

## Phase Equilibria of PEG/Sulfate Salt Aqueous Two-Phase Systems: Effects of pH and Molecular Weight of Polymer

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(Received 2 December 2020, Accepted 28 February 2021)

In this study, the liquid-liquid equilibrium (LLE) in the aqueous two-phase system (ATPS) formed by polyethylene glycol (PEG1500 and PEG6000) and magnesium sulfate is investigated. The experimental measurements were performed at temperature of 298.15 K and pH values of 3.60, 5.00 and 6.67. Densities and refractive indices of the mixtures were first measured to obtain the compositions from the plotted tie lines. The effects of pH and molecular mass of polymers on the binodal curve, tie lines length (TLL) and slope of tie line (STL) were examined. It was found that the pH values and molecular weight rise the heterogeneous region for each system. The binodal curve was fitted to the Merchuk and Pirdashti equations. The Othmer-Tobias and Bancroft equations were subsequently selected to correlate the compositions of the tie lines at equilibrium where the fitted parameters are derived. In addition, the Guan's equation was utilized to correlate the experimental binodal curves. Finally, the effectively excluded volume (EEV) was determined and the values were found to increase with pH.

**Keywords:** ATPS, Phase diagram, Tie Line, Polyethylene glycol, Magnesium sulfate

### INTRODUCTION

The aqueous two-phase system (ATPS) can be comprised of the liquid-liquid extraction (LLE) method with a hydrophilic polymer. Compared to ATPS, a mixture of polymer, salt, and water, which consists of two hydrophilic polymers and water, proved to be more economical and more powerful to the separation of different biomolecules from the crude fermentation broth and their partial purification [1]. Besides, ATPS has been applied in the extractions of metallic ions [2-4] and sulfide minerals [6], extractive crystallization of inorganic salts [5-6], separation of cell particles, removals of color from textile plant wastes [8], organic pollutants from the environment [9], textile effluents [10], metal from effluents [11], as well as

recoveries of nano-particles and bio-molecules from varied industrial effluents [7,12-15]. In addition, the ATPS presents a powerful separation technique because of its easy to scale-up feasibility [16-18], low cost [19-20], good resolution and high yield [21-22]. Polyethylene glycol (PEG) is a rather cheap, non-toxic, non-flammable, and non-volatile polymer which is highly soluble in water [23]. Polymer-salt systems are mostly prepared by PEG and its derivatives. In fact, PEG-salt biphasic systems have been described and characterized by numerous references in the literature [24-25]. PEG-salt ATPSs are formed through a wide application of phosphate and sulfate salts [26]. Lei *et al.* (1990) [27] reported liquid-liquid equilibrium (LLE) data for various PEGs with potassium phosphate systems, namely, PEG400, PEG600, PEG1000, PEG1500, PEG3400, PEG8000 and PEG20000, at 277.15 K. Based on the Lei *et al.*'s results, as the molecular weight is increased, the

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binodal curve shifts to a lower PEG and lower phosphate concentrations, and also as the system becomes more basic, the binodals shift to a lower PEG and lower phosphate concentrations, as was observed for the molecular weight effect. The difference in position between the binodals begins to diminish at high pH, while the binodals for pHs 8 and 9.2 are almost identical. Another study by Snyder *et al.* (1992) [28] published the phase equilibrium data for PEG-based mixtures with various salts; *i.e.*, PEG1000, PEG3350 and PEG8000 with sodium sulfate, magnesium sulfate potassium phosphate and sodium carbonate at 298.15 K. They found that increasing the molecular weight of the polymer had a direct effect on the expansion of the biphasic region. Also, in our previous work, phase diagrams and LLE data for ATPSs containing zinc sulfate, magnesium sulfate or aluminum sulfate and PEG 300, 400 and 600 were determined at 298.15 K. It was attempted to show how the PEG molecular weight and the type of cation influence the binodal curve, tie line length (TLL) and slope of the tie line (STL). The results showed that as the PEG molecular weight increases, the two-phase region becomes extended and the binodal curve shifts to the origin [29]. In the present work, the effects of pH and molecular weight of aqueous PEG with magnesium sulfate on binodal curve, LLE data, TLL, STL, effectively excluded volume (EEV), and density difference were obtained at 298.15 K and at pH values of 3.60, 5.00 and 6.67. The Merchuk and the Pirdashti equations were selected to correlate the binodal curve [30, 31]. Further, the Othmer-Tobias and the Bancroft equations were used to fit the experimental ATPS data [32-33].

## EXPERIMENTAL

### Materials

PEG with an average molecular weight of 1500 and 6000 g mol<sup>-1</sup> as well as magnesium sulfate were obtained from Merck with purities better than 99.5%. These chemicals were used without further purification. Deionized water with conductivity of 17.39 μs cm<sup>-1</sup> was used during the experiment.

### Apparatus and Procedure

The experimental approach used in this study consists of two stages that have been fully reported in previous works

[34,35-38]. Briefly, the titration method was used to construct the binodal curve [8] followed by the construction of the calibration curve of the mixture to determine the concentration of components. Temperature was kept as constant as it is important throughout the process and the equipment used in this study was essentially similar to the previous report [34]. A summary of the method used to test and determine the polymer-salt phase diagram is shown in Fig. 1.

**Analytical method.** The refractive indices and densities for the studied systems at various pH values (3.60, 5.00 and 6.67) at 298.15 K were obtained by using a CETI refractometer (Belgium) with an accuracy of 0.0001 n<sub>D</sub> and using an Anton Paar oscillation U-tube densimeter (model: DMA 500, Austria) with a precision of ±10<sup>-4</sup> g cm<sup>-3</sup>. The values of these two physical properties together with the values from the calibration equation coefficients for the mixtures are presented in Tables 1 and 2, respectively. In order to confirm the accuracy of the calculated values from the calibration equation, mass balance calculations were performed to confirm that the amount of the feed mixture will be equal to the amount of polymer and salt in the upper and lower phases.

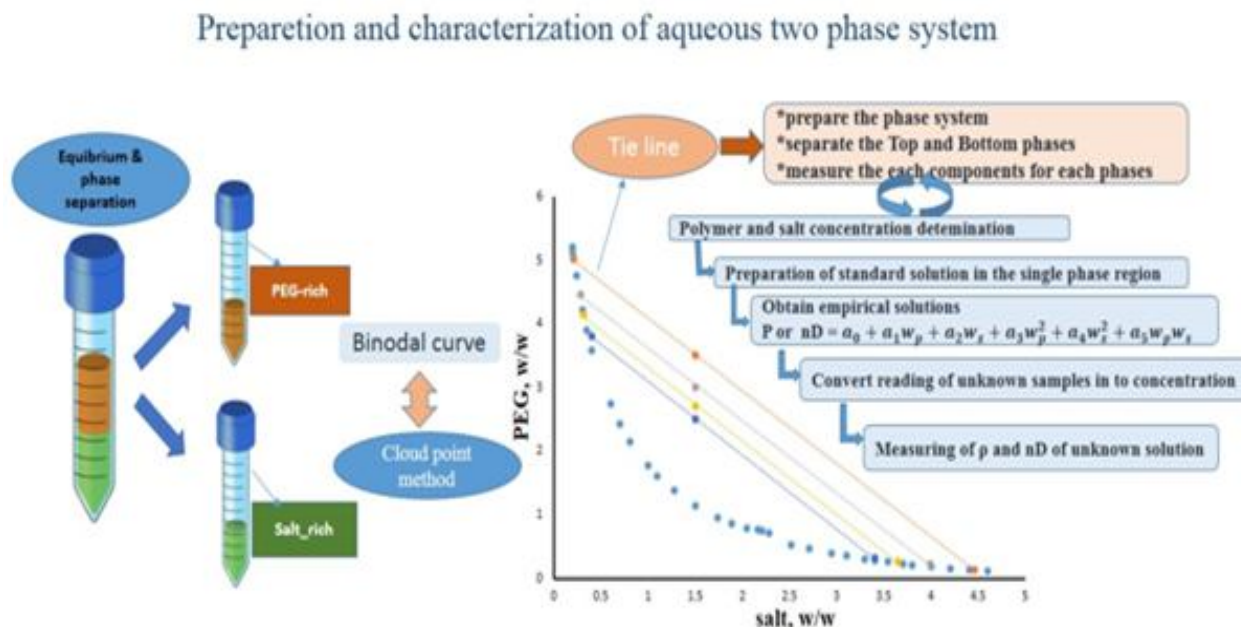
**Phase diagram and determination of tie line.** Once the phase diagram has been obtained from the titration method, the Merchuk [30] and Pirdashti [31] equations (Eqs. (1)-(2)) are appropriately employed for the construction of the binodal curves.

$$w_p = ae^{(bw_s^{0.5} - cw_s^2)} \quad (1)$$

$$w_p = (a + bw_s)^{\frac{-1}{c}} \quad (2)$$

where *a*, *b*, and *c* represent the fitting parameters, and *w<sub>p</sub>* and *w<sub>s</sub>* are polymer and salt compositions (w/w), respectively.

According to the two-phase region, the feed composition for each system was selected. Then, feed composition was prepared and after forming two phases, the composition for top (t) and bottom (b) phases were calculated from the calibration curve. Furthermore, the TLL and STL were determined by using Eqs. (3) and (4) as expressed below.



**Fig. 1.** Schematic diagram for the determination of phase diagram of PEG-salt ATPS.

**Table 1.** Density,  $\rho$  and Refractive Index,  $n_D$ , for the Binary and Ternary Mixtures Composed of PEG (1500, 6000) (p) + Magnesium sulfate (s) + Water at 298.15 K and 101 kPa<sup>b</sup> at Various Polymer Compositions (w/w),  $w_p$

Magnesium sulfate	PEG1500	$\rho$ ( $\pm 0.0001$ ) ( $\text{g cm}^{-3}$ )	$n_D$ ( $\pm 0.0001$ )
$w_s$	$w_p$		
0.05	0.00	1.0216	1.3327
0.10	0.00	1.0476	1.3370
0.15	0.00	1.0728	1.3421
0.00	0.05	1.0060	1.3380
0.00	0.10	1.0146	1.3444
0.00	0.15	1.0235	1.3602
0.05	0.05	1.0338	1.3380
0.10	0.10	1.0759	1.3562
	PEG6000		
0.00	0.05	1.0053	1.3391
0.00	0.10	1.0143	1.3466
0.00	0.15	1.0257	1.3536
0.05	0.05	1.0251	1.3441
0.10	0.10	1.0587	1.3634

Standard uncertainties:  $u(w_i) = 0.01$ ,  $u(n_D) = 0.0001$ ,  $u(\rho) = 0.0001 \text{ g cm}^{-3}$ ,  $u(T) = 0.05 \text{ K}$  and  $u(P) = 5 \text{ kPa}$ .

**Table 2.** The Value of the Coefficients from the Experimental Data

System	Physical properties	a <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	a <sub>4</sub>	a <sub>5</sub>	R <sup>2</sup>
PEG1500 + Magnesium sulfate(s)	n <sub>D</sub>	1.3351	-0.0684	-0.0236	0.7810	1.2589	1.0000	0.9921
	ρ (g cm <sup>3</sup> )	0.9962	0.5119	0.1950	-0.0073	-0.0926	1.0000	0.9999
PEG6000 + Magnesium sulfate(s)	n <sub>D</sub>	1.3301	0.0410	0.1860	0.2600	-0.2000	1.0000	0.9996
	ρ (g cm <sup>3</sup> )	0.9967	0.5009	0.0151	0.0452	0.0027	1.0000	0.9998

$$TLL = \sqrt{(w_p^t - w_p^b)^2 + (w_s^b - w_s^t)^2} \quad (3)$$

$$STL = \frac{w_p^t - w_p^b}{w_s^t - w_s^b} \quad (4)$$

The Othmer-Tobias [32] and Bancroft [33] equations (Eqs. (5) and (6)) were further utilized to examine the reliability of the measured tie line compositions:

$$\left( \frac{1 - w_{pt}}{w_{pt}} \right) = k \left( \frac{1 - w_{sb}}{w_{sb}} \right)^n \quad (5)$$

$$\left( \frac{w_{wb}}{w_{sb}} \right) = k_1 \left( \frac{w_{wt}}{w_{pt}} \right)^r \quad (6)$$

where  $w_{pt}$  and  $w_{sb}$  represent the weight fractions of PEG in the top phase and the weight fraction of magnesium sulfate in the bottom phase, respectively. The compositions of water (w/w) in the bottom and top phases are shown by  $w_{wb}$  and  $w_{wt}$ ,  $k$ ,  $n$ ,  $k_1$  and  $r$  are the correlated parameters, and the values of the parameters are tabulated in Table 6.

The EEV of the salt into the aqueous PEG solution was first introduced by Guan *et al.* [39,40]:

$$\ln \left( V^* \cdot \frac{w_p}{Mw_p} \right) + V^* \cdot \frac{w_s}{Mw_s} = 0 \quad (7)$$

In this equation,  $M_w$  is molecular weight and  $V^*$  indicates the EEV.

## RESULTS AND DISCUSSION

### Fitting Parameters of Calibration Equation

Density and refractive index for the binary and ternary mixtures composed of PEG (1500, 6000) (p) + magnesium sulfate (s) + water at various polymer compositions are shown in Table 1. The values of the coefficients  $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$ ,  $a_5$  and  $f$  for the investigated mixtures are shown in Table 2.

### Binodal Curve

The binodal curve data for the ternary mixture of PEG + magnesium sulfate + H<sub>2</sub>O are presented in Table 3. Figure 2 depicts the influence of pH to the binodal curve of the aqueous two-phase PEG1500 + magnesium sulfate system at various pH values of 3.60, 5.00 and 6.67 at 298.15 K. From this figure, it is observed that an increasing pH can expand the two-phase area. This trend is also congruent with the experimental data reported in the previous references [35,36,40] for other aqueous PEG + salt systems. Likewise, Fig. 3 demonstrates the effect of the molecular mass of PEG 6000 on the binodal curve of this system. Here, the increase of molecular mass of polymer causes the expansion of a single phase.

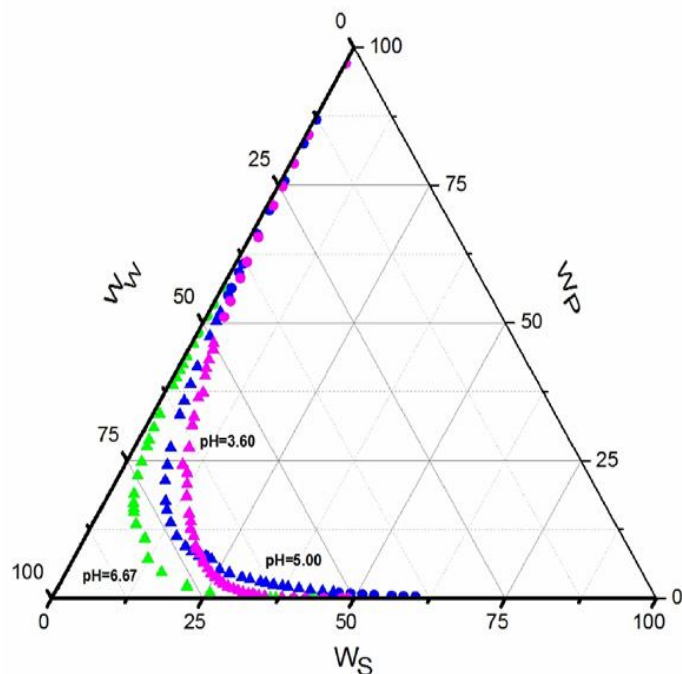
### TLL and STL

The composition of the tie line is tabulated in Table 4 and plotted in Fig. 4. Similarly, Figs. 5-8 depict the tie lines and the binodal curve for the studied system at 298.15 K. In the present work, the determination of the tie lines is performed by connecting each of the corresponding set of

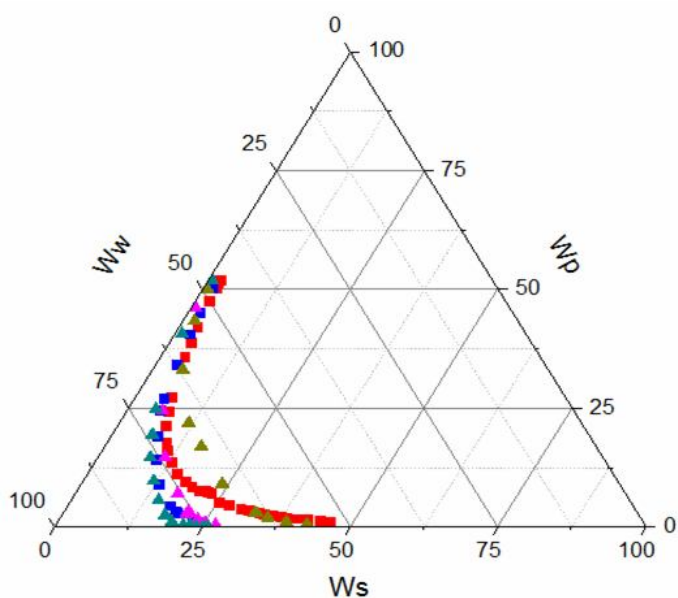
**Table 3.** Binodal Curve Data of the PEG + Magnesium Sulfate(s) + Water System at 298.15 K and 0.1 MPa

PEG1500 + Magnesium sulfate(s) pH = 3.60		PEG1500 + Magnesium sulfate(s) pH = 5.00		PEG1500 + Magnesium sulfate(s) pH = 6.67		PEG6000 + Magnesium sulfate(s)	
100 w <sub>p</sub>	100 w <sub>s</sub>	100 w <sub>p</sub>	100 w <sub>s</sub>	100 w <sub>p</sub>	100 w <sub>s</sub>	100 w <sub>p</sub>	100 w <sub>s</sub>
46.35	3.65	50.34	2.10	46.30	0.24	50.21	1.54
45.16	4.10	51.98	1.95	43.99	0.34	45.16	1.98
43.36	4.36	51.31	2.01	42.58	0.41	40.64	2.41
41.79	4.69	47.62	2.38	41.49	0.47	34.31	3.52
40.41	5.21	42.12	3.04	40.18	0.55	27.15	4.83
37.38	6.36	40.31	3.26	38.80	0.66	24.6	5.54
36.46	6.03	38.91	3.51	33.51	1.12	19.23	7.73
33.07	7.01	35.89	4.03	28.80	1.73	14.36	9.91
31.48	7.52	27.40	6.01	27.60	1.98	8.98	13.11
27.43	9.05	24.28	7.02	24.77	2.51	4.55	17.25
24.32	9.55	21.45	8.08	22.29	3.12	3.41	18.61
22.79	11.02	17.70	10.02	19.00	4.16	3.27	18.89
20.74	12.06	16.09	11.02	17.30	4.93	2.99	19.24
18.54	13.07	13.80	12.79	16.40	5.41	1.43	22.45
15.42	15.04	11.34	15.03	15.70	5.76		
13.97	16.02	9.49	17.40	13.50	7.24		
12.68	16.63	8.52	18.92	10.90	9.99		
11.36	17.82	7.78	20.46	7.18	12.35		
9.53	19.04	7.68	21.62	7.21	12.32		
8.92	19.51	7.47	22.11	4.77	15.8		
8.09	20.57	7.16	22.88	2.20	21.30		
6.96	21.53	5.30	25.13	1.01	25.69		
6.51	21.88	4.62	27.08	0.26	31.63		
5.48	23.04	3.89	29.51	0.09	35.02		
4.66	24.06	3.48	31.06	0.07	36.14		
3.93	25.09	3.03	33.01	0.05	37.02		
3.28	26.17	2.55	35.42	0.04	38.12		
2.71	27.03	2.82	34.03	0.02	40.11		
2.21	28.07	2.10	38.05	0.01	42.18		
1.79	29.12	2.27	37.01				
1.43	30.10	1.81	40.02				
1.13	31.05	1.56	42.02				
0.86	32.12	1.32	44.12				
0.71	32.85	1.13	46.02				
0.64	33.21						
0.52	34.01						
0.39	35.06						
0.15	38.04						

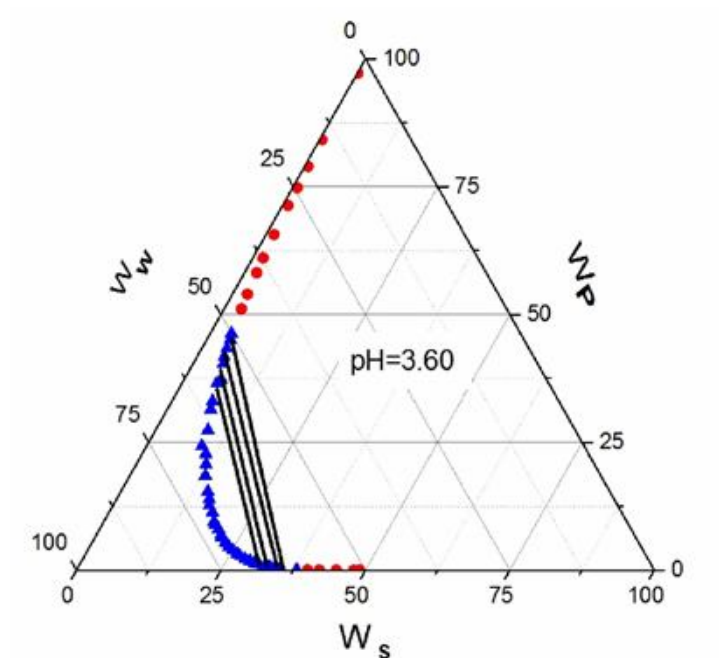
Standard uncertainties:  $u(w_i) = 0.01$ ;  $u(P) = 5$  kPa;  $u(T) = 0.05$  K.



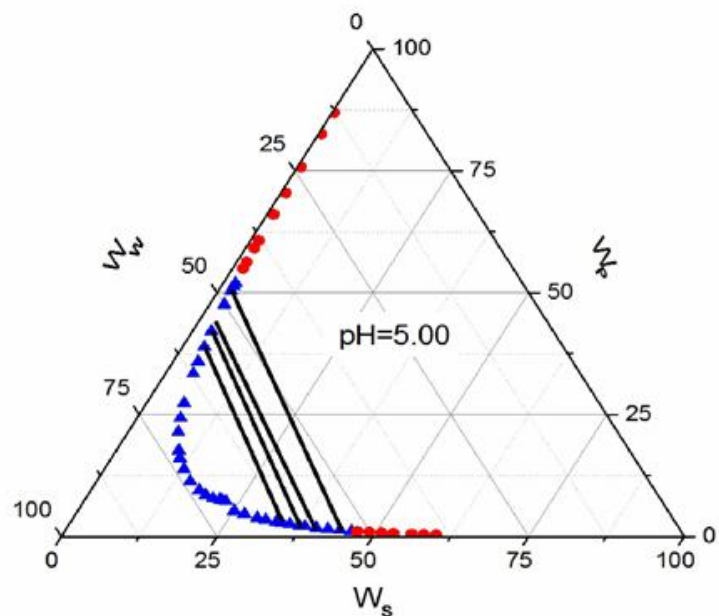
**Fig. 2.** Phase diagram of the PEG1500 + magnesium sulfate + water two-phase system at  $T = 298.15$  K and various pHs (3.60, 5.00 and 6.67): ( $\blacktriangle$ ) experimental binodal (3.60 (pink), 5.00 (blue) and 6.67 (green)); ( $\bullet$ ) calculated binodal using the Merchuk equation (Eq. (3)) (3.60 (pink), 5.00 (blue) and 6.67 (green)).



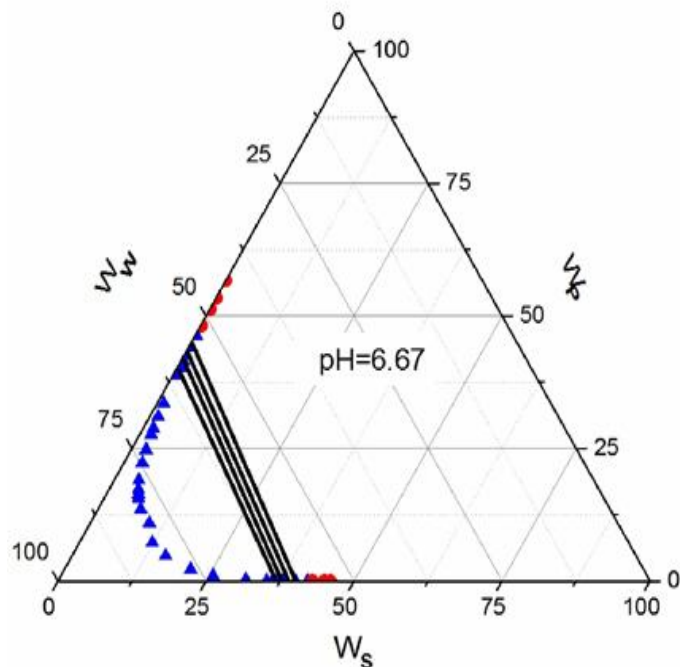
**Fig. 3.** Phase diagram of the PEG6000 + magnesium sulfate + water two-phase system at  $T = 298.15$  K ( $\blacktriangle$ ) experimental binodal in assay of González-Tello *et al.* [41] (PEG1000 (green), PEG 3350 (purple) and PEG8000 (blue)); ( $\blacksquare$ ) experimental binodal (PEG1500 (red) and PEG6000 (blue)).



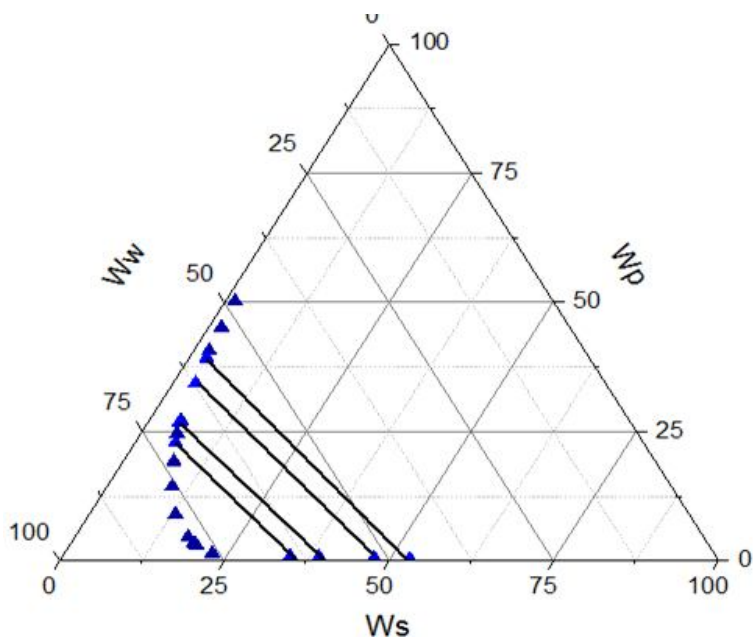
**Fig. 4.** Phase diagram and pH impacts on the compositions of the equilibrium phase, the STL and TLL of PEG1500 + magnesium sulfate + water two-phase system at  $T=298.15$  K and pH 3.60: (-▲-) experimental binodal; (- - -● - - -) calculated by using Eq. (4).



**Fig. 5.** Phase diagram and pH effects on the equilibrium phase compositions, STL, and TLL of PEG1500 + magnesium sulfate + water two-phase system at  $T=298.15$  K and pH 5.00: (-▲-) experimental binodal; (- - -● - - -) calculated by using Eq. (4).

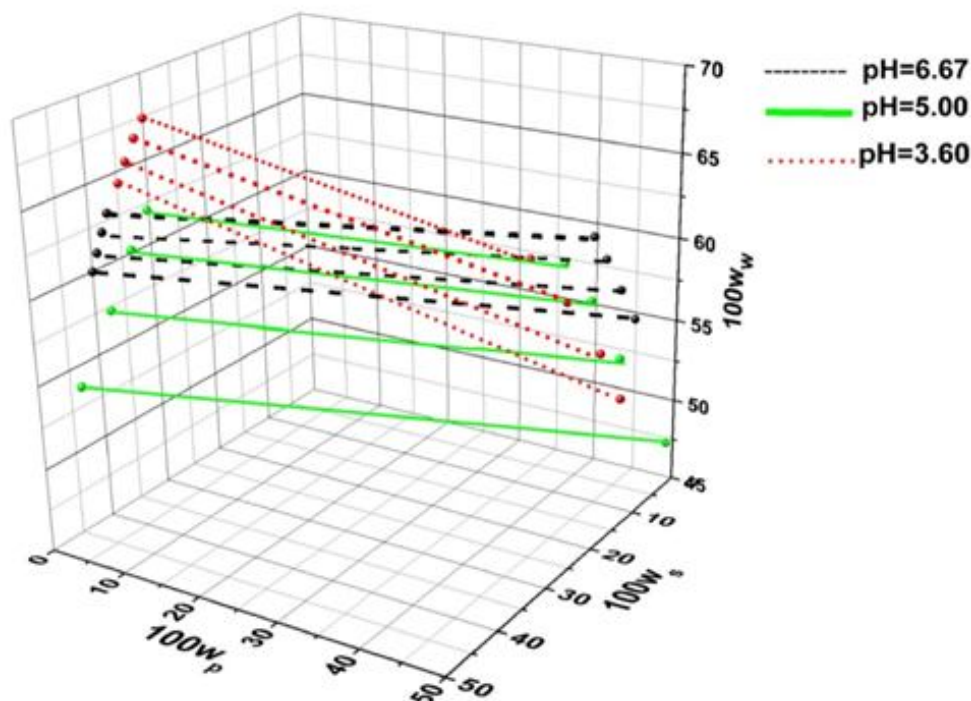


**Fig. 6.** Phase diagram and pH effects on the equilibrium phase compositions, STL, and TLL of PEG1500 + magnesium sulfate + water two-phase system at  $T = 298.15$  K and pH 6.67: (-▲-) experimental binodal; (- -●- -) calculated by using Eq. (4).



**Fig. 7.** Phase diagram and molecular mass of polymer on the equilibrium phase compositions, STL, and TLL of PEG6000 + magnesium sulfate + water two-phase system at  $T = 298.15$  K: (-▲-) experimental binodal.





**Fig. 8.** The tie line of PEG1500 + magnesium sulfate + water at different pHs (3.60, 5.00 and 6.67) two-phase system at  $T = 298.15$  K; experimental tie line; (...) pH 3.60; (—) pH 5.00; pH 6.67 (---).

compositions related to the total, top, and bottom phases. Similar compositions are observed for the coexisting phases. Based on the equilibrium composition, the mass balance between the top and bottom phases and the initial weight of each component were confirmed. By measuring the volume and density, the calculation of each phase mass was performed. It was found that the relative error of the data to the calculated mass balance was less than 3%. Furthermore, the range of the density of the top phases was between  $1.06 \text{ g cm}^{-3}$  and  $1.09 \text{ g cm}^{-3}$ , while density of the bottom phases was found to be close to  $1.2 \text{ g cm}^{-3}$ . The length of the tie line made a greater difference in the densities of the phases. Likewise, the enhancement on the TLL and pH resulted in the increment of density ( $\Delta\rho$ ) and reduction in refractive index ( $n_D$ ) differences between the phase. Besides, the relationship between density and refractive index differences between the phases, and TLL (Fig. 9) was found to follow linear trend. This tendency is confirmed with the published references elsewhere [31,34,37,38].

### Binodal Curve and Tie Line Data Correlation

Table 5 exhibits the corresponding standard deviations (SDs) of the systems investigated, as well as the coefficients in Eqs. (1) and (2), respectively.

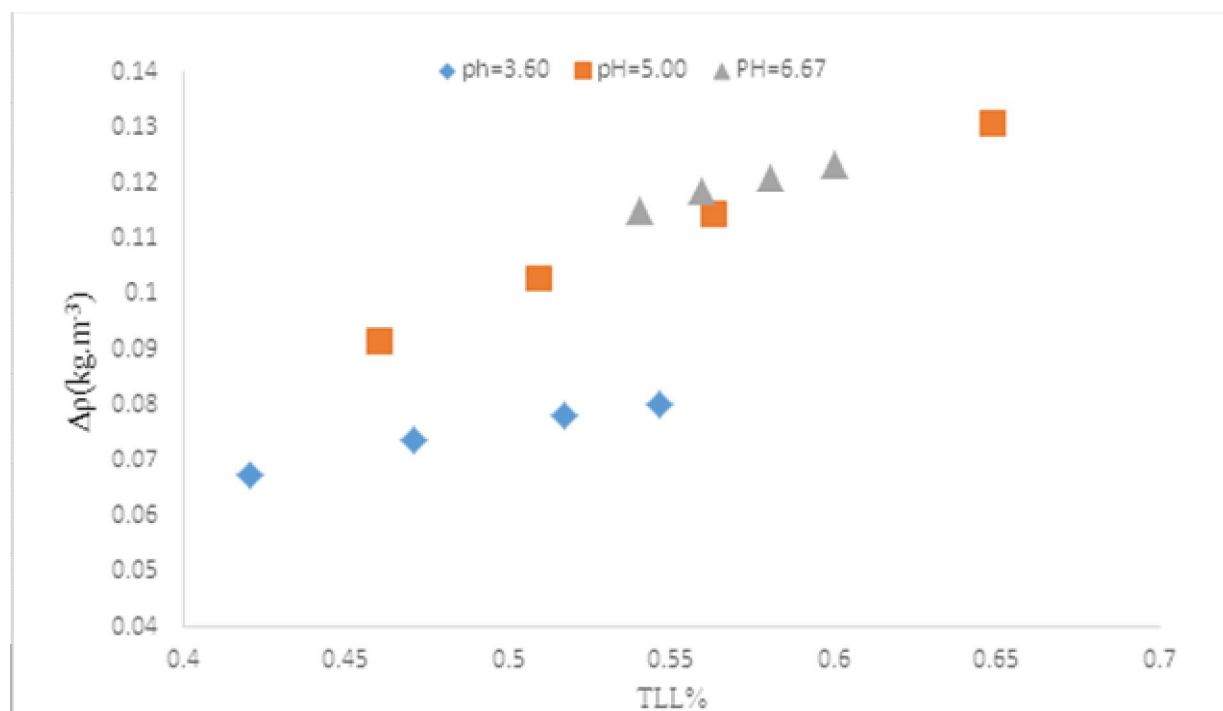
Based on the calculated standard deviation, it can be concluded that Eqs. (1) and (2) can be employed to correlate the experimental data obtained in this work. It was found that the binodal curves of the studied mixtures can be correlated by using Eqs. (1) and (2) with satisfactory results. The reliability of these models were further confirmed from the binodal curves. Furthermore, two logarithmic plots, namely  $\log\left(\frac{1-w_{pt}}{w_{pt}}\right)$  vs.  $\log\left(\frac{1-w_{sb}}{w_{sb}}\right)$  and  $\log\left(\frac{w_{wb}}{w_{sb}}\right)$  vs.

$\log\left(\frac{w_{wr}}{w_{pt}}\right)$  found to be in linear dependency, indicating the consistency of the experimental results. Table 6 gives the corresponding correlation coefficient values, or  $R_1$  and  $R_2$ . The EEV values from the experimental data are presented in Table 7. Here,  $V^*$  denotes the salt EEV in the PEG aqueous

**Table 4.** Phase Composition, Tie Line Data, and Physical Properties of PEG + Magnesium Sulfate(s) + Water ATPS System at 298.15 K and 0.1 MPa

Total system		Top phase				Bottom phase				TLL	STL
(%Mass)											
100w <sub>p</sub>	100w <sub>s</sub>	100w <sub>p</sub>	100w <sub>s</sub>	$\rho$ ( $\pm 0.0001$ ) (g cm <sup>-2</sup> )	n <sub>D</sub>	100w <sub>p</sub>	100w <sub>s</sub>	$\rho$ ( $\pm 0.0001$ ) (g cm <sup>-2</sup> )	n <sub>D</sub>		
PEG1500 + MgSO <sub>4</sub> + water, pH = 3.6											
20.00	17.00	35.00	6.53	1.0860	1.3858	1.05	31.29	1.1532	1.3640	42.02	1.37
25.00	18.00	35.35	4.24	1.0918	1.3975	0.36	35.24	1.1718	1.3669	54.65	1.45
25.00	17.00	42.80	4.30	1.0877	1.3941	0.52	34.00	1.1659	1.3659	51.69	1.42
20.00	18.00	38.97	4.12	1.0856	1.3897	0.76	32.59	1.1592	1.3649	47.06	1.39
PEG1500 + MgSO <sub>4</sub> + water, pH = 5.00											
35.00	15.00	50.14	2.12	1.0892	1.4019	1.27	44.66	1.2203	1.3803	64.79	1.15
30.00	15.00	44.53	2.89	1.0837	1.3951	2.17	39.96	1.1983	1.3742	56.29	1.14
27.00	15.00	41.00	3.12	1.0790	1.3905	2.61	36.50	1.1818	1.3721	50.87	1.15
25.00	15.00	38.00	3.98	1.0783	1.3873	3.11	34.00	1.1702	1.3702	46.02	1.16
PEG1500 + MgSO <sub>4</sub> + water, pH = 6.67											
35.00	9.00	45.05	0.31	1.0717	1.3933	0.02	40.00	1.1950	1.3711	60.02	1.13
33.00	9.00	43.29	0.42	1.0693	1.3910	0.03	39.06	1.1903	1.3702	58.01	1.12
32.00	9.00	41.47	0.50	1.0667	1.3886	0.04	38.02	1.1851	1.3692	55.89	1.10
31.00	9.00	40.00	0.70	1.0653	1.3868	0.05	37.04	1.1802	1.3683	54.00	1.10
PEG6000 + MgSO <sub>4</sub> + water											
20.00	10.00	22.80	6.20	1.0456	1.4080	0.80	34.60	1.1783	1.4075	35.92	0.775
20.00	15.00	26.80	4.80	1.0379	1.3812	0.70	39.00	1.2017	1.4297	43.02	0.769
30.00	10.00	34.30	3.50	1.0318	1.3680	0.50	47.50	1.2472	1.4796	55.48	0.768
30.00	15.00	39.20	2.70	1.0272	1.3749	0.30	53.00	1.2765	1.4917	63.58	0.765

Standard uncertainties:  $u(w_i) = 0.01$ ,  $u(n_D) = 0.0001$ ,  $u(\rho) = 0.0001$  g cm<sup>3</sup>,  $u(T) = 0.05$  K and  $u(P) = 5$  kPa.



**Fig. 9.** The relationship between density difference ( $\Delta\rho$ ) and TLL for the PEG1500 + magnesium sulfate + water system at different pH values (3.60, 5.00 and 6.67).

solution. Nonlinear regression was employed to obtain the EEV values.

Despite the poor performance of this model compared to Bleasdale, EEV found to have a stronger theoretical background from statistical geometry, which enables the evaluation of various salts to the salting-out effect in ATPS systems. Besides, both models have been widely employed to correlate the binodal data of ATPS composed of polymer + polymer and polymer + salt systems [31,35-38]. Finally, a simple model based on the binodal theory with only two-parameters was chosen to correlate the phase equilibrium data (Guan and co-workers [39]):

$$\ln(w_s^t/w_s^b) = \beta + k(w_p^b - w_p^t) \quad (8)$$

In this model,  $\beta$  and  $k$  give the fitting parameters which can be referred as “effective” viral or activity coefficients and the salting-out coefficient of the salt. Here,  $w_i$  is the

composition of PEG and salt (w/w), the superscripts in the equation indicate the top and bottom phases. The evaluation of these parameters was performed by using the linear regression method (Table 8).

## CONCLUSIONS

Liquid-liquid equilibrium data for the PEG (p) + magnesium sulfate (s) + water (w) system were obtained at temperature of 298.15 K. The data were measured at three different pH values (3.60, 5.00 and 6.67) and for different molecular weights of polymer. The experimental binodal and tie line data at the mentioned pH values were also reported in this work. It was found that the tie lines were successfully correlated by using the equation proposed by Guan and co-workers based on the binodal theory and statistical geometry. Furthermore, the Othmer-Tobias, Bancroft, Merchuk, and Pirdashti equations were selected to correlate the tie line and binodal data for this system with

**Table 5.** Correlations and Parameters for PEGs + Magnesium Sulfate + Water System with Varied Molecular Weights at Different pHs, at  $T = 298.15$  K

Correlation	pH	$T$ (K)	$A$	$B$	$C$	$R^2$
PEG1500 + Magnesium sulfate						
$w_p = (a + bw_s)^c$	3.60	298.15	1.0000	11.9719	0.4816	0.9976
(Pirdashti <i>et al.</i> [43])	5.00	298.15	1.1501	11.5971	0.4792	0.9987
	6.67	298.15	1.4852	11.2709	0.5275	0.9981
PEG6000 + Magnesium sulfate						
	-	298.15	0.1221	2.3038	0.1221	0.9987
PEG1500 + Magnesium sulfate						
$w_p = ae^{(bw_s^{0.5} - cw_s^2)}$	3.60	298.15	1.1206	-4.5223	69.7699	0.9992
(Merchuk <i>et al.</i> [29])	5.00	298.15	1.2114	-6.0584	5.7606	0.9995
	6.67	298.15	0.6144	-5.7283	70.8791	0.9999
PEG6000 + Magnesium sulfate						
	-	298.15	1.0523	-6.0162	124.9284	0.9995

**Table 6.** Values of the Parameters of Eqs. (5) and (6) for PEG + Magnesium Sulfate(s) + Water at Different pH Values

pH (PEG1500)	k	n	$R^2$	$k_1$	r	$R^2$
3.60	0.258567	2.496230	0.9941	1.759395	0.406899	0.9967
5.00	0.791928	1.088472	0.9989	1.257352	0.908053	0.9988
6.67	0.628709	1.645217	0.9975	1.329224	0.618669	0.9950
(PEG 6000)						
-	1.730881	1.046183	0.9994	0.600180	1.005355	0.9994

**Table 7.** Correlation Results for EEV of the Investigated System

pH (PEG1500)	EEV (g mol <sup>-1</sup> )	LSE <sup>a</sup>
3.60	2400.0	0.0154
5.00	2560.1	0.0704
6.67	3547.1	0.8299
PEG 6000		
	5000.0	0.1465

<sup>a</sup>Least Square Error  $(\min \frac{1}{n} \sum_{i=1}^n (error)^2)$ .

**Table 8.** Parameter for Eq. (8) from the Linear Regression Method

pH	<i>k</i>	<i>β</i>	R <sup>2</sup>
3.60	0.542485	0.257256	0.9736
5.00	0.646913	0.087558	0.9825
6.67	1.742190	2.965933	0.9760

satisfactory results. From the results, it was found that increase in pH and decrease in polymers' molecular weight increase in STL and TLL. Similarly, a direct relationship between the EEV and pH was obtained and it was found that increase in the EEV resulted in the increment of pH. As a result, the findings suggest that PEG 6000 + magnesium sulfate produces ATPS with the largest EEV and heterogeneous region.

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