

Combination of size selective binding ability of 18-crown-6 dissolved in aqueous phase and extractive properties of an amic acid; toward enhancement of rare earths separation

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Abstract The separation of La(III), Eu(III) and Er(III) ions by an amic acid, *N,N*-dioctyldiglycolamic acid (HL), dissolved in carbon tetrachloride has been improved in the presence of 18-crown-6 (18C6) in aqueous phase as a selective masking agent. The interaction between the studied metal ions and 18C6 resulted a shift in the extraction curve of the studied metal ions versus pH toward higher pH region. The displacement of the extraction curves was more pronounced for lanthanum ions and was varied as La(III) > Eu(III) > Er(III). This order of complexing ability of 18C6 toward the studied ions was attributed to the size adaptation of the ions and that of the crown ether cavity. The stability constants of the lanthanide–crown ether complexes in aqueous phase were evaluated. The influence of temperature on the extraction of studied metal ions from aqueous phase in the absence and the presence of 18C6 was tested in the range 298–308 K. This investigation allowed evaluating the thermodynamic parameters associated with the extraction process and those of the complexation of cations by 18C6 in the aqueous phase.

Keywords Lanthanides · Separation · Solvent extraction · Amic acid extractant · Crown ether · Masking effect

Introduction

The rare earths are known as important elements due to their vast applications in a variety of industries such as production of rechargeable nickel–metal hydride (NiMH) batteries, lamp phosphors, permanent magnets and catalysis [1, 2]. The worldwide demand for high purity rare earths is increasing [3–5], and thus, it is requested for more efficient separation strategies in order to produce these metals with the industrial desired purity. Due to the similar chemical properties of the rare earth ions [6], their intergroup separation requires sophisticated techniques. To this end, a number of approaches have been investigated and developed. Among these, approaches are solid phase extraction [7], ion exchange [8] and liquid chromatography [9]. In spite of the progress in these techniques, liquid–liquid extraction is the most general applied method for intergroup separation of rare earths [10, 11].

A survey on the reported studies confirms that in much of the works concerning on the liquid–liquid extraction of rare earths, organophosphorus compounds such as di(2-ethylhexyl)phosphoric acid, bis(2,4,4-trimethylpentyl)phosphinic acid, 2-ethylhexylphosphonic acidmono-2-ethylhexyl ester, bis(2,4,4-trimethylpentyl)monothiophosphinic acid, bis(2,4,4-trimethylpentyl)dithiophosphinic acid, alkylated phosphine oxides and their mixtures [12–20], have been extensively applied as extractant. Although these compounds are known as efficient extractants for rare earth ions, they suffer from incombustibility and they leave phosphorus residues, which are known as environmental menace. Besides, they present relatively low selective attitude

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in intergroup separation of rare earths [21]. These deficiencies conduct the interests toward development and application of different types of extractants [22–28]. The organic extractants composed of only C, H, O and N atoms (the CHON-principle) have attracted much attention as green extractants to establish a new residual waste-free extraction process based on their complete combustibility. However, almost all CHON-type extractants provide low extraction and separation performances for rare earths in comparison with organophosphorus extractants [29, 30]. Carbamoyl-carboxylic acids, called also amic acids, are among the phosphorus-free extractants [23], in which binding potential of amide groups cooperates with the pH-dependent selectivity of carboxylic acid functionalities [30, 31].

Among the strategies investigated for enhancing the extraction performance in solvent extraction of rare earths is the application of mixture of two extractants. This strategy is called synergistic extraction [32–34]. Application of masking agents in aqueous phase with a particular selectivity to some analytes is another contrivance for improving the separation factor in solvent extraction process [35–42].

Our recent investigation on the extractive properties of *N,N*-dioctyldiglycolamic acid (HL) toward La(III), Eu(III) and Er(III) ions, from chloride aqueous solutions, confirmed its potential toward these ions [28]. Lanthanum, europium and erbium ions have been selected as representative ions for light, middle and heavy rare earths. The selectivity presented by HL dissolved in dichloromethane, carbon tetrachloride and ethyl acetate toward the investigated rare earths varies as Er(III) > Eu(III) > La(III). Analysis of the extraction data confirmed that the studied ions were extracted by formation of LaL_3 , EuL_3 and ErL_2Cl complexes. In addition, the ability of the crown ether 18C6 to complex these ions has been also reported [38, 43]. This ability allowed us to use crown ethers for amelioration of the separation of lanthanides/actinides [37, 38]. Following to this investigation, the present report concerns on the application of water-soluble crown ether 18-crown-6 (18C6), as a size selective masking agent in the aqueous phase, in conjunction with the solvent extraction of La(III), Eu(III) and Er(III) ions by HL dissolved in carbon tetrachloride, in order to improve the intergroup separation of rare earths.

Experimental

Materials

The synthesis and characterization of *N,N*-dioctyldiglycolamic acid (HL) were performed based on the previously reported procedure [28]. The stock solutions of La(III),

Eu(III) and Er(III) ions were prepared by dissolving an appropriate amount of their oxides (Fluka) in concentrated nitric acid (Merck). These solutions were standardized by complex formation titrations with disodium salt of ethylenediaminetetra acetic acid (Merck) solutions, in the presence of xylenol orange (Fluka) as indicator [44]. Working solutions were prepared by dilution of the stock solution with deionized water (resistance $\geq 18.2 \text{ M}\Omega$). Crown ether 18C6, sodium hydroxide, hydrochloric acid, Arsenazo III (Merck), lithium hydroxide, lithium chloride and formic acid (Fluka) were used as received. Carbon tetrachloride (Merck) was washed three times with deionized water, in order to remove the solvent stabilizers and saturated it with water.

Apparatus

A DR-5000 UV–Vis spectrophotometer was used for spectrophotometric determination of the studied rare earths, using Arsenazo III as indicator [41]. The pH adjustments were done by a Metrohm digital pH meter (model 780) using a combined glass electrode. Efficient mixing of the phases was achieved by using a Heidolph (MR 3001) magnetic stirrer. Temperature of the extraction vessels was controlled ($\pm 0.1 \text{ }^\circ\text{C}$) by a thermostated water circulator (Julabo MP5). A Labofuge 300 Heraeus centrifuge was used for aqueous/organic phases separations.

Extraction procedure

Extraction experiments were performed by contacting two equal volumes (5 mL) of organic (0.01 mol L^{-1} HL in CCl_4) and aqueous phases ($1 \times 10^{-4} \text{ mol L}^{-1}$ of the rare earth ions) in glass vials. The ionic strength of aqueous phase was adjusted at 0.1 mol L^{-1} , by using LiCl. Lithium chloride was used, because the interaction of lithium ions with 18C6 is negligible. The pH of the aqueous phases was varied by addition lithium hydroxide or hydrochloric acid solutions (0.1 mol L^{-1}). Carbon tetrachloride was used because distribution ratio of 18C6 between this diluent and water is low; therefore, it can be considered that the crown ether remains quantitatively in the aqueous phase. The temperature of the vials was controlled by placing the vessels in a double layer containing water adjusted at given temperature by circulating thermostated water through its jacket. Except for the thermodynamic study of the extraction process, all the experiments have been performed at 298 K. After equilibration (30 min) and disengagement of the phases, the equilibrium concentration of the metal in the aqueous phase was measured spectrophotometrically by Arsenazo III [37, 38, 41].

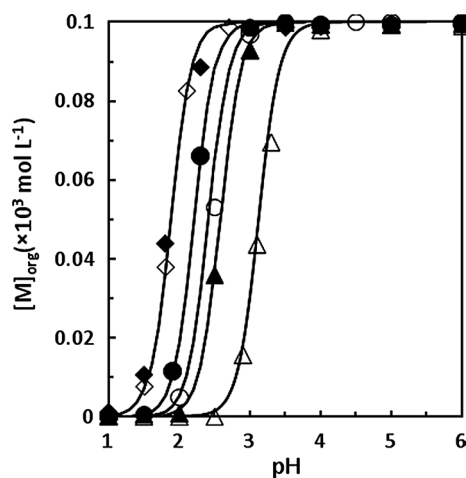


Fig. 1 Extraction of lanthanum (filled triangle, open triangle), europium (filled circle, open circle) and erbium (filled diamond, open diamond) ions (initial concentration 1×10^{-4} mol L $^{-1}$) in the absence (filled symbols) and presence (empty symbols) of 18C6 (0.05 mol L $^{-1}$) and 0.1 mol L $^{-1}$ lithium chloride, by HL (0.01 mol L $^{-1}$) dissolved in carbon tetrachloride at 298 K

Results and discussion

Influence of dissolved 18C6 in the aqueous phase

Individual extraction experiments of La(III), Eu(III) and Er(III) ions from aqueous phase containing 0.1 mol L $^{-1}$ lithium chloride and 0.05 mol L $^{-1}$ the crown ether 18C6 by HL in carbon tetrachloride (0.01 mol L $^{-1}$) as a function of aqueous phase were performed, at 298 °C. The results, together with those found in the absence of the crown ether, are shown in Fig. 1.

The extraction curves of lanthanum and europium ions shifted toward higher pH values, revealing a complex formation in the aqueous phase, between these ions and the crown ether, are taken place. These observations can be described by the formation of water-soluble complexes of the metal ions by 18C6, which results a displacement of the extraction curves versus aqueous phase pH toward higher pH values. In fact, the crown ether forms sufficiently strong complexes with the metal and thus limits its reaction with the extractant at the organic/aqueous phase interface. These outcomes allowed considering the crown ether 18C6 as a masking agent. The results clearly showed that the order of the interaction between the studied ions and 18C6 varies as La(III) > Eu(III) > Er(III). This order is in agreement with a better complexation of La(III) ions in comparison with the other tested ions by 18C6. In fact, this can be attributed to the ionic size of lanthanum ions (1.032 Å [45]) which is more close to the cavity radius of 18C6 (1.34–1.43 Å [43]). It is noteworthy that the ionic radius of trivalent europium and erbium ions has been reported to be as 0.947 and 0.89 Å [45].

Table 1 $pH_{0.5}$ and $\Delta pH_{0.5}$ values of the extraction of La(III), Eu(III) and Er(III) ions derived from data presented in Fig. 1

Ion	$pH_{0.5}$		$\Delta pH_{0.5}$
	Without 18C6	With 18C6	
La(III)	2.55	3.10	0.55
Eu(III)	2.20	2.40	0.20
Er(III)	1.81	1.81	–

Quantification of the effect of 18C6

A quantitative description of the effect of 18C6 on the extraction process of the studied ions can be presented by comparing the displacement of $pH_{0.5}$ values. It is worth of note that a pH value at which 50 percent of an analyte is extracted into the organic phase is called $pH_{0.5}$. Table 1 contains the $\Delta pH_{0.5}$, i.e., the difference of the $pH_{0.5}$ values of the extraction curves of the studied rare earths in the absence and presence of the crown ether. A positive $\Delta pH_{0.5}$ value for lanthanum and europium ions revealed a complex formation in the aqueous phase between these ions and the crown ether. The $pH_{0.5}$ value for the extraction of La(III) in the absence of 18C6 was 0.35 and 0.71 higher than that of Eu(III) and Er(III), respectively. These differences were increased to 0.7 and 1.29, by intervention of crown ether 18C6 in the extraction process, which means an enhanced separation can be achieved. This enhancement of separation is also seen for Eu(III)/Er(III) separation. In fact, the difference between $pH_{0.5}$ values of europium and erbium ions increases from 0.39 in the absence of 18C6 to 0.59 in the presence of this crown ether.

Effect of organic diluent

It was emphasized that carbon tetrachloride was used because the solubility of the applied crown ether (18C6) in this solvent is negligible. The effect of the organic diluent was studied by using a polar diluent dichloromethane in the same conditions shown in Fig. 1. The results are shown in Fig. 2. For comparison, the results of the extraction of the studied ions by HL dissolved in carbon tetrachloride are also given in Fig. 2. As the dissolved 18C6 did not affect the extraction of Er(III) by HL into both organic diluents, the corresponding results are not presented. The corresponding $pH_{0.5}$ and $\Delta pH_{0.5}$ of the extraction of the ions by HL dissolved in dichloromethane are shown in Table 2.

A comparison of the $pH_{0.5}$ values given in Tables 1 and 2 shows a more efficacious extraction of the studied ions by using carbon tetrachloride with respect to dichloromethane. The higher extraction efficiency of both ions by HL dissolved in carbon tetrachloride in comparison with that found by using dichloromethane, in the presence or absence

Fig. 2 Variation of the extraction of (a) La(III) and (b) Eu(III) ions (initial concentration 1×10^{-4} M) from aqueous solutions ($\text{LiCl } 0.1 \text{ mol L}^{-1}$) without (field markers) and with (open markers) the presence of 18C6 by HL (0.01 mol L^{-1}) dissolved in carbon tetrachloride (triangle markers) and in dichloromethane (round markers), at 298 K

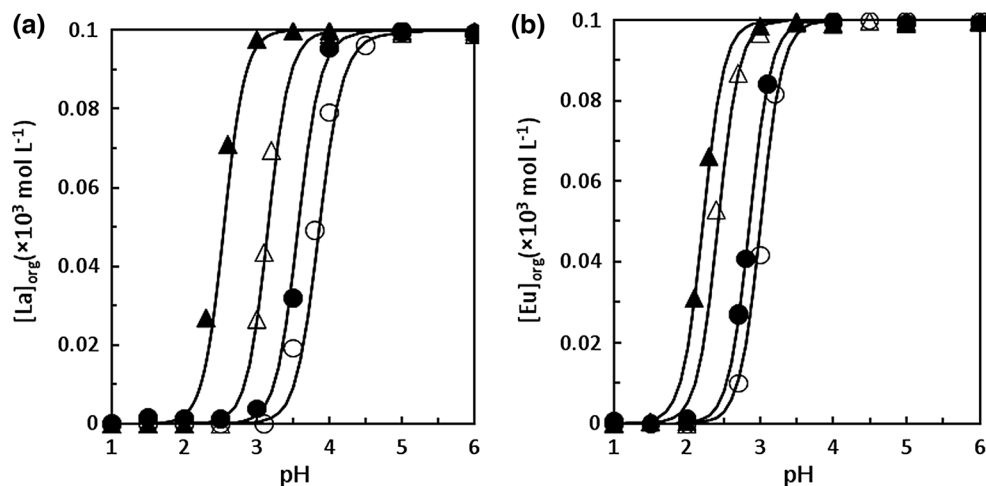


Table 2 Values of $\text{pH}_{0.5}$ and $\Delta\text{pH}_{0.5}$ of the extraction of La(III) and Eu(III) ions by HL dissolved in dichloromethane

Ion	$\text{pH}_{0.5}$		$\Delta\text{pH}_{0.5}$
	Without 18C6	With 18C6	
La(III)	3.45	3.80	0.35
Eu(III)	2.80	2.90	0.10
Er(III)	1.95	1.95	–

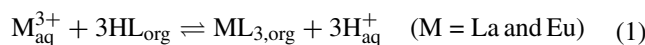
Experimental conditions: see Fig. 2

of 18C6, can be attributed to the difference in the polarity of the examined diluents [46]. The polarity of a diluent can affect the efficiency of an extraction process that depends on its mechanism [46]. The observed data confirm the extraction efficiency can be improved with decrease in the organic diluent polarity.

Lower displacement of the extraction curve of La(III) and Eu(III) ions toward higher pH region in the presence of 18C6 by HL dissolve in dichloromethane can be explained by considering the higher solubility of the crown ether in this polar solvent. Despite this, the difference in $\text{pH}_{0.5}$ values of the La(III)/Eu(III) and Eu(III)/Er(III) pairs (which is 0.65 and 0.85 in the absence of 18C6 and 0.9 and 0.85 in the presence of the crown ether, respectively) allows concluding the higher separation efficiency of the extraction process by using dichloromethane as diluent. Nevertheless, it is of important to note that the extraction at higher pH values is a negative point of this system with respect to the extraction process using carbon tetrachloride.

Quantification of La(III)/18C6 and Eu(III)/18C6 interactions

The equation describing the extraction equilibrium of La(III) and Eu(III) ions from chloride medium into carbon tetrachloride solution of HL has been demonstrated as [28]:



The corresponding equilibrium constant of Eq. 1 is:

$$K_{\text{ex}} = \frac{[\text{ML}_3]_{\text{org}}[\text{H}^+]_{\text{aq}}^3}{[\text{M}^{3+}]_{\text{aq}}[\text{HL}]_{\text{org}}^3} \quad (2)$$

The $\log K_{\text{ex}}$ values have been evaluated by analyzing the extraction experiments data of these ions and have been reported as -1.30 and -0.30 [28]. As the metal organic concentrations are much lower than that of the initial ligand concentration, and by considering the distribution of the ligand between aqueous and organic phases is negligible, the equilibrium ligand concentration can be considered equal to its initial concentration:

$$[\text{HL}]_{0,\text{org}} \approx [\text{HL}]_{\text{org}} \quad (3)$$

On the other hand, the equation describing the metal ion interaction with crown ether (CE) in the aqueous phase and the corresponding stability constant can be described by Eqs. 3 and 4:



$$\beta = \frac{[\text{M}(\text{CE})^{3+}]_{\text{aq}}}{[\text{M}^{3+}]_{\text{aq}}[\text{CE}]_{\text{aq}}^3} \quad (5)$$

The experimental condition with respect to the crown ether concentration has been selected as the initial concentration of the crown ether equaled to its equilibrium concentration,

$$[\text{CE}]_{\text{aq}} = [\text{CE}]_{0,\text{aq}} \quad (6)$$

In addition, the mass balance equation of La(III) and Eu(III) ions (M^{3+}) is given by:

$$[M^{3+}]_{\text{aq}} = [M^{3+}]_{0,\text{aq}} - [M]_{\text{aq}} - [M(\text{CE})^{3+}]_{\text{aq}} \quad (7)$$

in which,

$$[M]_{\text{org}} = [\text{ML}_3]_{\text{org}} \quad (8)$$

A combination of Eqs. 2, 3, 5, 6, 7 and 8 allows defining the concentration of La(III) and Eu(III) from the aqueous phase containing 18C6 into carbon tetrachloride solution of HL, as below:

$$[M]_{\text{org}} = \frac{K_{\text{ex}}[M^{3+}]_{0,\text{aq}}[\text{HL}]_{0,\text{org}}^3}{[\text{H}^+]_{\text{aq}}^3(1 + \beta[\text{CE}]_{0,\text{aq}}) + K_{\text{ex}}[\text{HL}]_{0,\text{org}}^3} \quad (9)$$

By applying $[\text{HL}]_{0,\text{org}}$ (0.01 mol L⁻¹), $[\text{CE}]_{0,\text{aq}}$ (0.05 mol L⁻¹) and K_{ex} values, which were determined previously [28], the experimental values of the extracted metal ions in the presence of 18C6 as a function of pH can be fitted by applying an appropriate value for β (curves corresponding to the extraction of lanthanum and europium into carbon tetrachloride solution of HL in Fig. 2). The values of $\log\beta$ allow to interpret quantitatively the variation in the selectivity presented by the extraction procedure using amic acid in the absence and in the presence of 18C6. The calculated complexation constant for $[\text{La}(\text{CE})^{3+}]$ and $[\text{Eu}(\text{CE})^{3+}]$ complexes was found to be 3.10 (± 0.06) and 1.81 (± 0.05), respectively. These values were close to those reported previously for the complexation of these ions by 18C6 in methanol [35].

Thermodynamics of the extraction process

In order to assess the effect of temperature on the extraction of La(III), Eu(III) and Er(III) ions in the absence of 18C6 by carbon tetrachloride solution of HL and determination of corresponding thermodynamic parameters (ΔH° , ΔS° and ΔG°), a series of extraction experiments were performed in the range 293–308 K.

The free-energy change (ΔG°) for the extraction equilibrium is calculated from the extraction constant K_{ex} by Eq. 7:

$$\Delta G^\circ = -RT \ln K_{\text{ex}} \quad (10)$$

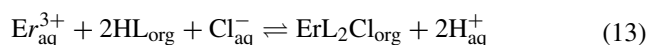
The Gibbs-Helmholtz equation relates the Gibbs free energy to the corresponding enthalpy and entropy changes:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

By combining the Eqs. 7 and 8, it is possible to calculate the equation describing the temperature dependency of the extraction constants:

$$\ln K_{\text{ex}} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (12)$$

It is noteworthy that the extraction equilibrium and its corresponding extraction equilibrium constant for the Er(III) ions from chloride medium by HL into carbon tetrachloride have been shown to be described by Eqs. 13 and 14 [28]:



$$K_{\text{ex}} = \frac{[\text{ErL}_2\text{Cl}]_{\text{org}}[\text{H}^+]_{\text{aq}}^2}{[\text{Er}^{3+}]_{\text{aq}}[\text{Cl}^-]_{\text{aq}}[\text{HL}]_{\text{org}}^2} \quad (14)$$

The slope and the intercept of the plots of $\ln K_{\text{ex}}$ values as a function of T^{-1} (Fig. 3) permitted calculating ΔH° , ΔS° and ΔG° values for the extraction process of La(III), Eu(III) and Er(III) by HL into carbon tetrachloride (Table 3).

The thermodynamic parameters correspond to the complexation of La(III) and Eu(III) ions in the aqueous phase were also investigated by performing a series of extraction of these ions from aqueous solutions (0.1 mol L⁻¹ LiCl) containing 18C6 (0.05 mol L⁻¹) into carbon tetrachloride solution of HL (0.01 mol L⁻¹), in the range of 293–308 K. The evaluated β values, calculated based on the procedure described in “Quantification of La(III)/18C6 and Eu(III)/18C6 interactions” section, were related to the ΔH_c° and ΔS_c° values of the complexation of La(III) and Eu(III) ions in the aqueous phase by using Eq. 12:

$$\ln \beta = -\frac{\Delta H_c^\circ}{RT} + \frac{\Delta S_c^\circ}{R} \quad (15)$$

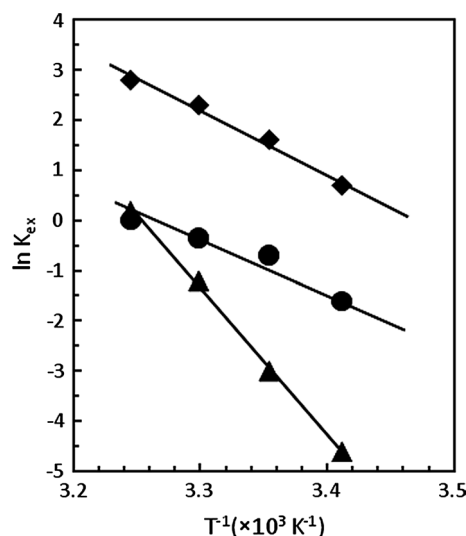


Fig. 3 Variation of $\ln K_{\text{ex}}$ as a function of T^{-1} (K^{-1}) for lanthanum (filled triangle), europium (filled circle) and Erbium (filled diamond) ions extraction from aqueous phase containing 0.1 mol L⁻¹ LiCl into carbon tetrachloride solution of HL (0.01 mol L⁻¹)

Table 3 Thermodynamic parameters (in kJ mol^{-1}) associated with the liquid–liquid extraction of La(III), Eu(III) and Er(III) ions from LiCl (0.1 mol L^{-1}) aqueous phase solutions into carbon tetrachloride

Ion	Extraction by HL			Complexation with 18C6		
	ΔH°	$T\Delta S^\circ$	ΔG°	ΔH°	$T\Delta S^\circ$	ΔG°
La(III)	242.7	235.4	7.3	−27.2	9.6	−17.6
Eu(III)	77.9	75.6	2.3	−54.2	−44.0	−10.2
Er(III)	105.7	109.4	−3.7	–	–	–

Calculation using the least-squares method; $\delta_{N-1} \leq \pm 5 \%$

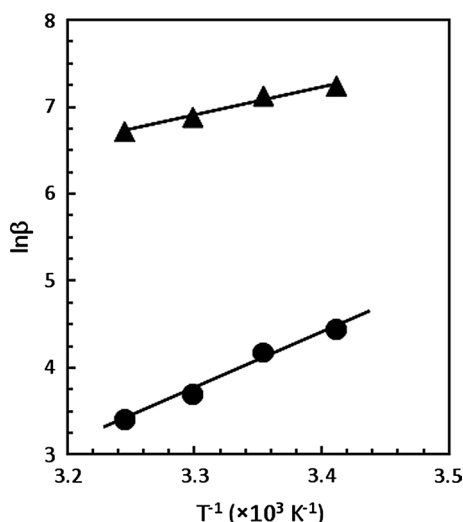


Fig. 4 Variation of $\ln \beta$ values as a function of T^{-1} (K^{-1}) for lanthanum (filled triangle) and europium (filled circle) ions extraction from aqueous phase containing 18C6 (0.05 mol L^{-1}) and LiCl (0.1 mol L^{-1}) by HL (0.01 mol L^{-1}) dissolved in carbon tetrachloride

This equation reveals that, by plotting the variation in $\ln \beta$ values versus T^{-1} (Fig. 4), it is possible to determine the enthalpy and entropy changes in La(III) and Eu(III) ions interaction with 18C6. The values of ΔG_C° were calculated by Eq. 13:

$$\Delta G_C^\circ = \Delta H_C^\circ - T\Delta S_C^\circ \quad (16)$$

Table 3 contains ΔH_C° , ΔS_C° and ΔG_C° values for the complexation process of lanthanum and europium ions in the aqueous phase.

The values of the thermodynamic parameters given in Table 3 signify that the extraction of all the studied ions is endothermic and the process is controlled by positive entropy changes. In contrast, the complexation process of La(III) and Eu(III) ions is exothermic. This means that an increase in the temperature can enhance the extraction efficiency, while it decreases the complexation of the studied ions in the aqueous phase and thus a decrease in the separation of the ions can be taken place.

solution of HL, and those of the complexation of La(III) and Eu(III) ions by 18C6 in aqueous phase solution containing 0.1 mol L^{-1} LiCl, at 298 K

Conclusions

The selectivity presented by *N,N*-dioctyldiglycolamide acid (HL) dissolved in carbon tetrachloride for the extraction of La(III), Eu(III) and Er(III) ions was just opposite to that of the complexation of these ions by crown ether 18C6 in aqueous phase. This allowed 18C6 to be applied as masking agent for improving extraction–separation of La(III), Eu(III) and Er(III) as representative ions of light, middle and heavy rare earths. The analysis of the liquid–liquid extraction data was performed as an indirect route for evaluation of the stability constant of the studied rare earths complexes with 18C6. Thermodynamic investigations of the extraction and complexation processes demonstrated that an increase in temperature enhances the extraction efficiency, while it causes a decrease in the separation of the studied ions.

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