



# Solvent extraction study of rare earth elements from chloride medium by mixtures of *sec*-nonylphenoxy acetic acid with Cyanex301 or Cyanex302

Shanshan Tong <sup>a</sup>, Xiaowei Zhao <sup>a</sup>, Naizhong Song <sup>a</sup>, Qiong Jia <sup>a,\*</sup>, Weihong Zhou <sup>a</sup>, Wuping Liao <sup>b,\*</sup>

<sup>a</sup> College of Chemistry, Jilin University, Changchun 130022, China

<sup>b</sup> State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

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## ABSTRACT

The extraction of rare earth elements from chloride medium by mixtures of *sec*-nonylphenoxy acetic acid (CA100) with bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex301) or bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex302) in *n*-heptane has been studied. The synergistic enhancement of the extraction of lanthanum (III) by mixtures of CA100 with Cyanex301 has been investigated using the methods of slope analysis and constant mole. The extracted complex of lanthanum (III) is determined. The logarithm of the equilibrium constant is calculated as  $-1.41$ . The formation constants and the thermodynamic functions,  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  have also been determined. Moreover, the different extraction effects of rare earth elements in the mixing systems of CA100 with Cyanex301 or Cyanex302 have been employed to consider the possibility of separating rare earth elements according to their separation factors.

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## 1. Introduction

Synergistic solvent extraction, the extraction of metal ions with two kinds of extractants, has attracted much attention in the last decades. It not only enhances the extraction efficiency but also improves the selectivity significantly (Mathur, 1983). Different kinds of mixing systems containing acidic organophosphorus extractants have been applied to the extraction of rare earth elements (REEs) (Bari et al., 2007; Belova et al., 2009; Bhattacharyya et al., 2006; Coupez et al., 2003; Ionova et al., 2001; Jia et al., 2009a,b; Joshi et al., 2009; Reddy et al., 1999; Sun et al., 2005, 2006; Wang et al., 2001, 2002; Wu et al., 2007; Xu et al., 2004). Reddy et al. (1999) have investigated the synergistic extraction of REEs from nitrate solutions using mixtures of bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex301, hereafter abbreviated as C301) and trialkyl phosphine oxide (Cyanex923) in xylene. The addition of Cyanex923 to the REEs extraction system improves the extraction efficiency and the selectivities between yttrium and heavy lanthanoids.

Carboxylic acids are another kind of extractant for the extraction of REEs (Singh et al., 2006). However, the synergistic effects of REEs with carboxylic acids have not been studied as extensively as with organophosphorus acids (Cordier et al., 1998; Jia et al., 2009a,b; Sun et al., 2005, 2006; Wu et al., 2007). In our previous work (Jia et al., 2009a), the synergistic extraction of  $\text{Sm}^{3+}$  with mixtures of C301 and *sec*-octylphenoxy acetic acid (CA12) has been studied in detail. The

equilibrium constants and the thermodynamic functions have been obtained. Synergistic effects are also found when  $\text{La}^{3+}$  is extracted with mixtures of di-(2-ethylhexyl)phosphoric acid (D2EHPA) and CA12 (Jia et al., 2009b).

*Sec*-nonylphenoxy acetic acid (CA100), a novel organic carboxylic acid extractant developed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, has several advantages including low solubility and stronger acidity in aqueous phase. Sun et al. (2006) have studied the synergistic extraction of Sc, Y, La, Gd, and Yb with mixtures of bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) and CA100. The authors regarded the mixtures would be of practical value in the extraction and separation of REEs.

In the present paper, the solvent extraction of REEs by mixtures of CA100 with C301 or bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex302, hereafter abbreviated as C302) from chloride medium has been studied. The synergistic coefficient, the extraction mechanism and the thermodynamic functions are determined for lanthanum (III) when extracted by mixtures of CA100 with C301. Based on the various extraction effects on REEs, the possibilities of separating them are discussed according to the separation factors.

## 2. Experimental

### 2.1. Reagents and apparatus

High purity REEs (>99.95%) were purchased from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China). Stock solutions of REEs were prepared from these oxides by dissolving in concentrated hydrochloric acid and diluting with

\* Corresponding authors. Tel./fax: +86 431 85095622.

E-mail address: [jiaqiong@jlu.edu.cn](mailto:jiaqiong@jlu.edu.cn) (Q. Jia).

distilled water. The REEs were analyzed by titration with a standard solution of EDTA at pH 5.5 using xylenol orange as an indicator. All the initial metal concentrations were maintained at  $5 \times 10^{-3} \text{ mol L}^{-1}$ . An amount of  $0.3 \text{ mol L}^{-1}$  NaCl was used in all extraction experiments to keep the constant of ionic strength ( $\mu = 0.3 \text{ mol L}^{-1}$ ). HCl or NaOH solutions were employed for pH adjustments.

C301 and C302 were supplied by Cytec Canada Inc. CA100 with a purity greater than 98% was purchased from Shanghai Rare-Earth Chemical Co., Ltd. Both of the extractants were used as received and dissolved in *n*-heptane to the required concentration. All other reagents were of analytical reagent grade.

The concentrations of REEs were determined by spectrophotometry using a Cintra 10e spectrophotometer (GBC Scientific Equipments, Australia). A pHS-3C digital pH meter was employed for pH measurements (Shanghai Rex Instruments Factory, China). Deionized water was prepared by the Milli-Q SP system (Millipore, Milford, MA, USA).

## 2.2. Extraction procedures

The extraction procedures were carried out as follows: equal volumes (5 mL each) of aqueous and organic solutions were mixed and shaken for 30 min, which was determined to be sufficient for equilibrium attainment in preliminary experiments. All the experiments were conducted at  $293 \pm 1 \text{ K}$  unless otherwise stated. The solutions were then settled and separated by gravity. After the separation of the phase, the concentrations of REEs in the aqueous phase were determined by spectrophotometry at 654 nm with Arsenazo (III) as an indicator. The concentrations in the organic phase were determined by difference. Distribution ratios (*D*) were calculated as the ratios of the concentrations of REEs in the organic phase to those in the aqueous phase.

## 2.3. Stripping test

The loaded organic phase was equilibrated with hydrochloric acid of different concentrations. The mixtures were shaken at  $293 \pm 1 \text{ K}$  for 30 min. The aqueous solution was separated from the organic phase and the REE concentrations were quantified to evaluate the stripping ratio,  $St = ([\text{REEs}]_{(a)} / [\text{REEs}]_{(o)}) \times 100\%$ .

## 3. Results and discussion

### 3.1. Synergistic extraction of $\text{La}^{3+}$ by CA100 + C301

The extraction of  $\text{La}^{3+}$  by C301 ( $\text{H}_2\text{A}_2$ ), CA100 ( $\text{H}_2\text{B}_2$ ), and C301 + CA100 is shown in Fig. 1, where  $X_{\text{C301}}$  denotes the mole fraction of C301 in the organic phase. According to Xu et al.'s (1963) method, the synergistic enhancement coefficient can be calculated as the following:

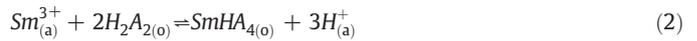
$$R = \frac{D_{\text{mix}}}{D_A + D_B} \quad (1)$$

where  $D_{\text{mix}}$ ,  $D_A$ , and  $D_B$  denote the distribution ratios of  $\text{La}^{3+}$  when extracted by CA100 + C301, C301, and CA100, respectively. *R* can thus be obtained as 2.11. *R* values determine whether synergism or antagonism occurs.  $R > 1$  means synergistic extraction whereas  $R < 1$  means antagonism. It is evident that the mixtures of CA100 and C301 have synergistic effects on  $\text{La}^{3+}$ .

### 3.2. Extraction stoichiometry of $\text{La}^{3+}$ by CA100 + C301

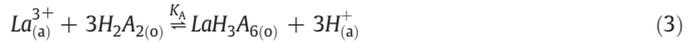
The extracted complex of REEs by C301 from nitrate medium has been reported as  $\text{LnA}_3 \cdot 3\text{HA}$  or  $\text{LnA}_2 \cdot \text{NO}_3$  (Reddy et al., 1999; Bhattacharyya

et al., 2006). In our previous work (Jia et al., 2009a), the extraction reaction of  $\text{Sm}^{3+}$  from chloride medium has been determined as:



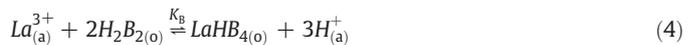
where the subscripts "a" and "o" express the aqueous and organic phases, respectively.

In this work, the effects of pH and C301 concentration on the extraction of  $\text{La}^{3+}$  are investigated when other experimental conditions are fixed. Results show that the extraction reaction is as the follows:



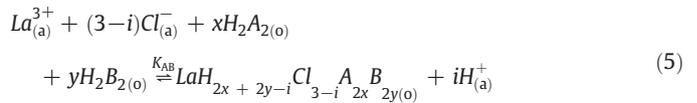
where  $K_A$  denotes the equilibrium constant when  $\text{La}^{3+}$  is extracted by C301 alone.

Similarly, the extraction of  $\text{La}^{3+}$  by CA100 can thus be obtained based on the results of the effects of pH and CA100 concentration on the extraction:



where  $K_B$  expresses the equilibrium constant when  $\text{La}^{3+}$  is extracted by CA100 alone.

In order to study the synergistic effect in the mixtures of C301 and CA100, the following reaction is proposed:



the distribution ratio  $D_{AB}$  can be written as:

$$\log D_{AB} = x \log [\text{H}_2\text{A}_2]_{(o)} + y \log [\text{H}_2\text{B}_2]_{(o)} + ipH + \log K_{AB} + (3-i) \log [\text{Cl}^-]_{(a)}. \quad (6)$$

At fixed concentrations of C301, CA100, and ionic strength, the effects of pH on the extraction of  $\text{La}^{3+}$  are investigated. The results are shown in Fig. 2, giving a straight line with a slope of about 3.0. When the concentration of one extractant is varied at fixed pH and the concentration of the other extractant, the relationship between  $\log D_{AB} - 3pH$  and extractant concentrations can be obtained. As shown in Fig. 3, the straight lines of the plots of  $\log D_{AB} - 3pH$  versus

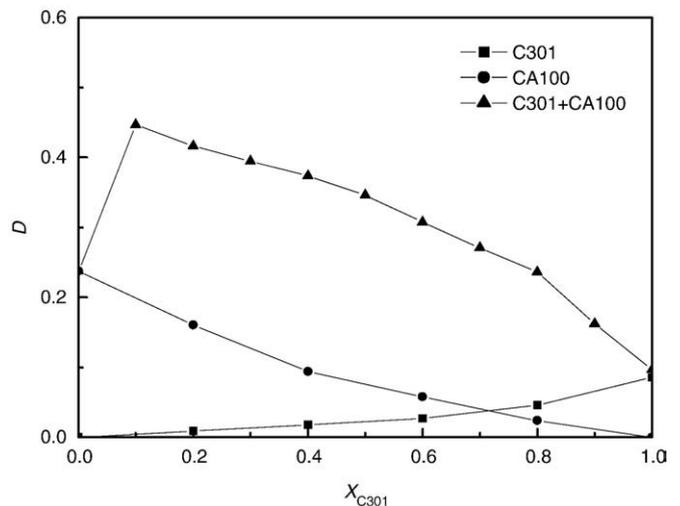
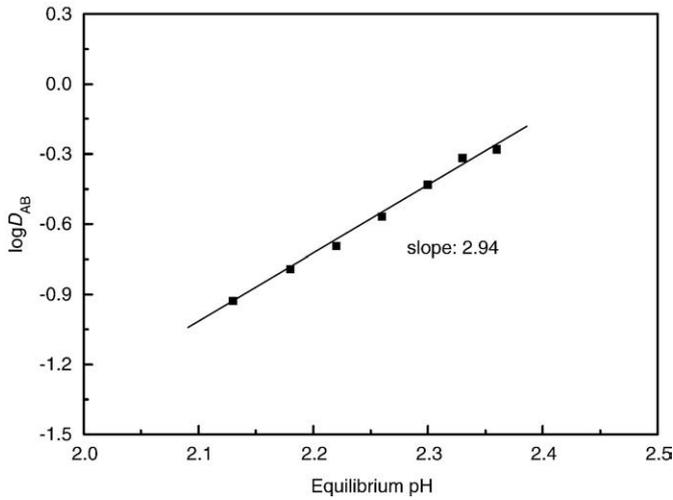
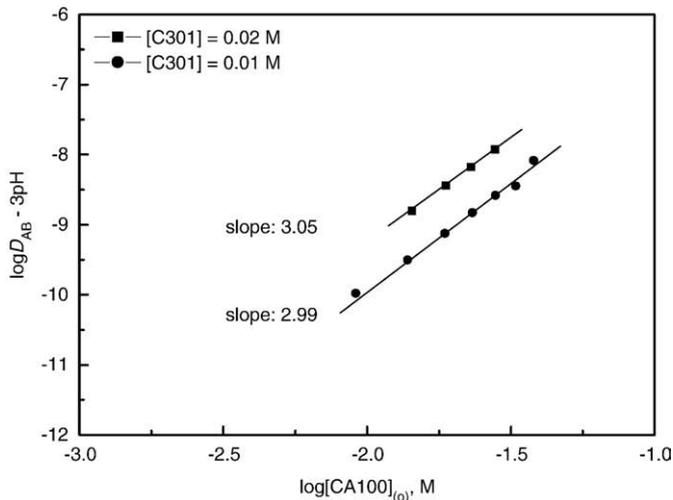
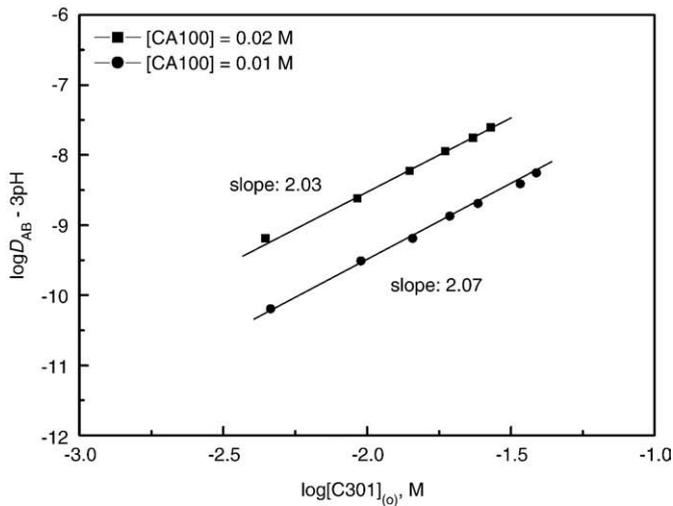
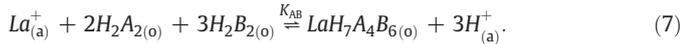


Fig. 1. Extraction of  $\text{La}^{3+}$  by C301, CA100, and CA100 + C301.  $[\text{La}^{3+}] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$ ,  $pH = 3.0$ ,  $\mu = 0.3 \text{ mol L}^{-1}$ ,  $[\text{CA100}]_{(o)} + [\text{C301}]_{(o)} = 0.05 \text{ mol L}^{-1}$ .



**Fig. 2.** Effect of pH on the extraction of  $\text{La}^{3+}$  by CA100 + C301.  $[\text{La}^{3+}] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$ ,  $\mu = 0.3 \text{ mol L}^{-1}$ ,  $[\text{C301}]_{(o)} = 0.02 \text{ mol L}^{-1}$ ,  $[\text{CA100}]_{(o)} = 0.03 \text{ mol L}^{-1}$ .

$\log [\text{H}_2\text{A}_2]_{(o)}$  and  $\log [\text{H}_2\text{B}_2]_{(o)}$  have slopes of about 2.0 and 3.0, respectively. Based on these results, Eq. (5) can be rewritten as:



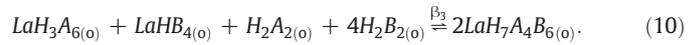
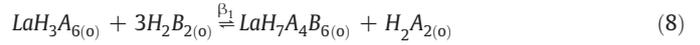
**Fig. 3.** Effects of extractant concentration on the extraction of  $\text{La}^{3+}$  by CA100 + C301.  $[\text{La}^{3+}] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$ ,  $\text{pH} = 3.0$ ,  $\mu = 0.3 \text{ mol L}^{-1}$ .

**Table 1**

Equilibrium constants and formation constants of  $\text{La}^{3+}$  extracted by C301 and CA100.

$\log K_A$	$\log K_B$	$\log K_{AB}$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
$-4.97 \pm 0.05$	$-4.88 \pm 0.07$	$-1.41 \pm 0.03$	3.56	3.47	7.03

According to Eqs. (3), (4), and (7), the formation reactions can be described as the following:



The formation constants,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  can thus be calculated:

$$\log \beta_1 = \log K_{AB} - \log K_A \quad (11)$$

$$\log \beta_2 = \log K_{AB} - \log K_B \quad (12)$$

$$\log \beta_3 = 2 \log K_{AB} - \log K_A - \log K_B \quad (13)$$

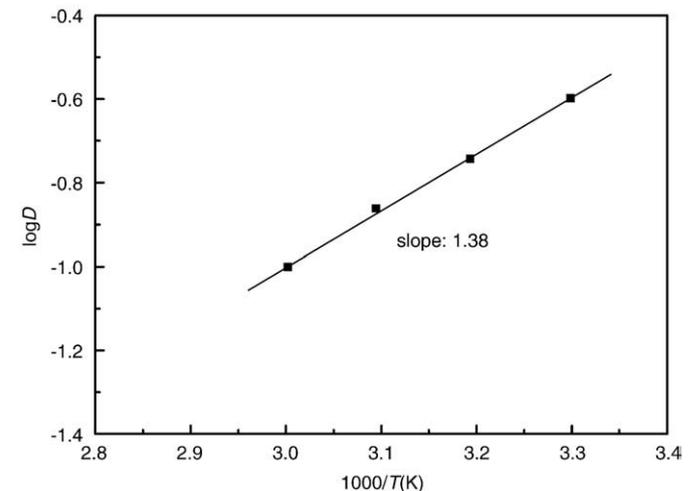
The values of  $K_A$ ,  $K_B$ ,  $K_{AB}$ ,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  are all shown in Table 1. It is obvious that  $\beta_3$  is bigger than  $\beta_1$  and  $\beta_2$ , which implies that Eq. (10) contributes most to the synergistic extraction. The extracted complexes of  $\text{La}^{3+}$  by C301 and CA100, i.e.,  $\text{LaH}_3\text{A}_6$  and  $\text{LaHB}_4$ , are more prone to form the final synergistic complex,  $\text{LaH}_7\text{A}_4\text{B}_6$ .

### 3.3. Influence of temperature on the extraction of $\text{La}^{3+}$ by CA100 + C301

When  $\text{La}^{3+}$  concentration, pH, and concentrations of C301 and CA100 are fixed, the influence of temperature on the extraction of  $\text{La}^{3+}$  by C301 + CA100 has been studied. Fig. 4 shows the plots of  $\log D$  versus  $1000/T$ . The change of enthalpy ( $\Delta H$ ), the change of Gibbs free energy ( $\Delta G$ ), and the change of entropy ( $\Delta S$ ) can thus be obtained as the following:

$$\frac{\Delta \log D}{\Delta \frac{1}{T}} = \frac{-\Delta H}{2.303R} \quad (14)$$

$$\Delta G = -RT \ln K \quad (15)$$



**Fig. 4.** Relationship between distribution ratio  $D$  and temperature.  $[\text{La}^{3+}] = 5 \times 10^{-3} \text{ mol L}^{-1}$ ,  $\text{pH} = 3.0$ ,  $\mu = 0.3 \text{ mol L}^{-1}$ ,  $C_{\text{C301}} = 0.02 \text{ mol L}^{-1}$ ,  $C_{\text{CA100}} = 0.03 \text{ mol L}^{-1}$ .

**Table 2**  
Separation factors of REEs in C301/CA100 + C301 systems.

C301/C301 + CA100	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
La	1.04/0.52	1.06/0.48	1.72/0.46	2.08/0.52	3.02/0.75	3.54/0.48	3.60/0.35	3.72/0.38	3.84/0.38	3.90/0.31	4.59/0.18	5.00/0.45	5.27/0.30	3.74/0.11
Ce		1.02/0.93	1.65/0.89	2.00/1.01	2.91/1.44	3.40/0.93	3.46/0.68	3.57/0.74	3.69/0.73	3.75/0.61	4.41/0.35	4.81/0.86	5.06/0.58	3.59/0.22
Pr			1.62/0.96	1.96/1.09	2.85/1.56	3.34/1.00	3.39/0.74	3.50/0.80	3.62/0.79	3.67/0.65	4.32/0.37	4.71/0.93	4.96/0.62	3.52/0.24
Nd				1.21/1.13	1.76/1.62	2.06/1.04	2.09/0.77	2.16/0.83	2.23/0.82	2.27/0.68	2.67/0.39	2.91/0.97	3.06/0.65	2.17/0.38
Sm					1.45/1.43	1.70/0.92	1.73/0.67	1.79/0.73	1.85/0.72	1.87/0.60	2.21/0.34	2.40/0.85	2.53/0.57	1.80/0.22
Eu						1.17/0.64	1.19/0.47	1.23/0.51	1.27/0.50	1.29/0.42	1.52/0.24	1.65/0.60	1.74/0.40	1.24/0.15
Gd							1.02/0.73	1.05/0.80	1.08/0.78	1.10/0.65	1.30/0.37	1.41/0.93	1.49/0.62	1.06/0.23
Tb								1.03/1.09	1.07/1.07	1.08/0.89	1.27/0.51	1.39/1.27	1.46/0.84	1.04/0.32
Dy									1.03/0.98	1.05/0.82	1.24/0.47	1.35/1.17	1.42/0.78	1.01/0.29
Ho										1.02/0.83	1.19/0.47	1.30/1.19	1.37/0.79	0.97/0.30
Er											1.18/0.57	1.28/1.43	1.35/0.95	0.96/0.36
Tm												1.09/2.50	1.15/1.67	0.81/0.63
Yb													1.05/0.67	0.75/0.25
Lu														0.71/0.38

The separation factors with single C301 system are from Jia et al. (2009a).

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (16)$$

where  $\Delta G$  and  $\Delta S$  are determined when  $T$  is 298.15 K.

The  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  values are calculated as  $-26.38 \text{ kJ mol}^{-1}$ ,  $7.91 \text{ kJ mol}^{-1}$ , and  $-116.97 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. It can be seen that  $\Delta H$  is smaller than zero, indicating that the extraction of  $\text{La}^{3+}$  in CA100 + C301 system is an exothermic reaction.

#### 3.4. Separation of rare earth elements by mixtures of CA100 with C301 or C302

The extraction effects of REEs by mixtures of CA100 with C301 or C302 have been studied in detail. In CA100 + C301 system, the synergistic enhancement coefficients decrease with increasing atomic number of lanthanoids. However, such an order cannot be found in CA100 + C302 system.

The different extraction effects may be used to investigate the separation of REEs. If  $D_M$  and  $D_N$  represent the distribution ratios of M and N under the same extraction conditions, the separation factor between M and N can be expressed as:

$$\beta_{M/N} = \frac{D_M}{D_N} \quad (17)$$

The further  $\beta_{M/N}$  values are from 1, the better can the two metals be separated. Tables 2 and 3 show the separation factor values of REEs by C301 (Jia et al., 2009a), CA100 + C301, C302, CA100 + C302 systems. It can be concluded that the separation factors for many REE pairs by CA100 + C301 are greater than those by C301 alone. It is very important to note that the separation factors between Y and all the lanthanoids are enhanced by the mixing system since Y is well known to be difficult to be separated from other REEs, especially heavy lanthanoids. There is great potential to separate Y from lanthanoids by CA100 + C301 system proposed in the present work. However, the greater separation abilities to separate REEs cannot be obtained by CA100 + C302 system than by single C302 system.

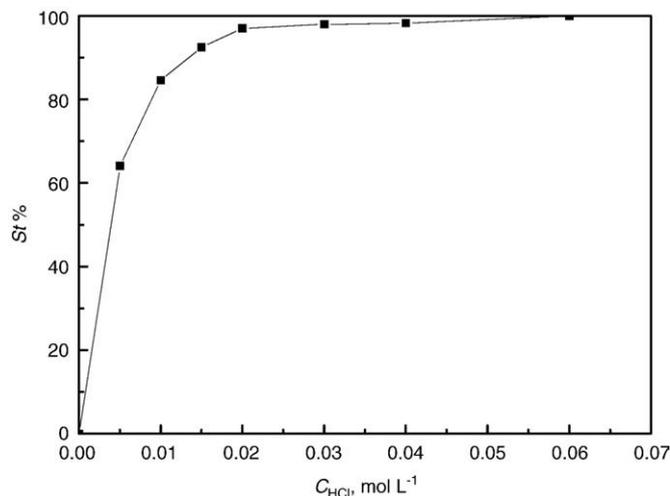
**Table 3**  
Separation factors of REEs in C302/CA100 + C302 systems.

	Nd	Sm	Tb	Er	Yb	Y
La	3.09/0.87	9.26/1.01	12.87/2.82	19.13/2.57	28.70/1.73	18.63/1.34
Nd		3.00/1.16	4.17/3.24	6.20/2.95	9.30/1.98	6.04/1.53
Sm			1.39/2.79	2.07/2.54	3.10/1.71	2.01/1.32
Tb				1.49/0.91	2.23/0.61	1.45/0.47
Er					1.50/0.67	0.97/0.52
Yb						0.65/0.77

The aqueous medium is an important factor that may affect the extraction behavior of metal ions. In the present work, the extraction of REEs by CA100 + C301 from chloride medium is compared with that from thiocyanate medium in which  $0.3 \text{ mol L}^{-1} \text{ NH}_4\text{SCN}$  is employed for keeping the ionic strength instead of NaCl (Sun et al., 1981). Results show that CA100 + C301 do not have evident synergistic effects on all REEs from thiocyanate medium. The separation factors between Y and lanthanoids by CA100 + C301 can also be obtained, e.g.,  $\beta_{Y/La} = 0.65$ ,  $\beta_{Y/Tb} = 0.81$ ,  $\beta_{Y/Yb} = 0.95$ . It can be concluded that the separation abilities between Y and lanthanoids from thiocyanate medium are weaker than those obtained from chloride medium.

#### 3.5. Stripping properties

The loading capacities of REEs by CA100 + C301 have also been investigated by studying the influence of REE concentrations on the distribution ratios. Results show that the distribution ratios decrease with increasing REE concentrations and then keep constant. An amount of  $0.03 \text{ mol L}^{-1}$  CA100 +  $0.02 \text{ mol L}^{-1}$  C301 organic phase loaded with REEs ( $5 \times 10^{-3} \text{ mol L}^{-1}$ ) has been back-extracted with hydrochloric acid. The stripping efficiency versus the concentration of HCl is shown in Fig. 5, indicating that the majority of REEs can be stripped by one single stage stripping if the concentration of hydrochloric acid is greater than  $0.02 \text{ mol L}^{-1}$ . Therefore, the low stripping acidity in the CA100 + C301 mixing system will have the potential of practical application.



**Fig. 5.** Relationship between stripping concentration of HCl and stripping ratio.  $[\text{C301}] = 0.02 \text{ mol L}^{-1}$ ,  $[\text{CA100}] = 0.03 \text{ mol L}^{-1}$ .

#### 4. Conclusions

In the present study, the mixtures of CA100 with C301 or C302 are applied to the extraction of REEs from chloride medium. The mixtures exhibit different extraction effects on different REEs. The synergistic extraction of  $\text{La}^{3+}$  has been investigated by graphical and numerical methods.  $\text{La}^{3+}$  is determined to be extracted as  $\text{LaH}_7\text{A}_4\text{B}_6$  by the synergistic mixture of CA100 and C301. The equilibrium constants and formation constants are calculated and an extraction mechanism is proposed. The synergistic extraction of  $\text{La}^{3+}$  is an exothermic reaction. Furthermore, the mixtures of CA100 with C301 are proved to have great potential for the separation of Y from lanthanoids according to the separation factors.

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