Research Article

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Solvent extraction studies of Sm(III) from nitrate medium and separation factors of rare earth elements with mixtures of *sec*-octylphenoxyacetic acid and 1,10-phenthroline

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Abstract

BACKGROUND: Liquid–liquid extraction is widely used for the separation of rare earths, among which synergistic extraction has attracted more and more attention. Numerous types of synergistic extraction systems have been applied to rare earths with high extraction efficiency and selectivities. In the present study, mixtures of *sec*-octylphenoxyacetic acid (CA12, H_2A_2) and 1,10-phenanthroline (phen, B) have been used for the extraction of rare earths from nitrate medium. The stoichiometry of samarium(III) extraction has been studied using the methods of slope analysis and constant molar ratio. The possibility of using synergistic extraction effects to separate rare earths has also been studied.

RESULTS: Mixtures of CA12 and phen display synergistic effects in the extraction of rare earth elements giving maximum enhancement coefficients of 5.5 (La); 13.7 (Nd); 15.9 (Sm); 24.5 (Tb); 45.4 (Yb) and 12.3 (Y). Samarium(III) is extracted as $SmHA_4B_3$ with mixtures of CA12 and phen instead of $SmHA_4$ when extracted with CA12 alone. The calculated logarithm of the equilibrium constant is 6.0 and the thermodynamic functions, ΔH, ΔG, and ΔS, have been calculated as 4.3 kJ mol^{-1}, −33.7 kJ mol^{-1} and 129.7 J mol^{-1} K^{-1}, respectively.

CONCLUSION: Mixtures of CA12 and phen exhibit synergistic effects on rare earth elements. Graphical and numerical methods have been successfully used to determine their stoichiometries. The different synergistic effects may provide the possibility of separating yttrium from heavy lanthanoids at an appropriate ratio of CA12 and phen.

Keywords: synergistic extraction; rare earths; samarium; *sec*-octylphenoxyacetic acid; 1,10-phenanthroline

INTRODUCTION

With the increasing demand for rare earths, their separation and purification has gained considerable importance. Liquid–liquid extraction is commonly used and plays an important role in separating rare earths.[1] Synergistic extraction is a feature of liquid–liquid extraction that not only enhances the extraction efficiency, but also in some cases significantly improves the selectivity.[2] In synergistic systems, the extracting ability of the mixture of extractants exceeds the sum of the individual extracting abilities of its components. To date, numerous types of synergistic extraction systems have been investigated and applied extensively to rare earths with high extraction efficiency and selectivities.

A variety of extractants have been used in synergistic extraction including: acidic organophosphorus extractants,[3–11] neutral organophosphorus extractants,[4,5,12–14] carboxylic acids,[6,8–12] amines,[15] β-diketones,[13,14,16–27] crown ethers,[28] calix[4]arenes,[29] and neutral nitrogen donors.[5,7,15–27] For example, Luo *et al*[3] have studied the synergistic extraction of cerium from sulfuric acid using mixtures of di-(2-ethylhexyl) phosphoric (D2EHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEHEHP) and have determined the synergistic enhancement coefficients, the nature of the extracted complex, and the equilibrium constants. Zhao *et al*.[13] investigated the synergistic extraction of rare earths with mixtures of di-(2-ethylhexyl)-2-ethylhexylphosphonate (DEHEHP) and a β-diketone extractant, 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP).

Nitrogen bases such as 1,10-phenanthroline (phen), which have high proton affinity, are appropriate auxiliary ligands and separation scientists have used phen as an extractant to

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separate rare earths and the combination of phen with chelating extractants has been shown to have good synergistic effects. There have been many papers concerning the synergistic extraction of rare earths with phen and β-diketones.[16–27] For instance, Hasegawa *et al.*[17] studied the extraction of europium (III) with pivaloyltrifluoroacetone and phen into different diluents such as $CHCl_3$, $CHBr_3$.

Sec-octylphenoxyacetic acid (CA12), a carboxylic acid with the formula s-$C_8H_{17}C_6H_4OCH_2$-COOH, has several advantages including stable composition, low aqueous solubility, easy preparation and little emulsification during extraction. Several studies have been reported on the extraction of rare earths with a mixed system containing CA12.[6,9,11,12] In previous work, mixtures of CA12 with D2EHPA or bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex301) were employed for the extraction of rare earths.[6,11] However, the (CA12 + D2EHPA) and (CA12 + Cyanex301) systems only have synergistic effects on the light lanthanoids and in addition, the separation abilities of rare earths are not greatly improved. This led to the exploration of some new mixed systems including CA12 to enhance the extraction and separation abilities of rare earths.

In the present work, a novel synergistic extraction system using CA12 and phen has been developed for the extraction of rare earths from nitrate medium. The possibility of separating rare earths and its potential application are discussed. The synergistic effect, extraction mechanism and thermodynamic parameters of samarium(III) are investigated in detail.

EXPERIMENTAL

Reagents and apparatus

High-purity rare earth oxides (>99.95%) were obtained from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China). Stock solutions of rare earths were prepared by dissolving their oxides in concentrated nitric acid and diluting to the required volume with distilled water. The rare earths were analyzed by titration with a standard solution of EDTA with xylenol orange as indicator in hexamethylenetetraamine buffer solutions. All the initial metal concentrations were maintained at 1×10^{-3} mol L^{-1}. The pH of the aqueous phase was adjusted by the addition of HNO_3 or NaOH solutions. All extraction experiments were performed at constant ionic strength with $NaNO_3$ ($\mu = 0.6$ mol L^{-1}). All other reagents were of analytical reagent grade.

CA12 and phen were supplied by Shanghai Rare-Earth Chemical Co. Ltd and Tianjin Kermel Chemical Reagent Co. Ltd, respectively. Both of the extractants were used without further purification and dissolved in benzene to the required concentrations.

The concentrations of rare earths 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).

EXTRACTION PROCEDURES

Equal volumes (5 mL) of aqueous and organic solutions were mixed and shaken for 30 min at 298 ± 1 K unless otherwise stated. The solutions were allowed to settle and were separated by gravity. After phase separation, the concentrations of rare earths in the aqueous phase were determined by spectrophotometry at 654 nm with Arsenazo III as an indicator. The concentrations in the organic phases were determined by difference. Distribution ratios (*D*) were calculated from these concentrations.

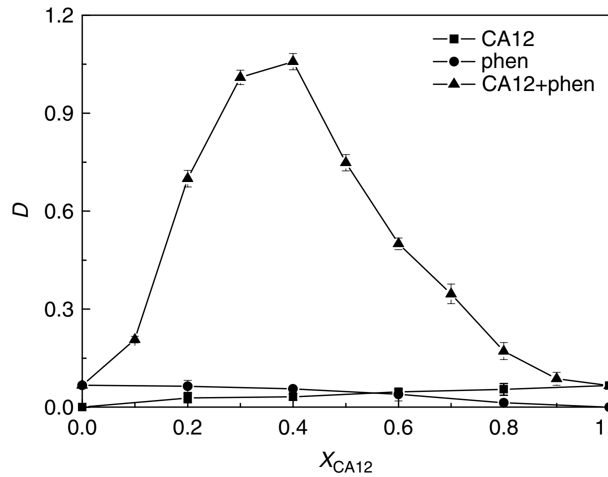

Figure 1. Extraction of Sm^{3+} with mixtures of CA12 and phenanthroline: $[Sm^{3+}] = 1 \times 10^{-3}$ mol L^{-1}, pH = 3.0, $\mu = 0.6$ mol L^{-1}, $[CA12]_{(o)} + [phen]_{(o)} = 0.01$ mol L^{-1}.

RESULTS AND DISCUSSION

Extraction and separation of rare earths with mixtures of CA12 and phen

According to Xu *et al.*[30] the synergistic enhancement coefficient *R* is expressed as:

$$R = D_{mix}/(D_{CA12} + D_{phen}) \quad (1)$$

where D_{mix}, D_{CA12}, and D_{phen} represent the distribution ratios with (CA12 + phen), CA12, and phen, respectively with synergistic extraction when $R > 1$ and antagonism when $R < 1$.

The extraction of several rare earths, La, Nd, Sm, Tb, Yb, and Y with CA12, phen, and their mixtures has been investigated. The mixtures exhibit synergism with all the rare earths studied, the order of increasing synergism being La < Y < Nd < Sm < Tb < Yb, with maximum enhancement coefficients, R_{max}, calculated as 5.5 (La); 13.7 (Nd); 15.9 (Sm); 24.5 (Tb); 45.4 (Yb) and 12.3 (Y), indicating synergism increases with increasing atomic number. As an illustration the distribution ratios of Sm^{3+} extracted with CA12, phen, and (CA12 + phen) are shown in Fig. 1, where X_{CA12} represents the mole fraction of CA12 in the organic phases.

Besides the extraction ability, the selectivity of rare earths is an important parameter in evaluation of an extraction system with the separation factor, β, often used to describe the separation between two substances:

$$\beta_{M/N} = D_M/D_N \quad (2)$$

where D_M and D_N represent the distribution ratios of M and N under the same extraction conditions.

Table 1 shows the β values between Y and lanthanoids in (CA12 + phen) mixtures. It is interesting to note that (CA12 + phen) mixtures are more effective in separating Y from heavy lanthanoids than from light lanthanoids. As has been reported, using CA12 it is difficult to separate Y from heavy lanthanoids,[9] and in the present work, the addition of phen to

Table 1. Separation factors of rare earths in CA12 + phen system

	La	Nd	Sm	Tb	Yb
Y	1.0	1.8	3.1	5.7	6.5
La		1.9	3.3	5.9	6.8
Nd			1.8	3.2	3.7
Sm				1.8	2.1
Tb					1.2

The extraction of rare earths with CA12 + phen was carried out separately.

enhance the selectivity between Y and the heavy lanthanoids is attractive. There have been some reports of the separation of rare earths with mixtures containing an acidic extractant and phenanthroline. Zhang *et al.*[22] explored the extraction of La, Pr, Nd, Sm, Gd, Dy and Y with mixtures of 1,5-bis(1′-phenyl-3′-methyl-5′-oxopyrozole-4′-yl)-pentanedione-[1,5] and phenanthroline. The observed synergistic enhancement coefficient of La was 5.2 and the separation factors between La/Y, Pr/Y, Nd/Y, Sm/Y, Gd/Y and Dy/Y was calculated as 4.1, 2.1, 1.7, 0.7, 0.3 and 0.3, respectively. As shown in Table 1 it is obvious that there is great potential for the separation of Y from heavy lanthanoids with mixtures of CA12 and phenanthroline.

Extraction equilibrium of Sm^{3+} with CA12 and (CA12 + phen) systems

The extraction of rare earths with CA12 (HB) in *n*-heptane from nitrate medium has been studied in previous work,[6] giving the following extraction reaction for La^{3+}:

$$La^{3+}{}_{(a)} + 2H_2A_{2\,(o)} \rightleftharpoons LaHA_{4\,(o)} + 3H^+{}_{(a)} \tag{3}$$

In the present study, benzene is employed as diluent instead of *n*-heptane. The relationships between the distribution ratio, D_A, and pH (Fig. 2) or the extractant concentration show that the extraction of Sm^{3+} with CA12 in benzene is as follows:

$$Sm^{3+}{}_{(a)} + 2H_2A_{2(o)} \rightleftharpoons SmHA_{4(o)} + 3H^+{}_{(a)} \tag{4}$$

The equilibrium constant can be calculated as $\log K_A = -5.8$

If the synergistic extraction equation with (CA12 + phen) is written as:[7,15]

$$Sm^{3+}{}_{(a)} + xH_2A_{2(o)} + yB_{(o)} \rightleftharpoons SmH_{2x-n}A_{2x}B_{y(o)} + iH^+{}_{(a)} \tag{5}$$

then the relationship between the equilibrium constant, K_{AB}, and the distribution ratio, D_{AB}, should be:

$$\log D_{AB} = x\log[H_2A_2]_{(o)} + y\log[B]_{(o)} + i\text{pH} + \log K_{AB} \tag{6}$$

In order to determine the equilibrium stoichiometry, a series of experiments have been carried out using the methods of slope analysis and constant molar ratio. First of all, the relationship between distribution ratios and pH is determined at fixed ionic strength and concentrations of Sm^{3+} and extractants. Results (Fig. 2) indicate that $\log D_{AB}$ versus pH gives a straight line with a slope of about 3.0. Second, the influence of the concentration of the extractant is investigated at fixed pH, ionic strength, and concentration of the other extractant. The plots of $\log D_{AB} - 3\text{pH}$

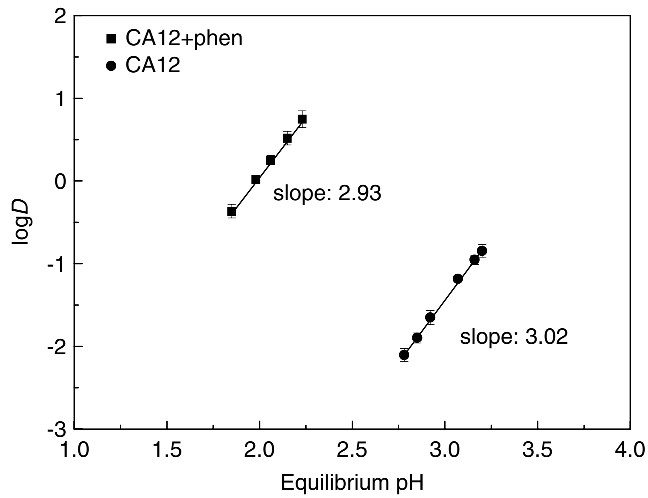

Figure 2. Effect of pH on the extraction of Sm^{3+} with CA12 and (CA12 + phen): $[Sm^{3+}] = 1 \times 10^{-3}$ mol L^{-1}, $\mu = 0.6$ mol L^{-1}, $[CA12]_{(o)} = 0.004$ mol L^{-1}, $[phen]_{(o)} = 0.006$ mol L^{-1}.

versus $\log[CA12]_{(o)}$ or $\log[phen]_{(o)}$ (Fig. 3), give straight lines with slopes of about 2.0 and 3.0 for CA12 and phen, respectively. Therefore, Equation (5) can be rewritten as:

$$Sm^{3+}{}_{(a)} + 2H_2A_{2(o)} + 3B_{(o)} \rightleftharpoons SmHA_4B_{3(o)} + 3H^+{}_{(a)} \tag{7}$$

The equilibrium constant of Sm^{3+} extracted with (CA12 + phen) can be calculated as $\log K_{AB} = 6.0$

The influence of temperature on the extraction of Sm^{3+} with CA12, phen and (CA12 + phen) is shown in Fig. 4. The plots of $\log D$ versus $(1000/T)$ indicate that the distribution ratio of Sm^{3+} increases with increasing experimental temperatures. Therefore, the change of enthalpy of the reaction, ΔH, can be determined according to the equation:

$$\frac{\Delta \log D}{\Delta 1/T} = -\frac{\Delta H}{2.303R} \tag{8}$$

The change of Gibbs free energy, ΔG, and the change of entropy, ΔS of the system at 293 K can thus be obtained as well.

$$\Delta G = -RT\,\ln K \quad \text{with } \Delta G = -33.7\ \text{kJ mol}^{-1} \tag{9}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{and therefore } \Delta S = (\Delta H - \Delta G)/T = 129.7\ \text{J mol}^{-1}\,\text{K}^{-1} \tag{10}$$

The positive sign of ΔH implies that the extraction of Sm^{3+} with (CA12 + phen) is endothermically driven. The positive sign of ΔS means that the mixed system is more disordered. Synergistic extraction may occur in accordance with the theory of increase of entropy from the view of statistics. The positive entropy change in the mixed system may also be explained by the release of water molecules from the inner coordination sphere of the metal ion.

CONCLUSIONS

A new mixed extractant system (CA12 + phen) for the extraction and separation of rare earths from nitrate medium is reported. The mixture has synergistic effects on all the rare earths investigated and the synergism increases with increasing atomic

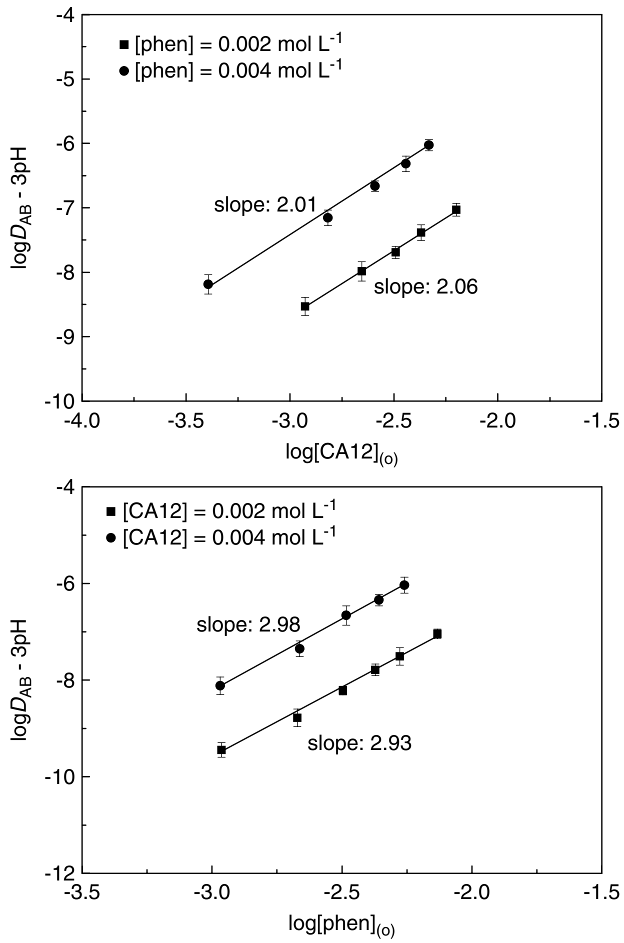

Figure 3. Relationship between distribution ratio D_{AB} and equilibrium concentration of CA12 and phen in (CA12 + phen) systems: $[Sm^{3+}] = 1 \times 10^{-3}$ mol L^{-1}, pH = 3.0, $\mu = 0.6$ mol L^{-1}.

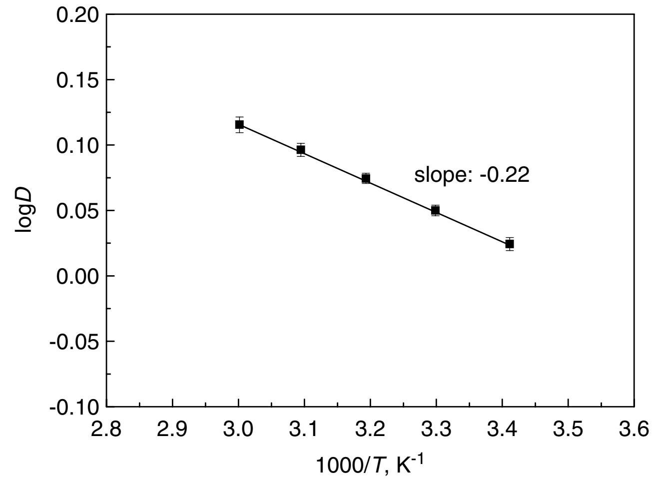

Figure 4. Relationship between distribution ratio D and temperature: $[Sm^{3+}] = 1 \times 10^{-3}$ mol L^{-1}, pH = 3.0, $\mu = 0.6$ mol L^{-1}, $[CA12]_{(o)} = 0.004$ mol L^{-1}, $[phen]_{(o)} = 0.006$ mol L^{-1}.

number of the rare earth. The separation of Y from heavy lanthanoids is also feasible with this system. The extraction stoichiometry of Sm^{3+} has been determined and indicates an extracted compound of $SmHA_4B_3$ stoichiometry. According to the thermodynamic functions the synergistic extraction reaction of Sm^{3+} is endothermic.

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