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THERMODYNAMIC INVESTIGATIONS OF AQUEOUS-MOLTEN PARAFFIN WAX LIQUID–LIQUID EXTRACTIONS AND SYNERGISTIC EXTRACTIONS OF SOME TRIVALENT RARE EARTH ELEMENTS*

JINZHANG GAO,† GUANGLIN HU, JINGWAN KANG, HAIYAN FAN and GUANGBI BAI
Department of Chemistry, Northwest Normal University, Lanzhou 730070, China

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Summary—In this paper, liquid–liquid extraction behaviour of RE(III) (RE = La, Sm, E, Yb) by the use of 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (PMBP) in liquid paraffin with cersin has been investigated at 343.2 K. Under some conditions, the synergistic extraction behaviour with PMBP and Phen has also been studied. The slope analysis method shows that the compositions of the extracted species are REA_3 and REA_3B. $pH_{1/2}$ values were also obtained. Equilibrium extraction constants and thermodynamic parameters were calculated. The results showed that increasing temperature is favourable to extraction of heavy rare earth ions with PMBP and more favourable to synergistic extraction with PMBP and Phen. Synergistic extraction can be carried out at lower pH.

As a good extractant, PMBP has been used widely in liquid–liquid extraction to separate rare earth elements.[1–5] Lou and his coworkers[6] reported the liquid–liquid synergistic extraction behaviour lanthanid ions with PMBP and Phen. Separation and concentration using molten paraffin as a solid solvent is relatively new.[7–10] However, few studies concern the mechanism of solid–liquid extraction. Tokehiro[11] reported the mechanism of extraction of UO_2^{2+} with TOPO in molten naphthalene–diphenyl mixture, obtaining enhancement of thermodynamic parameters. The mechanism of synergistic extraction in molten liquid has never been studied. Wu[12] suggested that molten liquid extraction is a special liquid–liquid extraction, and the mechanism of molten liquid extraction is similar to that of liquid–liquid extraction. Based on our previous work,[10] phase separation in the present study was achieved directly at high temperature so that extraction distribution ratios at high temperature could be obtained. The molten liquid extraction behaviour of RE(III) with PMBP and its synergistic behaviour with PMBP and Phen were investigated. $pH_{1/2}$ values, equilibrium extraction constants and enhancement of thermodynamic parameters were determined.

EXPERIMENTAL

Reagents and apparatus

PMBP (m.p.t. 91° ~ 92°) was purified with 1:3(v:v)chloroform–petroleum. Phen was dissolved in 36% acetic acid and diluted to the desired volume with distilled water.

Paraffin with cersin (PC, m.p.t. 48 ~ 50°) was purified by the method in Ref. 13. The specific gravity is 0.7715 g/ml. Stock solutions of rare earth ions ($1.0 \times 10^{-2} M$) were prepared by dissolving calculated amounts of the respective oxide (99.99%) in hydrochloric acid. The buffer solution (NH_4Ac–HAc) pH was adjusted with acetic acid. Arsenazo III (0.15%) aqueous solution was newly prepared. All other chemicals used were of analytical grade.

The experiment was carried out with the device shown in Fig. 1. A mode I DF-101B magnetic stirrer (Zhejiang, China), a super thermostat (Chongqing, China).model CS501. with an accuracy of ±0.07%, a model 721 spectrophotometer (Shanghai, China), a model U-3400 Hitachi spectrophotometer and a model PHS-10A digital acidity ionometer (Xiaoshan, China) were used.

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†Author for correspondence.

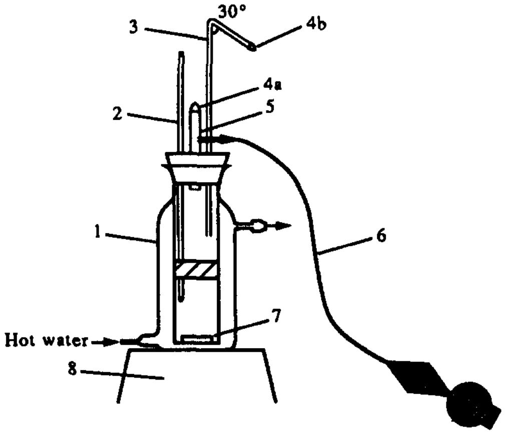

Fig. 1. Galass extraction vessel. 1. Water jacket. 2. 100° mercury thermometer. 3. Curved galass tube whose height can be modulated. 4a, 4b. Rubber cover. 5. "T" shape glass tube. 6. Double connected rubber ball. 7. Stirring bar. 8. Magnetic stirrer.

Procedure

Preparation of the solid extractant. A given weight of PMBP and paraffin were transferred to a 50-ml beaker which was heated on a water-bath till the solid substance melted completely. The obtained yellow transparent solution was brought to room temperature.

Experiment and analysis of extraction equilibrium. A given volume of $10^{-4}M$ RE^{3+} and 5 ml of NH_4Ac–HAc buffer solution were transferred to the extraction vessel (see Fig. 1). The mixture was diluted to 10 ml with distilled water. The ionic strength of the aqueous phase was kept at 0.250 (when synergistic extraction was carried out, an appropriate amount of Phen solution was added and the total volume of aqueous phase was kept at 10 ml.) A stir bar was carefully placed into the vessel. A given weight of solid extractant was added and the phase ratio was 0.5 (v/v). High temperature circulating water was introduced into the water jacket with a super thermostat. When the solid phase was melted completely and the temperature was kept at 70°, the magnetic stirrer was started. After 10 min, the stirrer was stopped and the high temperature circulating water kept on flowing. The rubber cover 4a (see Fig. 1) was pulled out. The curved tube 3 (see Fig. 1) was inserted at the bottom of the extraction vessel and the rubber cover 4b was pulled out. The opening of the "T" shape tube was covered with a thumb while a 10-ml beaker was placed near the mouth of the curved tube 3. The double connected rubber ball was used to pump the air into the vessel, in this way the aqueous phase was separated at high temperature. When the synergistic extraction was studied by means of Job's method, the usual phase separation was employed. That is, extraction was performed at high temperature and separation was performed at room temperature. After the curved tube 3 was inserted at the bottom of the vessel, the high temperature circulating water was stopped. The mixture was cooled to room temperature, and the aqueous phase was separated directly. The pH value of the aqueous phase was measured with a model PHS-10A PH-meter at room temperature. The amount of rare earth ions contained in the aqueous phase was measured by Arsenazo III spectrophotometry.

RESULTS AND DISCUSSION

Solubility of the extractant in paraffin

At a certain temperature, above 50°, PMBP can dissolve in paraffin. Phen can hardly dissolve in paraffin and dissolves slightly in cool water, but fully in hot water or diluted acid.

Extraction of RE(III) with PMBP

Determination of composition of the extracted complex. In the system of RE(III) ($2.0 \times 10^{-5}M$)/HAc–NH_4Ac($\mu = 0.250$)/PMBP-PC, the extraction process can be described as follows:

$$RE^{3+} + (x+y)HA_{(o)} + zAc^- \xrightleftharpoons{343.2\,K} REA_x(HA)_y(Ac)_{z(o)} + xH^+ \quad (1)$$

Where RE = La, Sm, Er, Yb, (o) denotes organic phase, the extraction constant (K_{ex}) is written as

$$K_{ex} = [REA_x(HA)_y(Ac)_z]_o[H^+]^x / [RE^{3+}][HA]_o^{(x+y)}[Ac^-]^z$$
$$= [REA_x(HA)_y(Ac)_z]_o[H^+]^x / \gamma_{RE^{3+}} C_{RE^{3+}} [HA]_o^{(x+y)}[Ac^-]^z \quad (2)$$

Where $C_{RE^{3+}}$ and $\gamma_{RE^{3+}}$ are the equilibrium concentration of RE^{3+} in aqueous phase and activity coefficient. Because concentration in the organic phase are very low, concentration can substitute for activity. The activity coefficient of RE^{3+} can be calculated from $\log \gamma_{\pm} = (-AZ_+Z_- \sqrt{I})/(1 + \alpha B\sqrt{I})$, where A, B are constants which can be found in literatures.[14,15]

The distribution ratio between two phase was written as $D = C_{RE(o)}/C_{RE}$, where $C_{RE(o)}$ and C_{RE} are the analytical concentrations of

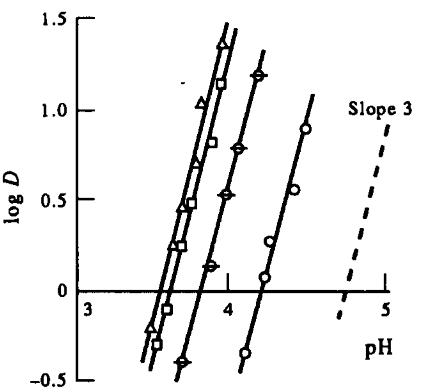

Fig. 2. Relationship between log D and pH in extractions with PMBP ○—La; ⌀—Sm; □—Er; △—Yb, $[Ha]_o = 0.01103$ M.

RE^{3+} in the organic and aqueous phase respectively. Moreover, $C_{RE(o)} = [REA_x(HA)_y(Ac)_z]_o$, $C_{RE} = C_{RE^{3+}} = [RE^{3+}/\gamma_{RE^{3+}}$, therefore, K_{ex} can be simplified as

$$K_{ex} = D[H^+]^x/\gamma_{RE^{3+}}[HA]_o^{(x+y)}[Ac^-]^z$$

$$\log D = \log K_{ex} + x\text{pH} + \log \gamma_{RE^{3+}} + (x+y)\log[HA]_o + z\log[Ac^-]$$

From Fig. 2 we obtain $x = 3$ and the $pH_{1/2}$ value of La^{3+}, Sm^{3+}, Er^{3+} and Yb^{3+} are 4.21, 3.82, 3.61, 3.55 respectively.

From Fig. 3 we calculate $x + y = 3$, $y = 0$. According to the change balance principle, $x + y + z = 3$, therefore, $z = 0$. The composition of the extracted complex is REA_3. The reaction equation and K_{ex} can be given as follows:

$$RE^{3+} + 3HA_{(o)} = REA_{3(o)} + 3H^+ \quad (3)$$

$$K_{ex} = \frac{[REA_3]_o[H^+]^3}{[RE^{3+}][HA]_o^3} = \frac{D[H^+]^3}{\gamma_{RE^{3+}}[HA]_o^3} \quad (4)$$

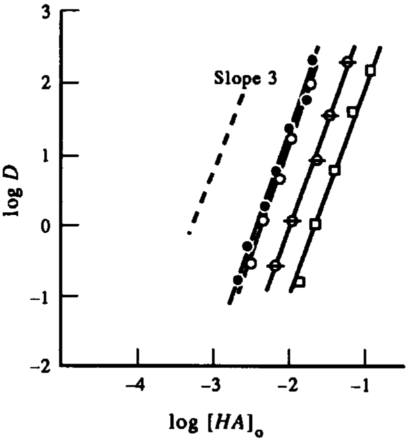

Fig. 3. Relationship between log D and $\log[HA]_o$ in extractions with PMBP □—La, pH = 4.10; ⌀—Sm, pH = 3.80, ○—Er, pH = 3.70; ●—Yb, pH = 3.70.

Calculation of thermodynamic parameters. The variation of the distribution ratio with temperature in the range 55–85° was measured. For this system, the K_{ex} values at different temperatures was calculated from equation (4). Log K_{ex} *vs.* $1/T$ gives four straight line slopes of 2250, 561.5, −1575 and −1637, for La^{3+}, Sm^{3+}, Er^{3+} and Yb^{3+}, respectively. Moreover, $\log K_{ex} = (-\Delta H_{ex}/2.303RT) + \text{constant}$, $\Delta G = -RT \log K_{ex}$ and $\Delta S_{ex} = (\Delta H_{ex} - \Delta G_{ex})/T$. The extraction constants and thermodynamic parameters in the extraction of RE^{3+} with PMBP are summarized in Table 1 (see Fig. 4).

Molten-liquid synergistic extraction of RE(III) with PMBP and Phen

Synergistic extraction of RE(III) by means of Job's method. The temperature was kept at 343.2 K. The initial concentration of RE(III) in the aqueous phase was $2.00 \times 10^{-5}M$. The ionic strength of the aqueous phase was kept at 0.250.

Table 1. Extraction constants and thermodynamic parameters in reaction of Re^{3+} and $HA_{(o)}$

The extraction equation	$\log K_{ex}$	ΔH_{ex}(kJ)	ΔG_{ex}(kJ)	$\Delta S_{ex}(JK^{-1})$
$La^{3+} + 3HA_{(o)} \rightleftharpoons LaA_{3(o)} + 3H^+$	−5.425	−48.8	35.7	−246.2
$Sm^{3+} + 3HA_{(o)} \rightleftharpoons SmA_{3(o)} + 3H^+$	−2.031	−10.75	13.35	−70.22
$Er^{3+} + 3HA_{(o)} \rightleftharpoons ErA_{3(o)} + 3H^+$	−1.33	30.16	8.74	62.41
$Yb^{3+} + 3HA_{(o)} \rightleftharpoons YbA_{3(o)} + 3H^+$	−1.214	31.35	7.98	68.09

Table 2. R and R_{HA} in synergistic extraction system of RE^{3+} (2.00×10^{-5})/HAc–NH_4Ac ($\mu = 0.250$)/Phen, PMBP-PC

Synergistic extraction system	R	R_{Ha}
$La^{3+}(2 \times 10^{-5})$/HAc–$NH_4$Ac ($\mu = 0.250$)/Phen, PMBP-PC	6.59	5.27
$Sm^{3+}(2 \times 10^{-5})$/HAc–$NH_4$Ac ($\mu = 0.250$)/Phen, PMBP-PC	10.30	15.14
$Er^{3+}(2 \times 10^{-5})$/HAc–$NH_4$Ac ($\mu = 0.250$)/Phen, PMBP-PC	22.55	32.22
$Yb^{3+}(2 \times 10^{-5})$/HAc–$NH_4$Ac ($\mu = 0.250$)/Phen, PMBP-PC	31.12	43.83

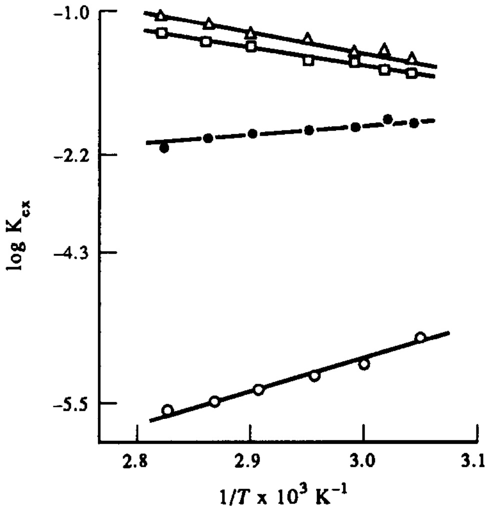

Fig. 4. Relationship between log K_{ex} and $1/T$ in extractions with PMBP ○—La, $[HA]_o = 0.01103M$, pH = 4.46, ○/A = 1/2; ●—Sm, $[HA]_o = 0.01103M$, pH = 3.85, ○/A = 1/2; □—Er, $[HA]_o = 0.01103M$, pH = 3.62, ○/A = 0.26; △—Yb, $[HA]_o = 0.01103M$, pH = 2.94, ○/A = 1/2.

The total amount of extractant ($n\Delta$) was fixed at 38.9μ mol($n\Delta = n_{HA(o)} + n_B$, where $n_{HA(o)}$ and n_B were the initial amount of PM-BP in organic phase and Phen in aqueous phase, respectively), while the molar ratio of Phen x_B($x_B = n_B/n\Delta$) was changed. The extraction of RE(III) from acetic acid medium with PMBP and Phen was investigated at pH 4.10, 3.71, 3.53 and 3.49, respectively. Phase separation was performed at room temperature. Distribution ratios were determined. Log D vs. x_B showed the synergistic effect. The synergistic extraction coefficient R and acid synergistic extraction coefficient R_{HA} were calculated[16] (see Table 2). In this experiment, the distribution ratio between two phase can be written as $D = D_{AB} + D_B + D_{HA}$, where D_{HA} was the distribution ratio of extraction with PMBP, D_B was the distribution ratio of extraction with Phen, and D_{AB} was the distribution ratio of the synergistic extraction with PMBP and Phen. From Fig. 5, $D_B = 0$, therefore, $D_{AB} = D - D_{HA}$. Because D and D_{HA} can be determined under experimental conditions, D_{AB} can be calculated from $D_{AB} = D - D_{HA}$.

Slope analysis method to obtain the composition of synergistic extracted complex. In the molten-liquid synergistic extraction system of $RE^{3+}(2.00 \times 10^{-5}M)$/H Ac–$NH_4Ac(\mu = 0.250)$ /Phen, PMBP-PC, the extraction equation and synergistic extraction constant K_{ex} was written as

$$\mathrm{RE^{3+}} + (q + r)\mathrm{HA_{(o)}} + s\mathrm{Ac^-} + t\mathrm{B} \xrightleftharpoons{343.2\ \mathrm{K}} \mathrm{REA}_q(\mathrm{HA})_r(\mathrm{Ac})_s\mathrm{B}_{t(o)} + q\mathrm{H^+} \quad (5)$$

$$\begin{aligned} K_{ex} &= [\mathrm{REA}_q(\mathrm{HA})_r(\mathrm{Ac})_s\mathrm{B}_t]_o[\mathrm{H^+}]/ \\ &\quad [\mathrm{RE^{3+}}][\mathrm{HA}]_o^{(x+y)}[\mathrm{Ac^-}]^s[\mathrm{B}]^t \\ &= [\mathrm{REA}_q(\mathrm{HA})_r(\mathrm{Ac})_s(\mathrm{B})_t]_o[\mathrm{H^+}]_q/ \\ &\quad C_{\mathrm{RE^{3+}}}\gamma_{\mathrm{RE^{3+}}}[\mathrm{HA}]_o^{(x+y)}[\mathrm{Ac^-}]^s[\mathrm{B}]^t \qquad (6) \end{aligned}$$

Moreover,

$$D_{AB} = [\mathrm{REA}_q(\mathrm{HA})_q(\mathrm{Ac})_s(\mathrm{B})_t]_o/C_{\mathrm{RE^{3+}}},$$

therefore,

$$D_{AB} = K_{ex}\gamma_{\mathrm{RE^{3+}}}[\mathrm{HA}]_o^{(x+y)}[\mathrm{Ac^-}]^s[\mathrm{B}]^t/[\mathrm{H^+}]^q,$$

$$\begin{aligned} \log D_{AB} &= \log K_{ex} + \log \gamma_{\mathrm{RE^{3+}}} \\ &\quad + (q + r)\log[\mathrm{HA}]_o + s\log[\mathrm{Ac^-}] \\ &\quad + t\log[B] + q\mathrm{pH} \qquad (7) \end{aligned}$$

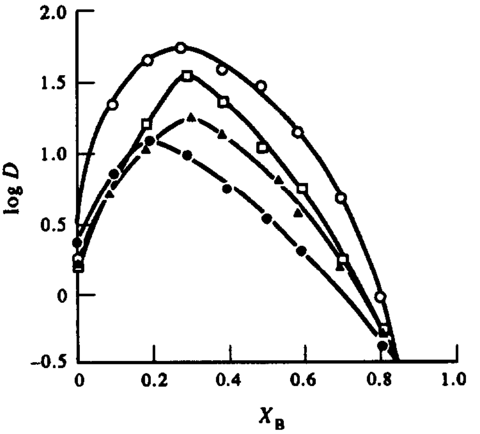

Fig. 5. Synergistic extraction curve of RE(III). ●—La, ▲—Sm, □—Er, ○—Yb.

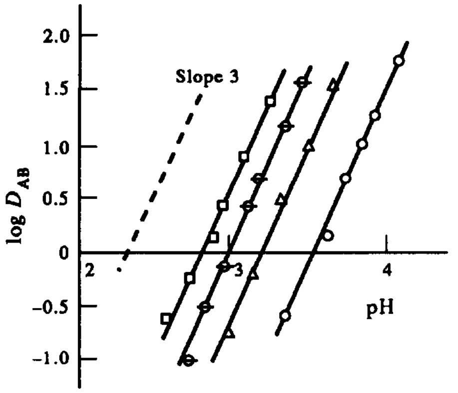

Fig. 6. Relationship between log D_{AB} and pH in synergistic extraction with PMBP and Phen. ○—La, △—Sm, ∅—Er, □—Yb $[HA]_o = 0.01103M$, $[B] = 5 \times 10^{-4}M$.

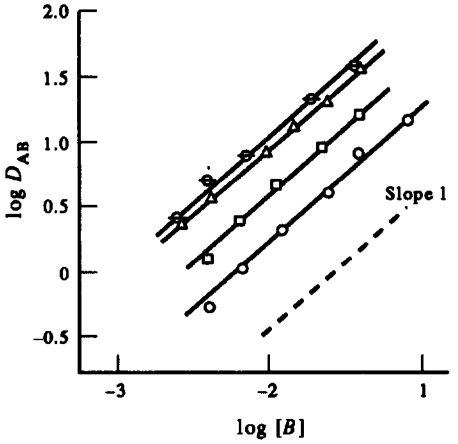

Fig. 7. Relationship between $\log D_{AB}$ and log[B] in synergistic extraction with PMBP and Phen ○—La, pH = 3.60; □—Sm, pH = 3.18; △—Er, pH = 3.03; ∅—Yb, pH = 2.90; $[HA]_o = 0.01103M$.

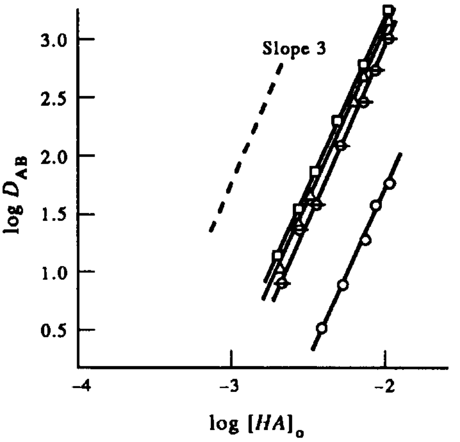

Fig. 8. Relationship between $\log D$ and $\log[Ha]_0$ in synergistic extraction with PMBP and Phen; ○—La, pH = 4.10, [B] = 0.00389*M*; ∅—Sm, pH = 3.69, [B] = 0.01167*M*; △—Er, pH = 3.53, [B] = 0.01167*M*; □—Yb, pH = 3.43, [B] = 0.01167*M*.

By the use of slope analysis, we obtained $t = 1$ (see Fig. 7), $q = 3$ (see Fig. 6), $q + r = 3$ (see Fig. 8), that is, $r = 0$. According to the charge balance, $q + r + s = 3$, therefore, $s = 0$. The composition of the synergistic extracted complex is REA_3B. The extraction equation and K_{ex} can be simplified as

$$RE^{3+} + 3HA_{(o)} + B = REA_3B_{(o)} + 3H^+ \quad (8)$$

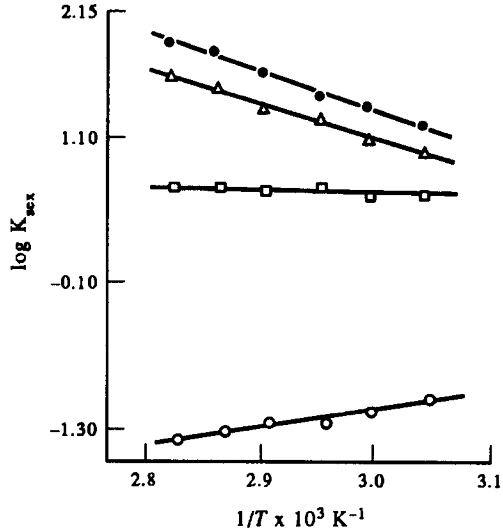

Fig. 9. Relationship between $\log K_{sex}$ and $1/T$ in synergistic extraction with PMBP and Phen; ○—La, pH = 3.85, $[HA]_o = 0.01103M$, [B] = 0.00389*M*, O/A = 0.26; □—Sm, pH = 2.92, $[HA]_o = 0.01103M$, [B] = 0.01167*M*, O/A = 1/2; △—Er, pH = 2.96, $[HA]_o = 0.01103M$, [B] = 0.01167*M*, O/A = 1/2; ●—Yb, pH = 2.75, $[HA]_o = 0.01103M$, [B] = 0.01167*M*, O/A = 1/2.

$$K_{ex} = D_{AB}[H^+]^3/\gamma_{RE^{3+}}[HA]_o^3[B] \quad (9)$$

From Fig. 6, the $pH_{1/2}$ values for La^{3+}, Sm^{3+}, Er^{3+} and Yb^{3+} were 3.63, 3.20, 2.97, and 2.82, respectively.

Calculation of the thermodynamic parameters in the synergistic extraction. Variation of the distribution ratio D_{AB} with temperature in the range 55–85° was determined. The K_{ex} values at the different temperatures were calculated from equation (9). $\log K_{ex}$ *vs.* $1/T$ shows four straight lines of slopes 1460, −239, 2797 and 3126, respectively, from each slope value and the thermodynamic equations, the synergistic equilibrium extraction constants and the thermodynamic parameters were calculated (see Table 3 and Fig. 9).

CONCLUSION

Table 1 shows that from light rare earth elements to heavy rare earth elements, enthalpy

Table 3. Synergistic extraction constants and thermodynamic parameters at 343.2 K

Synergistic extraction equation	$\log K_{sex}$	ΔH_{sex}(kJ)	ΔG_{sex}(kJ)	$\Delta S_{sex}(JK^{-1})$
$La^{3+} + 3HA_{(o)} + B \rightleftharpoons LaA_3B_{(o)} + 3H^+$	−1.26	−27.96	8.3	−105.6
$Sm^{3+} + 3HA_{(o)} + B \rightleftharpoons SmA_3B_{(o)} + 3H^+$	0.68	4.6	4.4	0.4
$Er^{3+} + 3HA_{(o)} + B \rightleftharpoons ErA_3B_{(o)} + 3H^+$	1.35	53.6	−8.9	181.9
$Yb^{3+} + 3HA_{(o)} + B \rightleftharpoons YbA_3B_{(o)} + 3H^+$	1.65	59.9	−10.8	206.0

increases gradually. Changing from negative to positive, the extraction reaction changes from releasing heat to absorbing heat. Therefore, increasing temperature is favourable to the extraction of heavy rare earth elements. The enhancement of Gibbs free energy reduces from L-a^{3+} to Yb^{3+}, that is, the heavy rare earth elements are easier to extract in this system. With increased atomic number, the extractability of PMBP is enhanced.[17] Table 3 shows that the enhancement of enthalpy (ΔH_{sex}) and Gibbs free energy (ΔG_{sex}) in synergistic extractions are consistent with the enhancement of enthalpy (ΔH_{ex}) and Gibbs free energy (ΔG_{ex}) in extraction with single extractant. For a given RE(III), ΔH_{sex} is larger than ΔH_{ex}, ΔG_{sex} is smaller than ΔG_{ex}. The synergistic extraction reaction of heavy rare earths absorbs heat greatly, that is, increased temperature is more favourable to the molten-liquid synergistic extraction of heavy rare earth elements. Because ΔGs_{ex} for the heavy rare earths is negative, the extraction reaction of heavy rare earths have higher extraction efficiency. For the given RE(III), $pH^{sex}_{1/2}$ is smaller than $pH^{ex}_{1/2}$ assuming $\Delta pH_{1/2} = pH^{sex}_{1/2} - pH^{ex}_{1/2}$, the $\Delta pH_{1/2}$ for La^{3+}, Sm^{3+}, Er^{3+} and Yb^{3+} is -0.58, -0.62, -0.64 and -0.73, respectively. Therefore, the synergistic extraction can be performed at lower pH value.

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