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Liquid–Liquid Equilibrium and Thermodynamic Modeling of Aqueous Two-Phase System Containing Polypropylene Glycol and $NaClO_4$ at T = (288.15 and 298.15) K

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Abstract In this work the phase equilibrium of an aqueous two phase system (ATPS) containing polypropylene glycol (PPG, molecular weight = 425 $kg \cdot mol^{-1}$) and $NaClO_4$ was investigated at atmospheric pressure and at 288.15 and 298.15 K. Two phase regions and composition of phases were determined. Our results show that as the temperature increases, the two-phase region expands. Also, the extended UNIQUAC (E-UNIQUAC) equation was used to correlate the equilibrium data. To reduce the number of adjustable parameters, ATPSs composed of PEG and PPG were collected from the literature and simultaneously correlated using the E-UNIQUAC model. Also, the effect of temperature on the liquid–liquid equilibrium (LLE) was considered by using temperature-dependent parameters. In the modeling, two different scenarios were supposed. In the first, polymer and salt were treated as solutes (Case A), while in the second, the pseudo-solvent approach was considered (Case B). The results showed good agreement with experimental data in both cases. The average absolute deviation of the model using Case B was about 0.2% and that for Case A was about 2% in the ATPS composed of PEG. Meanwhile, the reported errors in the ATPS containing PPG for Case A and Case B were almost equal.

Keywords Liquid–liquid equilibrium · Aqueous two-phase system · Electrolyte solution · Pseudo-solvent approach

List of symbols

G^{ex}	Excess Gibbs energy
n_D^o	Refractive index of water
A	Debye–Hückel constant
U_{ij}	Interaction parameters
b	Debye–Hückel constant

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d	Density ($kg\cdot m^{-3}$)
D	Mixed-solvent dielectric constant
I	Ionic strength on the molal scale
m	Molality
M	Molecular weight ($kg\cdot mol^{-1}$)
n_D	Refractive index
OF	Objective function
q	Surface parameter
r	Volume parameter
T	Temperature (K)
V	Molar volume
w	Weight percent
x	Mole fraction
Z	Charge number or coordination number (= 10)
γ	Activity coefficient
θ	Surface area fraction
φ and ϕ	Volume fraction

Superscripts

I	Bottom phase
II	Top phase
S	Number of tie lines
N	Number of components
cal	Calculated value
exp	Experimental value
UQ	UNIQUAC equation
DH	Debye–Hückel equation

1 Introduction

A mixture of aqueous solutions of two incompatible polymers (polymer/polymer system) or a polymer and a salt (polymer/salt system) can form a stable two-phase liquid system called an aqueous two-phase system (ATPS) [1–3]. In aqueous two-phase systems, 70 to 90% w/w of each phase is water, in this regard, they are considered to be environmentally friendly systems [4, 5]. Moreover, ATPSs are biocompatible, nontoxic and nonflammable [6, 7]. Ease of scale-up, lower interfacial tension, viscosity and cost of materials are some advantages of polymer/salt systems over the polymer/polymer systems [8, 9]. ATPS can be used for separation and purification of biomolecules [10] and metal ions [11, 12]. Polymer/salt systems spontaneously separate into a polymer-rich top phase and salt-rich bottom phase. Among all the polymers, polyethylene glycol (PEG) [13, 14], polypropylene glycol (PPG) [15, 16] and polyvinylpyrrolidone (PVP) [17, 18] have been most used. There are considerable numbers of experimental studies on application of PEG and PPG for ATPS in the literature. As example, Voros et al. [19] studied the equilibrium of ATPSs containing PEG_{1000} or PEG_{2000} in the presence of Na_2CO_3 or $(NH_4)_2SO_4$ at different temperatures and Mishima et al. [20] measured the LLE data of the PEG + K_2HPO_4 + H_2O system at 288.15, 308.15 and 318.15 K.

In addition to experimental studies, it is important to have a good thermodynamic model to describe and predict liquid–liquid equilibrium conditions in engineering and design. To obtain global and reliable parameters for thermodynamic models usually phase equilibrium data is suitable. As there is polymer, electrolyte and water in polymer/salt systems, all different types of interactions should be taken into account. Up to now, several models have been used, including NRTL [21–23], Chen–NRTL [24–26], Wilson [27], UNIQUAC [28], NRTL–NRF [29] and UNIFAC–NRF [30]. It has been shown that, in all cases, the models were successful in reproducing tie-line data of polymer/salt aqueous two phase systems. In most of the previous works, the excess Gibbs functions have been used for modeling. In this way, Jimenez et al. [31] determined the phase diagram and LLE results for ATPS containing PEG_{4000} and $NaClO_4$. They examined the Chen–NRTL, modified Wilson and UNIQUAC models to correlate the tie-line data in this system and reported that quality of fitting is better with the modified Wilson model. Recently, Valavi et al. [5] used the PHSC equation of state (PHSC EOS) for modeling of aqueous two phase systems. They found that PHSC EOS could correlate a considerable number of systems using just two adjustable parameters.

In this paper, in continuation of previous work [32–36], the experimental and thermodynamic behavior of system containing PPG, PEG, water and electrolyte is studied. The LLE data for the system containing PPG_{425} (polypropylene glycol with molecular weight of 425 $kg{\cdot}mol^{-1}$), $NaClO_4$ and water at 288.15, 298.15 K is measured experimentally at atmospheric pressure. Considering industrial applications of ATPSs, the experiments were carried out at moderate temperatures. The data are then modeled using the E-UNIQUAC model considering two scenarios (A and B). In the Case A, water is solvent while in the Case B, water–polymer was treated as a pseudo-solvent. Finally, the performance of the model in representing of the experimental data of the ATPS is examined in each case.

2 Experimental

2.1 Chemicals Used

The polypropylene glycol (purity above 99.9%) and sodium perchlorate of analytical grade (purity greater than 98%) were obtained from Sigma–Aldrich. All chemicals were used as received without further purification. In this work doubly distilled deionized water was used in all experiments.

2.2 Apparatus and Procedure

Sodium perchlorate was dried before use in an oven at 378.15 K for 3 days. The experiments were carried out in 15 mL test tubes. Feed samples were prepared by mixing appropriate amounts of materials. The sample solutions were mixed for 1 h and then were placed in a water bath at constant temperatures for 36 h to reach equilibrium with clear phases. The temperature was controlled using a water bath with a precision of ± 0.1 K. Samples of both phases were taken with plastic syringes. In order to increase the accuracy of experiments, the samples of upper phase were taken 0.5 cm above the interface and the remaining of the top phase was discarded. Samples of both phases were taken for chemical analysis. Each experiment was carried out three time and average values of the results are reported. After separation of the two phases, the concentrations of sodium perchlorate in the top and bottom phases were determined by inductively coupled plasma atomic emission spectrophotometry (ICPS-7000, VER 2). The precision of the mass fraction of sodium perchlorate was better than ± 0.001 and this was checked by measuring standard salt solutions. The concentration of PPG in both phases was determined by refractive index measurements performed at 298.15 K using a refractometer (OPTECH) with a precision of ± 0.0001. To ensure the accuracy of the linear response, the concentration of sample solutions must be near the concentration of unidentified solutions. The relation between the mass fraction of polymer (w_1), salt (w_2) and the refractive index (n_{D}) is given by:

$$n_{\mathrm{D}} = n_{\mathrm{D}}^{\mathrm{o}} + a_1 w_1 + a_2 w_2 \tag{1}$$

where a_1 and a_2 are adjustable parameters and $n_{\mathrm{D}}^{\mathrm{o}}$ is refractive index of pure water. The values of the a_1 and a_2 can be obtained by measuring the refractive index of standard solutions. The $n_{\mathrm{D}}^{\mathrm{o}}$ is 1.3325 [37] and the values of a_1 and a_2 for the system were obtained as 0.1385 and 0.105, respectively. It must be mentioned that the precision of the mass fraction of PPG achieved using Eq. 1 was better than 0.002.

3 Thermodynamic Modeling

Sander et al. [38] presented a model to be used for electrolyte solutions by adding an extended Debye–Hückel term to the UNIQUAC model in 1986. Using this model, the excess Gibbs energy, G^{ex}, can be calculated as a sum of two contributions as follows [39]:

$$G^{ex} = G_{\mathrm{UQ}}^{\mathrm{ex}} + \mathrm{G}_{\mathrm{DH}}^{\mathrm{ex}} \tag{2}$$

In Eq. 2 $\mathrm{G}_{\mathrm{UQ}}^{\mathrm{ex}}$ is the original UNIQUAC equation and $\mathrm{G}_{\mathrm{DH}}^{\mathrm{ex}}$ is the extended Debye–Hückel term and accounts for the contribution of long-range interactions. Therefore, the activity coefficients of the solvents (γ_i, given in the symmetrical convention) and the activity coefficients of the ions ($\gamma_i^* = \gamma_i / \gamma_i^{\infty}$, given in the unsymmetrical convention) are also given as the sum of two terms as follows:

$$\ln\gamma_i = \ln\gamma_i^{\mathrm{UQ}} + \ln\gamma_i^{\mathrm{DH}} \tag{3}$$

$$\ln\gamma_i^* = \ln\gamma_i^{*\mathrm{UQ}} + \ln\gamma_i^{*\mathrm{DH}} \tag{4}$$

It must be mentioned that a value of unity is assigned to the activity coefficients at infinite dilution in the unsymmetrical convention and a value of unity is assigned to the activity coefficients in the pure state in the symmetrical convention. The UNIQUAC term for the activity coefficient can be calculated using Eq. 5:

$$\begin{aligned}\ln\,\gamma_i^{\mathrm{UQ}} = {} & \ln\left(\frac{\phi_i}{x_i}\right) + 1 - \frac{\phi_i}{x_i} - \frac{z}{2} q_i \left[\ln\left(\frac{\phi_i}{\theta_i}\right) + 1 - \frac{\phi_i}{\theta_i}\right] \\ & + q_i \left[1 - \ln\left(\sum_k \theta_k \psi_{ki}\right) - \sum_k \frac{\theta_k \psi_{ki}}{\sum \theta_k \psi_{lk}}\right]\end{aligned} \tag{5}$$

where the subscripts i and k are used to denote the components in the system, z is the coordination number and taken as $z = 10$. ϕ_i and θ_i are the volume fraction and the surface area fraction of component i, respectively, that can be calculated as Eqs. 6 and 7.

$$\phi_i = \frac{x_i r_i}{\sum x_i r_i} \tag{6}$$

$$\theta_i = \frac{x_i q_i}{\sum x_i q_i} \tag{7}$$

where q_i and r_i are the pure component area and volume parameters of the UNIQUAC model, respectively. Here, it is supposed that the sodium perchlorate in the aqueous phase is completely dissociated into ions; therefore, in Eq. 5, x_i is the mole fraction of component i, which can be calculated as follows:

$$x_1 = \frac{n_1}{n_1 + 2n_2 + n_3} \tag{8}$$

$$x_2 = \frac{2n_2}{n_1 + 2n_2 + n_3} \tag{9}$$

$$x_3 = \frac{n_3}{n_1 + 2n_2 + n_3} \tag{10}$$

where n is mole number of species. In this work two scenarios (A and B) are considered in the modeling, in Case A, water (3) is solvent and the polymer (1) and ions (2) are solutes, while in Case B, water–polymer was treated as a pseudo-solvent, this case is known as the mixed solvent model.

Meanwhile, infinite dilution in pure water was taken as the reference state for the solute (sodium perchlorate and PPG), and the pure liquid state for water as described by Gao et al. [40]. The contribution of long–range interaction in the electrolyte solutions was modeled using the extended Debye–Hückel (DH) equation of Fowler–Guggenheim [41]. In Case B, the electrostatic term of the activity coefficient for neutral molecule i was calculated based on Eq. 11, while in the Case A, the electrostatic term is zero for the polymer species.

$$\ln \gamma_i^{\mathrm{DH}} = M_i \frac{2A}{b^3}\left[1 + bI^{\frac{1}{2}} - \frac{1}{1 + bI^{\frac{1}{2}}} - 2\ \ln\left(1 + bI^{\frac{1}{2}}\right)\right] \tag{11}$$

where M_i is molar mass of component i. The ionic activity coefficient, γ_i^*, of salt can be written as:

$$\ln \gamma_i^{*\mathrm{DH}} = -z_i^2 \frac{AI^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} \tag{12}$$

The ionic strength (I) is calculated as:

$$I = \frac{1}{2}\sum Z_i^2 m_i \tag{13}$$

where Z_i is the charge number of ion i, m_i is the molal concentration and can be calculated using Eqs. 14 and 15 for Case A and Case B, respectively.

$$m_i = \frac{x_i}{M_3 x_3}, \text{ Case A} \tag{14}$$

$$m_i = \frac{x_i}{M_1 x_1 + M_3 x_3}, \text{ Case B} \tag{15}$$

where M_i and x_i represent the molecular weight and the mole fraction, respectively.

In the asymmetric convention, in both cases, the reference is taken as pure water.

The DH constants (A and b), can be calculated as Eqs. 16 and 17. A value of 4 Å is assumed for closest distance between ions [42].

$$A = 1.327757 \times 10^5 \frac{d^{0.5}}{(DT)^{1.5}} \tag{16}$$

$$b = 6.359696 \frac{d^{0.5}}{(DT)^{1.5}} \tag{17}$$

where T, D and d represent temperature, dielectric constant and density of the mixed solvent, respectively. The values for D and d can be calculated using the following relations:

$$D = \sum \varphi'_k D_k \tag{18}$$

$$d = \sum \varphi'_k d_k \tag{19}$$

Table 1 Experimental phase equilibrium compositions for the PPG_{425} (1) + $NaClO_4$ (2) + H_2O system at T = 288.15 and 298.15 K

Overall composition		Top phase			Bottom phase		
w_1(wt%)	w_2(wt%)	w_1(wt%)	w_2(wt%)	n_D	w_1(wt%)	w_2(wt%)	n_D
288.15 K							
37.8561	10.0383	67.8149	4.9874	1.432	7.8973	15.0892	1.3725
38.3346	10.8096	68.8744	5.129	1.4361	7.7948	16.4902	1.371
40.5088	11.3601	74.6701	4.5718	1.44	6.3474	18.1485	1.367
40.1445	13.2318	82.2079	4.4462	1.4468	6.0810	21.0173	1.366
39.3723	14.6058	75.7091	5.0859	1.4551	3.0354	24.1256	1.364
298.15 K							
29.8341	6.6428	51.4697	2.6923	1.4405	8.1986	10.5933	1.3772
41.1810	7.3066	74.6271	2.0606	1.441	7.7349	12.5527	1.369
42.7193	9.2138	78.7295	1.8616	1.445	6.7090	16.5660	1.365
51.1493	10.2331	95.7204	1.1355	1.465	6.5781	19.3306	1.36
51.4292	13.3955	98.0089	0.7187	1.468	4.8494	26.0724	1.3575

Fig. 1 Binodal curves for ATPS containing PPG_{425} and $NaClO_4$ at different temperatures

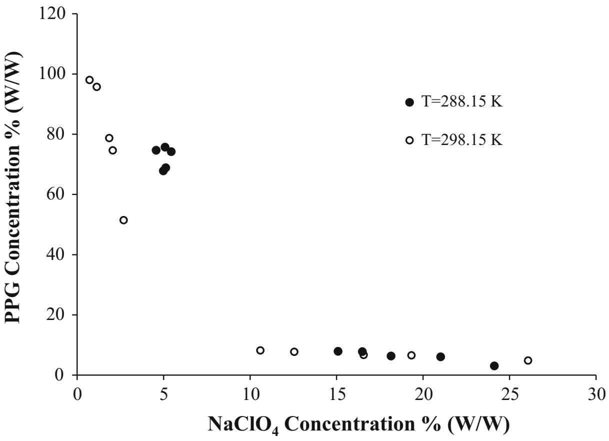

Table 2 Literature data for the PPG + salt + water and PEG + salt + water system

System	Number of data points	Temperature range	References
$PEG_{6000} + Na_3C_6H_5O_7 + H_2O$	21	298.15–318.15	[48]
$PEG_{4000} + Na_2SO_4 + H_2O$	16	298.15	[49]
$PEG_{1000} + NaH_2PO_4 + H_2O$	13	298.15–318.15	[50]
$PEG_{6000} + NaH_2PO_4 + H_2O$	15	298.15–318.15	[50]
$PEG_{1000} + Na_2HPO_4 + H_2O$	17	298.15–318.15	[50]
$PEG_{6000} + Na_2HPO_4 + H_2O$	21	298.15–318.15	[50]
$PEG_{4000} + NaClO_4 + H_2O$	14	288.15–308.15	[31]
$PPG_{400} + Na_2CO_3 + H_2O$	7	298.15	[51]
$PPG_{400} + Na_2SO_4 + H_2O$	6	298.15	[51]
$PPG_{425} + NaCl + H_2O$	37	278–333	[52]
$PPG_{725} + NaCl + H_2O$	14	278–298	[52]
$PPG_{425} + Na_2SO_4 + H_2O$	8	298.15	[53]
$PPG_{400} + Na_2HPO_4 + H_2O$	25	298.15–318.15	[15]
$PPG_{400} + Na_3PO_4 + H_2O$	25	298.15–318.15	[15]
$PPG_{400} + NaH_2PO_4 + H_2O$	25	298.15–318.15	[54]
$PPG_{425} + NaClO_4 + H_2O$	14	288.15–298.15	This work

where φ'_k is the salt-free volume fraction of non-ionic species k in the liquid phase and is defined as:

$$\varphi'_k = \frac{x_k V_k}{x_1 V_1 + x_3 V_3} \tag{20}$$

where V_i is the molar volume of i. A group contribution method can be used to calculate the molar volume of polymer. In this way, the molar volume of PPG_{425} was obtained as $V_1 = 425 \times 10^{-6}$ ($m^3 \cdot mol^{-1}$) using the group contribution data reported by Zana [43]. The dielectric constant of PPG was calculated according to the method proposed by Van et al. [44]. For water, the value of $D_3 = 82.22$ at 288.15 K and $D_3 = 78.34$ at 298.15 K

Table 3 The interaction parameters ($U_{kl}^{0} = U_{lk}^{0}$) of the UNIQUAC model for ATPS containing PEG ($U_{kl} = U_{kl}^{o} + U_{kl}^{T}(T - 298.15)$)

	PEG	H_2O	Na^+	$(C_6H_5O_7)^{3-}$	$(SO_4)^{2-}$	$(H_2PO_4)^-$	$(HPO_4)^{2-}$	$(ClO_4)^-$
PEG	− 7.1316	− 4.0781	145.6478	30.0078	1603.548	148.2142	12411.547	0.0405
H_2O		0*	733.286*	78.4094	752.879*	103.5017*	− 122.683*	− 8.6907
Na^+			0*	345.5401	845.135*	1918.884*	561.0501*	768.1165
$(C_6H_5O_7)^{3-}$				274.3811				
$(SO_4)^{2-}$					1265.83*			
$(H_2PO_4)^-$						199.3348*		
$(HPO_4)^{2-}$							− 89.3053*	
$(ClO_4)^-$								1.5835

An asterisk replaces parameter values in fields [37] (Case A)

Table 4 The interaction parameters ($U_{kl}^T = U_{lk}^T$) of UNIQUAC model for ATPS containing PEG ($U_{kl} = U_{kl}^o + U_{kl}^T(T - 298.15)$)

	PEG	H_2O	Na^+	$(C_6H_5O_7)^{3-}$	$(SO_4)^{2-}$	$(H_2PO_4)^-$	$(HPO_4)^{2-}$	$(ClO_4)^-$
PEG	0.5193	0.2668	28.5822	56.5730	0	2.3757	− 594.8814	0.5494
H_2O		0*	0.4872*	52.7435	9.4905*	0.1005*	− 0.7893*	1.0026
Na^+			0*	271.0626	11.681*	26.324*	1.5429*	13.1173
$(C_6H_5O_7)^{3-}$				53.6417				
$(SO_4)^{2-}$					8.3194*			
$(H_2PO_4)^-$						− 0.5030*		
$(HPO_4)^{2-}$							− 2.755*	
$(ClO_4)^-$								0.8175

An asterisk replaces parameter values in fields [37] (Case A)

Table 5 The interaction parameters ($U_{kl}^0 = U_{lk}^0$) of UNIQUAC model for ATPS containing PEG ($U_{kl} = U_{kl}^o + U_{kl}^T(T - 298.15)$)

	PEG	H_2O	Na^+	$(C_6H_5O_7)^{3-}$	$(SO_4)^{2-}$	$(H_2PO_4)^-$	$(HPO_4)^{2-}$	$(ClO_4)^-$
PEG	2.9749	0.3713	1080.79	− 201.8141	1291.553	57.8714	185.7970	− 11.4584
H_2O		0*	733.286*	− 236.7895	752.879*	103.5017*	− 122.683*	− 41.2258
Na^+			0*	− 6.9753	845.135*	1918.884*	561.0501*	206.5266
$(C_6H_5O_7)^{3-}$				− 499.5239				
$(SO_4)^{2-}$					1265.83*			
$(H_2PO_4)^-$						199.3348*		
$(HPO_4)^{2-}$							− 89.3053*	
$(ClO_4)^-$								− 71.6967

An asterisk replaces parameter values in fields [37] (Case B)

Table 6 The interaction parameters ($U_{kl}^{T} = U_{lk}^{T}$) of UNIQUAC model for ATPS containing PEG ($U_{kl} = U_{kl}^{o} + U_{kl}^{T}(T - 298.15)$)

	PEG	H_2O	Na^+	$(C_6H_5O_7)^{3-}$	$(SO_4)^{2-}$	$(H_2PO_4)^-$	$(HPO_4)^{2-}$	$(ClO_4)^-$
PEG	− 2.7573	− 1.2828	3.6489	− 1.7605	0	− 5.1105	28.2464	− 3.7534
H_2O		0*	0.4872*	− 2.8083	9.4905*	0.1005*	− 0.7893*	− 5.2691
Na^+			0*	− 27.6648	11.681*	26.324*	1.5429*	− 48.4844
$(C_6H_5O_7)^{3-}$				− 3.1222				
$(SO_4)^{2-}$					8.3194*			
$(H_2PO_4)^-$						− 0.5030*		
$(HPO_4)^{2-}$							− 2.755*	
$(ClO_4)^-$								− 7.7382

An asterisk replaces parameter values in fields [37] (Case B)

Table 7 The interaction parameters ($U_{kl}^{0} = U_{lk}^{0}$) of UNIQUAC model for ATPS containing PPG ($U_{kl} = U_{kl}^{o} + U_{kl}^{T}(T - 298.15)$)

	PPG	H_2O	Na^+	$(SO_4)^{2-}$	$(H_2PO_4)^-$	$(HPO_4)^{2-}$	$(ClO_4)^-$	$(CO_3)^{2-}$	$(PO_4)^{3-}$	Cl^-
PPG	− 1102.48	− 91.1952	− 105.912	− 902.115	− 1015.07	− 1515.6114	− 624.461	− 2635.33	− 1247.95	1937.609
H_2O		0*	733.286*	752.879*	103.5017*	− 122.683*	− 41.2258	328.141*	58.6402	1523.39*
Na^+			0*	845.135*	1918.884*	561.0501*	206.5266	476.956*	− 3915.67	1443.23*
$(SO_4)^{2-}$				1265.83*						
$(H_2PO_4)^-$					199.3348*					
$(HPO_4)^{2-}$						− 89.3053*				
$(ClO_4)^-$							− 125.1942			
$(CO_3)^{2-}$								1065.97*		
$(PO_4)^{3-}$									1671.856	
Cl^-										2214.81*

An asterisk replaces parameter values in fields [37] (Case A)

Table 8 The interaction parameters ($U_{kl}^T = U_{lk}^T$) of UNIQUAC model for ATPS containing PPG ($U_{kl} = U_{kl}^o + U_{kl}^T(T - 298.15)$)

	PPG	H_2O	Na^+	$(SO_4)^{2-}$	$(H_2PO_4)^-$	$(HPO_4)^{2-}$	$(ClO_4)^-$	$(CO_3)^{2-}$	$(PO_4)^{3-}$	Cl^-
PPG	− 4.0101	− 12.6385	42.2511	0	− 0.7736	0.5179	14.122	0	1.198	27.840
H_2O		0*	0.4872*	9.4905*	0.1005*	− 0.7893*	− 5.2691	− 0.5059*	11.3249	14.631*
Na^+			0*	11.681*	26.324*	1.5429*	− 48.4844	2.8191*	− 3.8673	15.635*
$(SO_4)^{2-}$				8.3194*						
$(H_2PO_4)^-$					− 0.5030*					
$(HPO_4)^{2-}$						− 2.755*				
$(ClO_4)^-$							− 23.2323			
$(CO_3)^{2-}$								− 4.4653*		
$(PO_4)^{3-}$									7.0352	
Cl^-										14.436*

An asterisk replaces parameter values in fields [37] (Case A)

Table 9 The interaction parameters ($U_{kl}^{0} = U_{lk}^{0}$) of UNIQUAC model for ATPS containing PPG ($U_{kl} = U_{kl}^{o} + U_{kl}^{T}(T - 298.15)$)

	PPG	H_2O	Na^+	$(SO_4)^{2-}$	$(H_2PO_4)^-$	$(HPO_4)^{2-}$	$(ClO_4)^-$	$(CO_3)^{2-}$	$(PO_4)^{3-}$	Cl^-
PPG	− 12.423	− 21.591	− 421.749	634.931	278.9161	29.7488	95.429	472.2241	− 401.649	7453.582
H_2O		0*	733.286*	752.879*	103.5017*	− 122.683*	− 41.2258	328.141*	− 622.408	1523.39*
Na^+			0*	845.135*	1918.884*	561.0501*	206.5266	476.956*	− 365.182	1443.23*
$(SO_4)^{2-}$				1265.83*						
$(H_2PO_4)^-$					199.3348*					
$(HPO_4)^{2-}$						− 89.3053*				
$(ClO_4)^-$							− 125.1942			
$(CO_3)^{2-}$								1065.97*		
$(PO_4)^{3-}$									− 1002.06	
Cl^-										2214.81*

An asterisk replaces parameter values in fields [37] (Case B)

Table 10 The interaction parameters ($U_{kl}^T = U_{lk}^T$) of UNIQUAC model for ATPS containing PPG ($U_{kl} = U_{kl}^o + U_{kl}^T(T - 298.15)$)

	PPG	H_2O	Na^+	$(SO_4)^{2-}$	$(H_2PO_4)^-$	$(HPO_4)^{2-}$	$(ClO_4)^-$	$(CO_3)^{2-}$	$(PO_4)^{3-}$	Cl^-
PPG	2.7652	31.5277	− 22.992	0	− 48.2613	− 53.8443	113.512	0	− 37.8749	− 41.3821
H_2O		0*	0.4872*	9.4905*	0.1005*	− 0.7893*	− 5.2691	− 0.5059*	− 13.274	14.631*
Na^+			0*	11.681*	26.324*	1.5429*	− 48.4844	2.8191*	− 1.3058	15.635*
$(SO_4)^{2-}$				8.3194*						
$(H_2PO_4)^-$					− 0.5030*					
$(HPO_4)^{2-}$						− 2.755*				
$(ClO_4)^-$							− 23.2323			
$(CO_3)^{2-}$								− 4.4653*		
$(PO_4)^{3-}$									− 166.618	
Cl^-										14.436*

An asterisk replaces parameter values in fields [37] (Case B)

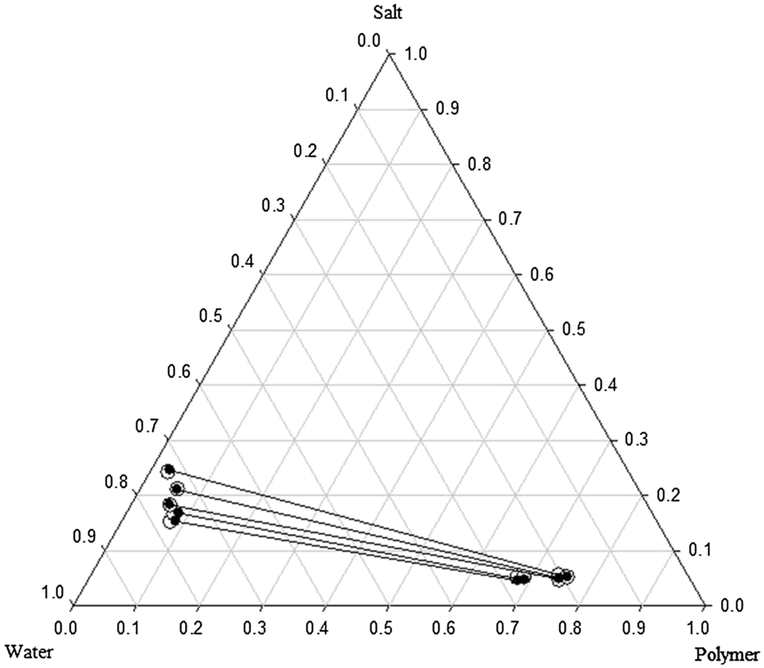

Fig. 2 Experimental (dotted circle) and calculated liquid–liquid equilibrium tie-lines (solid line) for the PPG(1)–$NaClO_4$ (2)–water(3) system at 288.15 K. Calculations have been performed using the extended UNIQUAC model (black circle) (Case A)

were used. The binary energy interaction parameters of the E-UNIQUAC model are defined as follows:

$$\psi_{ij} = \exp\left(-\frac{\Delta U_{ij}}{T}\right) \tag{21}$$

$$\Delta U_{ij} = U_{ij} - U_{jj} \tag{22}$$

where U_{ij} is the interaction parameter between species i and j. These parameters are symmetrical and temperature dependent as follows:

$$U_{ij} = U_{ij}^{\mathrm{o}} + U_{ij}^{T}(T - 298.15) \tag{23}$$

It must be noted that in the recent equations $U_{ij} = U_{ji}$. In this work, the interaction parameters of U_{kl}^{o} and U_{kl}^{T} were fitted to the experimental data. Therefore, the interaction parameters between polymer, salt and water were obtained using the E-UNIQUAC model.

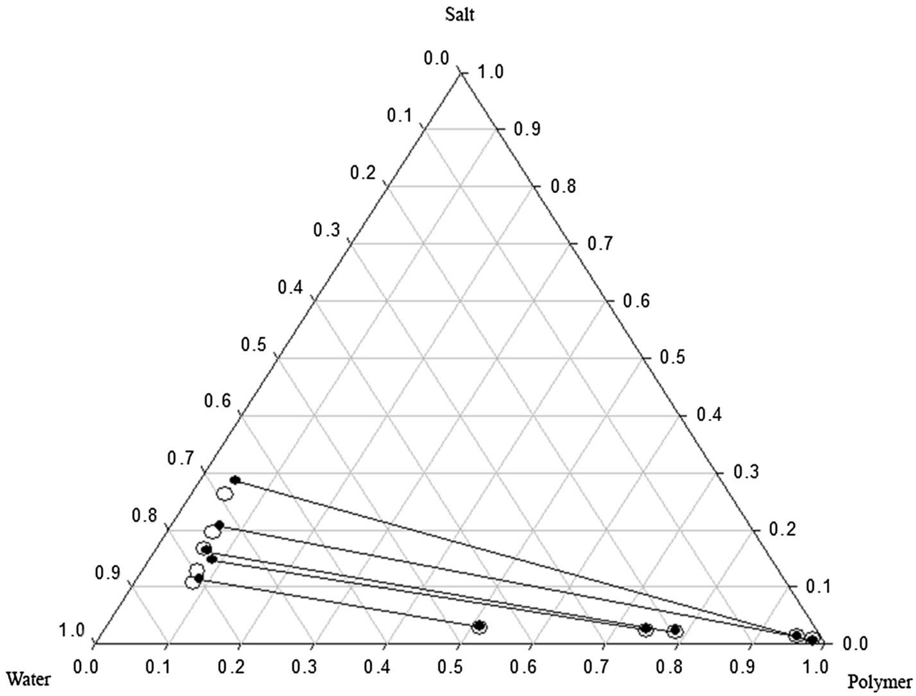

Fig. 3 Experimental (dotted circle) and calculated liquid–liquid equilibrium tie-lines (solid line) for the PPG (1)–$NaClO_4$ (2)–water (3) system at 298.15 K. Calculations have been performed using the extended UNIQUAC model (black circle) (Case A)

4 Results and Discussion

The experimental LLE data of the ATPS containing PPG_{425} and $NaClO_4$ was measured at different temperatures. The experimental data at 288.15 and 298.15 K are shown in Table 1.

As can be seen, the bottom phase is rich in salt and the upper one is polymer rich. Also, in Fig. 1, binodal curves at different temperatures have been presented. It is obvious that, as the temperature increases, the two-phase region expands and tie-line slopes increase. This phenomenon usually is explained by the higher solubility of the phase forming components at higher temperatures. Recently, Sadeghi et al. [45] recognized that the hydrophobic nature of polymers can be increased by increasing temperature, which expand the two-phase region.

To find the model parameters the ternary systems were modeled using E-UNIQUAC. In this way, the values of structural parameters (r and q) for water and polypropylene glycol have been taken from Larsen et al. [46], while the relevant values for the ions (Na^+ and ClO_4^-) have been extracted from Haghtalab et al. [47]. Considering the equality of component fugacity in two phases, the binary interaction parameters for PPG_{425} + $NaClO_4$ + H_2O system can be obtained using the binary LLE data (Table 1). To decrease the number of adjustable parameters, ion–water and ion–ion interaction parameters were obtained using experimental data from the literature, in this regard the ATPSs composed of sodium salts and PPG or PEG were used (Table 2). Meanwhile, it was assumed that a

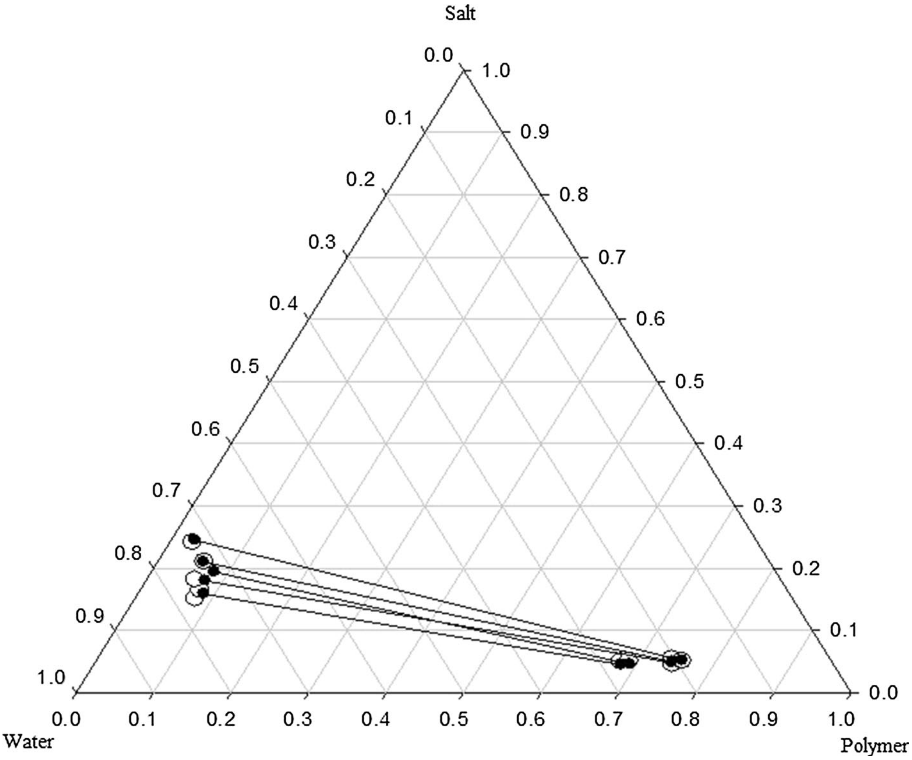

Fig. 4 Experimental (dotted circle) and calculated liquid–liquid equilibrium tie-lines (solid line) for the PPG (1)–$NaClO_4$ (2)–water (3) system at 288.15 K. Calculations have been performed using the extended UNIQUAC model (black circle) (Case B)

polymer with different molecular weight has the same interaction parameter with the ions; therefore, the effect of molecular weight of polymers can be considered in the UNIQUAC part because the structural parameters of UNIQUAC model are changed by changes in the molecular weights of polymers.

The adjustable parameters were obtained by minimizing following objective function for all tie lines:

$$\mathrm{OF} = \sum_{i=1}^{M} \sum_{j=1}^{N} \left(x_{ij}^{\mathrm{I}} \gamma_{ij}^{\mathrm{I}} - x_{ij}^{\mathrm{II}} \gamma_{ij}^{\mathrm{II}} \right)^2 \tag{24}$$

where the subscripts M and N represent the number of components and the number of tie lines, respectively, x_i and γ_i represent the experimental mole fraction and the activity coefficient of component i. The superscripts I and II represent the two liquid phases in equilibrium. The parameters obtained for the ATPS containing PEG are given in Tables 3 and 4 for Case A.

The parameters for Case B are given in Tables 5 and 6.

Due to lack of temperature dependent data on the PEG + Na_2SO_4 + H_2O system $U^{T}_{\mathrm{PEG-SO_4^{2-}}}$ was set to zero in Tables 4 and 6. The interaction parameters of ATPS

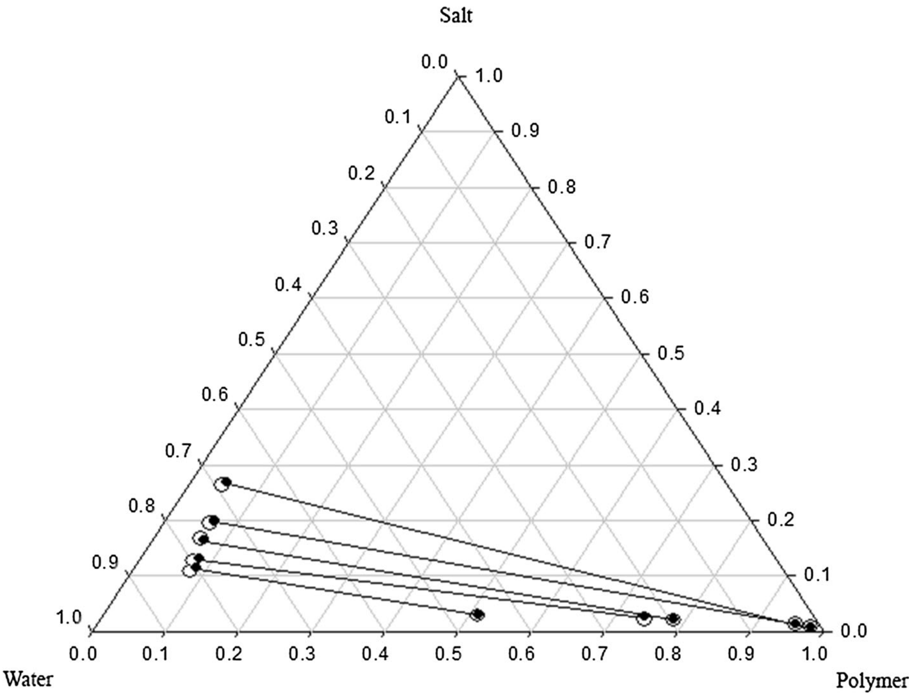

Fig. 5 Experimental (dotted circle) and calculated liquid–liquid equilibrium tie-lines (solid line) for the PPG (1)–$NaClO_4$ (2)–water (3) system at 298.15 K. Calculations have been performed using the extended UNIQUAC model (black circle) (Case B)

containing PPG and salt for Case A are reported in Tables 7 and 8; the same for Case B are given in Tables 9 and 10.

In these tables, the binary interaction parameters which previously were reported by Thomsen, are marked with an asterisk [39]. Due to lack of temperature dependent data on PPG + Na_2CO_3 + H_2O and PPG + Na_2SO_4 + H_2O systems, $U^{T}_{\mathrm{PPG-SO_4^{2-}}}$ and $U^{T}_{\mathrm{PPG-CO_3^{2-}}}$ were set as zero in Tables 8 and 10. In Figs. 2 and 3, the experimental and the calculated results (Case A), using reported binary interaction parameters, are compared at 288.15 and 298.15 K, respectively.

Furthermore, a comparison between the experimental and the calculated results (Case B), at 288.15 and 298.15 K are shown in Figs. 4 and 5.

As can be seen from these figures, there is good agreements between the calculated and experimental data at the studied temperatures.

The average absolute deviation ($\%\Delta X$) between calculated and experimental mole fractions is calculated as:

$$\%\Delta X = 100 \times \sqrt{\frac{\sum_{i=1}^{M}\sum_{j=1}^{N}\left\{\left(x_{ij}^{\mathrm{exp}} - x_{ij}^{\mathrm{cal}}\right)_{\mathrm{I}}^{2} + \left(x_{ij}^{\mathrm{exp}} - x_{ij}^{\mathrm{cal}}\right)_{\mathrm{II}}^{2}\right\}}{2MN}} \tag{25}$$

In Eq. 25, x^{exp} and x^{cal} represent the experimental and the calculated mole fractions,

Table 11 Average absolute deviation (%ΔX) between calculated and experimental mass fractions for ATPS containing PEG in Case A

System	T (K)	%ΔX
$PEG_{6000} + Na_3C_6H_5O_7 + H_2O$	298.15	0.31
	308.15	0.30
	318.15	0.42
$PEG_{4000} + Na_2SO_4 + H_2O$	298.15	2.05
$PEG_{1000} + NaHPO_4 + H_2O$	298.15	1.48
	308.15	1.22
	318.15	1.36
$PEG_{6000} + NaHPO_4 + H_2O$	298.15	1.50
	308.15	0.51
	318.15	0.81
$PEG_{1000} + Na_2HPO_4 + H_2O$	298.15	0.68
	308.15	0.65
	318.15	0.72
$PEG_{6000} + Na_2HPO_4 + H_2O$	298.15	1.57
	308.15	0.34
	318.15	0.35
$PEG_{4000} + NaClO_4 + H_2O$	288.15	0.11
	298.15	0.03
	308.15	0.30

Table 12 Average absolute deviation (%ΔX) between calculated and experimental mass fractions for ATPS containing PEG in Case B

System	T (K)	%ΔX
$PEG_{6000} + Na_3C_6H_5O_7 + H_2O$	298.15	0.01
	308.15	0.05
	318.15	0.05
$PEG_{4000} + Na_2SO_4 + H_2O$	298.15	0.07
$PEG_{1000} + NaHPO_4 + H_2O$	298.15	0.01
	308.15	0.001
	318.15	0.19
$PEG_{6000} + NaHPO_4 + H_2O$	298.15	0.10
	308.15	0.13
	318.15	0.06
$PEG_{1000} + Na_2HPO_4 + H_2O$	298.15	0.10
	308.15	0.13
	318.15	0.06
$PEG_{6000} + Na_2HPO_4 + H_2O$	298.15	0.02
	308.15	0.02
	318.15	0.01
$PEG_{4000} + NaClO_4 + H_2O$	288.15	0.29
	298.15	0.17
	308.15	0.32

Table 13 Average absolute deviation (%Δ*X*) between calculated and experimental mass fractions for ATPS containing PPG in Case A

System	*T* (K)	%Δ*X*
$PPG_{400} + Na_2CO_3 + H_2O$	298.15	0.45
$PPG_{400} + Na_2HPO_4 + H_2O$	298.15	0.16
	303.15	0.26
	308.15	0.23
	313.15	0.19
	318.15	0.18
$PPG_{425} + Na_2SO_4 + H_2O$	298.15	0.30
$PPG_{400} + Na_2SO_4 + H_2O$	298.15	0.47
$PPG_{400} + Na_3PO_4 + H_2O$	298.15	0.51
	303.15	0.38
	308.15	0.17
	313.15	0.14
	318.15	4.49
$PPG_{425} + NaCl + H_2O$	278.15	2.16
	298.15	1.15
	333.15	1.32
$PPG_{725} + NaCl + H_2O$	278.15	0.71
	298.15	0.62
$PPG_{400} + NaH_2PO_4 + H_2O$	298.15	0.35
	303.15	0.28
	308.15	0.26
	313.15	0.29
	318.15	0.33
$PPG_{425} + NaClO_4 + H_2O$	288.15	0.61
	298.15	0.76

respectively. The %Δ*X* between calculated and experimental data using the E-UNIQUAC model in ATPS containing PEG for Case A are given in Table 11.

The results (Table 11) show good agreement between calculated and experimental data. The %Δ*X* between calculated and experimental data in ATPS containing PEG for Case B are also reported in Table 12.

A comparison between Tables 11 and 12 shows that using the pseudo-solvent approach (Case B) increases the accuracy of the model and the average error of 0.095% was obtained in this case.

In Table 13, the %Δ*X* in ATPS containing PPG for Case A are reported. The same for Case B are shown in Table 14.

As can be seen from Tables 13 and 14, the results are similar in both cases and the reported errors are almost equal. In Tables 11–14, %Δ*X* is the average absolute deviation between calculated and experimental data at a fixed temperature. It must be mentioned that the reported parameters were obtained using experimental data at all temperatures.

In this work the ability of single solvent (Case A) and pseudo-solvent (Case B) approaches in correlation of ternary liquid–liquid phase equilibrium data were studied and it was found that pseudo-solvent theory gives better results compared to single solvent in

Table 14 Average absolute deviation (%ΔX) between calculated and experimental mass fractions for ATPS containing PPG in Case B

System	T (K)	%ΔX
$PPG_{400} + Na_2CO_3 + H_2O$	298.15	0.22
$PPG_{400} + Na_2HPO_4 + H_2O$	298.15	0.87
	303.15	0.19
	308.15	0.07
	313.15	0.20
	318.15	0.54
$PPG_{425} + Na_2SO_4 + H_2O$	298.15	0.69
$PPG_{400} + Na_2SO_4 + H_2O$	298.15	0.63
$PPG_{400} + Na_3PO_4 + H_2O$	298.15	0.19
	303.15	0.18
	308.15	0.49
	313.15	1.23
	318.15	1.62
$PPG_{425} + NaCl + H_2O$	278.15	2.16
	298.15	1.15
	333.15	1.18
$PPG_{725} + NaCl + H_2O$	278.15	1.22
	298.15	0.62
$PPG_{400} + NaH_2PO_4 + H_2O$	298.15	2.80
	303.15	0.44
	308.15	0.60
	313.15	0.74
	318.15	0.59
$PPG_{425} + NaClO_4 + H_2O$	288.15	1.03
	298.15	2.06

the systems containing PEG. Meanwhile, Case A and Case B showed similar results in the ATPS containing PPG.

5 Conclusions

In this work the liquid–liquid equilibrium of a ternary system composed of PPG_{425}, $NaClO_4$ and H_2O were determined at 288.15 and 298.15 K. It was found that increasing temperature expands the two-phase region and tie-line slopes. This phenomenon can be explained through the solubility of the phase forming components at different temperatures. The experimental data were correlated using the E-UNIQUAC model. In this regard, two procedures of single solvent and pseudo-solvent were used and unknown binary interaction parameters were estimated for future applications. To present global parameters, the available liquid–liquid experimental data were collected from the literature and were modeled simultaneously. The results showed that the model can correlate the experimental data efficiently. It was found that both scenarios (Case A and Case B) are fairly equal and there is no significant difference between them in modeling of ATPSs containing PPG while in the case of PEG, the pseudo-solvent scenario showed better results. In overall it must be mentioned that good agreement with the experimental data was obtained in all cases, however the performance of Case B was slightly better than the Case A. Finally, it is worth mentioning that the results in this work can enhance the experimental data and thermodynamic modeling approach to polymer/salt aqueous two-phase systems.

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