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The Role of Polyethylene Glycols Dissolved in Aqueous Phase on the Extraction-Separation of Zn(II) and Pb(II) by Bis(2-ethylhexyl)phosphoric Acid

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The present study describes the solvent extraction process of Zn(II) and Pb(II) from aqueous solutions by a cation exchanger extractant named bis(2-ethylhexyl)phosphoric acid (DEHPA). The results confirm that both of the extraction efficiency and extraction selectivity depend on the employed organic diluent. The applied extractant was selective towards zinc ions; this selectivity did not depend on the employed organic diluent. The possible interaction of the studied metal ions with the polyether compounds (PEGs) dissolved in the aqueous phase, and the effect of the presence of two PEGs with molecular masses 200 (PEG₂₀₀) and 2000 (PEG₂₀₀₀) on the selectivity characteristics of the proposed extraction system were appraised. The evaluated PEGs play the role of masking agents by complexing the lead ions in the aqueous phase, while the zinc ions did not interact with them. These interactions result in the transposition of the extraction curves of lead as a function of pH, towards higher pH regions, whereas the extraction curves of zinc remained almost unchanged. By replacing the organic diluent (CCl₄) by another one capability to dissolve the complexed lead ions with PEG200 (*e.g.* chloroform), a synergistic extraction was observed. The latter observation clearly showed the decisive impact of the employed solvent on the effect of the investigated PEGs to act as a masking or synergistic agent in the solvent extraction system studied.

Keywords: Lead, Zinc, Solvent extraction, Separation, Masking agent, Synergism

INTRODUCTION

Hydrometallurgical processes are well-known techniques used as conventional methods in metal production plants from the primary or the second-hand sources [1-3]. Solvent extraction is categorized as a type of hydrometallurgical technique. Although the application of solvent extraction is accompanied by environmental concerns, including the need to a considerable amount of organic solvents, presently, this method is extensively used in many metal mineral-rich countries as an efficient, reliable, simple and low-cost technique for metal production [4].

Two main objectives for applying the solvent extraction studies are (1) to approach to a method for efficient

recovery of the target species from its sources, and (2) to separate the analyte with the desired selectivity. Appropriate selection of the chemical composition of the phases involved in solvent extraction (*i.e.* organic and aqueous phases) is critical for a successful extraction-separation process. The organic diluent and the selected extractant in the organic phase are among the parameters determining the extraction characteristics of this phase. However, the presence of the complexing agents with one of the masking or synergistic effects are among the parameters influencing the solvent extraction processes regarding the extraction efficiency and extraction selectivity. Moreover, depending on the extractant nature (acidic, basic or neutral) and the type of the distribuend, the aqueous phase pH affects also the solvent extraction processes.

Acidic extractants, like phosphoric acid compounds [5], oximes [6], β -diketones [7], and carboxylic acids [8] are the

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most studied compounds applied in solvent extraction studies. Although the extraction process based on these extractants can be partly controlled by adjusting the pH of the aqueous phase, the obtained selectivity in some cases cannot fulfill the desired selectivity.

The acidic extractant bis(2-ethylhexyl)phosphoric acid, abbreviated conventionally as DEHPA, is one of the well-known extractant used for separation and recovery of a variety of metals [9-13]. However, due to the poor selectivity presented by this extractant, researchers in the corresponding field try to find the ways for achieving the more suitable separations.

Umetani and coworkers [14-16] reported the results of a study on the solvent extraction of lanthanides and alkali earth ions by acidic extractants dissolved in organic solvents in the systems in which the aqueous phase was charged by water-soluble crown ethers. The results revealed that the interaction between the studied crown ethers and the lanthanides and alkali earth ions increases by increasing the lanthanide ionic radius. This interaction affected the extraction percentage versus aqueous phase pH curves; the curves displaced towards higher pH region. Therefore, the selectivity factors towards lanthanides and alkali earths have been significantly enhanced. In 2004, we studied the solvent extraction of thorium and lanthanides by using DEHPA in cyclohexane. The separation of the studied ions was raised by employing a crown ether bearing a nitrobenzene group (nitrobenzo-18-crown-6, NB18C6) as an agent capable to complex lanthanum ions in the aqueous phase. In fact, the studied crown ether masked the lanthanum ions while it had no significant interaction with Th(IV). This attitude provided an ameliorated separation of the studied metal ions [17]. The separation of La(III) and Eu(III) by the solvent extraction technique using DEHPA in cyclohexane was also studied in the presence of the crown ether 12-crown-4 dissolved in the aqueous phase as a masking agent [18]. The enhanced separation of these ions was observed because the presence of the applied crown ether displaced the extraction curve of lanthanum ions *versus* pH towards the higher pH values. However, the extraction curve of Eu(III) was not influenced.

Shiri-Yekta *et al.* have studied the solvent extraction of Zn(II), Cd(II) and Pb(II) by the solution of DEHPA in cyclohexane [19]. The results confirm that the presence of

the Schiff base BPIE (*N,N'*-bis(2-pyridylmethylidene)-1,2-diiminoethane) in the aqueous phase improves the selectivity of the extraction process. This water-soluble Schiff base interacts with the metal ions and thus the extraction curves of the more interacted ions (Zn(II) < Pb(II) < Cd(II)) moved to the higher pH region. Zamani *et al.* have studied the impact of the dissolved crown ethers in the aqueous phase for improving the selectivity of the solvent extraction of zinc(II) and lead(II) by DEHPA [20]. This study revealed that the application of the crown ethers 12C4, 15C5 and 18C6 dissolved in aqueous phase can affect the separation of target ions by the extractant in cyclohexane. It was shown that the ability of the studied crown ethers for complexing the ions determines the degree of the extraction curves displacement towards a higher pH zone. Thus, the selectivity of the solvent extraction process can be influenced by such interactions and could enhance the selectivity of the extraction process.

The role of polyethylene glycols (PEGs) as a sequestering agent for improving the separation of lanthanum(III), europium(III) and erbium(III) by following their solvent extraction process using DEHPA was investigated by Heidari *et al.* [21]. The designed system was based on the chelating effect of DEHPA dissolved in cyclohexane, and the binding properties of the investigated PEGs in the aqueous phase. This strategy results in ameliorated separation of lanthanum, europium and erbium ions.

We have studied previously the effect of the water-soluble complexing molecules such as crown ethers [17,18,20] and Schiff base ligands [19] to enhance the separation of various metal ions. In continuation of these studies, we have examined the effect of dissolved PEGs in aqueous phase for amelioration of the extraction-separation efficiency of rare earths by using DEHPA as an extractant [21].

The selective recovery and efficient separation of Pb(II) from Zn(II) are important because these metals are usually found together in Zn-Pb ores and some industrial wastes [22-24]. Considering this importance, the present paper intends to demonstrate the potentials of two polyethylene glycols PEG₂₀₀ and PEG₂₀₀₀ (polyethylene glycols with the average molecular mass of 200 and 2000), dissolved in aqueous phase, as masking agent, for the amelioration of the

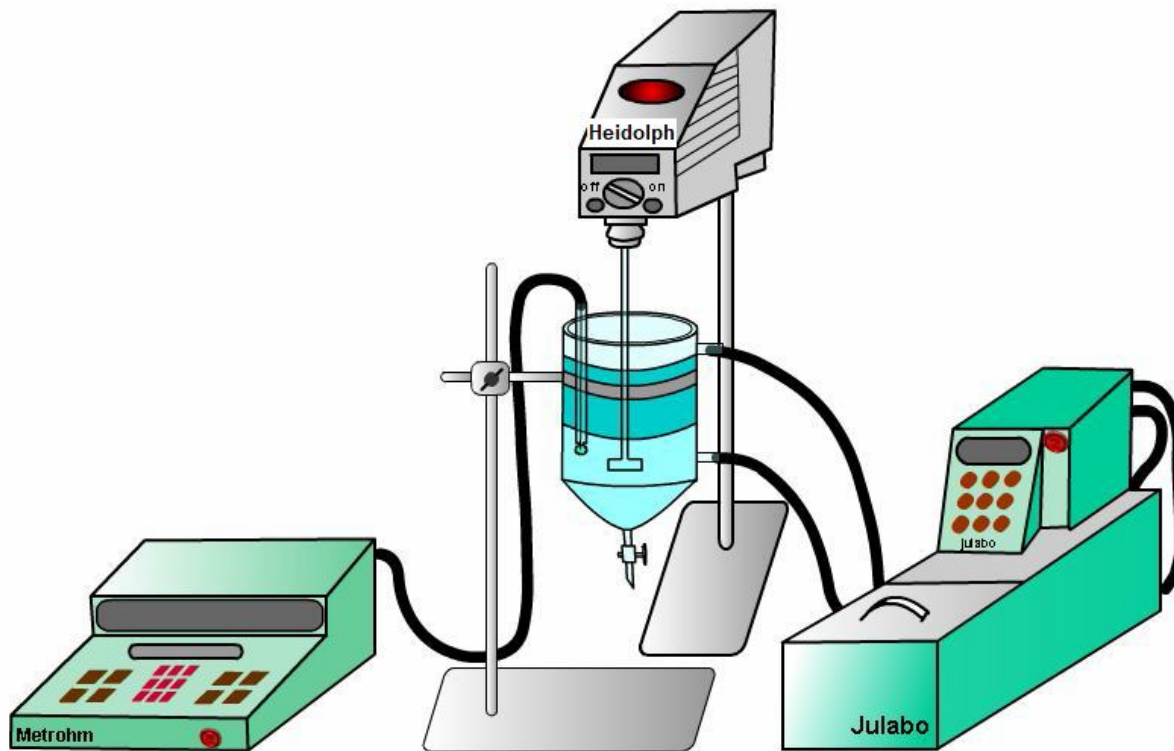


Fig. 1. Schematic representation of the experimental set-up used in this study.

separation efficiency of lead and zinc ions in a solvent extraction process using DEHPA as an extractant.

EXPERIMENTAL

Chemicals

The extractant bis(2-ethylhexyl)phosphoric acid (DEHPA) and the masking agents (polyethylene glycols with molecular weight 200 and 2000) were "for synthesis" and purchased from Merck chemical company. Kerosene (purum, Fluka), cyclohexane ($\geq 99.0\%$, Merck), carbon tetrachloride (extra pure, Merck), dichloromethane ($\geq 99.0\%$, Dr. Mojallali), 1,2-dichloroethane (for analysis, Merck), toluene ($\geq 99.0\%$, Merck), chloroform ($\geq 99.0\%$, Dr. Mojallali) sodium hydroxide (extra pure, Merck), zinc sulfate heptahydrate (extra pure, Merck), and lead nitrate ($\geq 99.0\%$, Merck) were the chemicals used in this study. The organic diluents were washed repeatedly before they were applied in solvent extraction experiments. This is important because it allows removing the solvent stabilizers

and providing the saturation of the organic diluent with water. The Zn(II) and Pb(II) solutions were prepared by dissolving a given weight of the corresponding salts in deionized water. The concentration of the stock solutions was determined complexometrically using the procedures reported elsewhere [25]. The working solutions were prepared by appropriate dilution of the stock solutions with deionized water.

Solvent Extraction Experiments

The solvent extraction experiments were carried out by mixing of the organic and aqueous phases (each 90 ml) in a double jacket cell equipped with a micro-valve at the bottom for sampling. The temperature of the cell was controlled by passing a thermostated water stream through the cell's jacket. The experimental set-up is shown schematically in Fig. 1. The mixing of the organic and aqueous phases was carried out with a Heidolph mechanical stirrer (model 2000, Germany). The pH of the aqueous

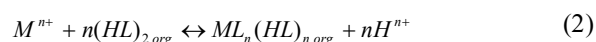
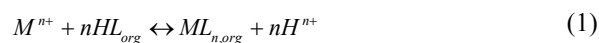
phase was varied by the addition of sodium hydroxide or hydrochloric acid solutions. After 15 min, the agitation has been stopped and the equilibrium pH value was recorded. Then, a given volume of the aqueous phase was taken and centrifuged (Heraeus, Labofuge 300, Germany). The aqueous phase was appropriately diluted and then metal ion content was measured by flame atomic absorption spectrometry spectrophotometrically (Varian model AA 220, Australia). Deionized water (resistivity ≥ 18.2 M Ω cm, Zolalan, m-uv-3+, Iran) was used for the preparation of all aqueous solutions.

RESULTS AND DISCUSSION

Organic Diluent Dependency of the Solvent Extraction of Pb²⁺ and Zn²⁺ by DEHPA

The employed organic diluent affects the ability and the selectivity of a solvent extraction by a given extractant [26]. To evaluate the potentials of DEHPA for the extraction-separation of Pb²⁺ and Zn²⁺, a series of the extraction experiments of these ions (9.65×10^{-4} M) into the DEHPA solutions (0.01 M) in different organic diluents including conventional solvents chloroform (CHCl₃), dichloromethane (CH₂Cl₂), 1,2-dichloroethane (C₂H₄Cl₂), carbon tetrachloride (CCl₄), toluene (C₇H₈), cyclohexane (C₆H₁₂) and kerosene have been performed. The variations of the extracted amount of Pb²⁺ and Zn²⁺ into the organic phase as a function of the aqueous phase pH are presented in Fig. 2.

The observed increase in the extracted amounts of ions by raising the pH of the aqueous phase, reveals that the mechanism of the extraction process obeys a cation exchange mechanism. It is known that DEHPA is in its monomeric form in polar diluents chloroform, and dichloromethane, whereas it is found as dimer form in non-polar diluent kerosene, cyclohexane, carbon tetrachloride and toluene [27]. Thus, the extraction reaction of a cation Mⁿ⁺ by DEHPA (shown as HL) depends on the diluent used, and can be presented by Eqs. (1) and (2).



where the subscribe "org" refers to the organic phase. Other species are presented in the aqueous phase. The corresponding equilibrium constants are:

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

$$K_{ex} = \frac{[ML_n(HL)_n]_{org} [H^+]^n}{[M^{n+}] [(HL)_2]_{org}^n} \quad (4)$$

For simplifying these equations, [ML_n]_{org} and [ML_n(HL)_n]_{org} are replaced by [M]_{org}. Also, the experimental conditions were selected so that the initial concentration of DEHPA in the organic solvent ([HL]_{0,org}) equals to its initial concentration (*i.e.* [HL]_{org} = [HL]_{0,org} and [(HL)₂]_{org} = [(HL)₂]_{0,org}). Besides, the metal ion concentration at equilibrium can be defined by Eq. (5).

$$[M^{n+}] = [M^{n+}]_0 - [M]_{org} \quad (5)$$

Thus, the variation of [M]_{org} as a function of H⁺ concentration in the aqueous phase ([H⁺]) can be derived by rearranging Eqs. (3) and Eq. (4), as demonstrated in Eqs. (6) and (7):

$$[M]_{org} = \frac{K_{ex} [M^{n+}]_0 [HL]_{org}^n}{[H^+]^n + K_{ex} [HL]_{org}^n} \quad (6)$$

$$[M]_{org} = \frac{K_{ex} [M^{n+}]_0 [(HL)_2]_{org}^n}{[H^+]^n + K_{ex} [(HL)_2]_{org}^n} \quad (7)$$

These equations were applied to the data acquired during the extraction of Pb²⁺ and Zn²⁺ ions (n = 2). The fitting of the experimental data allowed estimating K_{ex} and pH_{0.5}. pH_{0.5} is the pH that allows extracting 50% of the total amount of the ions. This parameter demonstrates the relative extraction selectivity of an acidic extractant towards two or more analytes. The curves shown in Fig. 2 and the logK_{ex} and pH_{0.5} values given in Table 1 are obtained by analyzing the experimental data by using Eqs. (6) and (7).

The results in Table 1 reveal that regardless of the type of diluent employed, the extraction of zinc is performed at the lower pH values in comparison with that observed for

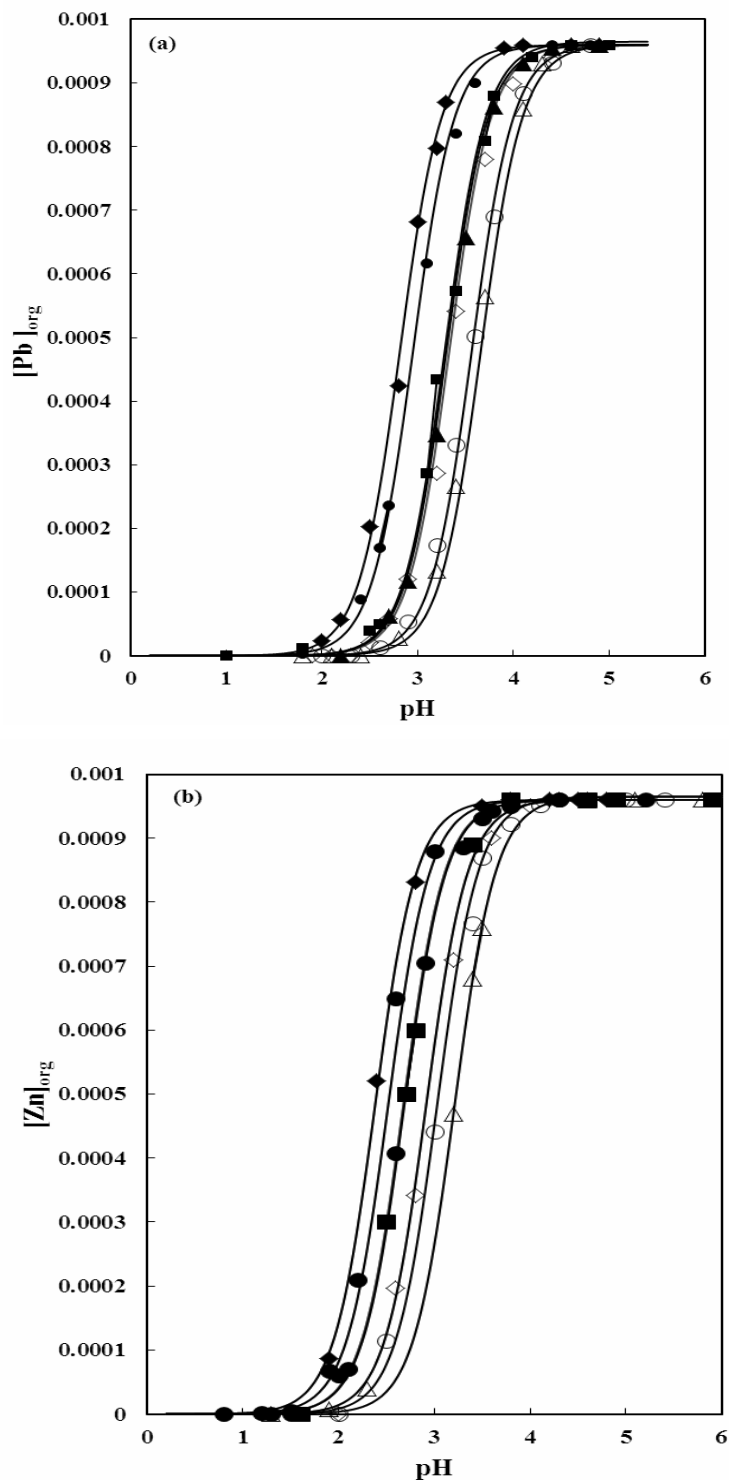


Fig. 2. Variation of the concentration of the extracted (a) Pb^{2+} and (b) Zn^{2+} (initial concentration 9.65×10^{-4} M) by DEHPA (0.01 M) dissolved in kerosene (\blacklozenge), cyclohexane (\bullet), 1,2-dichloroethane (\blacksquare), carbon tetrachloride (\blacktriangle), dichloromethane (\diamond), toluene (\circ), and chloroform (\triangle), as a function of pH, at 25 °C.

Table 1. Evaluated Extraction Equilibrium Constants and $\text{pH}_{0.5}$ Values of the Extraction of Lead and Zinc Ions by DEHPA Dissolved in Different Diluents^a

Diluent	Pb^{2+}		Zn^{2+}	
	$\log K_{\text{ex}}$	$\text{pH}_{0.5}$	$\log K_{\text{ex}}$	$\text{pH}_{0.5}$
Kerosene	-1.03	2.80	-0.15	2.40
Cyclohexane	-1.30	2.98	-0.43	2.50
Carbon tetrachloride	-2.00	3.30	-0.74	2.70
1,2-Dichloroethane	-2.57	3.30	-1.37	2.70
Dichloromethane	-2.66	3.33	-1.82	2.90
Toluene	-3.13	3.55	-1.45	3.05
Chloroform	-3.64	3.82	-2.42	3.20

^aExperimental conditions: see the caption of Fig. 1.

the extraction of lead. Besides, the $\log K_{\text{ex}}$ values confirm that the extraction efficiency of the DEHPA dissolved in the investigated diluents varies as kerosene > cyclohexane > carbon tetrachloride > 1,2-dichloroethane > dichloromethane > toluene > chloroform for lead ions, and kerosene > cyclohexane > carbon tetrachloride > 1,2-dichloroethane > toluene > dichloromethane > chloroform for zinc ions.

The logarithmic analysis has been used for approving the suggested extracted species as $\text{ML}_2(\text{HL})_2$ (M is Zn^{2+} and Pb^{2+}). The logarithmic form of Eqs. (3) and (4) are shown by Eqs. (8) and (9):

$$\log D = \log k_{\text{ex}} + n \log [\text{HL}]_{0,\text{org}} + npH \quad (8)$$

$$\log D = \log k_{\text{ex}} + n \log [(\text{HL})_2]_{0,\text{org}} + npH \quad (9)$$

where “D” in these equations are defined with Eqs. (10) and (11), respectively:

$$D = \frac{[\text{ML}_n]_{\text{org}}}{[\text{M}^{n+}]} \quad (10)$$

$$D = \frac{[\text{ML}_n(\text{HL})_n]_{\text{org}}}{[\text{M}^{n+}]} \quad (11)$$

A plot of $\log D$ versus aqueous phase pH (Fig. 3), under the condition in which the DEHPA concentration is constant, for the extraction process in polar and nonpolar organic diluents for lead and zinc ions allowed evaluating the term “n”. This analysis approved the suggested stoichiometry considered for the complexes of Pb^{2+} , Zn^{2+} extracted to the organic phase *i.e.* $n = 2$.

For evaluating the selectivity of the proposed solvent extraction of Pb^{2+} and Zn^{2+} by bid(2-ethylhexyl)phosphoric acid in the studied organic diluents, the definition of selectivity factor (SF) was applied (Eq. (12)):

$$SF_{\frac{M_1}{M_2}} = \log \frac{D_{M_1}}{D_{M_2}} \quad (12)$$

The term “D” (distribution ratio) is the concentration ratio of the metal ion in the aqueous phase to that in the organic phase. This term can be defined by rearranging Eqs. (3) and (4) as follows:

$$D_M = K_{\text{ex}} \frac{[\text{HL}]_{\text{org}}^n}{[\text{H}^+]^n} \quad (13)$$

$$D_M = K_{\text{ex}} \frac{[(\text{HL})_2]_{\text{org}}^n}{[\text{H}^+]^n} \quad (14)$$

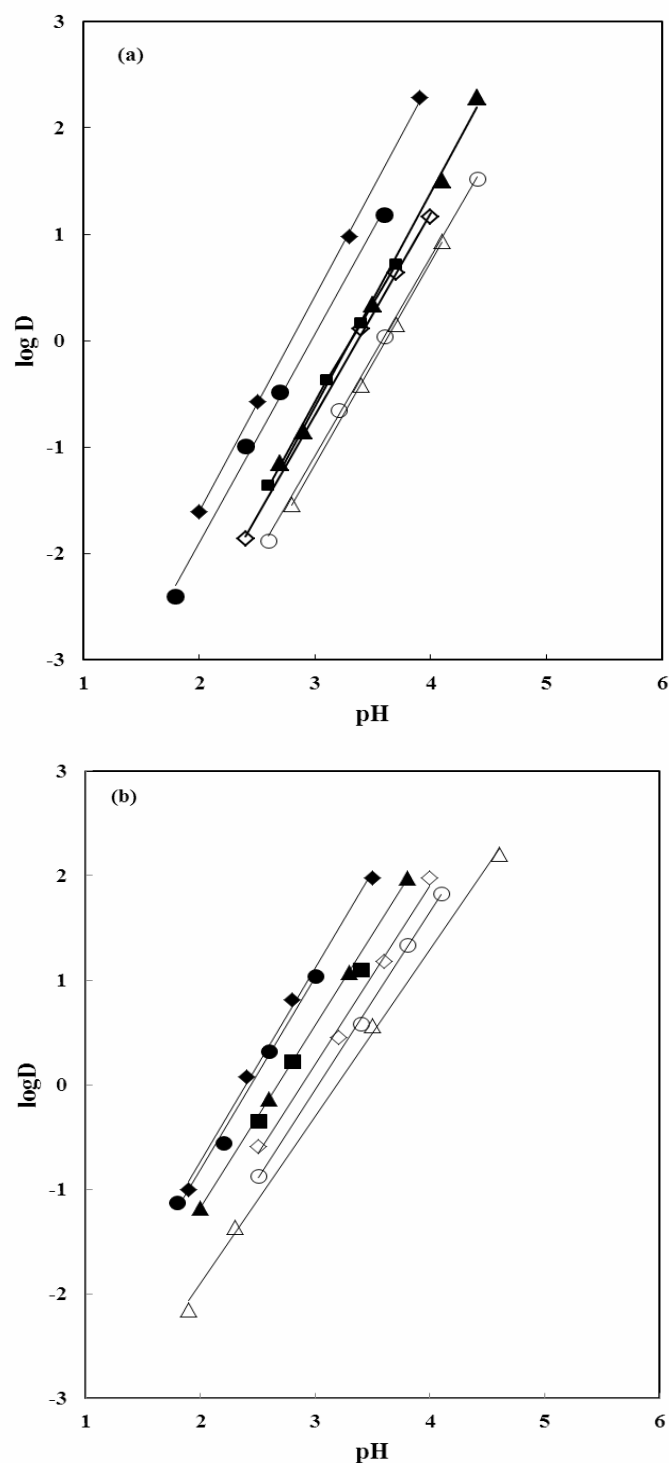


Fig. 3. The plot of $\log D$ versus the aqueous phase pH for the extraction of (a) Pb^{2+} and (b) Zn^{2+} (initial concentration $9.65 \times 10^{-4} \text{ M}$) by DEHPA (0.01 M) dissolved in kerosene (\blacklozenge), cyclohexane (\bullet), 1,2-dichloroethane (\blacksquare), carbon tetrachloride (\blacktriangle), dichloromethane (\diamond), toluene (\circ), and chloroform (\triangle), as a function of pH, at 25 °C.

Table 2. Calculated Selectivity of the Extraction of Zinc(II) with Respect to Lead(II) by DEHPA in Different Organic Diluents

Diluent	C ₇ H ₈	CCl ₄	CHCl ₃	C ₂ H ₄ Cl ₂	Kerosene	C ₆ H ₁₂	CH ₂ Cl ₂
SF _{Zn/Pb}	1.68	1.30	1.22	1.20	0.88	0.87	0.84

By inserting Eq. (8) or Eq. (9) in Eq. (12), and considering the equal charges of the studied ions ($n = 2$), the selectivity factor ($SF_{Zn/Pb}$) for both types of the extraction equilibrium is calculated by Eq. (11):

$$SF_{Zn/Pb} = \log \frac{K_{ex.Zn}}{K_{ex.Pb}} \quad (15)$$

The estimated selectivity factors in the examined organic diluents are given in Table 2. The results revealed that the maximum selectivity of DEHPA towards zinc to lead ions can be attained by using toluene as the organic diluent. This selectivity decreased by replacing toluene with carbon tetrachloride. The selectivity factor of Zn^{2+}/Pb^{2+} in this latter diluent was close to that found by using chloroform and 1,2-dichloroethane. The lowest but close values of the selectivity factors were observed by employing kerosene; cyclohexane and dichloromethane as organic diluents.

Extraction of Pb^{2+} and Zn^{2+} by DEHPA in the Presence of Ethylene Glycols

Although DEHPA is known as a powerful extractant, the extraction processes of metals based on this extractant suffer from poor selectivity for achieving efficient separations. As it was observed in the first part of this study, the organic diluents used in such extraction processes may be considered as a way to improve the separation of metals. However, this plan does not generally offer the desired selectivity. An alternative design has been proposed by the addition of a masking agent into the aqueous phase containing the cations, so that this agent binds selectively the cations to be extracted by DEHPA [14-21].

Polyethylene glycols (PEGs) with ethylene oxide units can wrap the cations *via* the interaction of the lone pair electrons of their oxygen atoms with cations [28]. This phenomenon allowed the extraction of the cation, which has

a more stable complex with the dissolved PEG in the aqueous phase, decreases and take place at higher pH value with respect to the competing cations. The applied PEG plays here the role of a masking agent which can improve the separation characteristics of a solvent extraction process [29].

The possible improvement in the separation of lead and zinc ions, the solvent extraction of these ions by DEHPA dissolved in carbon tetrachloride, as an organic phase, at 25 °C, was studied. The organic phase was contacted with the aqueous phase containing the target ions and the PEGs (PEG₂₀₀ and PEG₂₀₀₀, the polyethylene glycols with mean molecular weight of 200 and 2000) as masking agent. Carbon tetrachloride was selected because the studied PEGs have a negligible solubility in this diluent. The plots of the extracted amount of lead and zinc ions (initial concentration 9.65×10^{-4} M) in the absence and presence of PEG₂₀₀ (0.5 M) or PEG₂₀₀₀ (0.005 M) by DEHPA (0.01 M¹) dissolved in carbon tetrachloride versus the aqueous phase pH are presented in Fig. 4. The applied concentration of PEG₂₀₀₀ was determined by the solubility limit of this polyethylene glycol in the aqueous phase. It was seen that the extraction curve of Zn^{2+} *versus* the aqueous phase pH was not influenced by the presence of PEGs. In contrast, the extraction curves of the lead ions in the presence of the studied PEGs were displaced towards higher pH values. These results showed clearly the effective binding of lead ions by PEG₂₀₀ and PEG₂₀₀₀.

The quantification of these interactions can be achieved by comparing the values of $pH_{0.5}$ of the studied extraction systems (Table 3). The larger displacement of $pH_{0.5}$ for the solvent extraction of Pb^{2+} from the aqueous solution containing PEG₂₀₀₀ with respect to that of PEG₂₀₀ shows the higher interaction of lead ions with PEG₂₀₀₀. It is worthy of note that this higher displacement of $pH_{0.5}$ in the presence of PEG₂₀₀₀ was observed although its concentration was lower

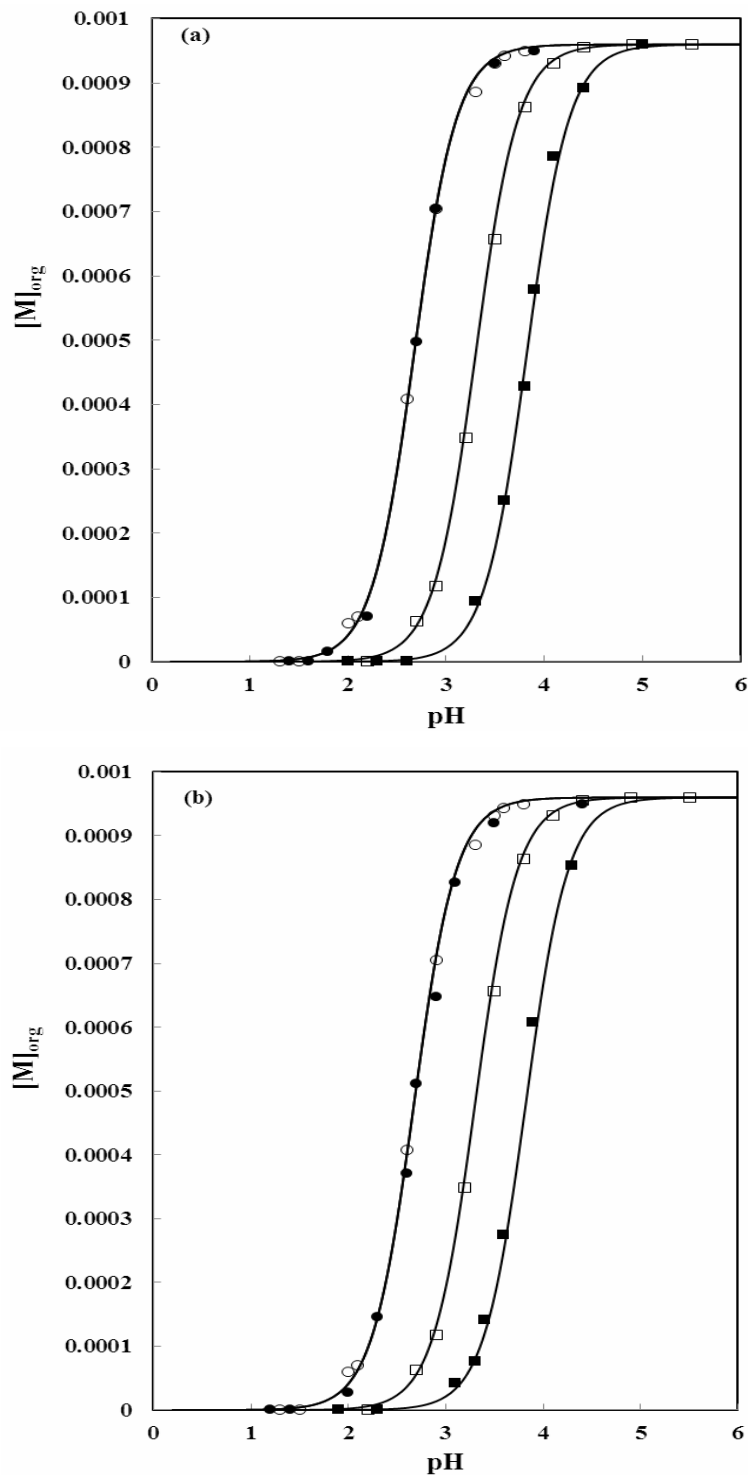


Fig. 4. Variation of the extracted amounts of lead (\square, \blacksquare) and zinc (\circ, \bullet) (initial concentration 9.65×10^{-4} M) by DEHPA (0.01 M) dissolved in carbon tetrachloride in the absence (open markers) and presence (filled markers) of PEG₂₀₀ (a) and PEG₂₀₀₀ (b) in the aqueous phase, as a function of the aqueous phase pH, at 25 °C.

Table 3. Evaluated $pH_{0.5}$ Values of the Extraction of Lead and Zinc Ions in the Absence and Presence of PEG₂₀₀ and PEG₂₀₀₀ by DEHPA Dissolved in Carbon Tetrachloride

Metal ion	$pH_{0.5}^a$	PEG ₂₀₀		PEG ₂₀₀₀	
		$pH_{0.5}$	$\Delta pH_{0.5}$	$pH_{0.5}$	$\Delta pH_{0.5}$
Pb ²⁺	3.30	3.58	0.28	3.95	0.65
Zn ²⁺	2.70	2.70	-	2.70	-

^aIn the absence of polyethylene glycols.

than that of PEG₂₀₀. This observation revealed the more selective separation of zinc from lead ions by the extraction system in which PEG₂₀₀₀ is chosen as a masking agent.

The mathematical description of the metal/PEGs interactions can be presented by analyzing the extraction data based on the extraction equilibrium reaction presented in Eq. (2) ($n = 2$) and the lead ion complexation reaction by the polyethylene glycols (Eq. (16)). It is noteworthy that a 1:1 stoichiometry was considered for the complex of Pb²⁺ and PEGs [28]. In fact, the metal cation is surrounded by one complexing molecule. The corresponding complexation reaction is:



and its equilibrium constant is:

$$\beta = \frac{[Pb(PEG)_2]^{2+}}{[Pb^{2+}][PEG]} \quad (17)$$

As the DEHPA and PEGs concentrations were significantly higher than those of the lead ions, the equilibrium concentration of DEHPA and PEGs can be considered as their initial concentrations:

$$[(HL)_2]_{org} = [(HL)_2]_{0,org} \quad (18)$$

$$[PEG] = [PEG]_0 \quad (19)$$

The mass balance for the lead species is defined by Eq.

(20):

$$[Pb^{2+}] = [MPb^{2+}]_0 - [Pb]_{org} - [Pb(PEG)^{2+}] \quad (20)$$

thus, the variation of the extracted lead ions with the pH of aqueous phase, when one of the PEGs are presented in the aqueous phase can be evaluated by fitting the experimental data using Eq. (21):

$$[Pb]_{org} = \frac{K_{ex}[Pb^{2+}]_0[(HL)_2]_{0,org}^2}{[H^+]^2(1 + \beta[PEG]) + K_{ex}[(HL)_2]_{0,org}^2} \quad (21)$$

Considering the evaluated K_{ex} (Table 1) and by using Eq. (21), the analysis of the data presented in Fig. 4 allowed evaluating the $\log\beta$ for the Pb²⁺ complexes by PEG₂₀₀ and PEG₂₀₀₀ which were 1.00 and 5.60, respectively.

Zinc ions did not have detectable interaction with dissolved PEGs, therefore Eq. (14) can be used for the definition of its distribution ratio (D) for such extraction conditions. However, for the extraction of Pb²⁺ from the aqueous solutions containing a masking agent (PEG₂₀₀ or PEG₂₀₀₀), the distribution coefficient is determined by Eq. (22).

$$D_{Pb} = K_{ex,Pb} \frac{[(HL)_2]_{org}^2}{[H^+]^2(1 + \beta_{Pb}[PEG]^2)} \quad (22)$$

The selectivity factor for the presented extraction system towards zinc ions with respect to the lead ions was appraised by employing Eq. (23).

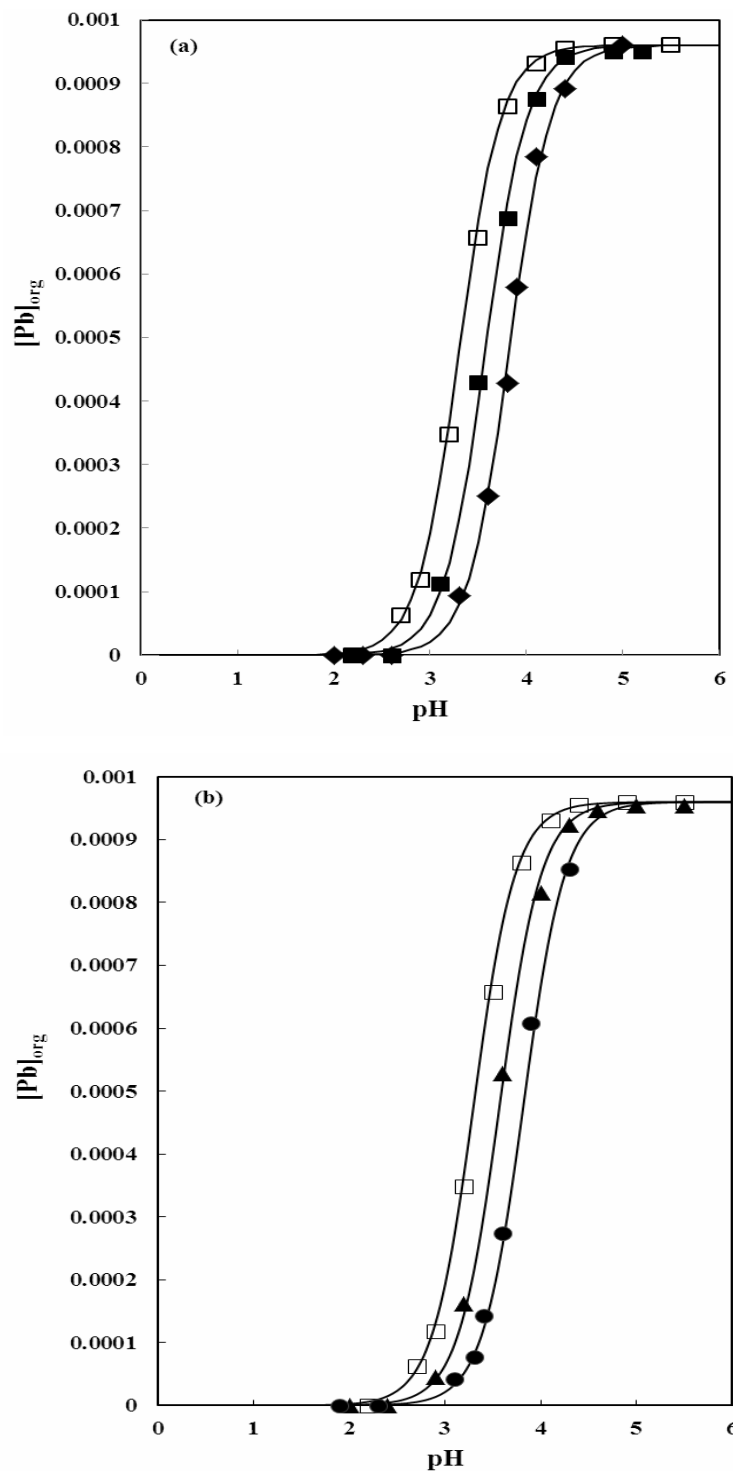


Fig. 5. Variation of the extracted amounts of Pb^{2+} (initial concentration 9.65×10^{-4} M) in the absence (open markers) and presence of (a) 0.5 (■) and 1 (◆) M PEG₂₀₀, and (b) 0.0025 (▲) and 0.005 (●) M PEG₂₀₀ as a function of the aqueous phase pH, at 25 °C.

$$SF_{\frac{Zn}{Pb}} = \log \frac{D_{Zn}}{D_{Pb}} = \log \left(\frac{K_{ex,Zn}(1 + \beta_{Pb})}{K_{ex,Pb}} \right) \quad (23)$$

The evaluated selectivity factors for the extraction system, in which PEG₂₀₀ and PEG₂₀₀₀ have been used as masking agents, have been appraised to be 2.30 and 6.86. A comparison of these data with those obtained in the absence of PEGs ($SF_{Zn/Pb} = 1.26$, Table 2) confirmed the role of these compounds as masking agents of lead ions which results in a significant improvement in the selective attitude for the extraction of Zn²⁺ by the proposed extraction process. Besides, these values revealed the more efficacious influence of PEG₂₀₀₀ (close to three times) in comparison with PEG₂₀₀ for the separation of Zn²⁺ and Pb²⁺.

The effect of the amount of PEGs used in the aqueous phase on the transposition of the extraction curves to the pH_{0.5} values ($\Delta pH_{0.5} > 0$) was monitored by following the solvent extraction experiments of Pb²⁺ by DEHPA dissolved in carbon tetrachloride, from the aqueous solution containing different concentrations of PEG₂₀₀ (0, 0.5 and 1.5 M) or PEG₂₀₀₀ (0, 0.0025 and 0.005 M).

Masking Versus the Synergistic Effect of Polyethylene Glycol; Effect of the Organic Diluent

As pointed out, the organic diluent was selected based on the insolubility of the studied PEGs in the organic phase. These characteristics prevent the distribution of both polyethylene glycols and their metal-complexes into the organic phase. This was desired for approaching to the aim of using PEGs as the masking agent. In fact, under such condition an improved selectivity for the studied extraction system can be accessed.

Otherwise, it was suggested that the distribution of PEGs might offer a cooperative (synergistic) effect on the solvent extraction of the ions bearing the potential to be complexed by PEGs. This suggestion came from this fact that the formation of more lipophilic species of lead ions with PEGs favors the transfer of the formed species to the organic phase capable to dissolve the lipophilic complex.

To examine this suggestion, the solvent extraction of Pb²⁺ from aqueous solution without and with PEG₂₀₀ (0.5 M) was performed by using a chloroform solution of DEHPA (0.01 M) as the organic phase by variation of the aqueous phase pH (Fig. 4). Chloroform was selected

because PEG₂₀₀ is soluble in this diluent. The results were compared with the extraction of lead into the organic phase composed of DEHPA in carbon tetrachloride in the absence and presence of PEG₂₀₀ (Fig. 6).

The extraction curve of lead into chloroform in the presence of PEG₂₀₀ displaced to the lower pH value region with respect to that in the absence of PEG (pH_{0.5} values were 3.82 and 3.15, in the absence and presence of PEG₂₀₀, respectively). In contrast, by using carbon tetrachloride a masking effect was demonstrated for PEG₂₀₀ towards lead ions (pH_{0.5} values were 3.30 and 3.58, in the absence and presence of PEG₂₀₀, respectively). The results denote the crucial role of the organic diluent as masking or synergistic agent on the solvent extraction of Pb²⁺ in the presence of PEG₂₀₀.

CONCLUSIONS

Bis(2-ethylhexyl)phosphoric acid (DEHPA) dissolved in the organic diluents chloroform, dichloromethane, 1,2-dichloroethane, carbon tetrachloride, toluene, cyclohexane and kerosene acts as an efficient extractant towards both of the lead and zinc ions with a preference towards the latter ions. The combination of chelating properties of DEHPA in carbon tetrachloride and the complexation of lead ions by polyethylene glycols with the molecular mass 200 (PEG₂₀₀) and 2000 (PEG₂₀₀₀), in the aqueous phase, enhances the extraction-separation of zinc and lead ions. The source of such modification is attributed to the insolubility of the studied polyethylene glycols in carbon tetrachloride and the binding of lead ions by PEG₂₀₀ and PEG₂₀₀₀ in the aqueous phase. The diluent used influences profoundly the effect of PEGs in the solvent extraction as masking or synergistic effect. It was demonstrated that the application of chloroform, which can dissolve PEG₂₀₀, results in a synergistic effect for the extraction of Pb²⁺.

The low price and commercially available polyethylene glycols make them suitable candidates for their application in industrial extraction processes. This potential can be appraised by developing this study to other aspects which are important for an industrial application. Among these considerations, employing the more environmentally-friendly organic diluents is crucial.

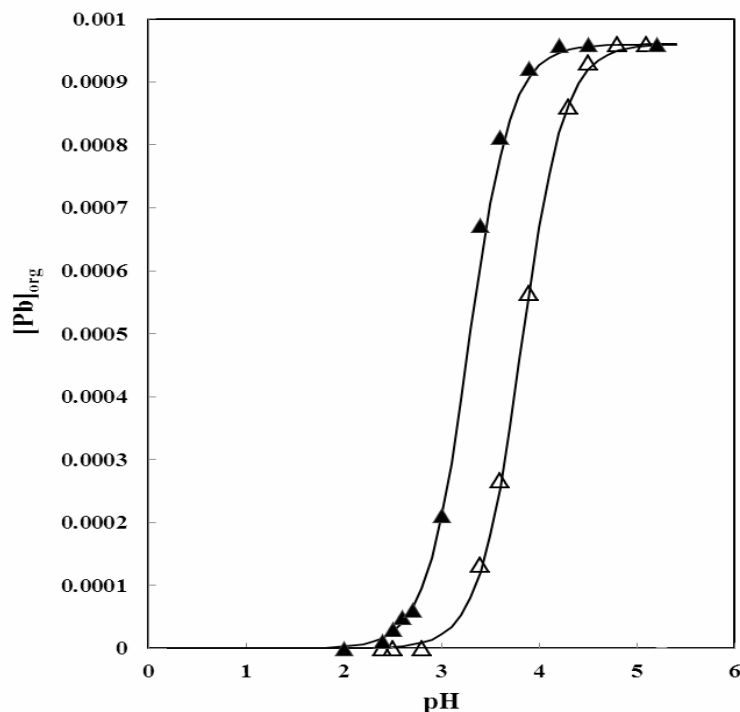


Fig. 6. Variation of the extracted amounts of Pb^{2+} (initial concentration 9.65×10^{-4} M) in the absence (Δ) and presence (\blacktriangle) of PEG_{200} (0.5 M) as a function of the aqueous phase pH, at 25 °C.

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