

Water soluble crown ethers: selective masking agents for improving extraction-separation of zinc and lead cations

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Abstract The presence of crown ethers 12C4, 15C5 and 18C6 (CE) in aqueous phase influences extraction-separation of zinc and lead ions (M^{2+}) by acidic extractant bis(2-ethylhexyl)phosphoric acid (DEHPA) in cyclohexane. In fact, higher complexing ability of the crown ethers towards lead ions causes a greater shift toward higher pH region of the extraction curves versus aqueous phase pH, and consequently an enhancement in the extraction selectivity. The order of extraction selectivity in the presence of the crown ethers varies as $18C6 > 15C5 > 12C4$. The analysis of extraction data allows evaluating the stability constants of $[M \cdot CE]^{2+}$ complexes in the aqueous phase. It is demonstrated that the influence of aqueous crown ethers on the extraction process is deeply affected by the organic diluent used. The influence of temperature on the extraction process was studied in the range 286–302 K. This study lets estimating the thermodynamic parameters, i.e., free-energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes associated with the extraction process as well as the complexation of cations by the crown ethers in water.

Keywords Crown ethers · Masking effect · Extraction · Zinc · Lead · Bis(2-ethylhexyl)phosphoric acid

Introduction

Beside the vast applications and economic importance of zinc, lead, and their related compounds [1], they have been

recognized among ecotoxicological hazardous materials [2, 3]. This provokes the removal, separation and purification of these metals from different sources to be an important subject of many fundamental and industrial investigations [4, 5].

It is well known that liquid–liquid extraction techniques play an important role in the development of processes for recovering and separation of different metal ions [6]. Undoubtedly, the selectivity and efficiency of these techniques is mainly determined by the extracting agents.

Acidic ligands such as carboxylic acids [7], pyrazolons [8] and β -diketones [9] have been frequently used as extractant for separation of a variety of metal ions. One of the most important advantages of this type of extractants is the possibility to tune the selectivity and efficiency of extraction by controlling the pH of aqueous phases.

Bis(2-ethylhexyl)phosphoric acid (DEHPA) is among the acidic extracting agents used in many studies concerned to the extraction-separation of metal ions [10–12]. During the time, attempts were performed to improve the extraction processes in which DEHPA is involved. A part of the studies is focused on its application in cooperative extraction with a second extracting agent, known as synergistic extractions [13–16]. In addition, the application of water soluble molecules, as masking agents, is also investigated as a method for improving the extraction selectivity of metal ions [17–20].

Due to their ion size selective nature and ability to transfer metal ions into organic media, crown ethers have been frequently used as extractants and phase transfer reagents in solvent extraction and liquid membrane techniques, respectively [21–27]. This class of synthetic macrocyclic compounds has been extensively used as synergistic agents for modifying the efficiency of extraction processes [28–30]. Substantial progress has been made

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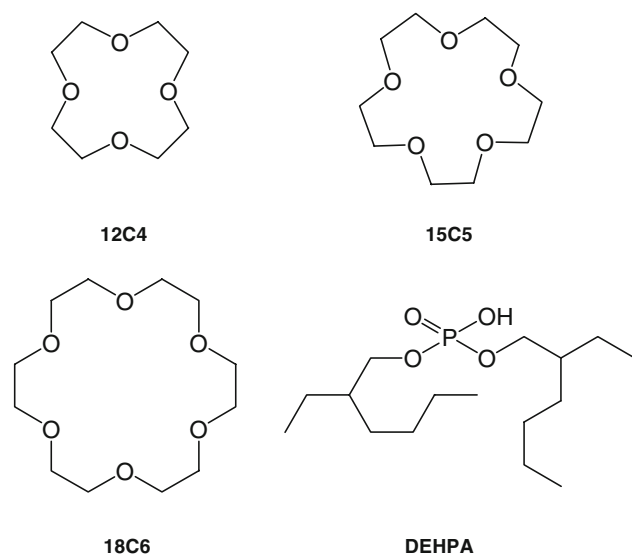


Fig. 1 Chemical structure of the ligands used in this study

in the application of neutral water soluble crown ethers as masking agents for improving the solvent extraction selectivity [17–20].

Following to our previous studies on the complexing [19, 20], extractive [26] and mobile carrier properties [25, 27, 31] of crown ethers towards metal ions, we report here, the application of water soluble crown ethers 12C4, 15C5, and 18C6 (Fig. 1) for improving the extraction-separation of zinc and lead ions by bis(2-ethylhexyl)phosphoric acid (DEHPA) in cyclohexane. This study allows for the indirect evaluation of the stability constants of metal ion-crown ethers complexes in water. The effect of diluent and temperature on the extraction in the absence and presence of the studied crown ethers are also investigated and discussed.

Experimental

Bis(2-ethylhexyl)phosphoric acid, 12C4, 15C5, and 18C6 (Merck) were used as received. Cyclohexane, carbon tetrachloride, chloroform, dichloromethane, and 1,2-dichloroethane (Merck) were washed twice with distilled water. Stock solutions of zinc and lead were prepared by dissolving a proper quantity of corresponding nitrate salts (Fluka) in water. These solutions were standardized complexometrically [32]. Extraction experiments were carried out by contacting two equal volumes (90 mL) of organic and aqueous 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 lithium hydroxide (Fluka) or hydrochloric acid (Merck) 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 by flame atomic absorption spectrometry (FAAS: Varian 220AA).

Results and discussion

Effect of diluent on the extraction of Zn(II) and Pb(II) ions by DEHPA

In order to evaluate the extraction efficiency of DEHPA toward zinc and lead ions, the extraction of these ions by the extractant into different diluents (cyclohexane, carbon tetrachloride, chloroform, dichloromethane, and 1,2-dichloroethane) as a function of pH has been investigated at 298 K. Figure 2 shows, as an example, the variation of extraction value of zinc ions versus aqueous phase pH by DEHPA in the investigated diluents. For both metal ions the extraction values were increased by varying the diluent as: cyclohexane > 1,2-dichloroethane \approx carbon tetrachloride > dichloromethane > chloroform.

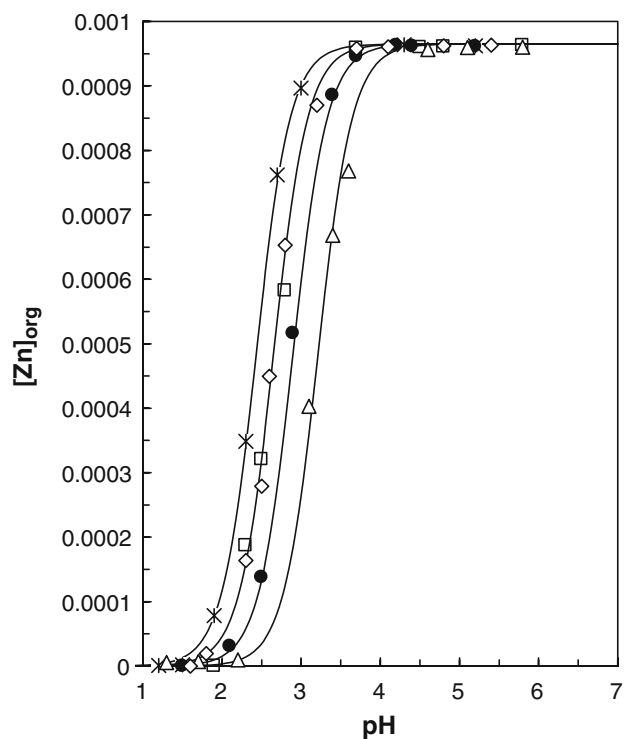
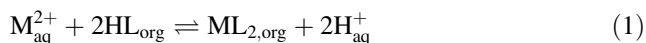


Fig. 2 Extraction of zinc ions (9.65×10^{-4} M) by DEHPA (0.01 M) in cyclohexane (*), carbon tetrachloride (\diamond), 1,2-dichloroethane (\square), dichloromethane (\bullet) and chloroform (\triangle) as a function of aqueous phase pH at 298 K

Based on the existence of DEHPA as monomer in polar (chloroform, dichloromethane, and 1,2-dichloroethane) and dimer in nonpolar (carbon tetrachloride and cyclohexane) diluents [33], two types of equations can be used for describing the extraction equilibrium:



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:

$$K_{ex} = \frac{[ML_2]_{org} [H^+]_{aq}^2}{[M^{2+}]_{aq} [HL]_{org}^2} \quad (3)$$

$$K_{ex} = \frac{[ML_2(HL)_2]_{org} [H^+]_{aq}^2}{[M^{2+}]_{aq} [(HL)_2]_{org}^2} \quad (4)$$

As the metal concentrations in the organic phase are much lower than that of the initial ligand concentration, the equilibrium ligand concentration can be considered equal to its initial concentration:

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

$$[(HL)_2]_{0,org} \approx [(HL)_2]_{org}$$

By introducing the following mass balance equation for metal ions,

$$[M^{2+}]_{0,org} = [M^{2+}]_{aq} + [M^{2+}]_{org}$$

$$\begin{aligned} \text{(in which } [M^{2+}]_{org} &= [ML_2]_{org} \text{ or } [M^{2+}]_{org} \\ &= [ML_2]_{org} \text{ or } [M^{2+}]_{org} = [ML_2(HL)_2]_{org}) \end{aligned}$$

and rearrangement of Eqs. 3 and 4, the variation of metal ions in the organic phase as a function of hydrogen ion concentration in the aqueous phase can be driven:

$$[M]_{org} = \frac{K_{ex} [M^{2+}]_{0,org} [HL]_{org}^2}{[H^+]_{aq}^2 + K_{ex} [HL]_{0,org}^2} \quad (5)$$

$$[M]_{org} = \frac{K_{ex} [M^{2+}]_{0,org} [(HL)_2]_{org}^2}{[H^+]_{aq}^2 + K_{ex} [(HL)_2]_{0,org}^2} \quad (6)$$

The analysis of experimental results 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} (curves in Fig. 2). The evaluated K_{ex} with corresponding $pH_{0.5}$ values (pH of the extraction of 50% of metal ions into organic phase) are presented in Table 1. The results reveal that, regardless to the type of diluent used, DEHPA extracts zinc ions more efficacious than lead ions.

By introducing the distribution ratio,

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

The logarithmic expression of Eqs. 3 and 4 is:

$$\log D = \log K_{ex} + n \log [HL]_{0,org}^2 + pH \quad (7)$$

$$\log D = \log K_{ex} + n \log [(HL)_2]_{0,org}^2 + pH \quad (8)$$

The conventional log–log analysis of the extraction data for zinc and lead ions in the studied diluents confirms the stoichiometry considered for the extracted species. Figure 3 illustrates, as an example, this analysis for the extraction of the studied metal ions by DEHPA in cyclohexane.

Effect of the presence of aqueous 12C4, 15C5, and 18C6

Application of masking agents is known as one of the ways for improving the selective separation of metal ions in the extraction processes [18]. In order to verify the possible enhancement of the separation of zinc and lead ions in the solvent presence of 12C4 (0.05 M), 15C5 (0.05 M), and 18C6 (0.01) as masking agents, the extraction of these ions from aqueous phase containing these crown ethers into cyclohexane solution of DEHPA has been studied (Fig. 4). Cyclohexane was used because distribution ratio of the

Table 1 Extraction equilibrium constants and corresponding $pH_{0.5}$ values for the extraction of zinc and lead ions by DEHPA in different diluents

M^{2+}	C_6H_{12}		CCl_4		$CHCl_3$		CH_2Cl_2		CH_2ClCH_2Cl	
	$\log K_{ex}$	$pH_{0.5}$	$\log K_{ex}$	$pH_{0.5}$	$\log K_{ex}$	$pH_{0.5}$	$\log K_{ex}$	$pH_{0.5}$	$\log K_{ex}$	$pH_{0.5}$
Zn^{2+}	-0.26	2.43	-0.70	2.65	-1.82	3.21	-1.19	2.90	-0.7	2.65
Pb^{2+}	-1.96	3.30	-2.06	3.33	-3.35	3.98	-2.65	3.62	-2.06	3.33

Experimental conditions: initial metal concentration, 9.65×10^{-4} M; initial ligand concentration, 0.01 M; temperature, 298 K

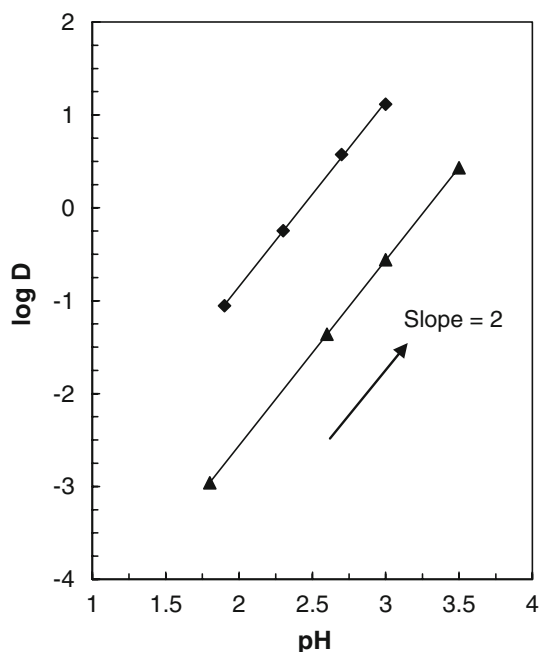


Fig. 3 Plot of log D versus pH in the extraction of zinc (◆) and lead (▲) ions (9.65×10^{-4} M) by DEHPA (0.01 M) in cyclohexane at 298 K

studied crown ethers between this diluent and water is low, therefore the crown ethers remains quantitatively in the aqueous phase. It is noteworthy that, we used higher concentration for 12C4 and 15C5 in order to obtain a higher shift in extraction curves and therefore a lower uncertainty in treatment of the data. As it is seen in Fig. 4, the presence of the crown ethers affects the extraction curve of lead ions. Except for 15C5, other crown ethers do not influence the extraction curve of zinc ions.

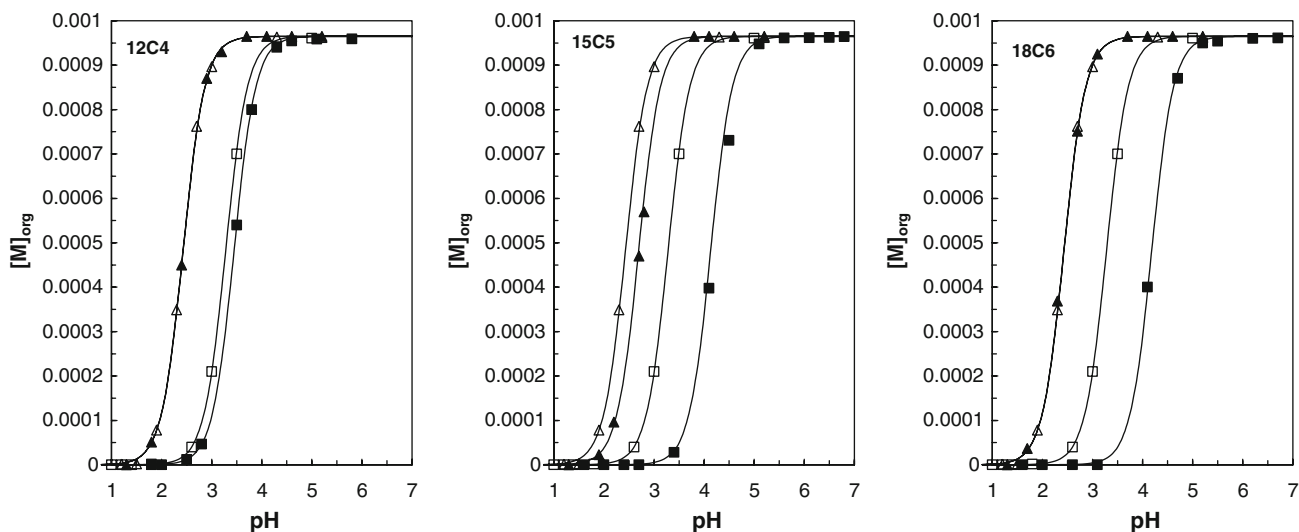


Fig. 4 Extraction of zinc (△, ▲) and lead (□, ■) ions (initial concentration 9.65×10^{-4} M) in the absence (empty symbols) and presence (filled symbols) of 12C4 (0.05 M), 15C5 (0.05 M) and 18C6 (0.01 M) by DEHPA (0.01 M) dissolved in cyclohexane at 298 K

Table 2 $\text{pH}_{0.5}$ and $\Delta\text{pH}_{0.5}$ values of the extraction of zinc and lead ions (9.65×10^{-4} M) in the absence and presence of 12C4 (0.05), 15C5 (0.05) and 18C6 (0.01 M) by DEHPA dissolved in cyclohexane (0.01 M) at 298 K

M^{2+}	$\text{pH}_{0.5}^a$	12C4		15C5		18C6	
		$\text{pH}_{0.5}$	$\Delta\text{pH}_{0.5}$	$\text{pH}_{0.5}$	$\Delta\text{pH}_{0.5}$	$\text{pH}_{0.5}$	$\Delta\text{pH}_{0.5}$
Zn^{2+}	2.43	2.43	–	2.70	0.27	2.43	–
Pb^{2+}	3.30	3.50	0.20	4.20	0.90	4.25	0.95

^a In the absence of the crown ethers

The shift of $\text{pH}_{0.5}$ values ($\Delta\text{pH}_{0.5}$) of the extraction curves demonstrates a quantitative measure for the metal ion–crown ethers interactions in the aqueous phase. These values are extracted from Fig. 4 and are regrouped in Table 2. It is seen that all crown ethers are able to complex Pb(II) more stable than Zn(II) ions. The binding ability of the studied crown ethers varies in the order $18\text{C6} > 15\text{C5} > 12\text{C4}$.

Quantitative investigation of the metal ion–crown ether interactions was performed by evaluating the stability constant of $[\text{M}\cdot\text{CE}]^{2+}$ complexes ($\text{M} = \text{Zn}, \text{Pb}$; $\text{CE} =$ crown ether) in water using the extraction data. Equilibrium describing the metal ion complexation by crown ethers in the aqueous phase is considered as,



For which the equilibrium stability constant is:

$$\beta = \frac{[\text{M}(\text{CE})^{2+}]_{\text{aq}}}{[\text{M}^{2+}]_{\text{aq}}[\text{CE}]_{\text{aq}}} \quad (10)$$

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

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

Considering the mass balance equation for the metal ions,

$$[M^{2+}]_{aq} = [M^{2+}]_{0,aq} - [M]_{org} - [MCE^{2+}]_{aq}$$

the variation of metal concentration in the organic phase versus pH (Eq. 6) becomes,

$$[M]_{org} = \frac{K_{ex} [M^{2+}]_{0,aq} [(HL)_2]_{org}^2}{[H^+]_{aq}^2 (1 + \beta [CE]_{aq}) + K_{ex} [(HL)_2]_{org}^2} \quad (11)$$

Using the evaluated K_{ex} values (Table 1), the experimental values of the extracted metal ions in the presence of 12C4, 15C5, and 18C6 as a function of pH can be fitted by applying an appropriate value for β (curves in Fig. 4). Corresponding β values with those reported in DMSO/H₂O (90/10 v/v) [34], determined by conductometry, are presented for comparison in Table 3.

The influence of the concentration of the crown ethers dissolved in water on the extraction of lead by DEHPA in cyclohexane was tested. Figure 5 shows, as an example, the extraction curves of lead ions by DEHPA (0.01 M) as a function of aqueous pH values in the presence of different concentration of 18C6 in the aqueous phase. As it is expected, an increase in the crown ether concentration causes the $pH_{0.5}$ of the extraction shifts to higher value.

Evaluation of separation factor in the presence of crown ethers

In order to investigate quantitatively the separation efficiency of the extraction in the presence of the studied crown ethers, the corresponding separation factors (SF) were determined. This parameter is defined as,

$$SF = \log \left(\frac{D_{M_1}}{D_{M_2}} \right) \quad (12)$$

Separation factor in the absence of the crown ethers is derived from Eq. 4,

$$SF = \log \left(\frac{D_{M_1}}{D_{M_2}} \right) = \log \left(\frac{K_{ex,M_1}}{K_{ex,M_2}} \right) \quad (13)$$

In the presence of crown ether, the distribution value is:

Table 3 Logarithm of the complex formation constant (β) of zinc and lead ions by 12C4, 15C5 and 18C6 in water at 298 K

M ²⁺	18C6	15C5	12C4
Zn ²⁺	−(1.61)	1.90 (1.94)	–
Pb ²⁺	3.80 (3.87)	2.99 (2.85)	1.36

Values in parentheses, measured in DMSO/H₂O (90/10 v/v) by conductometry [34]

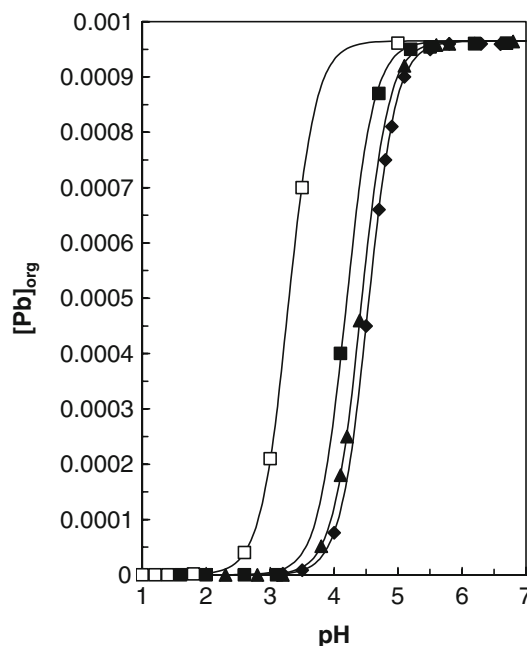


Fig. 5 Extraction of lead ions (initial concentration 9.65×10^{-4} M) in the absence (\square) and presence of 18C6 (0.01 M, \blacksquare ; 0.03 M, \blacktriangle ; 0.05 M, \blacklozenge) by DEHPA (0.01 M) dissolved in cyclohexane at 298 K

$$D_{M_1} = \frac{[M_1]_{org}}{[M_1^{2+}]_{aq} + [M_1(CE)^{2+}]_{aq}} = K_{ex,M_1} \frac{[(HL)_2]_{org}^2}{[H^+]_{aq}^2 (1 + \beta_{M_1} [CE]_{aq})} \quad (14)$$

Therefore, the separation factor is calculated as follow:

$$SF = \log \left(\frac{D_{M_1}}{D_{M_2}} \right) = \log \left(\frac{K_{ex,M_1}}{K_{ex,M_2}} \right) \left(\frac{1 + \beta_{M_2} [CE]_{aq}}{1 + \beta_{M_1} [CE]_{aq}} \right) \quad (15)$$

The evaluated separation factors are presented in Table 4. This factor is improved significantly in the presence of the studied crown ethers and thus an enhanced separation can be achieved. The best separation factor is found in the presence of crown ether 18C6.

Influence of the organic diluent

In order to evaluate the role of the organic diluent on the masking effect of aqueous crown ethers, the extraction of lead ions by DEHPA, dissolved in carbon tetrachloride,

Table 4 Separation factors for the extraction of zinc and lead ions in the absence and presence of 12C4, 15C5 and 18C6 by DEHPA in cyclohexane

Crown ether	–	18C6	15C5	12C4
SF _{Zn/Pb}	1.70	4.20	2.70	2.03

Table 5 Effect of the diluent on $\text{pH}_{0.5}$ of the extraction of lead ions by DEHPA in the presence of aqueous 12C4 (0.05 M), 15C5 (0.05 M) and 18C6 (0.01 M)

Diluent	$\text{pH}_{0.5}^a$	12C4		15C5		18C6	
		$\text{pH}_{0.5}$	$\Delta\text{pH}_{0.5}$	$\text{pH}_{0.5}$	$\Delta\text{pH}_{0.5}$	$\text{pH}_{0.5}$	$\Delta\text{pH}_{0.5}$
C_6H_{12}	3.30	3.50	0.20	4.20	0.90	4.25	0.95
CCl_4	3.33	3.57	0.24	3.80	0.47	4.55	1.22
CHCl_3	3.98	3.98	–	3.46	–0.52	3.42	–0.56
CH_2Cl_2	3.62	3.62	–	3.16	–0.46	3.36	–0.26
$\text{CH}_2\text{ClCH}_2\text{Cl}$	3.33	3.63	0.30	3.08	–0.25	3.57	0.24

^a In the absence of the crown ethers

chloroform, dichloromethane and 1,2-dichloroethane, in the presence of 12C4, 15C5, and 18C6 in the aqueous phase was studied. The obtained extraction data are presented in Table 5. Considering the results, one can conclude that, the organic diluent affect profoundly the role of the aqueous crown ethers on the extraction. A masking effect is presented by all the crown ethers in the extraction when cyclohexane and carbon tetrachloride are used as organic diluent. Although such effect is found for the extraction of lead ions in the presence of 12C4 and 18C6, this is not the case for 15C5. In fact, the presence of 15C5 and 18C6 in the extraction of lead ions into chloroform and dichloromethane provokes a synergistic effect. Such observation is also seen for 15C5 when 1,2-dichloroethane is used as organic diluent. It is noteworthy that there is no net masking or synergistic effect for 12C4 in the extraction of lead ions by DEHPA dissolved in chloroform or dichloromethane.

An interpretation for the observed results can be given by considering the distribution of the free crown ethers and their metal complexes between organic diluents and aqueous phase. By increasing this distribution it is presumed that the masking effect of the crown ether decreases and, in contrast, its cooperative effect on the extraction increases.

Thermodynamics of the extraction and complexation processes

In order to assess the effect of temperature on the extraction of zinc and lead ions by DEHPA in cyclohexane, a series of extraction experiments were performed in the range 286–302 K. These experiments allow evaluating the corresponding equilibrium extraction constants in the aqueous phase as a function of temperature, and the thermodynamic functions, i.e., ΔG° , ΔH° , and ΔS° of the process.

The free-energy change (ΔG°) for the extraction equilibrium is calculated from the extraction constant K_{ex} by Eq. 16,

$$\Delta G^\circ = -RT \ln K_{\text{ex}} \quad (16)$$

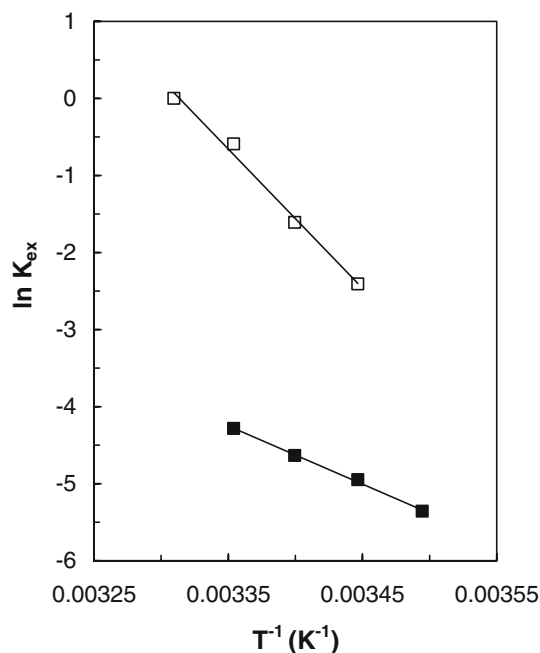
and is related to the enthalpic and entropic changes (ΔH° and ΔS°) through the Gibbs–Helmholtz equation,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

Combination of Eqs. 16 and 17 results Eq. 18, describing the temperature dependency of K_{ex} :

$$\ln K_{\text{ex}} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (18)$$

Plots of $\ln K_{\text{ex}}$ values as a function of the inverse absolute temperature gave straight lines (Fig. 6). The analysis of these plots allows calculating ΔG° , ΔH° and $T\Delta S^\circ$ (Table 6). The results reveal that the extraction of both cations is endothermic and driven by positive entropy changes. The differences between enthalpy and entropy changes for these ions can be interpreted considering the corresponding hydration free energies [6]. This is higher for zinc ions. In the case of zinc, more water molecules need to be released in the extraction process with respect to lead ions. Therefore, the energy spent for this process is

**Fig. 6** Plot of $\ln K_{\text{ex}}$ versus T^{-1} (K^{-1}) for zinc (\square) and lead (\blacksquare) ions in their extraction by DEHPA (0.01 M) in cyclohexane**Table 6** Thermodynamic parameters (ΔG° , ΔH° and $T\Delta S^\circ$) associated with the extraction of Pb and Zn ions at 298 K

M^{2+}	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	$T\Delta S^\circ$ (kJ mol^{-1})
Zn^{2+}	1.8	150.3	148.5
Pb^{2+}	10.6	64.0	53.4

higher and accordingly the net enthalpy changes, i.e., the difference of the energy corresponding to the formation of the extractable species and the energy spent in releasing the water molecules is more positive for zinc than lead ions. Furthermore, the net entropy change (i.e., the entropy gain due to water release and the entropy loss due to the binding with DEHPA) is more positive for zinc ions than that of lead ions.

Thermodynamic parameters associated to the lead ion complexation in water by 12C4, 15C5, and 18C6 has been measured by performing a series of extraction experiments of this cation in the presence of these crown ethers by DEHPA in cyclohexane at different temperatures (286–302 K). The corresponding β values have been evaluated as described before. The plots of variation of $\ln\beta$ as a function of T^{-1} for the complexation of lead ions by the studied crown ethers are shown in Fig. 7. The calculated thermodynamic functions are presented in Table 7.

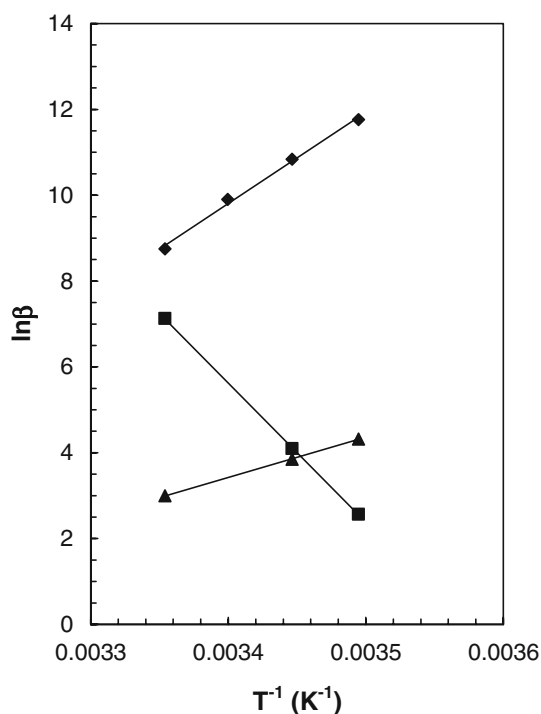


Fig. 7 Variation in $\ln\beta$ as a function of T^{-1} (K⁻¹) for lead ions by 12C4 (0.05 M, ▲), 15C5 (0.05 M, ■) and 18C6 (0.01 M, □) in water

Table 7 Thermodynamic parameters associated with the complexation of lead ions by 12C4, 15C5 and 18C6 in the aqueous phase at 298 K

Crown ether	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	$T\Delta S^\circ$ (kJ mol ⁻¹)
18C6	-21.9	-176.7	-154.8
15C5	-17.7	272.6	290.3
12C4	-7.4	-77.9	-70.5

Table 8 Values of $\Delta pH_{0.5}$, of the extraction of lead ions in the absence and presence of 12C4, 15C5 and 18C6 by DEHPA in cyclohexane at 290 and 298 K

Temperature (K)	$\Delta pH_{0.5}$		
	12C4	15C5	18C6
290	0.35	0.50	1.50
298	0.15	0.90	0.95

The complexation of lead ions by 12C4 and 18C6 is an exothermic reaction with a negative entropy changes. More negative values of enthalpy changes for the complexation process of lead ions by 18C6 with respect to that of 12C4 can be attributed to the higher number of donor oxygen atoms in the former. In contrast, Pb-15C5 interaction is endothermic and controlled by positive entropy changes. At this stage of study we do not have any interpretation for the determined thermodynamic functions of lead ion complexation by 15C5.

As it is shown in Table 8, the difference of the effect of temperature on the extraction and complexation process causes different overall result of the $\Delta pH_{0.5}$. In fact in the presence of 15C5 an increase in $\Delta pH_{0.5}$ value with temperature is observed. Although the extraction of lead ions increases with temperature, the higher $\Delta pH_{0.5}$ with temperature in the presence of 15C5 reveals that the complexation in the aqueous phase play a decisive role in the overall extraction-complexation temperature dependency of the processes. Contrarily, $\Delta pH_{0.5}$ diminishes by increasing the temperature in the presence of 12C4 and 18C6. This observation shows that an increase in temperature affects the extraction of lead ions by DEHPA more than complexation reaction of lead ions by 12C4 and 18C6.

Conclusions

The present study shows that the combination of chelating properties of acidic extractant DEHPA in cyclohexane and the aqueous crown ethers 12C4, 15C5 and 18C6, as selective masking agents, improves the extraction-separation of zinc and lead ions. The evaluated separation factors increase in the presence of the studied crown ethers as: 18C6 > 15C5 > 12C4. This order consists with the determined stability constants of metal ion-crown ether complexation in the aqueous phase. It is shown that the effect of crown ethers on the separation of zinc and lead ions is markedly affected by the organic diluent used. This work provides a series of thermodynamic data that contribute to a better understanding of the effect of temperature on the selectivity of the extraction of zinc and lead ions by DEHPA in cyclohexane in the presence of 12C4, 15C5, and 18C6 in water.

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