Improved Extraction-Separation of Lanthanum/ Europium Ions by Bis(2-ethylhexyl)phosphoric Acid Using 12-Crown-4 as an Ion Selective Masking Agent

Zamani, Abbas Ali; Yaftian, Mohammad Reza*[+]; Dallali, Naser

Department of Chemistry, Faculty of Science, Zanjan University, P. O. Box 45195-313 Zanjan, I.R. IRAN

ABSTRACT: *The extraction-separation of lanthanum and europium ions with bis(2-ethylhexyl) phosphoric acid (DEHPA) in cyclohexane was improved by adding 12-crown-4 (12C4) to the aqueous phase as a masking agent. In the presence of this crown ether the extraction curve of lanthanum ions versus pH shifts to the higher pH region, while the curve is not influenced for the europium ions. Consequently the separation of these ions is enhanced. The treatment of the extraction data in the presence of 12C4 allows to determine the stability constant of the lanthanum-crown ether complex in the aqueous phase. The results have been compared with those reported using 18-crown-6 (18C6). This comparison shows that the improvement in the separation of La/Eu in the presence of 12C4 is the same order as in the presence of 18C6. The influence of temperature on the extraction of the studied cations in the absence and the presence of 12C4 by DEHPA in cyclohexane is studied in the range 293-305 K. This study leads to assess the thermodynamic parameters i.e. the free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) changes associated with the extraction process as well as those of the complexation of lanthanum ions by 12C4 in aqueous phase.*

KEY WORDS: *Lanthanum, Europium, Extraction, Bis(2-ethylhexyl)phosphoric acid, 12-crown-4, Masking agent.*

INTRODUCTION

Because of similarities in chemical properties of lanthanides [1], their intra-group separation is among the most difficult processes and requires sophisticated techniques. Solvent extraction provides an appropriate way for achieving this goal [2]. Thus, there is much effort to design efficient and high selective extraction-separation systems. Masking agents have been frequently used for improving the separation of metal ions in solvent extraction process [3].

Acidic organophosphorus extractants such as bis(2-ethylhexyl)phosphoric acid (DEHPA) have been used for the extraction of lanthanides [4]. It is shown that the extraction of lanthanides by DEHPA [5], or their transport through a bulk liquid membrane [6] containing

* To whom correspondence should be addressed.
+ E-mail: yaftian@mail.znu.ac.ir
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this ligand increases with decreasing ionic radius of the metal ions. In contrast, the stability of lanthanide-crown ether complexes in homogenous phase increases with ionic radius [7,8]. Hasegawa et al. reported a similar tendency in the extraction of lanthanide picrates by crown ethers [9]. Therefore, a solvent extraction system combining the chelating effect of DEHPA and binding properties of crown ethers may provide an improved separation among lanthanide ions [10-13].

Following our previous studies concerning the separation of lanthanides [14], here we report the application of crown ether 12-crown-4 (12C4) for improving the separation of lanthanum and europium ions in their extraction by DEHPA in cyclohexane. The results are compared with those obtained using 18-crown-6 (18C6), reported previously [13]. Cyclohexane was employed as organic diluent to minimize the distribution of crown ethers to the organic phase. In the second part of this work the influence of the temperature on the extraction process and the complexation of lanthanum by 12C4 in the aqueous phase has been investigated and discussed.

EXPERIMENTAL

Bis(2-ethylhexyl)phosphoric acid and 12-crown-4 (Merck) were used as received without further purification. Cyclohexane (Fluka) was washed twice with distilled water to saturation with water and removal of the stabilizers. Stock 0.01 M solution of lanthanum and europium were prepared with dissolving a proper quantity of corresponding oxides (Fluka) in nitric acid (Merck) and then diluted with water. The stock solutions were standardized complexometrically. Extraction experiments were carried out with contacting two equal volumes (90 ml) of organic and aqueous phase in a double wall cell (110 mm height and 55 mm diameter) containing a micro-valve in the bottom. For controlling the temperature of the experiment vessel, thermostated water circulated through the jacket of the cell. An efficient mixing of the phases was achieved using a mechanical stirrer (Heidolph 2000). Adding lithium hydroxide (Fluka) provided variation of the pH. After equilibrium (20 min.) and engagement of the phases the concentration of the remained metal in the aqueous phase was measured spectrophotometrically (Shimadzo UV-160) using Arsenazo III (Fluka) as indicator [15].

RESULTS AND DISCUSSION

Bis(2-ethylhexyl)phosphoric acid is a well known and efficient acidic extractant for tri-valent rare-earth metal ions [5]. Since in non-polar diluents it is found as a dimer [16], the extraction of lanthanide (M) from water into cyclohexane by DEHPA is described by following equation [10]:

$$M^{3+}_{aq} + 3(HL)_{2,org} \rightleftharpoons ML_3(HL)_{3,org} + 3H^{+}_{aq} \qquad (1)$$

where, the subscribers "aq" and "org" denote the phase, aqueous or organic, in which the species are present.

Corresponding extraction equilibrium constant is defined as:

$$K_{ex} = \frac{[ML_3(HL)_3]_{org}[H^+]^3_{aq}}{[M^{3+}]_{aq}[(HL)_2]^3_{org}} \qquad (2)$$

The evaluated logarithm of K_{ex} for the extraction of lanthanum and europium ions is reported to be 0.7 and 2.5, respectively [13]. In addition the value of $pH_{0.5}$, i.e. pH of the extraction of 50 percent of metal ions into organic phase, is reported as 2.1 for lanthanum and 1.5 for europium ions [13].

Application of masking agents is one of the known methods for improving the selective separation of metal ions in the extraction processes [17]. Water-soluble crown ethers exhibit to be effective masking agents for enhancing separation factor in the extraction of rare-earth metal ions [10-13]. In order to verify a possible improvement of the separation of lanthanum and europium ions in the presence of 12C4, the extraction of these ions (initial concentration 1×10^{-4} M) from aqueous phase containing the crown ether (0.05 M) into cyclohexane solution of DEHPA (0.01 M) has been studied at 298 K (Fig. 1).

The results show that the extraction curve for lanthanum ions shifted towards higher pH values in the presence of 12C4 with respect to the curve in the absence of the crown ether. However, there was not any significant shift of the extraction curve of the europium ions. The $pH_{0.5}$ values in the absence and the presence of 12C4 and the corresponding $\Delta pH_{0.5}$ values are presented in Table 1. This table contains, also, the corresponding values for the extraction of the studied ions by DEHPA in the absence and the presence of 18C6 for comparison. In the presence of 12C4 and 18C6 the $pH_{0.5}$ values for the

Table 1 : $pH_{0.5}$ and $\Delta pH_{0.5}$ values of the extraction of lanthanum and europium ions in the absence and presence of 12C4 and 18C6[a] (0.05 M) by DEHPA dissolved in cyclohexane at 298 K.

M^{3+} (ionic radius)[b]	$pH_{0.5}$	12C4 (1.2 Å)[c]		18C6[a] (2.67-2.86 Å)[c]	
		$pH_{0.5}$	$\Delta pH_{0.5}$	$pH_{0.5}$	$\Delta pH_{0.5}$
La^{3+} (1.06 Å)	2.1	2.4	0.3	2.6	0.5
Eu^{3+} (0.95 Å)	1.5	1.5	-	1.7	0.2

a) Data are from reference [13]. b) From reference [1]. c) Cavity size of the crown ethers from reference [8].

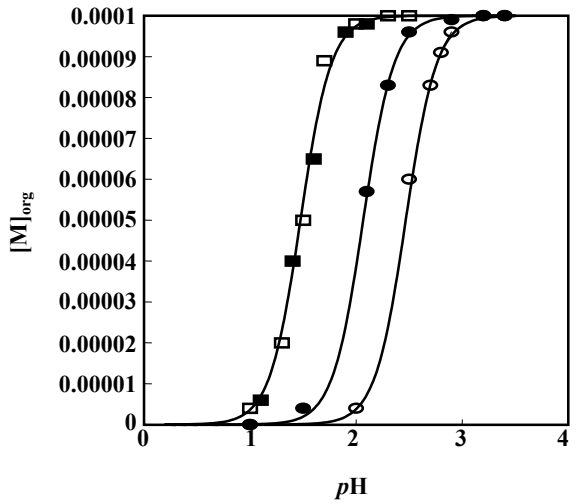

Fig. 1 : Extraction of lanthanum (●, ○) and europium (■, □) ions (initial concentration 1×10^{-4} M) in the absence (filled symbols) and presence (empty symbols) of 12C4 (0.05 M) in the aqueous phase by DEHPA (0.01 M) dissolved in cyclohexane at 298 K.

extraction of lanthanum ions are found to be 2.4 and 2.6 respectively.

Although a masking effect of 18C6 is also observed on the extraction of europium ions ($\Delta pH_{0.5}$ = 0.2), such effect is not demonstrated when 12C4 is used. This observation consists of the extraction order observed in the extraction of lanthanide picrates by crown ethers 15-crown-5, 18-crown-6 and dibenzo-18-crown-6 into chloroform [9] revealing that the extraction constants decreased through the lanthanide series. However, the examination of these results and a comparison of the ionic radius of the studied metal ions with the cavity size of the crown ethers revealed that these ions would not be trapped in the center of the cavity of the crown ethers.

For a quantitative investigation of the lanthanide-crown ethers interaction, the extraction of lanthanum and europium ions in the presence of 12C4 and 18C6 (0.05 M) has been studied. Equilibrium describing the metal ion complexation by crown ethers (CE) in the aqueous phase is considered:

$$M^{3+} + CE \rightleftharpoons M(CE)^{3+} \qquad (3)$$

for which the equilibrium stability constant is:

$$\beta = \frac{[M(CE)^{3+}]_{aq}}{[M^{3+}]_{aq}[CE]_{aq}} \qquad (4)$$

Since the crown ether's concentration is too high relative to the metal ion concentration, its equilibrium concentration equals to the initial concentration:

$[CE]_{aq} = [CE]_{0,\,aq}$

Considering the mass balance equation for the metal ions:

$[M^{3+}]_{aq} = [M^{3+}]_{0,\,aq} - [M]_{org} - [MCE^{3+}]_{aq}$

the variation of lanthanide concentration in the organic phase as a function of H^+ concentration (equation (2)) becomes:

$$[M]_{org} = \frac{K_{ex}[M^{3+}]_{0,\,aq}[(HL)_2]^3_{org}}{[H^+]^3_{aq}(1+\beta[CE]_{aq}) + K_{ex}[(HL)_2]^3_{org}} \qquad (5)$$

Using the evaluated K_{ex} values, the experimental values of the extracted metal ion in the presence of 12C4 and 18C6 as a function of pH can be fitted by applying an appropriate value for β (curves in Fig. 1). The logβ values for $[La\bullet 12C4]^{3+}$ complex was found to be 2.47.

In order to investigate quantitatively the separation ability of the extraction system in the presence of water-soluble crown ethers, the separation factors (SF) were evaluated. The separation factor between two metal ions is defined as:

$$Sf = \log\left(\frac{D_{M1}}{D_{M2}}\right) = \log\left(\frac{K_{ex,M1}}{K_{ex,M2}}\right)\left(\frac{1+\beta_{M2}[CE]_{aq}}{1+\beta_{M1}[CE]_{aq}}\right) \quad (6)$$

if $\beta >> 1$, Eq. (6) is used for calculating the separation factor:

$$SF = \log\left(\frac{K_{ex,M1}\beta_{M2}}{K_{ex,M2}\beta_{M1}}\right) \quad (7)$$

The evaluatez separation factors for Eu/La were 1.8 and 3 in the absence and presence of 12C4, respectively. The corresponding value in the presence of 18C6 was calculated to be 2.9 [13]. The results show a slightly better separation of the studied ions in the presence of 12C4.

Thermodynamic parameters associated with lanthanum binding in the aqueous phase by 12C4 has been measured by performing a series of extraction experiments of lanthanum and europium ions in the presence of the crown ethers by DEHPA in cyclohexane at different temperatures. Fig. 2 presents the extraction curve of the lanthanum ions in the presence of 12C4 by DEHPA in cyclohexane at the temperature range 293-308 K. The corresponding values of β have been evaluated as described before. The variation of lnβ as a function of T^{-1} for the extraction of lanthanum in the presence of 12C4 is shown in Fig. 3.

The thermodynamic values of the lanthanum extraction by DEHPA and those of its complexation in aqueous phase by 12C4 at 298 K determined by using Gibbs-Helmholtz equation [15], are given in Table 2. The corresponding values for lanthanum complexation by 18C6 in aqueous phase [13] are also shown in this table, for comparison. In contrast to the extraction of lanthanum, the complexation of these ions in the aqueous phase by 12C4 is exothermic and the process is controlled by enthalpy changes. However, the complexation of the metal ions with 18C6 is both enthalpy and entropy driven.

CONCLUSIONS

The separation of lanthanum/europium ions in their extraction by bis(2-ethylhexyl)phosphoric acid (DEHPA) is enhanced by using 12-crown-4 (12C6) in the aqueous phase. This improvement is due to the opposite size depending tendencies of DEHPA and 12C6 to bind lanthanide ions. Although a higher value of the stability

Table 2: Thermodynamic parameters associated with the extraction of lanthanum by DEHPA[a] and the complexation by 18C6[a] and 12C4 in the aqueous phase at 298 K.[b]

Process	Crown ether	ΔHº	TΔSº	ΔGº
Extraction	-	100.0	104.3	-4.3
Complexation	12C4	-47.9	-33.9	-14.0
	18C6	-13.2	3.9	-17.1

a) Data are given from ref. [13]. b) values in kJ/mol; calculation using least-squares method $\sigma N\text{-}1 \leq \pm 5$ %.

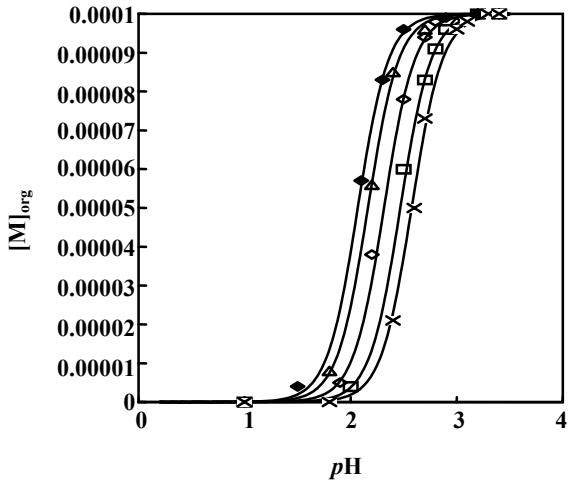

Fig. 2 : Variation of lanthanum ion concentration (initial concentration 1×10^{-4} M) in the organic phase as a function of pH by a solution of DEHPA (0.01 M) dissolved in cyclohexane in the absence (♦, 298 K) and presence of 12C4 in aqueous phase (0.05 M) at various temperatures (× 293 K; □ 298 K; ◊ 303 K; Δ 308 K).

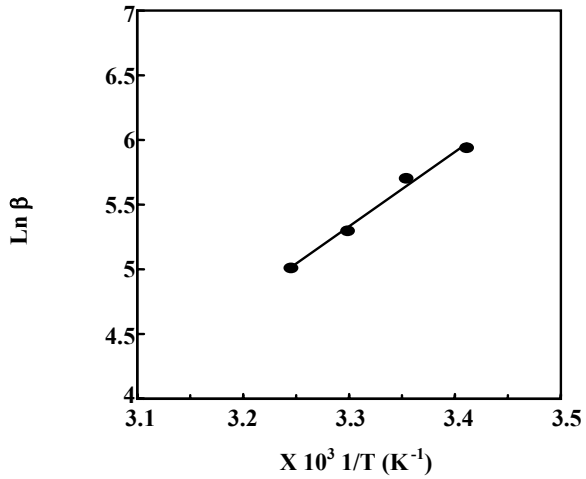

Fig. 3 : Variation in lnβ with 1/T (K^{-1}) in the presence of 12C4 (0.05 M) in the aqueous phase. Other experimental conditions are given in Fig. 2.

constant in water was reported for $[La\bullet 18C6]^{3+}$ complexes with respect to that of $[La\bullet 12C4]^{3+}$, a nearly similar separation improvement for Eu/La ions was observed for both systems. This result is attributed to the fact that 12C4, in contrast to 18C6, cannot interact with europium ions in the aqueous phase. The evaluated thermodynamic parameters reveal that the extraction of lanthanum ions by DEHPA is controlled by the entropy changes, while the complexation of La^{3+} with 12C4 is a enthalpy driven process.

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