Regular Article

Effect of Polyethylene Glycols Dissolved in Aqueous Phase on the Extraction-Separation of La(III), Eu(III) and Er(III) Ions with Bis(2-ethylhexyl)phosphoric Acid

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The present work concerns on the investigation of the role of polyethylene glycols (PEGs) as masking agent for amelioration of extraction-separation of La(III), Eu(III) and Er(III) ions by the acidic extractant bis(2-ethylhexyl)phosphoric acid (DEHPA). The studied solvent extraction system is based on the combination of chelating effect of DEHPA in the organic phase on the one hand, and the binding properties of the PEGs in the aqueous phase, on the other hand, to provide an improvement in separation of La(III), Eu(III) and Er(III) ions. The first part of this study deals with effect of diluent used as organic solvent on the separation efficiency of bis(2-ethylhexyl)phosphoric acid towards lanthanum, europium and erbium ions. Then, the influence of the presence of three polyethylene glycols, with molecular weights 200, 400 and 2000 (PEG_{200}, PEG_{400} and PEG_{2000}), in the aqueous phase on the separation of the studied metal ions was evaluated and discussed.

INTRODUCTION

The close ionic radii of trivalent rare-earth ions (0.848-1.061 Å) causes these ions exhibits very similar chemical properties [1] and, therefore, the intra-group separation of them to be difficult and requires sophisticated industrial processes [2]. In addition the elimination of rare-earth ions from high level liquid waste in nuclear waste management is crucial for a satisfactory transmutation of the minor actinides by neutron-irradiation process [3]. To surmount the difficulties encountered in intra-group separation of lanthanides and inter-group separation of actinides and actinides different process and techniques such as solvent extraction [3-5], ion exchange [6,7], aqueous biphasic system [8], solid phase extraction [9] and hollow fiber supported liquid membrane [10] have been studied and developed.

Solvent extraction is among the most popular methods used in fundamental as well as industrial studies for separation of a variety of chemical species [11]. Solvent extraction has been used both in the laboratory and on the industrial scale. This technique bears some advantages including; (a) it can be used for efficient, rapid and selective separations, (b) the partition coefficients are often approximately independent of concentration down to tracer levels, (c) in this method back extraction or stripping of the solute and recycling of the solvent and/or diluents are often feasible. it can usually be followed by back-extraction into aqueous solvents or, in some cases, the solution can be used directly in subsequent procedures, (c) it can be used for wide scope of applications, in fact the composition of the organic phase and the nature of extractants can be varied so that the number of practical combinations is almost unlimited, and (d) it can be performed with simple

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equipment, but can also be automated. Besides, the rapid extraction kinetics for many separations and their adaptability of the method to a wide variety of organic and inorganic solutes allow solvent extraction methods to be yet interesting from both pure and applied investigations.

It is well known that the type of extractant used in solvent extraction processes affects profoundly the efficiency and selectivity of the process. To improve these characteristics of solvent extraction methods, the investigations oriented towards preparation the new extractants [12] or application of mixed extractants (so called synergistic extractions) [13]. Alternatively, combination of complexation ability of a water soluble ligands and chelating effect of an extractant dissolved in an organic phase has been shown an achievement for improving the separation quality in solvent extraction methods [14].

Bis(2-ethylhexyl)phosphoric acid (DEHPA) has been used frequently for the extraction-separation of rare-earth ions [15,16]. These studies reveal that the good extraction efficiency of DEHPA towards rare-earths, is compensated with low selectivity of this extractant. It is demonstrated that combination of the non-selective but efficient extracting characteristics of DEHPA, by the size selective properties of water soluble crown ethers [14,17-19] or Schiff base ligands [20] allows acceding to efficient-selective extraction-separation processes for metal ions.

Polyethylene glycol (PEG) is a polymer of ethylene oxide produced by the interaction of this monomer with water. Depending on their molecular weight, polyethylene glycols are employed in various applications. They are used in wide range of medical, surfactants, cleaning agents and biological applications [21,22]. The potential of polyethylene glycols in solvent extraction process of alkaline earths [23] and lanthanides [24] is also demonstrated.

Similarities in chemical structure of polyethylene glycols with crown ethers have been considered in comparative complexation studies of these compounds [23-26]. Following to our studies concern on the application of water soluble crown ethers for improving extraction-separation of rare-earth ions [17,18], we report here the extraction-separation of lanthanum, europium and erbium ions in the absence and presence of three polyethylene glycols with molecular weight 200, 400 and 2000 (abbreviated as PEG_{200}, PEG_{400} and PEG_{2000}) in the aqueous solution by DEHPA dissolved in carbon tetrachloride, dichloromethane and ethyl acetate.

EXPERIMENTAL

Chemicals

Lanthanum oxide (purum, Fluka, Switzerland), europium oxide (puriss, Fluka, Switzerland), erbium oxide (puriss, Fluka, Switzerland), bis(2-ethylhexyl)phosphoric acid (for synthesis, Merck, Germany), polyethylene glycols with molecular weight 200, 400 and 2000 (for synthesis, Merck, Germany), carbon tetrachloride (extra pure, Merck, Germany), dichloromethane (laboratory reagent grade, Mojallali, Iran), ethyl acetate (extra pure, Merck, Germany), hydrochloric acid (extra pure, Mojallali, Iran), nitric acid (extra pure, Merck), sodium hydroxide (extra pure, Merck, Germany) and ArsenazoIII (metal indicator, Merck, Germany) were the chemical used in this study. Bis(2-ethylhexyl)phosphoric acid (DEHPA) was purified based on the method reported by Partridge and Jensen [27]. In order to remove solvent stabilizers and to ensure saturation with water, diluents were washed three times with distilled water before they were used in solvent extraction procedure. For preparing the stock solution of lanthanum, europium and erbium ions the weighed quantities of the corresponding oxides were dissolved in concentrated nitric acid and then diluted appropriately with distilled water. The stock solutions were standardized complexometrically [28].

Solvent Extraction Procedure

Were carried out by contacting two equal volumes (90 ml) of organic and aqueous Solvent extraction experiments phases in a double layer cell containing a micro-valve at the bottom. For controlling the temperature of the experiment vessel, thermostated water circulates through the jacket of the cell. An efficient mixing of the phases was achieved using a mechanical stirrer (Heidolph 2000). Adding sodium hydroxide or hydrochloric acid provided variation of the aqueous phase pH. After equilibration (30 min.) and disengagement of the phases, the equilibrium concentration of the metal in the aqueous phase was measured spectrophotometrically (DR-5000) using Arsenazo III as

the indicator [29].

RESULTS AND DISCUSSION

Effect of Diluent on the Extraction of La(III), Eu(III) and Er(III) Ions by DEHPA

In order to evaluate the effect of diluent on the extraction efficiency of DEHPA towards La(III), Eu(III) and Er(III) ions, the extraction of these ions by the extractant into carbon tetrachloride, dichloromethane and ethyl acetate as a function of the aqueous phase pH has been performed at 298 K. As instance, Fig. 1 shows the variation of extracted amount of erbium ions by DEHPA dissolved in the studied diluents.

Considering the existence of DEHPA as monomer and dimer in polar (dichloromethane and ethyl acetate) and non-polar (carbon tetrachloride) diluents, respectively [30], the equations describing the corresponding extraction equilibrium can be represented by Eqs. (1) and (2):

$$M_{aq}^{n+} + nHL_{org} \rightleftharpoons ML_{n,org} + nH_{aq}^{+} \qquad (1)$$

$$M_{aq}^{n+} + n(HL)_{2,org} \rightleftharpoons ML_{n}(HL)_{n,org} + nH_{aq}^{+} \qquad (2)$$

in which the subscribers "aq" and "org" indicate aqueous and organic phases, respectively. For these extraction equilibria, corresponding equilibrium constant is presented by Eqs. (3) and (4):

$$K_{ex} = \frac{[ML_{n}]_{org}[H^{+}]_{aq}^{n}}{[M^{n+}]_{aq}[HL]_{org}^{n}} \qquad (3)$$

$$K_{ex} = \frac{[ML_{n}(HL)_{n}]_{org}[H^{+}]_{aq}^{n}}{[M^{n+}]_{aq}[(HL)_{2}]_{org}^{n}} \qquad (4)$$

The equilibrium ligand concentration can be considered equal to its initial concentration, because the metal concentrations in the organic phase are much lower than that of the initial ligand concentration, it means,

$$[HL]_{0,org} \approx [HL]_{org}$$

$$[(HL)_{2}]_{0,org} \approx [(HL)_{2}]_{org}$$
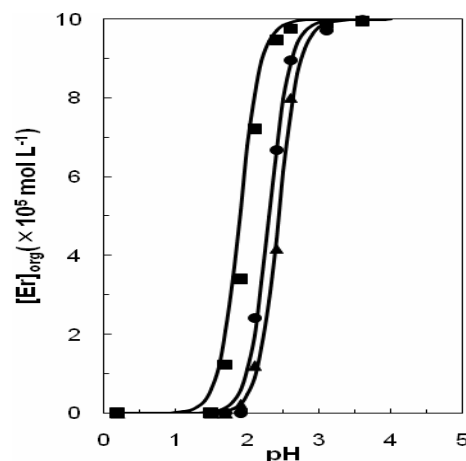
Using the mass balance equation for metal ions,

Fig. 1. Extraction of erbium ions (initial concentration 1×10^{-4} M) by DEHPA (initial concentration 0.01 M in carbon tetrachloride (■), dichloromethane (●) and ethylacetate (▲) at 298 K.

$$[M^{n+}]_{0,aq} = [M^{n+}]_{aq} + [M^{n+}]_{org}$$

(here

$$[M^{n+}]_{org} = [ML_{n}]_{org} \text{ or } [M^{n+}]_{org} = [ML_{n}(HL)_{n}]_{org})$$

and combining with Eqs. (3) and (4), the variation of metal ions in the organic phase as a function of pH (hydrogen ion concentration) in the aqueous phase can be calculated by Eqs. (5) and (6):

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

$$[M]_{org} = \frac{K_{ex}[M^{n+}]_{0,aq}[(HL)_{2}]_{org}^{n}}{[H^{+}]_{aq}^{n} + K_{ex}[(HL)_{2}]_{0,org}^{n}} \qquad (6)$$

Assuming n = 3, the analysis of experimental results (shown in Fig. 1 for erbium, as example) is carried out by means of a graphical representation (Excel). Whereby, the theoretical curves are normalized to the experimental results using an appropriate value of K_{ex} for Eqs. (5) and (6) (curves in Fig. 1). The evaluated K_{ex} with corresponding $pH_{0.5}$ values (pH of the extraction of 50 percent of metal ions into organic phase) are regrouped in Table 1. The

Table 1. Extraction Equilibrium Constants and Corresponding $pH_{0.5}$ Values for the Extraction of La(III), Eu(III) and Er(III) Ions by DEHPA in Different Diluents[a]

M(III)	Carbon tetrachloride			Dichloromethane			Ethyl acetate		
	$logK_{ex}$	$pH_{0.5}$	$\Delta pH_{0.5}$[b]	$logK_{ex}$	$pH_{0.5}$	$\Delta pH_{0.5}$[b]	$logK_{ex}$	$pH_{0.5}$	$\Delta pH_{0.5}$[b]
La(III)	-2.40	3.10	-	-1.40	2.50	-	-1.46	2.50	-
Eu(III)	0.20	2.24	0.86	-0.40	2.12	0.38	-1.00	2.36	0.14
Er(III)	1.23	1.90	1.20	-0.60	2.20	0.30	-1.00	2.35	0.15

[a]Experimental conditions: initial metal concentration, 1×10^{-4} M; initial ligand concentration, 0.01 M; temperature, 298 K. [b]$\Delta pH_{0.5} = pH_{0.5(La)} - pH_{0.5(M)}$, M = Eu(III) and Er(III) ions.

results bear the dependency of the extraction process of the studied ions by DEHPA on the diluents used. Although the extraction of lanthanum ions, with respect to europium and erbium ions, was taken place at higher pH region into the all examined diluents, the order of extraction efficiency of europium and erbium ions varies by the diluents. In fact, europium ions were extracted into dichloromethane more selective than erbium ions, whereas the selectivity presented by DEHPA dissolved in carbon tetrachloride was more significant towards erbium ions. The extracting behavior of DEHPA dissolved in ethyl acetate towards europium and erbium ions was very similar. Based on the evaluated K_{ex}, the order of extraction selectivity in the studied diluents varies as; Er(III) > Eu(III) > La(III) in carbon tetrachloride, Eu(III) > Er(III) > La(III) in dichloromethane and Er(III) ≈ Eu(III) > La(III) in ethyl acetate. The difference between $pH_{0.5}$ of lanthanum ions, as a reference, and those of europium and erbium ions is a quantitative sign for separation quality. Considering these values (Table 1), it is seen that the best separation of lanthanum ions from both erbium and europium ions can be achieved by using carbon tetrachloride as diluent.

In order to examine the suggestion n = 3 in Eqs. (5) and (6), the conventional log-log analysis has been used. By introducing the distribution ratio,

$$D = \frac{[M]_{org}}{[M]_{aq}}$$

the logarithmic expression of Eqs. (3) and (4) is:

$$logD = logK_{ex} + n \log[HL]_{0,org}^2 + n\,pH \tag{7}$$

$$logD = logK_{ex} + n \log[(HL)_2]_{0,org}^2 + n\,pH \tag{8}$$

A plot of logD *vs*. pH at constant ligand concentration lets evaluating the values of n. The results of the extraction of La(III), Eu(III) and Er(III) ions with DEHPA in the studied diluents (Fig. 2) confirm the considered stoichiometry *i.e.* n = 3.

Application of Polyethylene Glycols as Masking Agent

One of the methods used for improving the selectivity of a solvent extraction procedure is the application of masking agents [31]. In order to verify the possible enhancement of La(III), Eu(III) and Er(III) ions separation, the extraction of these ions from aqueous phase containing PEG_{200}, PEG_{400} (0.5 M) and PEG_{2000} (0.005 M) into carbon tetrachloride, dichloromethane and ethyl acetate solution of DEHPA was performed, at 298 K. A lower concentration of PEG_{2000} was selected because its solubility in water is limited with respect to the other studied PEGs. Figure 3 shows, as example, the results of extraction of La(III), Eu(III) and Er(III) ions in the presence of the studied polyethylene glycols by DEHPA dissolved in carbon tetrachloride. A shift of the extraction curves towards higher pH values demonstrates an interaction between the polyethylene glycol and the metal ions.

In order to quantify the metal ion/PEGs interactions, the analysis of the extraction data in the presence of PEGs has been considered. This was performed by considering the formation of $M \bullet PEG^{3+}$ complexes (M = La(III), Eu(III) and Er(III) ions) and evaluating the corresponding apparent
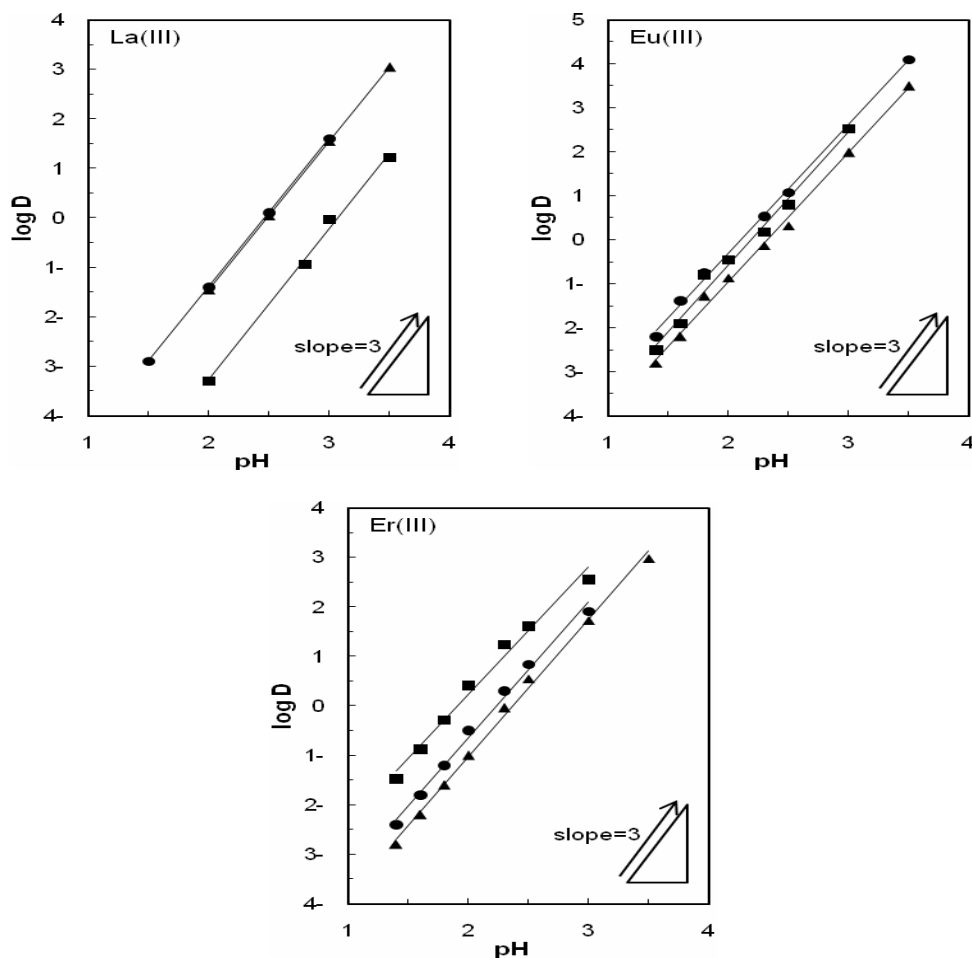
Fig. 2. Plot of logD *vs.* pH in solvent extraction of ions (initial concentration 1×10^{-4} M) by DEHPA in carbon tetrachloride (■), dichloromethane (●) and ethylacetate (▲) at different pH of the aqueous phase at 298 K.

binding ability in water using the extraction data. Equilibrium describing the metal ion complexation by PEG in the aqueous phase is considered as,

$$M^{3+} + PEG \rightleftharpoons M \bullet PEG^{3+} \qquad (9)$$

for which the apparent equilibrium stability constant is:

$$\beta = \frac{[M \bullet PEG^{3+}]_{aq}}{[M^{3+}]_{aq}[PEG]_{aq}} \qquad (10)$$

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

$$[PEG]_{aq} \approx [PEG]_{0,aq}$$

Considering the mass balance equation for the metal ions,

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

The variation of metal concentration in the organic phase *vs.* pH (Eqs. (5) and (6)) becomes,

$$[M]_{org} = \frac{K_{ex}[M^{3+}]_{0,aq}[(HL)_2]_{org}^3}{[H^+]_{aq}^3 (1 + \beta[PEG]_{aq}) + K_{ex}[(HL)_2]_{org}^3} \qquad (11)$$
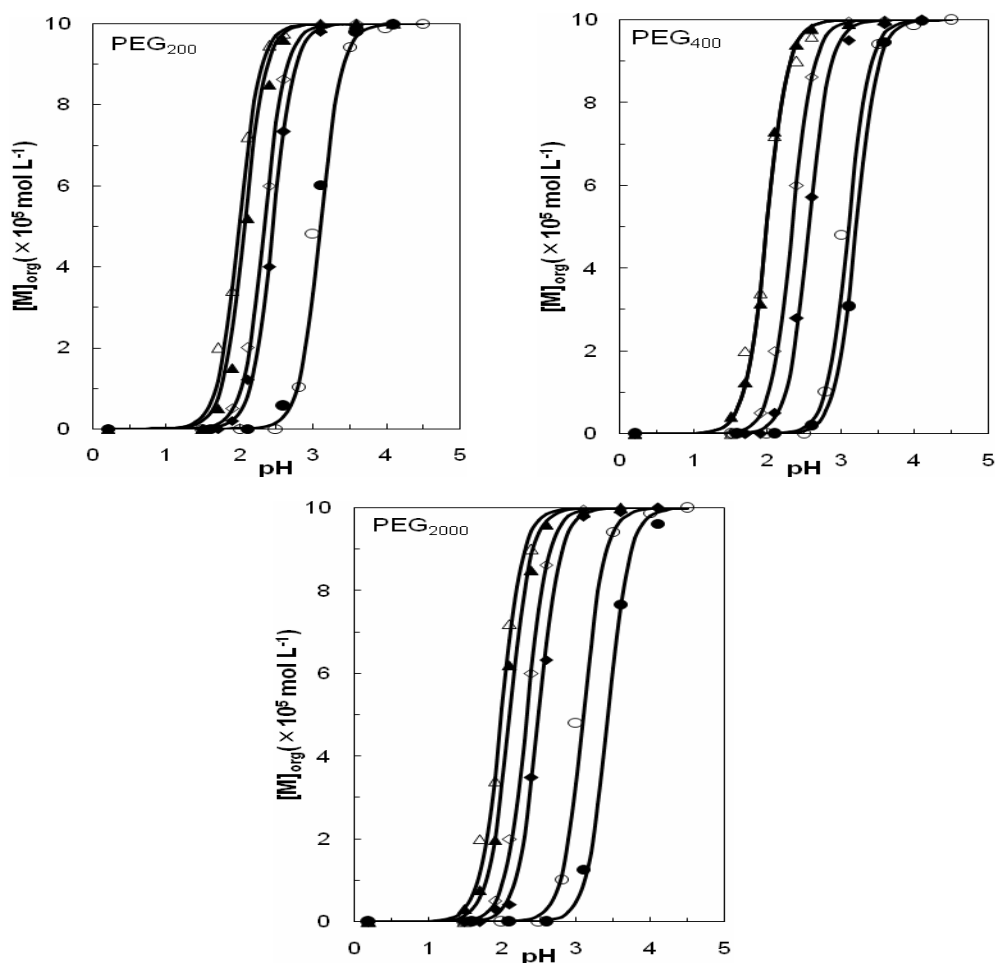
Fig. 3. Extraction of lanthanum ($\bigcirc$, $\bullet$) , europium ($\diamond$, $\blacklozenge$) and erbium ($\triangle$, $\blacktriangle$) ions (initial concentration 1×10^{-4} M) in the absence (empty symbols) and presence (filled symbols) of PEGs (PEG$_{200}$ and PEG$_{400}$ 0.5 M and PEG$_{2000}$ 0.005 M) by DEHPA (0.01 M) dissolved in carbon tetrachloride at 298 K.

Table 2. Logarithm of the Apparent Binding Constant (β) of the Studied PEGs Towards Lanthanum, Europium and Erbium Ions in Water at 298 K[a]

M(III)	PEG$_{200}$	PEG$_{400}$	PEG$_{2000}$
La(III)	-	-1.00	1.00
Eu(III)	0.39	3.07	4.90
Er(III)	-0.30	-1.30	2.36

[a]Standard deviation ≤ ±0.06.

Table 3. $pH_{0.5}$ and $\Delta pH_{0.5}$ Values of the Extraction of La(III), Eu(III) and Er(III) Ions in the Absence and Presence of the Studied PEGs[a]

Organic solvent	M(III)	$pH_{0.5}$[b]	$\Delta pH_{0.5}$[b,c]	PEG_{200}		PEG_{400}		PEG_{2000}	
				$pH_{0.5}$	$\Delta pH_{0.5}$[c]	$pH_{0.5}$	$\Delta pH_{0.5}$[c]	$pH_{0.5}$	$\Delta pH_{0.5}$[c]
CCl₄	La(III)	3.10	-	3.10	-	3.20	-	3.34	-
	Eu(III)	2.24	0.86	2.36	0.74	2.50	0.70	2.50	0.84
	Er(III)	1.90	1.20	2.10	1.00	2.00	1.20	2.10	1.24
CH₂Cl₂	La(III)	2.49	-	2.84	-	2.84	-	2.90	-
	Eu(III)	2.12	0.38	2.23	0.61	2.18	0.66	2.21	0.69
	Er(III)	2.20	0.30	2.50	0.34	2.40	0.44	2.66	0.24
C₄H₈O₂	La(III)	2.50	-	2.80	-	2.80	-	2.66	-
	Eu(III)	2.36	0.14	2.38	0.42	2.36	0.44	2.36	0.30
	Er(III)	2.35	0.15	2.40	0.40	2.46	0.34	2.35	0.31

[a]Experimental conditions: initial concentration of ions, 1×10^{-4} M; Concentration of PEGs, PEG_{200} 0.5 M, PEG_{400} 0.5 M, PEG_{2000} 0.005 M; Concentration of DEHPA 0.01 M; Temperature 298 K. [b]in the absence of PEGs. [c]$\Delta pH_{0.5}$ = $pH_{0.5(La)}$ -$pH_{0.5(M)}$, M = Eu(III) and Er(III) ions.

Using the evaluated K_{ex} values (Table 1), the experimental values of the extracted metal ions in the presence of PEG_{200}, PEG_{400} and PEG_{2000} as a function of pH can be fitted by applying an appropriate value for β (curves in Fig. 2). This analysis allows evaluating the apparent binding ability (β) of the complexes of La(III), Eu(III) and Er(III) by the investigated polyethylene glycols (Table 2). Based on these values the binding ability of PEGs towards examined metal ions in water varies as Eu(III) > Er(III) >> La(III) for PEG_{200}, Eu(III) > La(III) > Er(III) for PEG_{400} and Eu(III) > Er(III) > La(III) for PEG_{2000}. The higher binding properties of PEG_{2000} may be attributed to the larger size on this polyethylene glycol and a better wrap around of this polyethylene molecule, resulting higher number of oxygen atoms/metal ion interactions.

The metal ions/PEGs interaction results a shift of the extraction curves of metal ions *vs*. higher pH values (Table 3). The proximity of the shifts in $pH_{0.5}$ values in the absence and presence of PEG_{200} and PEG_{400} (0.5 M) with those in the presence of PEG_{2000} (0.005 M), reveals the higher binding ability of the latter polyethylene glycol for binding the studied metal ions, as it is reflected in logβ values shown in Table 2. The values presented in this table shows that PEG_{200} has no effect on the extraction of lanthanum in carbon tetrachloride.

A quantitative demonstration of the studied metal ions separation can be given by defining the $\Delta pH_{0.5}$ values which are defined as $pH_{0.5(La)}$ - $pH_{0.5(M)}$ (M = Eu(III) and Er(III) ions), in the absence and presence of the examined PEGs (Table 3). Comparison of these values reveals that although the effect of the presence of the PEGs for the extraction of the studied metal ions into carbon tetrachloride is more pronounced than that into dichloromethane and ethyl acetate, the selectivity remains practically the same as in the absence of the studied PEGs for the extraction of La(III), Eu(III) and Er(III) ions by DEHPA into carbon

tetrachloride. This comparison allows also considering an improvement in separation of the studied ions in the presence of PEGs by DEHPA dissolved in dichloromethane and ethyl acetate. It is noteworthy that this enhancement is taken place not only for the separation of lanthanum ions from europium and erbium ions, but also results an augmentation separation of these two latter ions. The solvent effect can be attributed to the distribution of the studied PEG's between aqueous and organic phase, and thus a change in the PEG concentration in the aqueous phase.

CONCLUSIONS

The present study shows that the diluent dependency of the selectivity presented by bis(2-ethylhexyl)phosphoric acid (DEHPA) towards rare-earth ions. Based on the determined extraction equilibrium constants (K_{ex}) the order of extraction selectivity varies as; Er(III) > Eu(III) > La(III) in carbon tetrachloride, Eu(III) > Er(III) > La(III) in dichloromethane and Er(III) ≈ Eu(III) > La(III) in ethyl acetate. The presence of polyethylene glycols with molecular weights 200, 400 and 2000 (PEG_{200}, PEG_{400} and PEG_{2000}, respectively) in the aqueous phase results generally a shift towards higher pH values of the extraction curve of La(III), Eu(III) and Er(III) *vs*. pH. This displacement affords an improvement in separation of lanthanide ions from europium and erbium ions by DEHPA dissolved in dichloromethane and ethyl acetate.

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