the value is less than that of sodium carboxylate. Conversely, the coordination mechanism is in the form of unidentate ligand, and the value of unidentate ligand is in the range of 120-160 cm^{-1}. According to the analysis in the Fig. 4, the value (Δv=119 cm^{-1}) of Nd^{3+}-Lac^- complex is less than that

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of sodium carboxylate ($\Delta v = v_{as} - v_s$ =1581-1413=168 cm^{-1}), indicating that the coordination mechanism between Nd^{3+}and Lac^{-} is in the form of carboxyl oxygen bridge bidentate ligand.

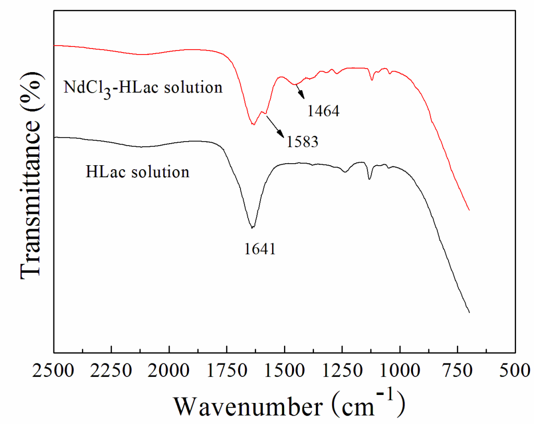

Fig. 4 IR transmittance spectra of HLac and NdCl$_3$-HLac solutions

From the above analyses of UV and FT-IR, it is found that Nd^{3+} can coordinate with Lac^{-}. The magnitude of the masking depends on complex formation constants, the agent concentration, and the pH value of the aqueous phase. The separation of the metals should thus be improved when the above conditions can be properly combined in the extraction system. Literature shows that adding HLac into the rare earth solution is beneficial for extraction and separation. It is interesting to study the extraction mechanism which can provide some information for the application of the chelating extraction system.

3.3. Separation possibility

The separation factor (*β*) is the ratio of distribution ratio (*D*) of two metals measured under the same condition. In this section, the concentrations of rare earths are set as 0.2 mol·L^{-1}. The relationship between *β* values and HLac concentration in the HCl-HLac system is shown in Fig. 5.

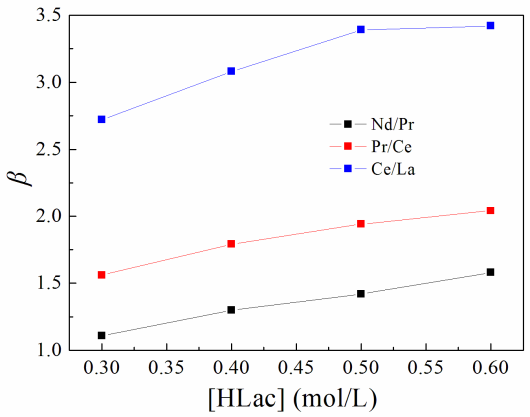

Fig. 5 Separation factors (*β*) between light rare earths in the D2EHPA−RECl$_3$−HLac system

It is interesting to note that the *β* values of La/Ce (3.42), Ce/Pr (2.04) and Pr/Nd (1.58) are nearly to

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those in the saponified HEH/EHP system. The results show that La/Ce, Ce/Pr and Pr/Nd can be separated from each other. Therefore, the studied system has the potential of separating light rare earths, and provides useful information for developing more efficient separation processes.

3.4. Stoichiometry of the complex formation

The solvent extraction of the Nd^{3+} with H_2A_2 has been studied previously. It has been found that the extraction mechanism can be represented by the following equation:

$$Nd^{3+}_{(a)} + 3H_2A_{2(o)} \xleftrightarrow{K} Nd(HA_2)_{3(o)} + 3H^+_{(a)} \tag{2}$$

where “a” and “o” represent aqueous and organic phase, respectively; K is the extraction equilibrium constant; H_2A_2 is the dimeric species of D2EHPA.

In the present study, the extraction reaction is expressed as follows according to the literature: [22]

$$Nd^{3+}_{(a)} + x(H_2A_2)_{(o)} + pL^-_{(a)} \xleftrightarrow{K} NdL_pA_{n-p}(HA)_{2x-n+p(o)} + (n-p)H^+_{(a)} \tag{3}$$

The relationship between the distribution ratio D and the equilibrium constant K can be expressed as:

$$\log D + \log Y = \log K + x\log[H_2A_2]_{(o)} + p\log[L^-]_{(a)} - (n-p)\log[H^+]_{(a)} \tag{4}$$

where L^- represents an anion in the aqueous phase; Y is the complexing degree at equilibrium, and is defined as the ratio of the total rare earth ion in the aqueous phase to the free rare earth ion in the aqueous phase, and is calculated based on the Eq. (5).

$$Y = \frac{[Nd^{3+}]_t}{[Nd^{3+}]} = \frac{[Nd^{3+}] + \sum_{i}^{3}[NdL_i^{3-i}]}{[Nd^{3+}]}$$

$$Y = 1 + \sum_{i}^{3} \beta_i [L^-]^i \tag{5}$$

where β is the coordination constant; ‘i’ is the number of the ligand.

In the present study, the concentration of Nd^{3+} is 5.0×10^{-3} $mol\cdot L^{-1}$, and concentration ratio of $[NdCl_3]$: [HLac] is 1 : 1, 1 : 2 and 1 : 3. The stoichiometry of the complex formation reaction between Nd(III) and D2EHPA in the presence of lactic acid has been evaluated by the method of saturation loading capacities at constant extractant concentration and studying log D + log Y on the logarithmic H_2A_2 concentration at a constant pH, which bases on the Eq. (4).

The extraction equilibrium for Nd(III) with D2EHPA in kerosene, up to high loading ratios, have been described in previous papers.[23, 24] It is well known that the aggregated species appear when the

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metals are extracted with acidic organophosphorus compounds. The maximum loading ratio ($\overline{[3H_2A_2]}_{feed} / \overline{[Nd^{3+}]}$) of Nd^{3+} with H_2A_2 is 3, which suggests that an aggregated species contains three dimeric extractants and a Nd^{3+} with the molar ratio of 3:1 at pH value 3. The plots of log D + log Y log $[H_2A_2]_{(o)}$ (shown in Fig. 6) yield straight lines. The slopes are approximately equal to 3.0, indicating that 3 mol H_2A_2 dimers are involved during the extraction of 1 mol of Nd^{3+} in the light of cation-exchange mechanism. Kinetic analysis shows that rare earth metal-ligand complex is not extracted into the organic phase, the extracted species in the presence of HLac is considered to be $Nd(HA_2)_3$ which do not contain HLac. This result is also confirmed by ^{13}C NMR analysis.[25] In addition, Matsuyama et al. studied the extraction rates by adding organic acid to aqueous phase in solvent extraction of rare earths in presence of DTPA, and found that organic acid is not extracted into the organic phase.[26] The studies of the stoichiometry of the complex formation-reaction between Nd(III) and H_2A_2 in the presence of lactic acid indicate that the extracted complex has the formula of $Nd(HA_2)_3$ whose structure is analyzed in sections 3.6 and 3.7, and the reaction could be considered using the Eq. (2). The above results are also confirmed by the subsequent kinetic studies. The equilibrium constant, log K for Nd(III) can be calculated to be 0.612 when the ratio of $[NdCl_3]$ to [HLac] is equal to 1 : 3.

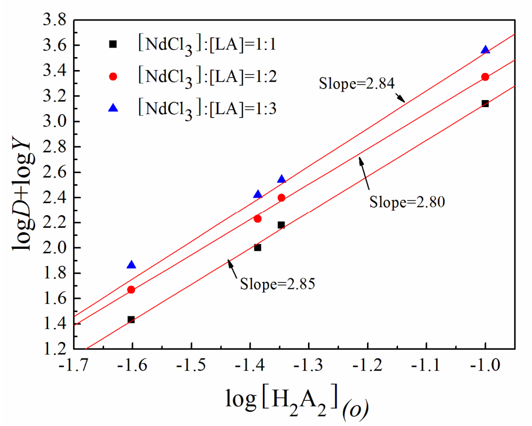

Fig. 6 Relationship between log$D$+log$Y$ and log$[H_2A_2]_{(o)}$ in extraction of Nd^{3+} by H_2A_2: $[Nd^{3+}]_{(a)} \approx 5.0\times10^{-3}$ mol·L^{-1}, pH≈3.0

Though it is mentioned that $Nd(Lac)_2^+$ is the main cationic species shown in Fig. 3 at pH 3, based on the kinetics analysis: the Nd^{3+} ions coordinate with ligands Lac^- to form complexes in the aqueous phase firstly, and then these complexes dissociate at the interface because the stability constant for the complex between Nd^{3+} and extractant is larger than that between Nd^{3+} and ligand (The stability constants are shown in Table 1); Nd^{3+} ions coordinate with H_2A_2 monomer to form $NdA^{2+}_{(i)}$ species at

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the interface, and reacts with HA step by step, lastly, to form the $NdA_{3(i)}$ species, at the same time, releasing three hydrogen ions; the $NdA_{3(i)}$ species are extracted by H_2A_2 in the organic phase to from the final $NdA_3 \cdot 3HA_{(o)}$ complex. So it is considered that the extraction reaction using the Eq. (2) is reasonable.

Table 1 Stability constants of different complexes

Complexes	Stability constants		
	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$
$[Nd(Lac)_n]^{3-n}$	2.47	4.37	5.80
D2EHPA-Nd		7.42	

3.5. Influence of temperature

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. Fig. 7 shows the effect of temperature on the extraction of Nd^{3+} with H_2A_2 at fixed pH, fixed concentrations of H_2A_2 and complexing agents in different systems, giving slopes of −0.7315 and −0.5663, respectively, which 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:

$$\log D + \log Y = \frac{-\Delta H^\circ}{2.303RT} + \mathrm{C} \tag{6}$$

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 298K can be obtained:

$$\Delta G^\circ = -RT \ln K \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \Rightarrow \Delta S^\circ = \frac{\Delta H^\circ - \Delta \mathrm{G}^\circ}{T} \tag{8}$$

ΔG°, ΔH° and ΔS° can be obtained as shown in Table 2. Using either method (distribution factor or Pitzer's polynomial) to calculate the thermodynamic properties of the extraction system, we can understand more than just knowing that the extraction is either endothermic or exothermic in nature.[27,28] The calculations of ΔH° (>0 $kJ \cdot mol^{-1}$) indicate that the extraction processes are endothermic reactions. ΔG° value from D2EHPA–HCl system to D2EHPA–HCl–HLac system changes to a negative value, indicate that the extraction system containing complexing agent is suitable to be carried at room temperature by comparing the ΔG° values in different systems. For an inner sphere complex,

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the reaction is disrupted more extensively, with a positive value for net changes in enthalpy and entropy of the system. The positive values of ΔS° suggest the extraction system is more disordered with a compensatory disruption of the reaction sphere, which is in accordance with the theory of increasing of entropy.

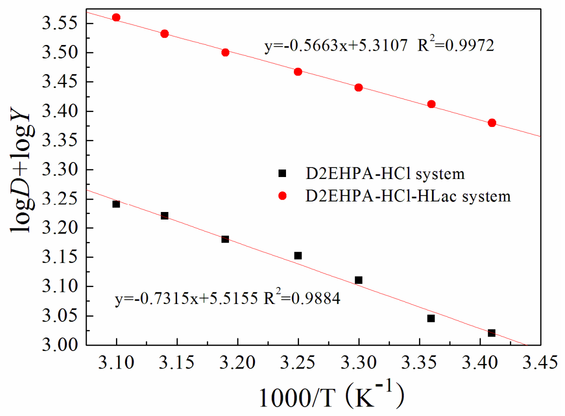

Fig. 7 Effect of temperature on the extraction of Nd^{3+} with H_2A_2 in different systems: $[Nd^{3+}]_{(a)}\approx 5.0\times10^{-3}$ mol·L^{-1}, $[H_2A_2]=0.20$ mol·L^{-1}, pH≈3.0, [HLac]=1.50×10^{-3} mol·L^{-1}

Table 2 Equilibrium constants and thermodynamic parameters of Nd^{3+} in different systems. [a].

Systems	log K	ΔH° (kJ·mol^{-1})	ΔG° (kJ·mol^{-1})	ΔS° (J·mol^{-1}·K^{-1})
D2EHPA–HCl system	-0.28	14.00	1.60	41.61
D2EHPA–HCl–HLac system	0.43	10.84	-2.45	44.60

[a] ΔG° and ΔS° have been calculated at 298K.

3.6. IR spectra

In the Fig. 8, the bands in the region 2700−2560 cm^{-1} and 2350−2080 cm^{-1} in the H_2A_2 spectra are due to P=O−(OH) vibrations between intermolecular hydrogen bonding in the dimeric form. The band at 1230 cm^{-1} is assigned to P=O stretch. In the H_2A_2-Nd spectra after extracting Nd in the HCl−HLac system, we found that the bands at 2730 cm^{-1}, 2327 cm^{-1} and 1672 cm^{-1} are all absent indicating that the hydrogen atom in P−OH is displaced, the P=O stretching at 1230 cm^{-1} shifts to 1200 cm^{-1}, which means that the oxygen of P=O participates the complex formation through coordination. These results suggest that when the dimeric H_2A_2 forms a complex with Nd^{3+}, a strong chelation of Nd by H_2A_2 anion occurs and thus confirms the cation exchange mechanism proposed in Eq. (2).

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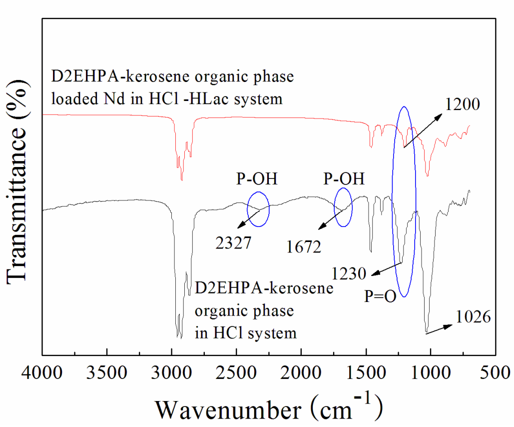

Fig. 8 IR transmittance spectra of saturated complexes between Nd^{3+} and H_2A_2 in different systems

3.7. ^{1}H NMR and ^{31}P NMR spectra

Nuclear magnetic resonance (NMR) is currently a promising option for characterizing the properties of extracted complexes. As for the organic phase, the diluent kerosene is replaced by n-heptane due to its higher boiling point and danger in this section. To further gain insight into the extraction mechanism, the ^{1}H NMR and ^{31}P NMR spectra of extracted complexes between Nd(III) and H_2A_2 are analyzed in Fig. 9. As can be seen, the chemical shift of reactive hydrogen of P−OH in H_2A_2 is at 11.857 ppm, while after extracting Nd^{3+}, the peak disappears, indicating that the extraction mechanism is a cation-exchange, which is in accordance with the analytical results in section 3.4.

The ^{31}P NMR spectra of extracted complexes between Nd(III) and H_2A_2 are given in Fig. 9(b) to analyze whether P=O and Nd(III) have coordination interaction or not. As can be seen, chemical shift of P=O at 1.074 ppm shifts to 0.3 ppm when the organic phase loads with Nd^{3+}, suggesting that the coordination interaction of Nd^{3+} with H_2A_2 is stronger.

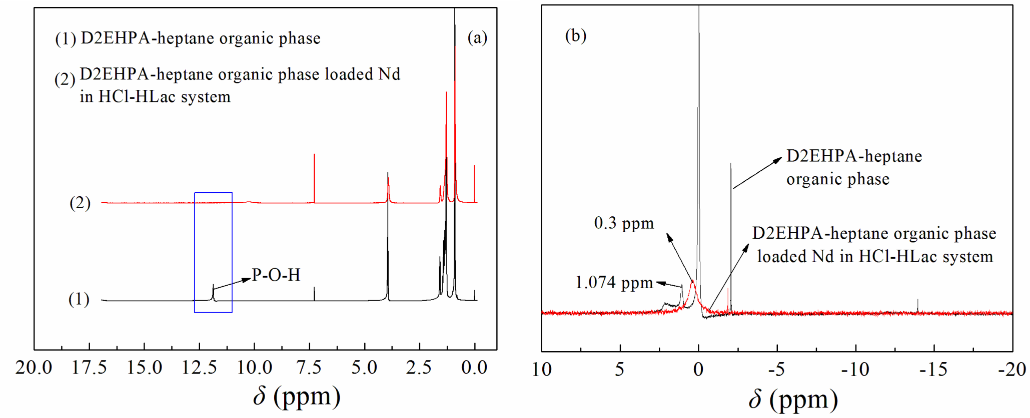

Fig. 9 ^{1}H NMR (a) and ^{31}P NMR (b) spectra of saturated organic phase extracted Nd^{3+} in different systems

Based on the above analysis of sections 3.6 and 3.7, the structure of extracted complex is shown in Fig. 10. Nd^{3+} locates in the center of the extracted complex which is formed by the chemical bond and

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the dative bond between the rare earth ion and the oxygen of P−OH as well as the oxygen of P=O, respectively.

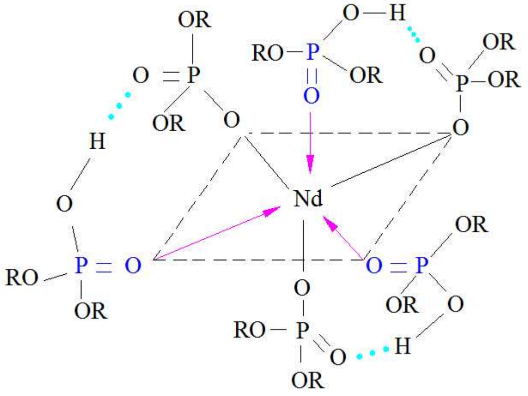
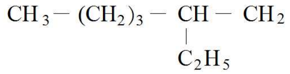


Fig. 10 The structure of extracted complex between Nd^{3+} and H_2A_2: R=



$CH_3-(CH_2)_3-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2$

4. Conclusions

The extraction of Nd^{3+} from chloride solution using a complexing agent lactic acid has been performed. It is found that:

(1) Nd^{3+} and Lac^- in the aqueous solution are coordinated to form the complexes like $Nd(Lac)^{2+}$ and $Nd(Lac)_2^+$ in the form of the carboxyl oxygen bridge bidentate ligand.

(2) The β values of La/Ce, Ce/Pr and Pr/ Nd indicate that the studied system would be a good option for the separation of light rare earths in industry.

(3) The extraction mechanism is analyzed by saturation loading capacities, FT-IR and NMR, and the complex extracted is determined to be $Nd(HA_2)_3$.

(4) 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.

Acknowledgements

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