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Selective separation of yttrium by CA-100 in the presence of a complexing agent

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Abstract

The selective separation of Y from yttrium solution containing small heavy rare earth (HRE) impurities (Ho, Er, Tm, Yb, Lu) by liquid–liquid extraction using CA-100 in the presence of a water-soluble complexing agent of ethylenediaminetetraacetic acid (EDTA) was experimentally studied at 298 K. Experiments were carried out in two feeds, Feed-I: $[\mathrm{RE}]_\mathrm{f} = 4.94 \times 10^{-3}$ M, Y = 98.5%, HRE (Ho, Er, Tm, Yb, Lu) = 1.5%; Feed-II: $[\mathrm{RE}]_\mathrm{f} = 4.94 \times 10^{-3}$ M, Y = 99.9%, HRE (Ho, Er, Tm, Yb, Lu) = 0.1%, as a function of equilibrium pH (pH_eq), the concentration ratio of [EDTA]:[HRE impurities]. It was shown that the extraction of HRE in the presence of EDTA was suppressed when compared to that of Y because of the masking effect, while the selective extraction of Y was enhanced and the separation factors increased to maximum at appropriate condition for Feed-I: Y/Ho = 1.53, Y/Er = 3.09, Y/Tm = 5.61, Y/Yb = 12.04, Y/Lu = 27.51 at pH 4.37 and [EDTA]:[HRE impurities] = 4:1, for Feed-II: Y/Ho = 1.32, Y/Er = 1.91, Y/Tm = 2.00, Y/Yb = 3.05, Y/Lu = 3.33 at pH 4.42 and [EDTA]:[HRE impurities] = 8:1. The separation and purification of Y by this method was discussed.

Keywords: Liquid–liquid extraction; Separation; Yttrium; Complexing agent; EDTA

1. Introduction

Yttrium (Y) is an important element and in great demand nowadays. It is widely used in astronavigation, luminescence, nuclear energy and metallurgical industries [1,2] and the purity of Y is strictly required, for example, the fluorescent grade Y_2O_3 requires the content of relevant RE impurities should be lowered to 1×10^{-4} level or even lower. However, the separation and purification of Y from HRE impurities is known to be difficult because of their similar chemical and physical properties. For the effective separation of rare-earth metals, various modification of the extraction system have been reported, one of the most effective methods for improving the separation is to modify the aqueous phase by adding EDTA, DTPA or HEDTA [3–6]. In the presence of the water-soluble complexing agent, a part of the metals in the aqueous phase is complexed with the complexing agent and thus hindered in the extraction by masking effect, and the separation of the metals should thus be improved. There were several reports about Y separation in the presence of water-soluble complexing agent [7–10]. Nishihama et al. reported the selective extraction of Y from Ho/Y/Er solution by EHPNA using EDTA as complexing agent [8].

S-Nonylphenoxy acetic acid (CA-100) is a novel organic carboxylic acid, developed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. It has been reported that the extraction sequence of rare earth by CA-100 is scandium > light (middle) lanthanide > heavy lanthanide > yttrium and CA-100 is superior to naphthenic acid for the separation of Y from light and middle lanthanides [11], but the separation of Y from HRE is very difficult. In order to overcome the problem, an attempt was, thus, made in this work to effectively separate Y from HRE impurities (Ho, Er, Tm, Yb, Lu) by adding water-soluble complexing

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agent (EDTA) to the aqueous solution as masking reagent for HRE.

In the present work, the selective separation of Y from Y solution containing small HRE impurities by CA-100 using EDTA as a complexing agent has been studied. Experiments were carried out at different concentration ratios of EDTA to HRE impurities, different aqueous $\mathrm{pH_{eq}}$ in two feeds. The results suggested that highly selective separation and purification of Y from small HRE impurities is possible.

2. Experimental

CA-100 (purity 98%) was supplied by Tianjin Xiandai Chemical Plant of China and purified as literature [11], then was diluted to required concentration in *n*-haptane. All of the inorganic chemicals were analytical grade. The rare-earth solutions were prepared by dissolution of the oxides (>99.9%) in heated hydrochloric acid and were standardized by EDTA. The aqueous feed solutions (Feed-I: $[\mathrm{RE}]_\mathrm{f} = 4.94 \times 10^{-3}$ M, Y = 98.5%, HRE (Ho, Er, Tm, Yb, Lu) = 1.5%; Feed-II: $[\mathrm{RE}]_\mathrm{f} = 4.94 \times 10^{-3}$ M, Y = 99.9%, HRE (Ho, Er, Tm, Yb, Lu) = 0.1%) were prepared by addition of the appropriate concentration of EDTA and NaOH to a rare-earth solution to achieve required pH value, the ionic strength of the aqueous solution was hold constant at 0.6 mol/L by adding (Na, H)Cl.

In the extraction procedure, equal volumes of aqueous and organic phase were shaken and equilibrated at 298 K for 30 min, after the phase separation, the concentration of RE in the aqueous phase were analyzed by TJA model POEMS inductive coupled plasma atomic emission spectroscopy (ICP-AES) and that in the organic phase were obtained by mass balance. An Orin model 720pH meter was used for pH measurement.

3. Results and discussion

3.1. Extraction equilibrium of rare-earth elements in CA-100-EDTA system

In the previous work, the extraction equilibrium was studied based on the assumption that: (1) all EDTA in the aqueous phase makes 1:1 complex with the rare earth; (2) this complex is inaction for extraction and only free rare-earth ions (not complexed with EDTA) can take part in the extraction. So in the present CA-100-EDTA system, the total feed concentration of RE, $\mathrm{RE_f}$, is shown as Eq. (1), where L and REL denote EDTA and RE–EDTA complex, respectively,

$$[\mathrm{RE}]_\mathrm{f} = [\mathrm{RE}] + [\mathrm{REL}] + [\overline{\mathrm{RE}}] \tag{1}$$

$$D_0 = \frac{[\overline{\mathrm{RE}}]}{[\mathrm{RE}]} \tag{2}$$

D_0 is the distribution in the absence of complexing agent. Thus, the concentration of RE in the organic phase is shown by Eq. (3):

$$[\overline{\mathrm{RE}}] = \frac{D_0([\mathrm{RE}]_\mathrm{f} - [\mathrm{REL}])}{1 + D_0} \tag{3}$$

Total concentration in the aqueous phase, $[\mathrm{RE}]_\mathrm{t}$, is:

$$[\mathrm{RE}]_t = [\mathrm{RE}] + [\mathrm{REL}] = [\mathrm{RE}]_\mathrm{f} - [\overline{\mathrm{RE}}] \tag{4}$$

Combine (3) and (4),

$$[\mathrm{RE}]_\mathrm{t} = \frac{[\mathrm{RE}]_\mathrm{f} + D[\mathrm{REL}]}{1 + D_0} \tag{5}$$

Combining these equations, the distribution ratio in the presence of EDTA, D, is expressed as follows:

$$D = \frac{[\overline{\mathrm{RE}}]}{[\mathrm{RE}]_\mathrm{t}} = \frac{D_0([\mathrm{RE}]_\mathrm{f} - [\mathrm{REL}])}{[\mathrm{RE}]_\mathrm{f} + D_0[\mathrm{REL}]} \tag{6}$$

Since all the complexing agents were assumed to complex with the rare-earth element, [REL] equals the concentration of the complexing agent in feed, $[\mathrm{L}]_\mathrm{f}$. Thus, Eq. (6) is expressed as:

$$D = \frac{D_0\left(\frac{[\mathrm{RE}]_\mathrm{f}}{[\mathrm{L}]_\mathrm{f}} - 1\right)}{\frac{[\mathrm{RE}]_\mathrm{f}}{[\mathrm{L}]_\mathrm{f}} + D_0} \tag{7}$$

The values of D are predicted by Eq. (7) and D_0 was determined in the system without EDTA. Fig. 1 shows the predicted D by solid line, which is agreement with the experimental data. It indicates that the proposed extraction scheme could be used to describe the extraction system, in the presence of EDTA.

3.2. The effects of EDTA concentration on the extraction of rare earths

The effect of [EDTA]:[HRE impurities] on the extraction of RE in two feeds with CA-100 was studied

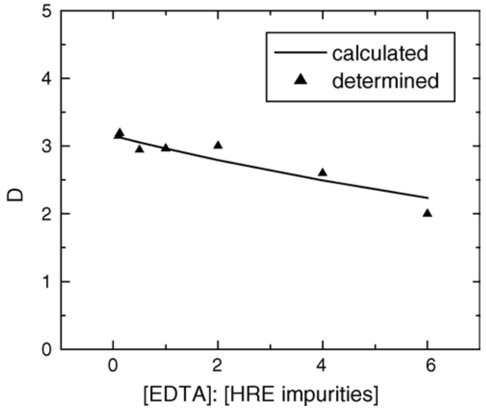

Fig. 1. Determined and calculated values of the distribution ratio of RE in CA-100-EDTA system. Feed-I: $[\mathrm{RE}]_\mathrm{f} = 4.94 \times 10^{-3}$ M, $[\mathrm{Y}] = 4.86 \times 10^{-3}$ M, $[\mathrm{Ho}] = [\mathrm{Er}] = [\mathrm{Tm}] = [\mathrm{Lu}] = 1.6 \times 10^{-5}$ M, $[\mathrm{Yb}] = 1.5 \times 10^{-5}$ M; $\mathrm{pH_{eq}} = 4.37$; [CA-100] = 0.08 M.

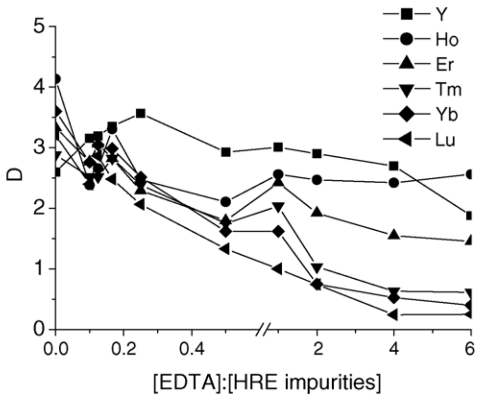

Fig. 2. The effect of the concentration ratio of [EDTA]:[HRE impurities] on the extraction of rare earths in Feed-I. $[RE]_f = 4.94 \times 10^{-3}$ M, $[Y] = 4.86 \times 10^{-3}$ M, $[Ho] = [Er] = [Tm] = [Lu] = 1.6 \times 10^{-5}$ M, $[Yb] = 1.5 \times 10^{-5}$ M; $pH_{eq} = 4.90$; [CA-100] = 0.08 M.

in detail and the results were shown in Fig. 2 and Table 1.

From Fig. 2, it can be found that HRE (Ho, Er, Tm, Yb, Lu) were extracted prior to Y in the absence of complexing agent (EDTA) and the reversed order was obtained in the presence of EDTA; we can also see the distribution ratios of Y (D_Y) in presence of EDTA were all larger than that without EDTA ($D_{0,Y}$) with [EDTA]:[HRE impurities] increasing from 0.1 to 4, while, the distribution ratios of HRE impurities were decreased, respectively, which means that the masking effect was firstly played on the HRE impurities and the masking effect for HRE was primary when compared to that for Y, which, thus, resulted in the increased D_Y ($D_Y > D_{0,Y}$). The distribution ratio sequence gradually became Y > Ho > Er > Tm > Yb > Lu, it can be ascribed to the K_1 order of RE–EDTA, Y < Ho < Er < Tm < Yb < Lu, which were given for $Y = 10^{17.38}$, $Ho = 10^{17.67}$, $Er = 10^{17.98}$, $Tm = 10^{18.59}$, $Yb = 10^{18.68}$, $Lu = 10^{19.06}$ in literature [12]. When the ratio of [EDTA]:[HRE impurities] was greater than 4, the distribution ratios of HRE almost unchanged, while D_Y decreased much, which indicated the masking effect for Y in this region was chief, while, for HRE was insensitive.

The separation factors (SF) of yttrium with respect to HRE (Y/HRE), which can further elucidate the selectivity of CA-100-EDTA system, were calculated and shown in Table 1. First, it is evident that Y/HRE values in the presence of EDTA are larger than those without complexing agent. Second, the SF values increase with the ratio of [EDTA]:[HRE impurities] increasing from 0.1 to 4, however, decrease when [EDTA]:[HRE impurities] is greater than 4. So, [EDTA]:[HRE impurities] value of 4 was, therefore, used thereafter. Third, comparing the SF values, we can expect that Y can be effectively separated and purified from Feed-I at the [EDTA]:[HRE impurities] = 4.

Table 1
Separation factors of yttrium with respect to HRE impurities at different [EDTA]:[HRE impurities] with CA-100 in the presence of EDTA

EDTA/RE	Y/Ho	Y/Er	Y/Tm	Y/Yb	Y/Lu
0	0.63	0.78	0.90	0.72	0.81
0.1	1.33	1.14	1.25	1.14	1.32
0.125	1.20	1.04	1.27	1.05	1.12
0.1667	1.02	1.19	1.19	1.12	1.35
0.25	1.45	1.56	1.50	1.42	1.73
0.5	1.39	1.63	1.67	1.81	2.20
1	1.16	1.22	1.46	1.83	2.96
2	1.21	1.56	2.91	4.03	4.05
4	1.18	1.68	4.13	4.95	10.73
6	0.74	1.29	3.08	4.73	7.58

The experiment was also carried out in Feed-II and the results indicated that, compared with Feed-I, the variation of *D* in Feed-II were similar to Feed-I. The distribution ratio of HRE attained to the minimum at the EDTA:RE (impurities) = 8:1, but the separation factors showed that compared to Feed-I, there were no advantages for separation of Y from Feed-II at [EDTA]:[HRE impurities] = 8:1 for Y/Ho = 1.88, Y/Er = 1.61, Y/Tm = 1.42, Y/Yb = 2.63 and Y/Lu = 2.40. But, the separation of Y from Feed-II at suitable condition is possible.

3.3. pH effects on the extraction of rare earth in two feeds

It should be noted that the equilibrium pH in the aqueous solution plays an important role in CA-100-EDTA extraction system. We assume that the relevant reaction is expressed by Eqs. (8)–(11) (we take Y^{3+} as example).

$$H_2L^{2-} \rightarrow 2H^+ + L^{4-} \tag{8}$$

$$L^{4-} + Y^{3+} \rightarrow LY^- \tag{9}$$

$$4H_2A_2 + Y^{3+} \rightarrow YA_3(HA)_5 + 3H^{+[11]} \tag{10}$$

$$Y^{3+} + iOH^- \rightarrow Y(OH)^{3-i} \tag{11}$$

First, the ability of EDTA to complex with rare-earth metals depends on the pH value of the aqueous solution because only the dissociated ligand of EDTA (L^{4-}) forms a complex with rare-earth metals (Eqs. (8)–(9)), therefore, the masking effect on rare-earth metal would be enhanced with the increasing of pH. Second, the increasing pH would attribute to the extractability of RE with CA-100 as shown in Eq. (10). Third, from Eq. (11), it is noted that with pH increasing, the rare-earth metal on aqueous solution is apt to hydrolyze with OH^-, and the free rare-earth metal in aqueous solution would decrease. Therefore, the extraction result is affected by the interaction of the three factors.

The effects of equilibrium pH on the distribution ratio of rare-earth metals in two different feeds were studied, it is found that both Feed-I (Fig. 3) and Feed-II have the similar variation and the extractability of RE increases first with the increasing of equilibrium pH and reaches a maximum at the pH about 4.4, and then decreases when pH beyond 4.4.

Table 2 shows the SF values of Y/HRE at different pH_{eq} in Feed-I. From Table 2, we can see that the SF values reach maximum at pH 4.37and the selectivity of Y/HRE

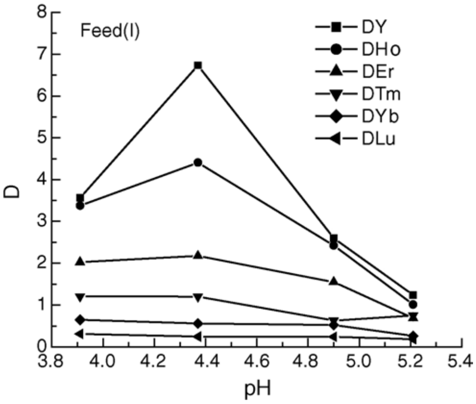

Fig. 3. The effect of pH on the extraction of rare-earth ions in Feed-I with CA-100 in the presence of EDTA, $[RE]_f = 4.94 \times 10^{-3}$ M, $[Y] = 4.86 \times 10^{-3}$ M, $[Ho] = [Er] = [Tm] = [Lu] = 1.6 \times 10^{-5}$ M, $[Yb] = 1.5 \times 10^{-5}$ M; [CA-100] = 0.08M; [EDTA]:[HRE impurities] = 4:1.

increases with decreasing ionic radii of the Ln^{3+}. So, yttrium can be more effectively separated from Feed-I at pH 4.37 and [EDTA]:[HRE] = 4:1; in addition, the SF values of HRE shown in Table 3 are so big that the mutual separation of HRE impurities may realize at this condition. In Feed-II, the SF values were Y/Ho = 1.32, Y/Er = 1.91, Y/Tm = 2.00, Y/Yb = 3.05, Y/Lu = 3.33 at the condition of pH 4.42 and [EDTA]:[HRE impurities] = 8:1, the selective extraction of Y from Feed-II is possible.

Table 2
Separation factors of yttrium with respect to HRE impurities in Feed-I at various pH in the presence of EDTA

PH	Y/Ho	Y/Er	Y/Tm	Y/Yb	Y/Lu
3.91	1.06	1.76	2.96	5.53	11.48
4.37	1.53	3.09	5.61	12.04	27.51
4.90	1.07	1.68	4.13	4.95	10.73
5.21	1.22	1.81	1.65	4.70	6.70

Table 3
Separation factors of mutual rare-earth impurities in Feed-I at pH 4.37 in the presence of EDTA

$SF_{(DLn2/DLn1)}$	Yb/Ln	Tm/Ln	Er/Ln	Ho/Ln
Lu	2.28	4.90	8.88	17.99
Yb		2.15	3.89	7.88
Tm			1.81	3.67
Er				2.03

4. Conclusions

In the CA-100-EDTA system, the extraction equilibrium was expressed and confirmed by experimental data. The extraction is affected by the stability constant of the EDTA–RE complex, the aqueous pH, the concentration ratio of EDTA to rare-earth impurities. The SF values of Y/HRE increased in the system and yttrium can be more effectively separated and purified from Feed-I at [EDTA]:[HRE impurities] = 4:1 and pH 4.37, moreover, the mutual separation of HRE impurities would be obtained. The selective extraction of yttrium from Feed-II was possible if the condition is suitable. The present method was suit for separation and purification of yttrium from Y solution containing small HRE impurities and the smaller amount of complexing agent needed.

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