

Behavior of Sec-Octylphenoxy Acetic Acid (CA-12) in Yttrium Recovery from High Concentrated Heavy Rare Earths Mixture

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Abstract The solvent extraction technique is the only industrial way used to separate and purificate yttrium from other rare earths. In order to improve this process several extractants have been tested during last years. In this work, the behavior of sec-octylphenoxy acetic acid (CA-12) in Yttrium recovery from high concentrated heavy rare earth mixture was investigated. Sodium hydroxide solution was used in order to presaponify organic phase composed by CA-12 and Tributyl phosphate (TBP) diluted in kerosene. In the investigated condition, TBP confirmed its role of phase modifier not significantly altering the extraction behavior of CA-12. The CA-12-TBP system showed a high affinity in extraction for lighter rare earths such as Sm, Eu, and Gd, leaving yttrium in aqueous phase. Using a feed concentration (\sum [RE]) of 1 M, organic mixture is capable to extract around the 70% of metals in a single extraction test showing this extraction sequence $Y < Lu < Yb < Tm < Er < Ho < Dy < Tb < Gd < Eu < Sm$. Moreover for [CA-12] = 1.79 M and [RE] = 2 M the instability of extraction system occurs.

Keywords CA-12 • Solvent extraction • Rare earths • Liquid-liquid extraction

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Introduction

In last years, heavy rare earths and yttrium are reported as Critical Raw Materials in the Strategic paper of EU community [1]. Yttrium is widely used for luminescent lamps production [2], Light Emitting Diode and other electronical devices [3]. Yttrium is produced from minerals [4] and naphthenic acid is the extractant most used to separate it from other heavy rare earths [5]. Minerals such as loparite, fergusonite, xenotime, monazite and bastnasite are the main source of rare earths, while a lower amount of REs are also contained in rock phosphate which is considered as secondary source for rare-earth elements. Yttrium separation and purification is a difficult task and solvent extraction technique is used to perform it [6–10]. Valiente et al. [7] studied the distribution of yttrium (III) between acidic aqueous chloride solutions and organic solutions of di-(2-ethylhexyl)-phosphoric acid (D2EHPA) dissolved in kerosene. Sposato et al. [11] made a comparison among three different extractant such as (2-ethylhexyl)-mono (2-ethylhexyl) ester phosphonic acid (P507), secondary-octyl phenoxy acetic acid (CA-12)) and bis (2,4,4-trimethylpentyl)phosphinic acid (Cyanex272) in the separation of heavy rare earths from a yttrium-rich nitrate aqueous source. Extraction of yttrium and some trivalent lanthanides from nitrate and thiocyanate solutions using Cyanex 923 in xylene was investigated by Reddy et al. [12]; they studied lanthanides complexes built by TRPO extractant from nitrate and thiocyanate media. Ramachandra Reddy et al. [9] performed studies about extraction of Y (III) from phosphoric acid solutions with TOPS 99 (Talcher Organo phosphorus solvent) as extractant. Gupta et al. [13] studied the solvent extraction and separation of yttrium and lanthanides by using Cyanex 923 from different acid media. Solvent extraction of Sc, Y, La and Gd from hydrochloric acid solutions with bis(2,4,4-trimethylpentyl) monothio-phosphinic acid (Cyanex 302), was investigated by Li and coworkers [14]. In a further works [15] Wei Li et al. investigated extraction and separation of yttrium with CA-12) and TBP from other rare earths in chloride medium, TBP was used as phase modifier to achieve fast phase separation and higher stability of organic phase. In present work we study the behavior of CA-12 in Yttrium recovery from a mixture with a high concentration of heavy rare earth.

Experimental

Apparatus

Digital pH meter (Metrohm 780) was used for pH measurements. Automatic titrator (Metrohm 905 Titrand), equipped by an iSolvotrode probe, was used to determine the molar concentration of CA-12). Inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer, Optima 8300 model) was used for the analysis of rare earths in aqueous media.

Reagent

CA-12 was kindly provided by Treibacher Industrie and its concentration (3.58 M) was titrated by using standard NaOH. This extractant, used without any further purification, was diluted with kerosene. The kerosene (provided by oleotecnica S.p. A.) is a selected fraction of linear hydrocarbons compounds (C10–C13, aromatic compounds <2%). Pure Sodium hydroxide (provided by Carlo Erba ACS-ISO) was dissolved in demineralized water and used for the pre-saponification of the extractant. TBP >99% (provided by Sigma-Aldrich) was used as phase modifier. Stock solution containing all rare earths and yttrium were prepared dissolving their salts, of analytical grade, in demineralized water (kindly provided by Treibacher Industry) and their concentrations checked by using ICP-OES (Table 1). All other reagents were of analytical grade.

Methods

The experiments were carried out shaking equal volumes of aqueous solution (feed and CA-12) diluted with kerosene for 40 min with the support of a mechanical shaker at room temperature (298 ± 1 K) to ensure complete equilibration. The laboratory is provided with microclima control. The ingredients in the aqueous phase were analyzed by ICP-OES, and the concentration of rare earths in organic phase was determined by mass balance. The preliminary experiments, by using HCl stripping solution, indicated that the concentration of metals in organic phase by mass balance was consistent. Distribution ratio was obtained as $D = [RE]_o/[RE]_a$, where 'a' and 'o' denote aqueous and organic phase. The value of pH was determined after extraction and phase separation. An amount of 15 vol.% of Tributyl phosphate (TBP), used as phase modifier, is added to the extractant mixture before kerosene dilution.

Results and Discussion

The Role of the Phase Modifier

CA-12 is an organic carboxylic acid extractant composed by an aromatic 6 carbons-ring with two functional groups in meta position ($-C_8H_{17}$ and $-OCH_2COOH$). Complexes of CA-12 and rare earths make easily emulsion in alkyl

Table 1 Feed relative concentration of rare earth elements

	Dy	Er	Eu	Gd	Ho	Lu	Sm	Tb	Tm	Y	Yb
Feed (wt%)	9.3	5.4	1.5	11.7	2.3	0.5	4.1	1.7	0.8	58	4.6

solution due to their small solubility, so it is necessary to add a modifier (usually an alcohol like iso-octanol) to avoid it [16]. Li studied the use of aliphatic alcohols as modifiers in CA12 system for long term industrial tests [17]. The concentration of CA-12 with iso-octanol as modifier decreases with time degrading the extraction system, probably the esterification of CA-12 and iso-octanol occurs. Otherwise, the concentration of CA-12-TBP system is constant for long time making this system a better choice [18]. For these reasons we decided to work using CA-12) with TBP as extractant system.

In Fig. 1 is reported the amount of rare earth extracted (calculated as $\sum \text{RE}$ extracted in organic phase/ $\sum \text{RE}$ in feed * 100) as a function of pH with and without the use of TBP. We observed that the use of a phase modifier does not significantly alter the amount of rare earth extracted from the feed. Separation factors (β) of rare earth elements versus Yttrium, calculated as $D_{\text{of single element}}/D_{\text{of yttrium}}$ are not influenced by presence of TBP (Table 2). Moreover, with the use of TBP we observe a better separation of the phases in term of rate and to avoid emulsification.

CA-12 Behavior for Feed Concentration = 0.2 M

The amount of rare earths extracted (calculated as $\sum \text{RE}$ extracted in organic phase/ $\sum \text{RE}$ in feed * 100) versus pH at different CA-12) concentration is reported in Fig. 2.

Fig. 1 The effect of phase modifier on the rare earth extracted. $[(\text{CA-12})] = 0.7 \text{ M}$, $\text{TBP} = 15 \text{ vol.}\%$ (if present), $[\text{feed}] = 0.2 \text{ M}$

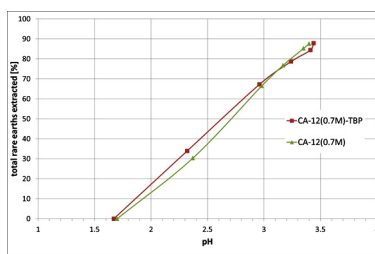


Table 2 Separation factors (β) of mixture rare earths elements $[(\text{CA-12})] = 0.7 \text{ M}$ with and without TBP

	0.7 M + TBP	0.7 M
Gd	4.26	4.34
Dy	2.45	2.58
Er	1.50	1.53
Sm	8.93	9.03
Yb	1.15	1.07
Ho	2.20	2.27
Tb	4.63	4.75
Eu	7.07	7.19
Tm	1.38	1.39
Lu	0.98	0.96

As expected, at higher extractant concentration, we observe an increased amount of extracted rare earths with the increase of pH. For $[CA-12] = 1.79 \text{ M}$, just at $\text{pH} = 3.4$, we can obtain the total extraction of rare earths contained in the feed. In this case, we don't have the possibility to separate rare earths metals but this underline that CA-12 is a strong extractant. The lowest value of pH, for each curves, is reached without adding sodium hydroxide, and this result shows as CA-12 doesn't work as extractant for $\text{pH} < 2$.

Data reported in Figs. 3 and 4 shows the effect of D versus pH on the mixture rare earths using the feed at 0.2 M and changing CA-12 concentration.

With pH increasing we observe an improvement of rare earths extraction.

Compared with other rare earths, yttrium and lutetium are the most difficult to be extracted by CA-12 which means that it is possible to be separated from other rare earths. The results shows that the value of D is $Y \leq Lu < Yb < Tm < Ho < Er < Dy < Gd < Tb < Eu < Sm$. The values of D increase with the increasing of extractant concentration, in particular from 0.5 to 0.7 M concentration

Fig. 2 Total amount of rare earths extracted versus pH at different CA-12-TBP-kerosene solution concentration for [feed] = 0.2 M

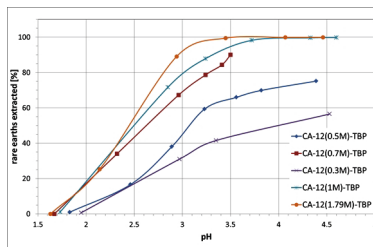


Fig. 3 Relationship between logarithm distribution ratio D and pH of aqueous phase: $[CA-12] = 0.5 \text{ M}$; TBP = 15%; [feed] = 0.2 M

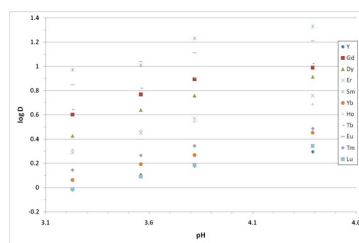


Fig. 4 Relationship between logarithm distribution ratio D and pH of aqueous phase: $[CA-12] = 0.7 \text{ M}$; TBP = 15%; [feed] = 0.2 M

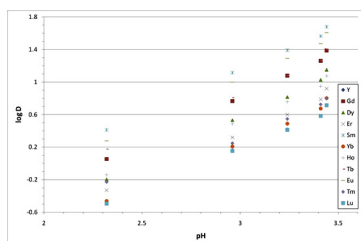
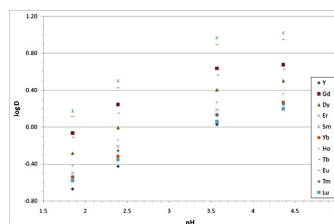


Table 3 Separation factors (β) of mixture rare earths elements

	CA-12 molar concentration			
	0.3 M	0.5 M	0.7 M	1 M
Gd	4.33	4.67	4.26	3.96
Dy	2.98	3.25	2.45	2.68
Er	1.88	2.34	1.50	1.59
Sm	8.56	9.62	8.93	8.36
Yb	1.98	1.20	1.15	1.36
Ho	2.29	2.49	2.20	1.94
Tb	3.81	5.51	4.63	3.57
Eu	7.30	8.25	7.07	7.61
Tm	1.99	1.39	1.38	1.39
Lu	1.62	0.90	0.98	1.08

Fig. 5 Relationship between logarithm distribution ratio D and pH of aqueous phase: [(CA-12)] = 1.79 M; TBP = 15%; [feed] = 1 M

of CA-12, at pH = 3.24 this increasing is around 160% (this value is calculated as $(D_{\text{element [0.5M]}} - D_{\text{element [0.7M]}})/D_{\text{element [0.5M]}} * 100$).

Separations factors (β), reported in Table 3, are calculated as $D_{\text{of single element}}/D_{\text{of yttrium}}$. The separation coefficient values are nearly constant for all CA-12) concentration. Lutetium and yttrium are the most difficult to be extracted from aqueous phase by using CA-12 as extractant. CA-12 presents the best selectivity for Sm, Eu, Tb and Gd with the higher values of separation factors. CA-12 presents a good affinity for all rare earths and the selectivity increase with the decrease of ionic radio dimension [19], except for an inversion for Holmium/Erbium and Terbium/Gadolinium, probably due to their relative concentrations in feed.

CA-12 Behavior for High Feed (1 and 2 M) Concentration

Data reported in Fig. 5 shows the effect of D versus pH with [feed] = 1 M. The results shows that the value of Distribution factors are $Y < Lu < Yb < Tm < Er < Ho < Dy < Tb < Gd < Eu < Sm$. Enhancing feed concentration, the selectivity for the extraction increase with the decrease of ionic radio dimension without exception. Moreover, with [(CA-12)] = 1.79 M is possible to extract about the 70%

Table 4 Separation factors (β); [CA-12] = 1 M, 1.79 M and [RE] = 1 M

Element	[CA-12] = 1 M	[CA-12] = 1.79 M
Gd	4.3	3.8
Dy	2.8	2.3
Er	1.8	1.4
Sm	7.2	7.1
Yb	1.36	1.2
Ho	2.2	1.6
Tb	3.7	3.2
Eu	6.4	6.3
Tm	1.6	1.23
Lu	1.4	1.05

of all rare earths contained in the feed at pH = 4.3 in a single step. These result underlines that CA-12-TBP solution presents a strong capability to extract rare earth from feed just in a single extraction step.

In the Table 4 are reported the separation factors (β) of rare earth elements versus Yttrium, calculated as $D_{\text{of single element}}/D_{\text{of yttrium}}$.

Best separation factors are for Samarium and Europium, 7.2 and 6.4 respectively, at [CA-12] = 1 M. The enhancing of extractant concentration decrease separation selectivity.

The possibility to separate yttrium and then the other rare earth became very interesting. In particular, we observe that yttrium is the metals most difficult to be extract, so it is left in aqueous phase to be separated. On the contrary, metals such as Sm, Eu and Gd present a very good affinity to CA-12-TBP system, so they are loaded in organic phase and separated/recovered after stripping by an HCl concentrated solution [15].

Tests carried out with [CA-12] = 1.79 M and [RE] = 2 M showed a total instability of extraction system. In particular, we observed the impossibility to separate aqueous and organic phase after the shaking of the system and the formation of a gel-phase occurs.

Conclusions

TBP showed to be a good phase modifier with a marginal effect on extractant power of the system. CA-12) + TBP showed a high affinity in extraction of lighter rare earths: the best extracted is Sm while the worst is Y ($Y < Lu < Yb < Tm < Er < Ho < Dy < Tb < Gd < Eu < Sm$). It resulted to be a very strong extractant system with an interesting potential to separate yttrium from other rare earths. It was impossible to work at feed concentration of 2 M for the incoming instability of the system.

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