

# Extraction of Lead Ions and Partitioning Behaviour in Aqueous Biphasic Systems Based on Polyethylene Glycol and Different Salts

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## **Abstract**

Lead ions are environmental pollutants often present in very low concentrations, which makes them difficult to detect and, thus, present problems for environmental monitoring. In this study, we examined the performance of aqueous biphasic systems based on polyethylene glycol (PEG, molecular mass of 4000 g mol<sup>-1</sup>) with ammonium sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, magnesium sulphate (MgSO<sub>4</sub>), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) and trisodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>) for the separation of lead (II) ions from aqueous solutions. We investigated the effects of salt types and the ratio of PEG4000 to salt on the extraction efficiency of lead (II) removal at constant temperatures of 303 K and 0.1 MPa. Additionally, we determined the cloud points (solubility equilibrium curve) and tie-lines for four ternary systems comprising PEG4000, water, and salt (either (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, or Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>) under the same conditions. A maximum lead (II) extraction efficiency of 74.4% was achieved using the PEG4000/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> system with a mass fraction ratio of PEG4000 to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> of 0.2:0.12. This outcome highlights the significant potential of utilizing aqueous biphasic systems based on PEG4000 to separate lead (II) from aqueous solutions efficiently.

## **Keywords:**

Aqueous two-phase system; Solubility; Polyethylene glycol; Lead extraction; Partition Coefficient

## 1. INTRODUCTION

Lead (Pb) is a heavy metal resistant to corrosion and radiation and, thus, widely used in various industries, including semiconductors, nuclear, mining, steel, and metallurgy [1-3]. Market demand for lead has increased in the last decade [4] due to the recent development in electronic devices, batteries, and cables [5]. Although the mineral industry has developed a highly efficient ion-exchange resin process for lead recovery, lead is still released into the environment with wastewater and distributed in the atmosphere, soil, and water [2,3].

Due to its toxicity, the released lead can severely affect the environment and human health [6, 7]. Plants and animals can ingest it since it accumulates in soil, water, and air. Contaminated soil and water are unsuitable for growing crops or other vegetation, harming aquatic life and reducing water quality [8]. Lead exposure can cause neurological problems in adults, developmental problems in children, and cardiovascular problems, including high blood pressure and heart disease [9]. Thus, improving its removal and disposal is paramount to prevent adverse effects.

Several processes were used to remove and separate heavy metal ions from natural waters, industrial wastewater, and contaminated soil [1]. The liquid-liquid extraction [10], cation adsorption [6], electrochemical treatment [11], coagulation-flocculation [12], biosorption [13] were reported to remove lead from aqueous solutions. In this context of separation, the aqueous two-phase system (ATPS) is more efficient than the typical liquid-liquid extraction in hydrometallurgical processes and has an intriguing possibility for use in the metal recovery process [14,15]. The characteristics of ATPS take advantage of being non-flammable, non-toxic and less harmful than organic solvents [16-18] as well as exhibiting lower interfacial tension [19-21]. Therefore, the ATPS technique is used in hydrometallurgical processes to selectively recover metals [16,19]. The ATPS is created by combining two aqueous solutions (such as polymer/salt or polymer/polymer systems). After complete phase separation, two liquid phases are formed: a polymer-rich top phase (TP) and a salt-rich bottom phase (BP) [22].

ATPS systems have been reported to extract lead from aqueous solutions, as summarized in Table 1. In 2012, Debashree Das et al. [23] used an ATPS consisting of a nonionic surfactant Triton X-100 in combination with trisodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) and magnesium sulphate ( $\text{MgSO}_4$ ) for the extraction of lead ( $\text{Pb(II)}$ ) from lead dithizone complex. They found that Pb from lead dithizone complex was not extracted in the Triton phase even though lead ( $\text{Pb(II)}$ ) from a metal mixture (Hg, Bi and Pb) was completely extracted at pH 8.9. In addition, Kaustab Ghosh et al. [24] studied the separation of no-carrier-added (NCA)  $^{203}\text{Pb}$  (lead radionuclide) from proton irradiated  $^{\text{nat}}\text{Tl}_2\text{CO}_3$  target and found that about 60% of (NCA)  $^{203}\text{Pb}$  was extracted by using ionic liquid, 1-butyl-3-methylimidazolium chloride ([bmim]Cl), and  $\text{K}_2\text{HPO}_4$  salt ATPS system. To the best of our knowledge, there is only one report on using aqueous biphasic systems based on polyethylene glycol, namely PEG1500/ $(\text{NH}_4)_2\text{SO}_4$  and PEG1500/ $\text{NaCl}$  to extract lead ions [25]. The authors reported that the maximum extraction yield was 51.8%.

In this study, we report the ATPS based on PEG4000 with either magnesium sulfate, sodium sulfate, ammonium sulphate or trisodium citrate to extract lead ions ( $\text{Pb(II)}$ ) from water at 303 K. Reported data include cloud points, solubility curves, critical points, tie-lines, partition coefficients and extraction efficiencies.

**Table 1** Extraction efficiency (*EE*) of  $\text{Pb(II)}$  ion in different ATPS systems.

Solvent <sup>a</sup>	Salt	Feed	<i>pH</i>	Maximum Extraction Efficiency <i>EE</i> (%)	Ref.
Triton X-100	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	$\text{Pb}(\text{NO}_3)_2$ solution	8.6	99.0	[23]
		Pb Dithizone complexes	8.6	0	
		Mixture of Hg, Bi and Pb	8.9	80.0	
		Dithizone complexes of Hg, Bi and Pb mixture.	8.9	0	
	$\text{MgSO}_4$	$\text{Pb}(\text{NO}_3)_2$ solution	9.5	65.0	
		Pb Dithizone complexes	9.5	0	
		Mixture of Hg, Bi and Pb	8.9	90.0	
		Dithizone complexes of Hg, Bi and Pb mixture.	8.9	0	
[bmim]Cl	$\text{K}_2\text{HPO}_4$	$^{203}\text{Pb}$ (lead radionuclide)	-	60.0	[24]
PEG1500	$(\text{NH}_4)_2\text{SO}_4$ (0.04 mol/L NaCl added)	$\text{Pb}(\text{NO}_3)_2$ solution	2.8	51.8	[25]

<sup>a</sup>Triton X-100 is Octyl phenol ethoxylate ( $\text{C}_{34}\text{H}_{17}\text{O}_7$ ); [bmim]Cl is 1-butyl-3-methylimidazolium chloride; PEG1500 is polyethylene glycol (molar mass  $1500 \text{ g mol}^{-1}$ ).

## 2. EXPERIMENTAL

### 2.1. Materials and Chemicals

All chemicals used in this work are summarized in Table 2. Polyethylene glycol (PEG) with a molar mass of 4000 g mol<sup>-1</sup> was purchased from Merck, Sigma-Aldrich. Ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> with purity ≥99.5 mass% was acquired from QReC. Magnesium sulfate (MgSO<sub>4</sub>) with purity ≥99 mass% was obtained from KemAus, while sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) with purity ≥99 mass% and trisodium citrate dihydrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>) with purity ≥99 mass% was obtained from Loba Chemie PVT Ltd. Lead (Pb(II)) standard solutions (1000 mg L<sup>-1</sup>) (Pb(NO<sub>3</sub>)<sub>2</sub> in HNO<sub>3</sub> 0.5 mol L<sup>-1</sup>) was purchased from PanReac AppliChem. Deionized water by MSECO DI-15A Model was used for solution preparations. All mixtures were gravimetrically prepared using an analytical balance (Sartorius TE214S with an accuracy of 0.0001 g).

**Table 2.** Chemicals Used in This Work.

Chemical	Source	Molecular Formula	Molecular mass (g mol <sup>-1</sup> )	Purity (%mass)
Polyethylene glycol (PEG)	Sigma Aldrich	C <sub>2n</sub> H <sub>4n+2</sub> O <sub>n+1</sub>	4000	100
Ammonium sulfate	QReC	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132.14	≥ 99.5
Magnesium sulfate	KemAus	MgSO <sub>4</sub>	138.36	≥ 99
Sodium sulfate	Loba Chemie	Na <sub>2</sub> SO <sub>4</sub>	142.04	≥ 99
Tri sodium citrate dihydrate	Loba Chemie	Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	294.10	≥ 99
Lead standard solution Pb(NO <sub>3</sub> ) <sub>2</sub> in HNO <sub>3</sub> 0.5 mol L <sup>-1</sup>	PanReac AppliChem	Pb(II)	207.19	1000 mg L <sup>-1</sup>

### 2.2. Cloud Points (Solubility Curves)

Cloud points of the ternary mixtures containing PEG4000, water, and salt (either Na<sub>2</sub>SO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> or MgSO<sub>4</sub>) were determined by the titration method at a constant temperature of 303 K and at a pressure of 0.1 MPa as described in our previous work [26]. Binary mixtures containing water and PEG4000 (40mass% PEG4000) were placed in septum-sealed glass vials with a magnetic stirrer bar. The vials were then immersed in a temperature-controlled bath using a complete set of heating and magnetic stirring equipment (C-MAG HS 7) with a temperature setting accuracy of 303 K (±1 K). The binary mixtures were slowly titrated with aqueous salt solutions 25 mass% Na<sub>2</sub>SO<sub>4</sub>, 25 mass%

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and 25 mass% Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, and 20 mass% MgSO<sub>4</sub> until the first turbidity was observed, which was taken as a cloud point. The final mixtures were weighed to calculate the composition corresponding to the cloud point. Three replicates of each assay were performed to validate the experimental method and the average reproducibility of the composition of cloud points (in mass fraction) was ±0.003.

The cloud points data were correlated by Merchuk's equation [27-29]:

$$x_{\text{PEG}} = A \cdot \exp[B \cdot x_{\text{salt}}^{0.5} - C \cdot x_{\text{salt}}^3] \quad (1)$$

where  $x_{\text{PEG}}$  and  $x_{\text{salt}}$  are mass fractions of PEG4000 and salt, respectively. Parameters  $A$ ,  $B$  and  $C$  were estimated from the regression of experimental cloud point data. The quality of Merchuk's equation [27] fitting was assessed in terms of the average standard error ( $ASE$ ) according to:

$$ASE(\%) = \frac{1}{N} \sum_i \frac{|x_{\text{PEG},i}^{\text{exp}} - x_{\text{PEG},i}^{\text{calc}}|}{x_{\text{PEG},i}^{\text{exp}}} \times 100 \quad (2)$$

where  $x_{\text{PEG},i}^{\text{exp}}$  and  $x_{\text{PEG},i}^{\text{calc}}$  are experimental and calculated mass fractions of PEG4000, respectively, and  $N$  is the number of cloud points data.

### 2.3. Tie-lines (TLs) and Critical Points

The methodology used for the tie-line determination has been described previously in great detail [20,29]. Here, only a short description is provided. Selected compositions of ternary mixtures containing PEG4000, water and salt (either Na<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, and MgSO<sub>4</sub>) were prepared gravimetrically in 15 mL glass vials. Firstly, the glass vials were agitated for at least two hours at a controlled temperature of (303 ± 1) K in a temperature-controlled bath using a complete set of heating equipment (C-MAG HS 7). Subsequently, the agitation was stopped, and mixtures were left still for at least 12 h. This was maintained at a consistent temperature using a temperature-controlled bath set to (303 ± 1) K. After this period, a complete phase separation was observed, with the top phase being PEG4000-rich and the bottom phase being salt-rich. Both phases were carefully separated and individually weighed using Sartorius TE214S analytical balance (an accuracy of ±0.0001 g). The same

experiment was repeated several times using different equilibrium times and it was estimated that 2 hours were sufficient to reach equilibrium. For convenience, the samples were left for at least 12 hours.

Parameters  $A$ ,  $B$ , and  $C$  obtained by the experimental regression of the composition cloud points from Eq. (1) and lever-arm rule were used to calculate the composition of PEG4000 and salt in the top and bottom phase of each individual TL, the following set of equations are obtained:

$$x_{\text{PEG}}^{\text{TP}} = A \cdot \exp[B \cdot (x_{\text{salt}}^{\text{TP}})^{0.5} - C \cdot (x_{\text{salt}}^{\text{TP}})^3] \quad (3)$$

$$x_{\text{PEG}}^{\text{BP}} = A \cdot \exp[B \cdot (x_{\text{salt}}^{\text{BP}})^{0.5} - C \cdot (x_{\text{salt}}^{\text{BP}})^3] \quad (4)$$

$$x_{\text{PEG}}^{\text{Total}} \cdot m_{\text{Total}} = x_{\text{PEG}}^{\text{BP}} \cdot m_{\text{BP}} + x_{\text{PEG}}^{\text{TP}} \cdot m_{\text{TP}} \quad (5)$$

$$x_{\text{salt}}^{\text{Total}} \cdot m_{\text{Total}} = x_{\text{salt}}^{\text{BP}} \cdot m_{\text{BP}} + x_{\text{salt}}^{\text{TP}} \cdot m_{\text{TP}} \quad (6)$$

where  $m_{\text{Total}}$ ,  $m_{\text{TP}}$ , and  $m_{\text{BP}}$  are the overall mass of the mixture, mass of the top phase, and mass of the bottom phase, respectively. Unknown variables  $x_{\text{PEG}}^{\text{TP}}$  and  $x_{\text{salt}}^{\text{TP}}$  are the mass fraction of the PEG4000 and salt in the top phase, respectively, while  $x_{\text{PEG}}^{\text{BP}}$  and  $x_{\text{salt}}^{\text{BP}}$  are the mass fraction of the PEG4000 and salt in the bottom phase, respectively. Four unknown variables ( $x_{\text{PEG}}^{\text{TP}}$ ,  $x_{\text{salt}}^{\text{TP}}$ ,  $x_{\text{PEG}}^{\text{BP}}$ , and  $x_{\text{salt}}^{\text{BP}}$ ) in a non-linear set of Eqs. (3)-(6) were solved by the Solver tool in Microsoft Excel® (Version 2304).

The slope of the tie-line ( $STL$ ) was calculated by the ratio between the mass fraction difference of PEG4000 and salt (either  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , and  $\text{MgSO}_4$ ) in the top and bottom phases according to:

$$STL = \frac{x_{\text{PEG}}^{\text{TP}} - x_{\text{PEG}}^{\text{BP}}}{x_{\text{salt}}^{\text{TP}} - x_{\text{salt}}^{\text{BP}}} \quad (7)$$

Tie-line length ( $TLL$ ) was calculated by the square root of the sum of the squares of the differences of PEG4000 and salt mass fractions in the coexisting phases according to Eq. (8):

$$TLL = \sqrt{(x_{\text{PEG}}^{\text{TP}} - x_{\text{PEG}}^{\text{BP}})^2 + (x_{\text{salt}}^{\text{TP}} - x_{\text{salt}}^{\text{BP}})^2} \quad (8)$$

The critical point (CP) for each ternary system was estimated using the so-called law of rectilinear diameter [30]. Firstly, the midpoints of each tie-line were plotted as a function of  $x_{\text{salt}}$  in the phase diagram, which defined the associated straight line using linear regression:

$$x_{\text{PEG}}^{\text{mid-point}} = f x_{\text{Salt}}^{\text{mid-point}} + g \quad (9)$$

where  $x_{\text{PEG}}^{\text{mid-point}}$  and  $x_{\text{Salt}}^{\text{mid-point}}$  are the mass fraction of PEG4000 and salt at the mid-point, respectively, while  $f$  and  $g$  are the fitting parameters. Finally, the critical point was determined as the interception of the line defined by Eq. (9) and the experimental binodal curve.

#### 2.4. Partition coefficient and extraction efficiency

The investigation of the partition coefficient of lead (Pb(II)) ion experiments was carried out in glass vials (15 mL) with a magnetic stirrer using the temperature-controlled bath at  $(303 \pm 1)$  K. The composition of PEG4000, distilled water, and salt (either  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , and  $\text{MgSO}_4$ ) was selected in such a way to form the aqueous biphasic system. The ternary mixtures were agitated by a magnetic stirrer at the same temperature. Subsequently, 100  $\mu\text{l}$  of lead (Pb(II)) standard solution (1000  $\text{mg L}^{-1}$ ) was added to the ternary mixtures. Therefore, the total mass of the Pb(II) ( $m_{\text{M}}^{\text{Total}}$ ) in all experiments was 0.1 mg. The mixtures were agitated for at least 2 h and then left still for at least 12 h at the constant temperature to reach equilibrium and complete phase separation. The bottom phase from the mixture was transferred to a 15 mL sample vial using a syringe. The samples were prepared for further analysis to determine the concentration of Pb(II) ions in the bottom phase ( $C_{\text{M}}^{\text{BP}}$ ) using flame atomic absorption spectrometry (Flame-AAS, Analyst 200 + flas 400; Perkin-Elmer).

The mass of Pb(II) in the bottom phase ( $m_{\text{M}}^{\text{BP}}$ ) was calculated using previously determined ( $C_{\text{M}}^{\text{BP}}$ ) and the volume of the bottom phase ( $V_{\text{BP}}$ ) determined by multiplying the density of the bottom phase by the measured mass of that phase, according to:

$$m_{\text{M}}^{\text{BP}} = C_{\text{M}}^{\text{BP}} \cdot V_{\text{BP}} \quad (10)$$

The mass of Pb(II) in the top phase ( $m_{\text{M}}^{\text{TP}}$ ) and Pb(II) concentration in the top phase ( $C_{\text{M}}^{\text{TP}}$ ) were calculated according to Eqs (11)-(12):



$$m_M^{TP} = m_M^{Total} - m_M^{BP} \quad (11)$$

$$C_M^{TP} = \frac{m_M^{TP}}{V_{TP}} \quad (12)$$

where  $V_{TP}$  is the volume of the top phase determined by multiplying the density of the bottom phase by the measured mass of that phase.

The partition coefficient was calculated using the following equation:

$$K = \frac{C_M^{TP}}{C_M^{BP}} \quad (13)$$

where  $C_M^{TP}$  and  $C_M^{BP}$  are the concentrations of Pb(II) ( $\text{mg L}^{-1}$ ) in the top and bottom phase, respectively.

The extraction efficiency ( $EE$ ) was calculated using the following equation:

$$EE(\%) = \frac{m_M^{TP}}{m_M^{Total}} \times 100 \quad (14)$$

where  $m_M^{TP}$  is the mass of Pb(II) in the top phase, and  $m_M^{Total}$  is the total mass (feed) of Pb(II) in the system [22,28].

All presented results are the average of three replicate analyses. The maximum observed standard error for obtained partition coefficients for different replicas of the same assays is <3%.

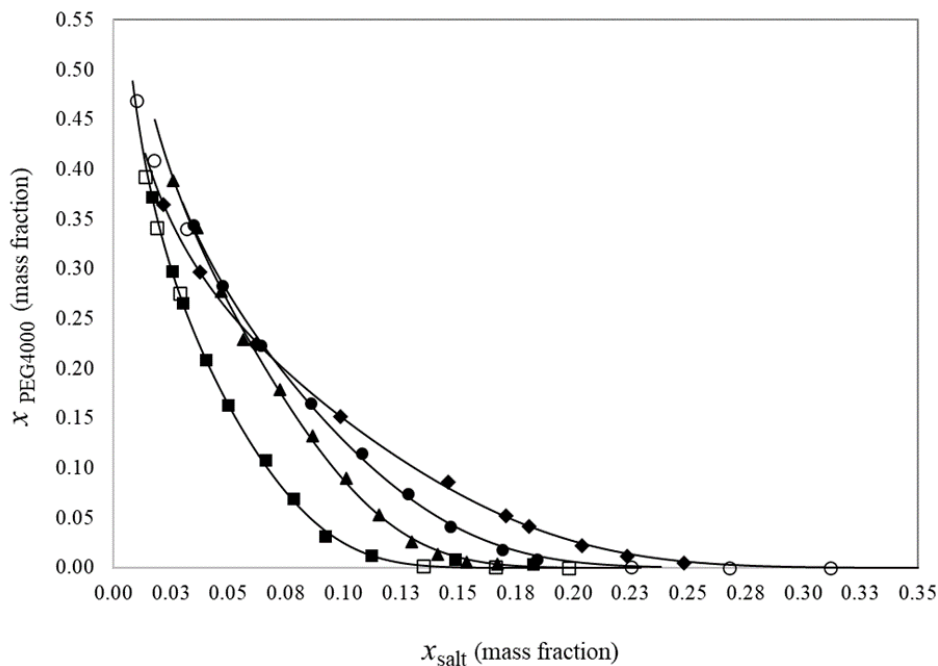
### 3. RESULTS AND DISCUSSION

#### 3.1 Cloud Points

Table S1 in the Supplementary Information presents experimental cloud points for the ternary mixtures containing PEG4000, water and salt (either  $\text{Na}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  or  $\text{MgSO}_4$ ) at 303 K and at a pressure of 0.1 MPa. These data were used to construct binodal lines, as shown in Figure 1. The area above and below the binodal curves denote the two-phase and single-phase regions, respectively. Components with a high phase segregation capacity are indicated by a binodal curve positioned closer to the origin, signifying that lower concentrations of the constituents are needed to

form a biphasic mixture. Both the type and concentration of salt significantly impacted the phase behaviour. In general, the ability of salt to induce phase separation followed the order  $\text{Na}_2\text{SO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 > \text{MgSO}_4$ . The experimental results for cloud points are consistent with the findings of Reinert Ramos Gandolfi et al. [18], who reported the cloud points of PEG4000 and salts ( $\text{Na}_2\text{SO}_4$  and  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) (white marker squares and circles in Fig.1).

The cloud point data were correlated using Eq. (1), as presented in Fig. 1. The obtained parameters  $A$ ,  $B$ , and  $C$  for each biphasic system are shown in Table 3, along with the coefficient of determination ( $r^2$ ) and the average standard error ( $ASE$ ) calculated according to Eq. (2). Correlations are reasonably good, with average standard deviations of 20.4%, 10.4%, 9.2%, and 8.7% for solutions with  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , and  $\text{MgSO}_4$ , respectively. Obtained parameters  $A$ ,  $B$ , and  $C$  were used to quantify the amount of each component in the top and bottom phases of the tie-lines by the lever rule.



**Figure 1.** Experimental solubility curves for the ternary mixtures containing polyethylene glycol (PEG4000), water, and salt ( $\text{Na}_2\text{SO}_4$ (■),  $(\text{NH}_4)_2\text{SO}_4$ (▲),  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (●), and  $\text{MgSO}_4$ (◆)), in mass fractions. Solid curves present fittings obtained by equation (1) using the obtained parameters given in Table 3. Literature solubility curve for the ternary solutions containing polyethylene glycol (PEG4000), water, and salt ( $\text{Na}_2\text{SO}_4$  (□) and  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  (○)) at 303 K and at 0.1 MPa [18].

**Table 3.** Parameters  $A$ ,  $B$  and  $C$  of Equation (1) Fitted to the Experimental Cloud Points for Four Ternary Systems at 303 K and at 0.1 MPa with associated standard deviations ( $\sigma$ ).<sup>a</sup>

System	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	$r^2$	$ASE$ (%)
PEG4000 + water + Na <sub>2</sub> SO <sub>4</sub>	0.928 ± 0.045	− 6.962 ± 0.314	1397.81 ± 128.31	0.9990	20.4
PEG4000 + water + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.873 ± 0.058	− 4.885 ± 0.359	740.96 ± 62.14	0.9982	10.4
PEG4000 + water + Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	0.888 ± 0.056	− 5.033 ± 0.301	343.53 ± 28.42	0.9989	9.2
PEG4000 + water + MgSO <sub>4</sub>	0.692 ± 0.017	− 4.315 ± 0.126	164.28 ± 8.77	0.9995	8.7

<sup>a</sup>  $r^2$  and  $ASE$  are the coefficient of determination and average standard error (Eq. (2)), respectively.

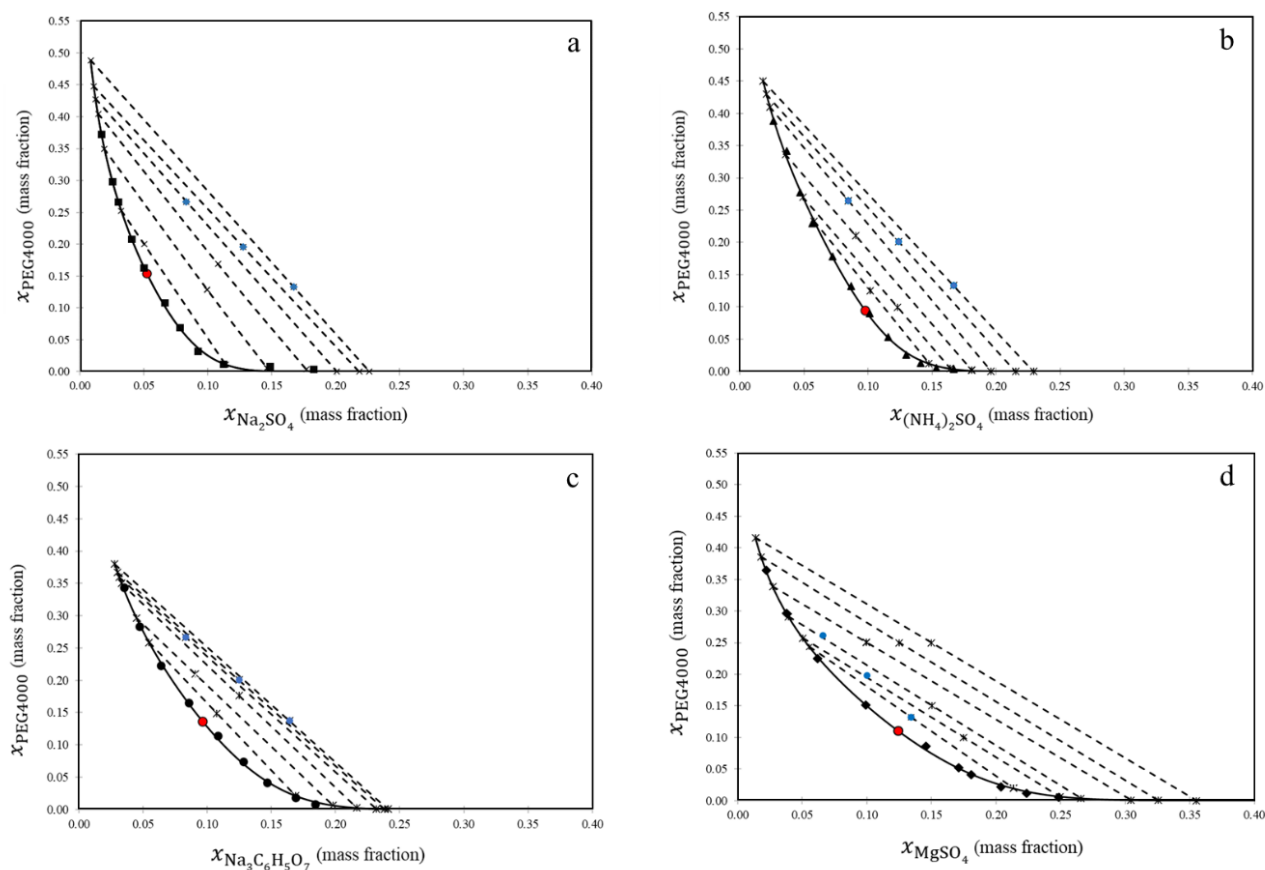
### 3.2. Tie-lines and Critical Points

Fig. 2 shows the cloud point curves with corresponding tie-lines for ternary solutions containing polyethylene glycol (PEG40000), water and salt (Na<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, and MgSO<sub>4</sub>) at 303 K and at 0.1 MPa. All tie-line data are included in Supplementary Information Table S2, along with the slope of the tie-line ( $STL$ ) and tie-line lengths ( $TLL$ ) calculated using Eq. (7) and Eq. (8), respectively. The increase in the overall salt or PEG4000 concentration enlarged the tie-line length for the four studied systems, indicating a larger difference between the compositions of the top and bottom phases (a higher degree of separation).

The critical points ( $x_{PEG}^{CP}$  and  $x_{Salt}^{CP}$ ), resulting from the intersection of the linear equation (Eq. (9)) with the binodal curve presented in Fig. S1, for each ternary system are given in Table 4. The table also includes the fitting parameters ( $f$  and  $g$ ) of the linear equation obtained from the tie-line relation point. The critical points of all the investigated systems are also illustrated in both Figs. 1 and 2. In the case of SO<sub>4</sub><sup>2-</sup>-based systems, salt composition at the critical point varies among all the studied systems. However, the composition of PEG4000 is similar for the (NH<sub>4</sub>)<sup>2+</sup> and Mg<sup>2+</sup> systems but is significantly different from the Na<sup>+</sup> system. When comparing the system of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> with Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, which differ in both the anion and cation, it was found that the salt concentration at the critical point was very similar, and the concentration of PEG4000 was different.

Table S1 in the Supplementary Information shows that the bottom phase of the systems had a greater water concentration than the upper phase. This is because salts and water have a higher degree of

similarity in terms of their polarity compared to the weakly polar PEG group, which leads to a stronger electrostatic interaction between water molecules and salts. The cations  $\text{Na}^+$ ,  $\text{NH}_4^+$ , and  $\text{Mg}^{2+}$  and the anions  $\text{C}_6\text{H}_5\text{O}_7^{3-}$  and  $\text{SO}_4^{2-}$  of salts interact significantly with water, affecting the hydrogen-bonding structure and thus their reactivity via the solubility property in water [31].



**Figure 2.** Cloud point curves (solid line) and corresponding tie-lines (dash line) for ternary solutions containing polyethylene glycol (PEG40000), water and salt at 303 K and at 0.1 MPa:  $\text{Na}_2\text{SO}_4$  (a);  $(\text{NH}_4)_2\text{SO}_4$  (b);  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  (c);  $\text{MgSO}_4$  (d); A polymer and salt composition in mass fraction ( $x_{\text{PEG4000}}$  and  $x_{\text{salt}}$ ) where partitioning behaviour of Pb(II) was evaluated (blue ●); critical point (red ●). Solid curves present fittings obtained by equation 1 using parameters given in Supplementary Information in Table S1.

**Table 4.** Critical Points of Four Ternary Systems Containing Polyethylene Glycol 4000 g mol<sup>-1</sup> (PEG4000), Water and Salt (either Na<sub>2</sub>SO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> or MgSO<sub>4</sub>) at 303 K and 0.1 MPa. <sup>a</sup>

System	The linear equation tie-line relation			Critical Point	
	<i>f</i>	<i>g</i>	<i>r</i> <sup>2</sup>	<i>x</i> <sub>PEG</sub> <sup>CP</sup>	<i>x</i> <sub>Salt</sub> <sup>CP</sup>
PEG4000 + water + Na <sub>2</sub> SO <sub>4</sub>	1.877	0.057	0.9611	0.155	0.052
PEG4000 + water + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	2.843	-0.182	0.9543	0.095	0.098
PEG4000 + water + Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	1.663	-0.023	0.9719	0.137	0.096
PEG4000 + water + MgSO <sub>4</sub>	1.317	-0.054	0.9692	0.110	0.125

<sup>a</sup> Parameters *f* and *g* of Eq. (9) fitted to the linear equation formed by the tie-line relation points and *r*<sup>2</sup> is the coefficient of determination. *x*<sub>PEG</sub><sup>CP</sup> and *x*<sub>Salt</sub><sup>CP</sup> are the mass fraction of the PEG4000 and salt at the critical point.

### 3.3. Partition Coefficient (*K*<sub>Pb</sub>) and Extraction Efficiency (%*EE*) of Lead (Pb(II)) Ions

The partition coefficient (*K*<sub>Pb</sub>) and extraction efficiency (%*EE*) of lead (Pb(II)) ion in the mixtures containing PEG4000, water, and salt (Na<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, and MgSO<sub>4</sub>) are provided in Table 5 as a function on the overall concentration, along with concentrations of lead (Pb(II)) ion in the top and bottom phase. As can be observed from Fig. 3, *K*<sub>Pb</sub> and *EE* were affected by the type of salt and composition of polymer per salt. The highest extraction efficiency of 74.7% was observed for the ATPS containing (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Comparing with the previous studies summarized in Table 1, this result is significantly higher than for other ATPS based on polyethylene glycol [24,25] but lower when some ATPS based on octyl phenol ethoxylate were used [23]. The second-highest extraction was achieved for the MgSO<sub>4</sub> system.

The partition coefficient in the Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> systems at all studied concentrations is less than unity, meaning that Pb(II) ion is more concentrated in the salt-rich phase. On the contrary, for the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> systems, the results indicate that the Pb(II) ion has a greater affinity for the more hydrophobic phase (*K*<sub>Pb</sub> > 1), which is the PEG-rich phase.

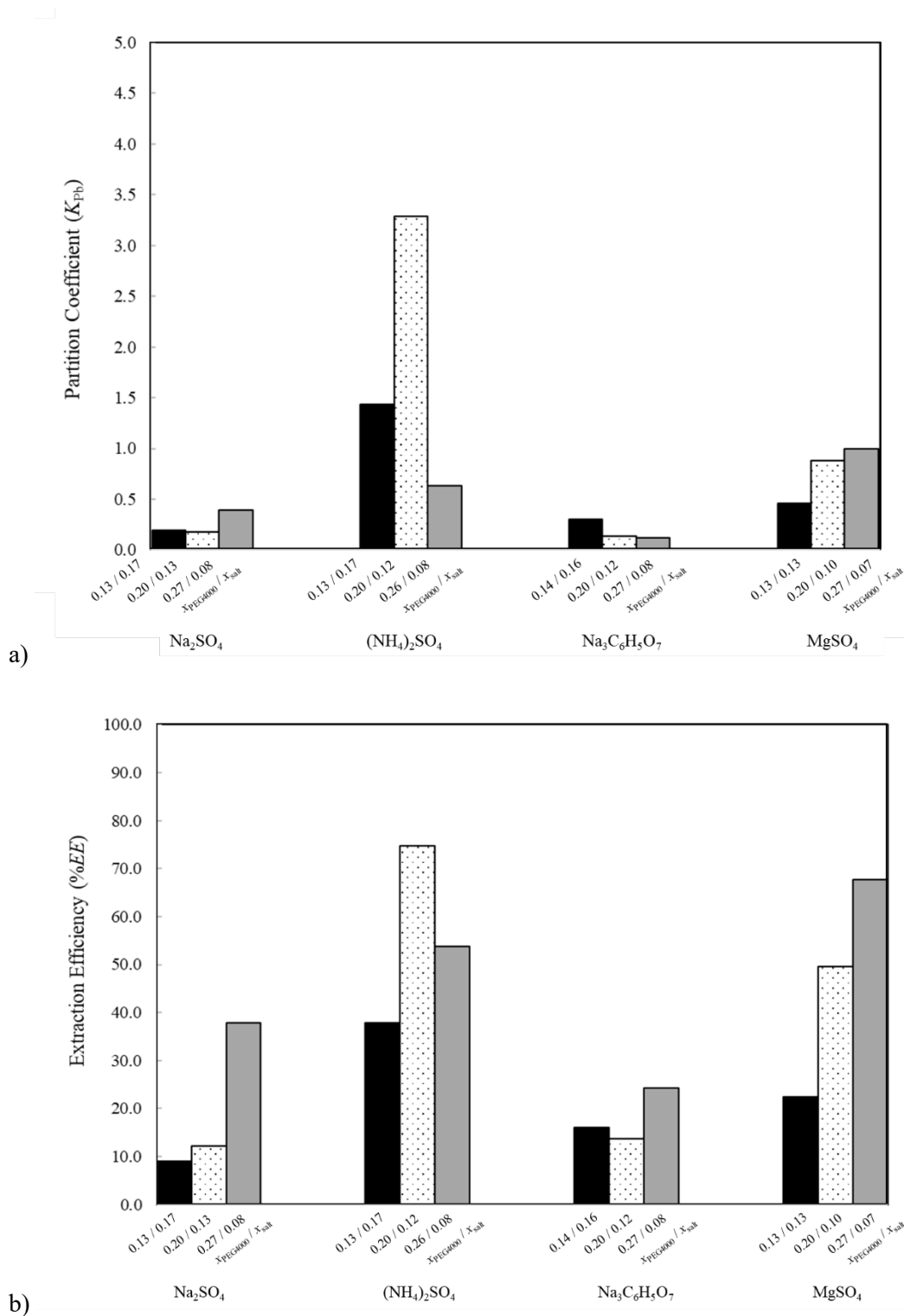
The tie-line length (*TLL*) is a parameter that indicates the difference in compositions between the polymer-rich and salt-rich phases in a liquid-liquid extraction system. It quantifies the extent of phase separation and reflects the influence of the two phases' compositions on the partitioning behaviour of specific components, such as Pb(II) in this case. A longer tie-line length implies a larger two-phase

region, providing more opportunities for the metal ions to partition between the phases. The blue solid points in Figure 2 represent a polymer and salt composition where the partitioning behaviour of Pb(II) was evaluated, along with the *TLL* provided in Table 5. In the Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> and MgSO<sub>4</sub> systems, an increased tie-line length led to a higher Pb(II) partitioning coefficient, indicating a stronger affinity of the metal ions for the polymer-rich phase. This could be attributed to specific interactions or complexations between Pb(II) and the polymer or salt components in these systems. On the other hand, in the Na<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> systems, an increase in tie-line length resulted in a decreased partitioning coefficient of Pb(II), indicating a reduced affinity for the polymer-rich phase. The reasons for this could include changes in the solvation or complexation behaviour of Pb(II) with the salt and polymer components [32-40], leading to a different distribution pattern. The variations in the polymer and salt concentrations in each phase can have a significant impact on the partitioning behaviour of Pb(II) and are important factors to consider when designing and optimizing the ATPS system for the extraction and separation of Pb(II).

**Table 5.** Partition Coefficients of Lead (Pb(II)) Ions in the Ternary Systems Containing Polyethylene Glycol 4000 g mol<sup>-1</sup> (PEG4000), Water and Salt (either Na<sub>2</sub>SO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> or MgSO<sub>4</sub>) at 303 K and 0.1 MPa. <sup>a</sup>

System	$x_{\text{PEG}}$ (g g <sup>-1</sup> )	$x_{\text{salt}}$ (g g <sup>-1</sup> )	$x_{\text{water}}$ (g g <sup>-1</sup> )	$C_{\text{Pb}}^{\text{Top Phase}}$ (mg L <sup>-1</sup> )	$C_{\text{Pb}}^{\text{Bottom Phase}}$ (mg L <sup>-1</sup> )	<i>TLL</i>	<i>K</i>	<i>EE</i> (%)
PEG4000 + water + Na <sub>2</sub> SO <sub>4</sub>	0.133	0.167	0.700	4.742	23.945	0.535	0.2	9.0
	0.196	0.128	0.677	4.849	27.462	0.494	0.2	12.1
	0.267	0.083	0.650	11.118	28.272	0.467	0.4	37.8
PEG4000 + water + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.133	0.167	0.700	22.306	15.520	0.497	1.4	37.9
	0.202	0.124	0.674	27.684	8.418	0.472	3.3	74.7
	0.265	0.085	0.651	14.528	23.124	0.444	0.6	53.8
PEG4000 + water + Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	0.137	0.164	0.699	7.254	24.012	0.435	0.3	16.0
	0.200	0.125	0.675	4.430	33.180	0.421	0.1	13.7
	0.267	0.083	0.650	5.907	50.520	0.410	0.1	24.2
PEG4000 + water + MgSO <sub>4</sub>	0.132	0.134	0.734	10.213	22.152	0.274	0.5	22.5
	0.198	0.101	0.701	16.507	18.696	0.320	0.9	49.5
	0.267	0.067	0.667	17.812	17.952	0.366	1.0	67.7

<sup>a</sup> The initial concentration of lead ion (Pb(II)) in feed solution was 17.540 mg L<sup>-1</sup>.  $x_{\text{PEG}}$ ,  $x_{\text{salt}}$  and  $x_{\text{water}}$  are mass fractions of PEG4000, salt, and water, respectively.  $C_{\text{Pb}}^{\text{Top Phase}}$  and  $C_{\text{Pb}}^{\text{Bottom Phase}}$  are concentrations of Pb(II) in the top and bottom phase, respectively. Standard uncertainties  $u$  is  $u(x) = \pm 0.003$ ,  $u(C_{\text{Pb}}) = \pm 0.003$  mg L<sup>-1</sup>,  $u(T) = \pm 1$  K, and  $u(p) = \pm 1$  kPa.



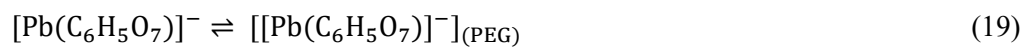
**Figure 3.** Partition coefficients of lead ion (Pb(II)) ( $K_{\text{pb}}$ ) (a) and Extraction Efficiency (%EE) (b), in biphasic systems composed of polyethylene glycol (PEG4000), water, and salt ( $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , and  $\text{MgSO}_4$ ) at 303 K and at 0.1 MPa, for different initial compositions in mass fraction ( $x_{\text{PEG4000}}/x_{\text{salt}}$ ). The initial concentration of lead ion Pb (II) in the feed solution was  $17.54 \text{ mg L}^{-1}$  in all partitioning experiments.

The partitioning of Pb(II) can be explained by the intermolecular forces in the mixture between metal ions with anions, complex metal with anions, and complex metal with polymer. The Pb(II) cation exists

in different forms in the initial solution and in two phases in equilibrium: polymer- and salt-rich phases. The interaction mechanism between Pb(II) ions and the components in the ATPS can be described according to the research literature [32-40]. In the salt-rich phase, the Pb<sup>2+</sup> cation forms a complex with the salt anion (SO<sub>4</sub><sup>2-</sup> and C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>3-</sup>) and water molecules, according to:



These complexes can establish hydrogen bonds with polyethylene glycol molecules [36,39] primarily by interaction through ionic forces with PEG ether oxygen atoms [33], enhancing their transfer into the PEG-rich phase:



On the other hand, some Pb<sup>2+</sup> cations will be retained in the bottom (salt-rich) phase due to interactions between the Pb(II) ions and the components of the ATPS, as described by Eqs. (15)-(17).

#### 4. Conclusion

This work focused on studying a polymer-based aqueous two-phase system for extracting Pb(II) ions. Aqueous two-phase system (ATPS) equilibrium data for the ternary mixtures (PEG4000 + Na<sub>2</sub>SO<sub>4</sub> + water), (PEG4000 + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + water), (PEG4000 + Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> + water), and (PEG4000 + MgSO<sub>4</sub> + water) were obtained at 303 K and at atmospheric pressure. The ability of salt to induce phase separation followed the order Na<sub>2</sub>SO<sub>4</sub> > (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> > Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> > MgSO<sub>4</sub>. The Pb(II) ion extraction was carried out at room temperature, and the behaviour of Pb(II) ions in ATPS was demonstrated through the assessment of the partition coefficient and extraction efficiency. The maximum extraction



efficiency of Pb(II) was 74.7% achieved with a mass fraction of PEG4000 per salt ratio of 0.2:0.12 in the PEG4000/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> system. The performance order of Pb(II) ion extraction efficiency was 74.7%, 67.7%, 37.8%, and 24.2% for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, and Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> systems, respectively. This suggests that the SO<sub>4</sub><sup>2-</sup> anion system could be a suitable option for extracting Pb(II) from aqueous solutions, particularly by utilizing (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> salts as additives in the PEG4000-based ATPS system for Pb(II) separation.

### **Acknowledgments**

The authors gratefully acknowledge the financial support provided by Thailand Science Research and Innovation under the Research and Researchers for Industries (RRi) Ph.D. Program (Grant No. PHD59I0016), Mektec Manufacturing Corporation (Thailand) Ltd. and Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University.

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