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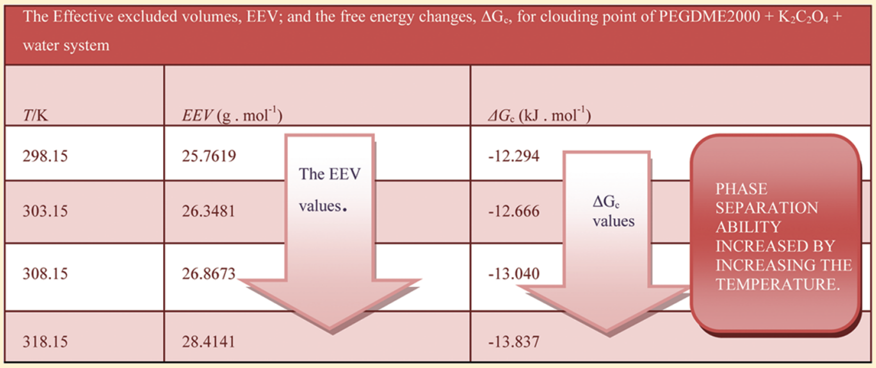
Effect of Temperature on the Aqueous Two-Phase System Containing Poly(ethylene glycol) Dimethyl Ether 2000 and Dipotassium Oxalate

Mohammed Taghi Zafarani-Moattar* and Vahid Hosseinpour-Hashemi

Physical Chemistry Department, University of Tabriz, Tabriz 51664, Iran



The Effective excluded volumes, EEV; and the free energy changes, ΔG_c, for clouding point of PEGDME2000 + $K_2C_2O_4$ + water system

T/K	EEV (g . mol^{-1})	ΔG_c (kJ . mol^{-1})
298.15	25.7619	-12.294
303.15	26.3481	-12.666
308.15	26.8673	-13.040
318.15	28.4141	-13.837

ABSTRACT: Liquid−liquid equilibria (LLE) of the poly(ethylene glycol) dimethyl ether 2000 (PEGDME2000) + dipotassium oxalate + H_2O system have been determined experimentally at T = (298.15, 303.15, 308.15, and 318.15) K. The effect of temperature on the binodal curves and tie-lines has also been studied. The Graber et al., Merchuk, and empirical equations were used to correlate the binodal data of this system with the temperature dependence expressed in the linear form with $(T - T_0)$ K as a variable. Furthermore, we used the Othmer−Tobias and Bancroft and a temperature-dependent Setschenow-type equation for the correlation and prediction of the liquid−liquid phase behavior of the studied system. The effective excluded volume (EEV) values obtained from the binodal model for this system and other aqueous PEGDME2000−salt systems were determined, and the relation between these values and salting-out ability of different salts was discussed. Also, the effects of type of the polymers PEGDME2000 and PEG2000 on LLE are discussed. Finally, the free energies of cloud points for this system were calculated. According to the results it was concluded that the increase of the entropy is a driving force for the formation of the studied aqueous two-phase system (ATPS).

1. INTRODUCTION

The aqueous two-phase system (ATPS) presents a powerful technique for the separation of the biological materials. There are two kinds of ATPS's: the polymer−polymer ATPS and the polymer−salt ATPS; the latter has more advantages. These systems, introduced in 1965 by the pioneering work of Albertsson, have been applied in the separation of biological materials, such as proteins, enzymes, and nucleic acids.[1−3]

Zaslavsky presented a useful summary of experimental liquid−liquid data and equilibrium (LLE) diagrams for systems formed by poly(ethylene glycol) (PEG), inorganic salts, and water.[3] Poly(ethylene glycol) dimethyl ether 2000 (PEGDME2000) is another polymer that has a similar structure to the PEG. Thus, PEGDME can be used to form ATPS's with kosmotropic (i.e., water structure) salts. As far as we know there are few experimental LLE data for ATPS's with this polymer.[4−8]

In this work, the phase diagrams have been determined for ATPS's containing PEGDME2000 and dipotassium oxalate ($K_2C_2O_4$) at T = (298.15, 318.15, and 318.15) K. There are no experimental liquid−liquid data in the literature for this system. The advantage of using oxalate is that it is biodegradable and therefore it could be discharged into biological wastewater plants in the separation of biological materials. Furthermore, plait points of system have been calculated in each temperature using linear least-squares regression method, and based on cloud point values the free energies of the clouding process have been estimated. In addition, the effective excluded volume (EEV) values obtained from the binodal model[9] for this system at T = (298.15, 303.15, 308.15, and 318.15) K have been used to study the effect of temperature on the phase-forming ability of the investigated system. The EEV values for the other previously studied PEGDME2000 + salt + water systems[6,8] were also calculated, and obtained values were used to compare the salting-out ability of different salts in these systems. On the basis of the Gibbs free energy of hydration of salts, the relations between these values and salting-out ability of different salts were also discussed. Also the effect of the polymers

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PEGDME2000 and PEG2000 on the phase-forming ability of these two-phase systems containing dipotassium oxalate was studied. The effect of temperature on the tie-lines was also studied.

An empirical equation[6] and the Graber et al.[10] and the Merchuk[11] equations as a function of temperature were used for the correlation of binodal data and the prediction of them at T = 303.15 K and compared with experimental data. The Othmer–Tobias and Bancroft[12] and Setschenow-type[13] equations have been used to correlate the experimental LLE data of investigated ATPS's. Likewise, the Setschenow-type equation[13] has also been used for the prediction of tie-line data at T = 303.15 K.

2. MATERIALS AND METHODS

2.1. Materials. PEGDME2000 with CAS Registry No. 24991-55-7 and PEG2000 with CAS Registry No. 25322-68-3 were obtained from Merck. The number average molar mass of the polymer was previously determined to be 2305 g·mol^{-1}, using gel permeation chromatography (GPC, Agilent, USA).[4] Dipotassium oxalate monohydrate ($K_2C_2O_4 \cdot H_2O$) with CAS Registry No. 6487-48-5 with a minimum mass fraction purity of 99 % was obtained from Merck. The polymers and salt were used without further purification, and double-distilled deionized water was used.

2.2. Apparatus and Procedure. The experimental apparatus employed is essentially similar to the one used in previous works.[4,5] The binodal curves were determined by clouding point titration method.[4] In this method the temperature was controlled using a thermostat (HETO BIRKERØD, type: 01 TE 623, Denmark) within ± 0.05 K. The composition of the mixture for each point on the binodal curve was calculated by mass using an analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan) with a precision of ± $1 \cdot 10^{-7}$ kg. The maximum uncertainty was found to be ± 0.002 in determining the mass fraction of both polymers and salt by using this method.

For the determination of the tie-lines, feed samples (about $2 \cdot 10^{-5}$ m^3) were prepared by mixing appropriate amounts of polymer, salt, and water in the vessel. The samples were stirred for 1 h and then placed in the thermostatted bath. The temperature of the thermostatted bath was controlled using a thermostat (JULABO model MB, Germany) with an accuracy of ± 0.02 K and allowed to settle for at least 48 h to separate into two clear phases. After separations of the two phases, the concentrations of dipotassium oxalate in the top and bottom phases were determined by flame photometry (Jenway PFP7, England). In this method, first we prepared about 11 standard solutions having the potassium ion in the concentration ranges of (150 to 250) ppm. Then, using these standard solutions the flame photometer has been calibrated. To measure potassium concentration in the samples taken from the top and bottom phases, it was necessary to dilute these solutions to place in the ranges of (150 to 250) ppm. The concentrations of samples were determined using obtained absorption values and the calibration curve. The maximum uncertainty was found to be ± 0.002 in determining the mass fraction of salt by using this method. The concentration of PEGDME in both phases was determined by refractive index measurements performed at T = 298.15 K using a refractometer (Atago DR-A$_1$, Japan) with a precision of ± 0.0001. The uncertainty in refractive index measurement is ± 0.0002. For dilute aqueous solutions containing a polymer and a salt, the relation between the refractive index, n_D, and the mass fractions of polymer, w_p, and salt, w_s is given by[14]

$$n_D = n_0 + a_p w_p + a_s w_s \tag{1}$$

where n_0 is the refractive index of pure water which is set to 1.3325 at T = 298.15 K. a_p and a_s are constants of the polymer and salt, respectively, for which linear calibration plots of the refractive index of the solution are obtained. However, it should be noted that eq 1 is only valid for dilute solutions. Therefore, it was necessary to dilute the samples before refractive index measurements, to be in the mass fraction range (C range) presented in Table 1. The uncertainty of the mass fraction of PEGDME achieved using eq 1 was better than 0.002. The values of these constants and respective correlation coefficient values, R^2, are given in Table 1.

Table 1. Values of the Parameters of Equation 1, a_i, for the PEGDME2000 (p) + $K_2C_2O_4$ (s) + H_2O (w) System

material	constant	value	C range (w/w)	$R^{2\,a}$
PEGDME2000	a_p	0.1358	0–0.15	0.9999
$K_2C_2O_4$	a_s	0.1373	0–0.12	0.9999

[a] R^2 represents the respective correlation coefficient value of the linear calibration plot of the refractive index against the mass fraction for PEGDME2000 or $K_2C_2O_4$ at the mass fraction range (C range) of each material.

3. RESULTS AND DISCUSSION

3.1. Experimental Results. For the PEGDME2000 + dipotassium oxalate + water system the experimental binodal data and the tie-line compositions at T = (298.15, 303.15, 308.15, and 318.15) K are given in Tables 2 and 3, respectively.

Table 2. Experimental Binodal Data in Mass Fraction, w_i, for the PEGDME2000 (p) + $K_2C_2O_4$ (s) + H_2O (w) System at T = (298.15, 303.15, 308.15, and 318.15) K

T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 318.15	
$100w_p$	$100w_s$	$100w_p$	$100w_s$	$100w_p$	$100w_s$	$100w_p$	$100w_s$
39.23	4.45	40.49	4.06	41.20	3.77	42.41	3.22
38.58	4.54	39.67	4.16	40.06	3.91	41.88	3.27
37.64	4.68	38.87	4.27	39.29	4.00	40.91	3.37
36.74	4.81	37.80	4.42	38.33	4.13	40.00	3.47
35.40	5.02	36.75	4.58	37.43	4.26	38.86	3.61
34.18	5.21	35.20	4.82	36.11	4.47	36.00	4.00
32.51	5.53	33.85	5.04	34.86	4.66	34.49	4.21
31.01	5.82	31.95	5.39	33.17	4.96	32.37	4.55
29.11	6.23	30.38	5.70	31.66	5.24	30.62	4.85
27.51	6.62	28.41	6.12	29.66	5.63	28.32	5.28
25.56	7.11	26.75	6.51	27.90	6.02	26.43	5.67
23.94	7.57	24.78	7.01	25.92	6.49	24.02	6.23
22.09	8.12	23.13	7.47	24.28	6.90	22.14	6.70
20.58	8.62	21.30	8.04	22.39	7.43	20.18	7.25
18.94	9.21	19.78	8.53	20.87	7.89	16.76	8.21
17.62	9.68	18.14	9.10	19.19	8.42	15.45	8.62
16.07	10.28	16.70	9.62	17.79	8.90		
				16.17	9.42		

3.1.1. Effect of Temperature. The effect of temperature on the phase-forming ability in the studied system is also shown in Figure 1. The locus for the experimental binodals shown in Figure 1 indicates that the two-phase area is expanded with an

Table 3. Experimental Tie-Lines Data in Mass Fraction, w_i, for the PEGDME2000 (p) + $K_2C_2O_4$ (s) + H_2O (w) System at T = (298.15, 303.15, 308.15, and 318.15) K together with Tie-Line Length, TLL, and Slope, S

feed sample[a]		top phase		bottom phase			
$100w'_p$	$100w'_s$	$100w_p$	$100w_s$	$100w_p$	$100w_s$	S	TLL
			T/K = 298.15				
18.00	10.00	24.53	7.39	2.72	16.08	−2.51	23.48
18.02	11.01	30.78	5.80	1.31	17.96	−2.42	31.87
17.96	11.99	34.26	5.13	0.59	19.19	−2.39	36.49
17.99	13.02	37.72	4.65	0.23	20.75	−2.33	40.81
18.03	14.00	39.88	4.28	0.23	22.02	−2.24	43.44
18.02	15.03	43.17	3.90	0.16	23.31	−2.22	47.19
18.00	16.01	45.54	3.71	0.12	24.04	−2.23	49.76
			T/K = 303.15				
18.01	10.00	26.58	6.57	2.13	16.43	−2.48	26.36
18.03	11.02	31.06	5.65	1.61	17.64	−2.46	31.80
18.01	12.00	35.24	4.87	0.65	19.07	−2.44	37.40
18.01	13.02	38.67	4.25	0.57	20.42	−2.36	41.39
18.03	13.99	41.90	3.93	0.47	21.86	−2.31	45.15
18.02	15.01	44.35	3.65	0.44	22.87	−2.28	47.93
18.04	15.99	46.96	3.41	0.33	23.83	−2.28	50.90
			T/K = 308.15				
18.03	10.00	27.66	6.09	2.13	16.57	−2.44	27.60
18.02	11.01	32.02	5.21	0.91	18.12	−2.41	33.68
18.00	12.00	35.82	4.56	0.37	19.39	−2.39	38.43
18.04	13.01	38.60	4.14	0.31	20.69	−2.31	41.72
17.76	13.80	40.54	3.86	0.18	21.49	−2.29	44.05
18.03	15.01	43.71	3.59	0.13	22.79	−2.27	47.62
18.03	15.80	45.77	3.47	0.09	24.10	−2.21	50.13
			T/K = 318.15				
18.00	10.00	33.17	4.37	0.52	16.72	−2.64	34.91
18.00	11.01	36.63	3.93	0.37	18.06	−2.57	38.91
18.06	12.00	39.00	3.69	0.29	19.33	−2.48	41.75
17.99	12.98	42.28	3.21	0.25	20.06	−2.49	45.28
18.03	14.00	44.22	3.00	0.18	21.47	−2.38	47.75
18.04	15.00	46.78	2.88	0.15	22.69	−2.35	50.67
18.03	16.00	48.92	2.71	0.11	23.92	−2.30	53.22

[a] w_p' and w_s' are the total mass fractions of polymer and salt in its feed samples, respectively.

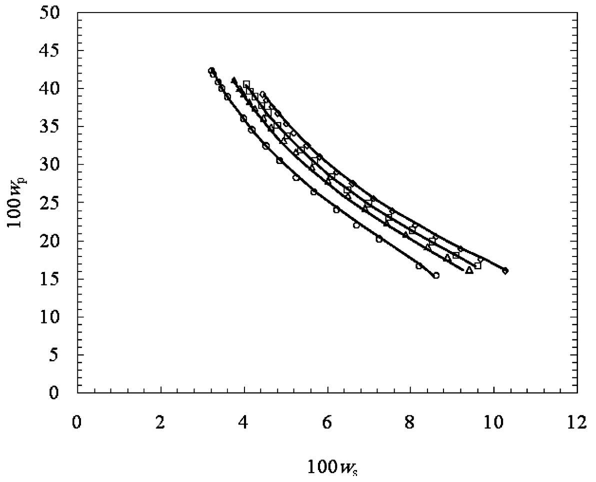

Figure 1. Plot of the mass fraction of polymer against the mass fraction of salt to show binodal curves for the PEGDME2000 (p) + $K_2C_2O_4$ (s) + water (w) two-phase system at different temperatures: ◊, T = 298.15; □, T = 303.15; △, T = 308.15 and ○, T = 318.15, and (solid line) calculated from eq 5.

Table 4. Effective Excluded Volumes, EEV (g·mol^{-1}), as Determined by the Regression of the Statistical Geometry Model[9] for PEGDME2000 + $K_2C_2O_4$+ H_2O at T = (298.15, 303.15, 308.15, and 318.15) K

T/K	EEV	R^2	SD[a]
298.15	25.7619	0.9990	0.02
303.15	26.3481	0.9989	0.00
308.15	26.8673	0.9994	0.01
318.15	28.4141	0.9993	0.09

[a] SD = $(\sum_{i=1}^{N}(100w_s^{\text{cal}} - 100w_s^{\text{exp}})^2/N)^{0.5}$, where N represents the number of binodal data, respectively.

increase in temperature. The effect of temperature on the obtained binodals can be explained using the binodal model.[9] This model is based on the statistical geometry methods from which the EEV can be determined. It was found that bigger EEV values correspond to a higher salting-out ability of salt in polymer + salt + water systems.[9] The binodal equation for the aqueous polymer−salt systems can be written as

$$\ln\left(V^*_{123}\frac{w_p}{M_p}\right) + V^*_{123}\frac{w_s}{M_s} = 0 \qquad (2)$$

where V^*_{123} is the EEV. M_p and M_s are the molar mass of polymer and salt, respectively. The EEV values obtained from the correlation of binodal data of investigated systems at T = (298.15, 303.15, 308.15, and 318.15) K along with the corresponding standard deviations (SD) are given in Table 4. The correlation coefficient values and the small standard deviations reported in Table 4 indicate that the binodal model[9] represents the obtained binodal data for the PEGDME2000 + $K_2C_2O_4$ + H_2O system with excellent accuracy at different working temperatures. Also as can be seen from Table 4, EEV values are increased by increasing the temperature. This means that the salting-out ability of the studied system is increased by increasing the temperature.

To show the effect of temperature on the equilibrium phase compositions for the investigated system, the experimental tie-lines are compared in Figure 2, for the temperatures T = (298.15 and 318.15) K. As shown in Figure 2, the slope and the length of the tie-lines increased with an increase in temperature. In other words, the concentration of salt in the bottom phase which is in equilibrium with a certain concentration of PEGDME in the top phase decreases by increasing temperature. This is because the PEGDME2000 becomes more hydrophobic with an increase in temperature.[15] Thus, by increasing temperature, water is driven from the polymer-rich phase to the salt-rich phase, so the polymer concentration at the polymer-rich phase increases, while the salt-rich phase will be somewhat more diluted (i.e., the salt concentration will be decreased).

3.1.2. Effect of Salt. To see the effectiveness of the anion in forming an ATPS with PEGDME, the experimental binodal curves of the {PEGDME2000 + $K_2C_2O_4$ + H_2O}, {PEGDME2000 + K_3PO_4 + H_2O}, and {PEGDME2000 + K_2HPO_4 + H_2O} systems[6,8] are shown in Figure 3 at T = 298.15 K. In Figure 3, considering that the salts have a common cation but contain different anions, it is easy to see that the salting-out ability of the anions follows the ordering PO_4^{3-} > HPO_4^{3-} > $C_2O_4^{2-}$. The salting-out ability can also be related to the Gibbs free energy of hydration of ions (ΔG_{hyd}). For PO_4^{3-},

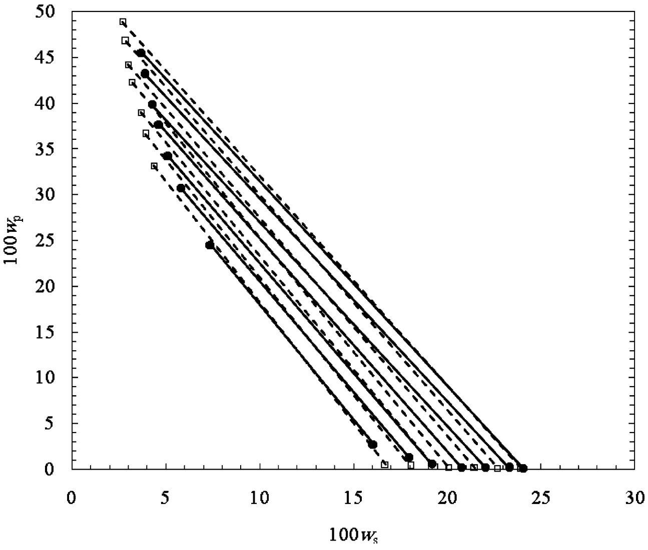

Figure 2. Plot of the mass fraction of polymer against the mass fraction of salt to illustrate the effect of temperature on the slope and length of tie-lines of the {PEGDME2000 (p) + $K_2C_2O_4$ (s) + H_2O (w)} system: ●, T = 298.15 K; □, T = 318.15 K; —, tie-lines at 298.15 K; - - -, tie-lines at 318.15 K. Tie-lines were obtained by connecting the experimental equilibrium phase composition data.

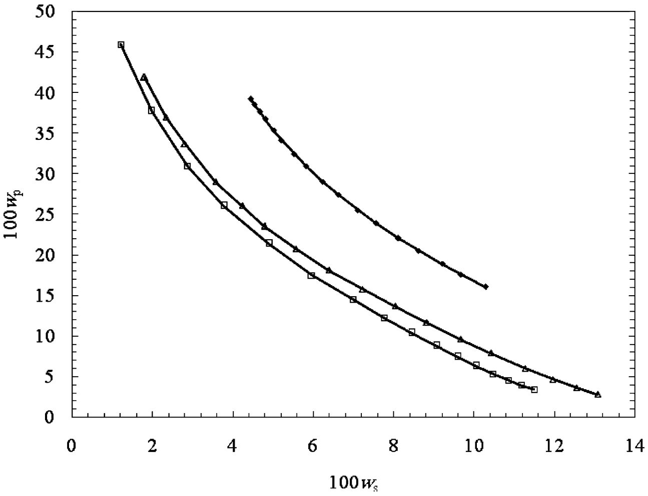

Figure 3. Binodal curves for the {PEGDME2000 (p) + salt (s) + H_2O (w)} systems at T = 298.15 K. ♦, $K_2C_2O_4$; △, K_2HPO_4; □, K_3PO_4.

the ΔG_{hyd} = −2835 kJ·mol^{-1} has been reported by Marcus.[16] For the anions HPO_4^{2-} and $C_2O_4^{2-}$, Zafarani-Moattar and Zaferanloo[17] estimated the ΔG_{hyd} values respectively (−1789 and −1577) kJ·mol^{-1}, using the procedure given by Marcus.[16] Therefore, it seems that better salting-out of PEGDME is observed when the anions of the salt have a more negative ΔG_{hyd} value. For studying the effect of salts on the salting-out ability in PEGDME2000 + salt + water systems, the binodal model[9] can also be used. Using the experimental binodal obtained in this work and other published data,[6,8] the EEV values were determined at T = 298.15 K by eq 2 for these systems and are collected in Table 5. The increase of EEV values in the order K_3PO_4 > K_2HPO_4 > $K_2C_2O_4$ indicates the same order of salting-out ability of these salts in the PEGDME2000 + salt + water systems. This trend is also evident from Figure 3.

Table 5. Comparison of Free Energies of Hydration for Anions, ΔG_{hyd} (kJ·mol^{-1}), and Effective Excluded Volumes, EEV (g·mol^{-1}), for PEGDME2000 + Salt + Water Systems at T = 298.15 K

salt	ΔG_{hyd}	EEV	R^2	SD
$K_2C_2O_4$	−1577	25.7619	0.9990	0.02
K_2HPO_4	−1789	34.8344	0.9744	0.61
K_3PO_4	−2835	42.0717	0.9786	0.99

3.1.3. *Effect of the Polymer.* PEGDME has a similar structure to PEG. In this regard, our interest lies in comparison of the phase-forming ability of these polymers. To accomplish this, we decided to determine the binodal curve of the system (PEG2000 + $K_2C_2O_2$ + H_2O) using PEG with the same molar mass of 2000 g·mol^{-1} for which there are no experimental binodal data in the literature. We determined binodals for the PEG2000 + $K_2C_2O_2$ + H_2O system at T = (298.15 and 318.15) K, and the binodal data are given in Table 6; and the corresponding binodal curves together with the binodal curves for (PEGDME$_{2000}$ + $K_2C_2O_2$ + H_2O) are shown in Figure 4a,b, at T = (298.15 and 318.15) K, respectively. Considering that both of the polymers have the same molar masses, from this figure we can conclude that when we have dipotassium oxalate the salting-out ability of PEGDME2000 is better than PEG2000.

Table 6. Experimental Binodal Data in Mass Fraction, w_i, for the PEGDME2000 (p) + $K_2C_2O_4$ (s) + H_2O (w) System at T = (298.15 and 318.15) K

T/K = 298.15		T/K = 318.15	
$100w_p$	$100w_s$	$100w_p$	$100w_s$
28.64	8.08	26.50	7.54
26.14	8.89	23.22	8.54
22.82	10.12	19.30	9.98
20.34	11.15	16.71	10.91
17.35	12.53	13.71	12.07
15.01	13.55	11.71	13.02
12.61	14.83	9.32	14.19
10.83	15.77	7.59	15.13
8.86	17.01	5.64	16.22
7.54	17.78	4.41	17.02
5.94	18.78	3.05	18.17
5.05	19.43	2.34	18.89
4.08	20.05	1.60	19.93
3.39	20.84	1.21	20.66
2.64	21.65	0.80	21.84
1.91	22.57	0.49	22.44
1.44	23.50	0.34	23.84
1.12	24.00		
0.78	25.30		
0.60	25.99		
0.39	26.67		

3.2. Correlation. *3.2.1. Binodal Curve Correlation.* The binodal curves for this system are shown in Figure 1. For the correlation of binodal data of polymer + salt + water systems, several empirical equations have been proposed. All of these commonly used equations are nonlinear empirical expressions of polymer mass fraction, w_p, as a function of salt mass fraction, w_p, or vice versa and at least have three parameters. In this work for the correlation of binodal data we examined the

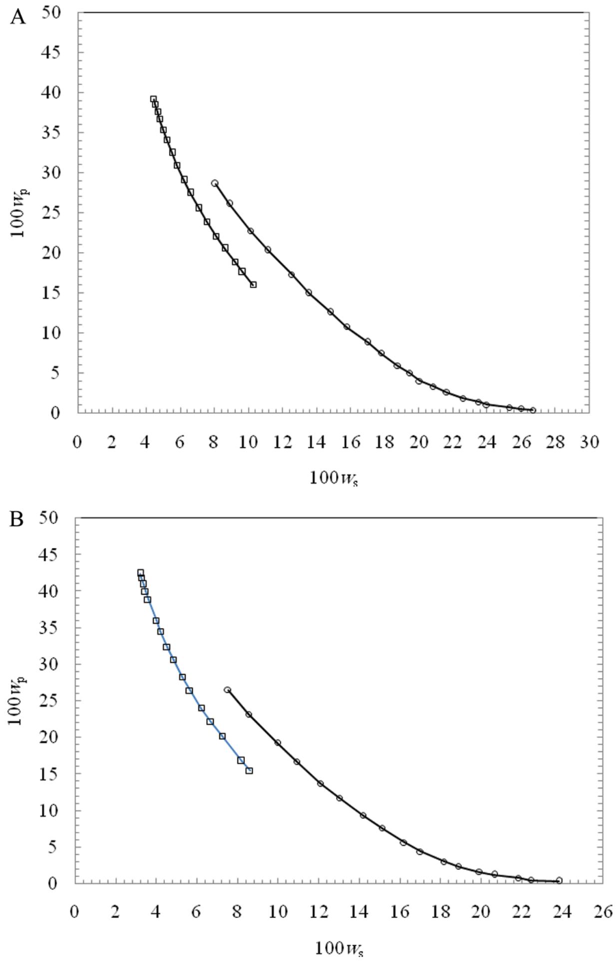

Figure 4. Binodal curves for the {PEGDME2000 (p) + $K_2C_2O_4$ (s) + H_2O (w)}, □, and {PEG2000 (p) + $K_2C_2O_4$ (s) + H_2O (w)}, ○, systems at: (a) T = 298.15 K, (b) T = 318.15 K.

performances of the temperature-dependent Merchuk equation[11] (eq 3) which has been successfully used previously,[18] the empirical equation (eq 4) that we proposed recently,[6] and the Graber et al.[10] equation with temperature dependency as given by eq 5. In these equations the temperature dependency of parameters was expressed in the linear form with $(T - T_0)$ K as a variable.

$$w_p = [a_0 + a_1(T - T_0)]\exp([b_0 + b_1(T - T_0)]w_s^{0.5} - [c_0 + c_1(T - T_0)]w_s^3) \tag{3}$$

$$w_p = [\alpha_0 + \alpha_1(T - T_0)] + [\beta_0 + \beta_1(T - T_0)]\ln(w_s) + [\gamma_0 + \gamma_1(T - T_0)]w_s \tag{4}$$

$$1/w_s = [d_0 + d_1(T - T_0)] + [e_0 + e_1(T - T_0)]w_p^{0.5} + [f_0 + f_1(T - T_0)]w_p \tag{5}$$

In these equations, T is the absolute temperature, and T_0 is assumed to be the reference temperature, T_0 = 273.15 K. Also (a_0, a_1, b_0, b_1, c_0, and c_1), (α_0, α_1, β_0, β_1, γ_0, and γ_1), and (d_0, d_1, e_0, e_1, f_0, and f_1) are independent temperature adjustable parameters of eqs 3 to 5.

The experimental binodal data at T = (298.15, 308.15, and 318.15) K were fitted by nonlinear least-squares regression method to eqs 3 to 5. The fitting parameters for these equations along with the corresponding standard deviation (SD) for each temperature are given in Table 7. The standard deviations show that all of these equations can be used to reproduce the binodal data with good accuracy; however, on the basis of the obtained standard deviations, we conclude that the performance of eq 5 is better than the other equations (eqs 3 and 4). To show the reliability of these equations and the prediction ability of the locus of the binodal curves for the investigated system at temperatures where no experimental data are available, we attempted to compare the experimental polymer compositions on the binodal curve of the PEGDME2000 + $K_2C_2O_4$ + H_2O system at T = 303.15 K with those predicted using eqs 3, 4, and 5 at the corresponding temperature. On the basis of the standard deviations reported in Table 7, it can be seen that eq 5 has the best prediction ability for the temperature T = 303.15 K.

3.2.2. Tie-Line Correlation.

For the correlation of LLE data of (polymer + salt + water) systems, several models have been developed. However, in this work we decided to use the Othmer–Tobias and Bancroft[12] equation which is usually used to assess the reliability of experimental tie-line data, and the Setschenow-type[13] equation which shows good performance in the correlation and prediction of the tie-lines for such two-phase systems.

3.2.2.1. Othmer–Tobias and Bancroft Equations.

The correlation equations given by Othmer–Tobias (eq 6a) and Bancroft[12] (eq 6b) have been used to correlate the tie-lines composition.

$$\left(\frac{1 - w_p^{top}}{w_p^{top}}\right) = k\left(\frac{1 - w_s^{bot}}{w_s^{bot}}\right) \tag{6a}$$

$$\left(\frac{w_w^{bot}}{w_s^{bot}}\right) = k_1\left(\frac{w_w^{top}}{w_p^{top}}\right)^r \tag{6b}$$

where k, n, k_1, and r represented fit parameters and "top" and "bot" represent top and bottom phases, respectively. These equations have also been used to assess the reliability of LLE data. Using the tie-line data reported in Table 3, a linear dependency of the $\log[(1 - w_p^{top})/w_p^{top}]$ plots against $\log[(1 - w_s^{bot})/w_s^{bot}]$ and $\log(w_w^{bot}/w_s^{bot})$ against $\log(w_w^{top}/w_p^{top})$ is obtained, which indicated an acceptable consistency of the results. The experimental LLE data were correlated to the eq 6 using the following objective function

$$\mathrm{OF} = \sum_T \sum_p \sum_l \sum_j (w_{T,p,l,j}^{cal} - w_{T,p,l,j}^{exp})^2 \tag{7}$$

where $w_{T,p,l,j}$ is the mass percent of the component j in the phase p for the lth tie-line at temperature T and the superscripts "cal" and "exp" refer to the calculated and experimental values, respectively. In eq 7 the species j can be polymer, salt, or solvent molecules. The corresponding correlation coefficient values, R^2, and the values of the fitted parameters together with the deviations (Dev) are given in Table 8. On the basis of correlation coefficient values, R^2, reported in Table 8, we conclude that the reported tie-line data have acceptable consistency. Also based on the obtained deviations, we conclude that eqs 6a and 6b can be satisfactorily used to correlate the tie-line data of the investigated system.

3.2.2.2. Seteschenow-Type Equation.

The Seteschenow-type equation[13] is a relatively simple two-parameter equation, which can be derived from the binodal theory.[9] The equation

Table 7. Values of Parameters of Equations 3, (a_i, b_i, c_i), 4, (α_i, β_i, γ_i), and 5, (d_i, e_i, f_i), for the PEGDME2000 + $K_2C_2O_4$ + Water System at T = (298.15, 308.15, and 318.15) K

Merchuk[11] equation as a function of temperature (eq 3)

T/K	a_0	a_1	b_0	$10^3\ b_1$	$10^5\ c_0$	$10^6\ c_1$	SD[a]
	155.4164	−0.2459	−0.5644	−2.6407	2.1706	6.6515	
298.15							0.30
303.15							0.26[b]
308.15							0.38
318.15							0.28
overall							0.32

empirical[6] equation as a function of temperature (eq 4)

T/K	α_0	α_1	β_0	β_1	γ_0	γ_1	SD
	247.4697	−0.5383	−97.165	0.2067	6.0402	−0.0163	
298.15							0.15
303.15							0.08[b]
308.15							0.23
318.15							0.18
overall							0.19

Graber et al.[10] equation as a function of temperature (eq 5)

T/K	d_0	$10^3\ d_1$	$10^3\ e_0$	$10^3\ e_1$	$10^3\ f_0$	$10^4\ f_1$	SD
	−0.0107	7.6394	9.0544	−3.1634	2.7082	3.8234	
298.15							0.05
303.15							0.02[b]
308.15							0.08
318.15							0.05
overall							0.06

[a] SD = $(\sum_{i=1}^{N}(100w_i^{\mathrm{cal}} - 100w_i^{\mathrm{exp}})^2/N)^{0.5}$. [b] Obtained from the comparison of the experimental polymer compositions, w_p, on the binodal curve of the PEGDME2000 + $K_2C_2O_4$ + H_2O system at T = 303.15 K reported in Table 2 and the corresponding data predicted using eqs 3 to 5 using the fitting parameters given in Table 7.

Table 8. Values of Parameters of Othmer−Tobias and Bancroft Equations, (K, n, k_1 , r), at T = (298.15, 303.15, 308.15, and 318.15) K, and the Steschenow Type, (k_p, k_s) (kg·K·mol^{-1}), Equation at T = (298.15, 308.15, and 318.15) K for the PEGDME2000 + $K_2C_2O_4$ + Water System

Othmer−Tobias and Bancroft equations

T/K	K	n	R^2	k_1	r	R^2	Dev[a]
298.15	0.1364	1.8698	0.9902	3.0119	0.5248	0.9860	1.08
303.15	0.1172	1.9265	0.9940	3.1317	0.5160	0.9917	0.61
308.15	0.1513	1.7552	0.9945	3.0459	0.5603	0.9914	0.58
318.15	0.1800	1.4997	0.9905	3.2477	0.6729	0.9911	0.12

Steschenow-type equation as a function of temperature

T/K	k_p	k_s·10^{-3}	Dev
	185.3783	1.0876	
298.15			0.02
303.15			0.01[b]
308.15			0.04
318.15			0.10
overall			0.05

[a] Dev = $\sum_p\sum_l\sum_j\sum_T ((100w_{p,l,j,T}^{\mathrm{cal}} - 100w_{p,l,j,T}^{\mathrm{exp}})^2/6N$, where $w_{p,l,j,T}$ is the mass fraction of the component j (i.e., polymer, salt, or water) in the phase p for the lth tie-line at temperature T and N represents the number of tie-line data points. [b] Predicted with the corresponding model parameters obtained from the correlation of data at T = (298.15, 308.15, and 318.15) K.

has the following form:

$$\ln\left(\frac{C_p^{\mathrm{top}}}{C_p^{\mathrm{bot}}}\right) = k_p + k_s(C_s^{\mathrm{bot}} - C_s^{\mathrm{top}}) \tag{8}$$

in which the k_s is the salting-out coefficient, k_p is a constant, and C_p and C_s are the molality of polymer and salt, respectively. Recently we successfully used eq 8 for the correlation of tie-line data for the aqueous poly(propylene glycol) + potassium citrate two-phase system.[19] In this work, for the temperature dependency of fitting parameters of eq 8, we adopted a simple form for each parameter as follows:

$$\ln\left(\frac{C_p^{\mathrm{top}}}{C_p^{\mathrm{bot}}}\right) = \left[\frac{k_p}{T} + \frac{k_s}{T}(C_s^{\mathrm{bot}} - C_s^{\mathrm{top}})\right] \tag{9}$$

The parameters of eq 9 which were obtained from the correlation of the experimental LLE data at T = (298.15, 308.15, and 318.15) K are also given in Table 8 along with the corresponding deviations. Here, the objective function (eq 7) was also used. On the basis of deviations reported in Table 8, it is interesting to note that eq 9 with only two parameters represents the experimental LLE data with excellent accuracy for the studied system at the temperatures T = (298.15 to 318.15) K.

Also, for the studied system, the tie-lines at T = 303.15 K that clearly have no contribution to obtaining the parameters, k_p and k_s, were predicted with the deviation of 0.01 in mass percent using the same parameters given in Table 8. Figure 5 shows the experimental and the predicted tie-lines at T = 303.15 K. On the basis of obtained deviations and from Figure 5, we conclude that eq 9 can accurately predict tie-lines at temperatures at which no experimental data are available.

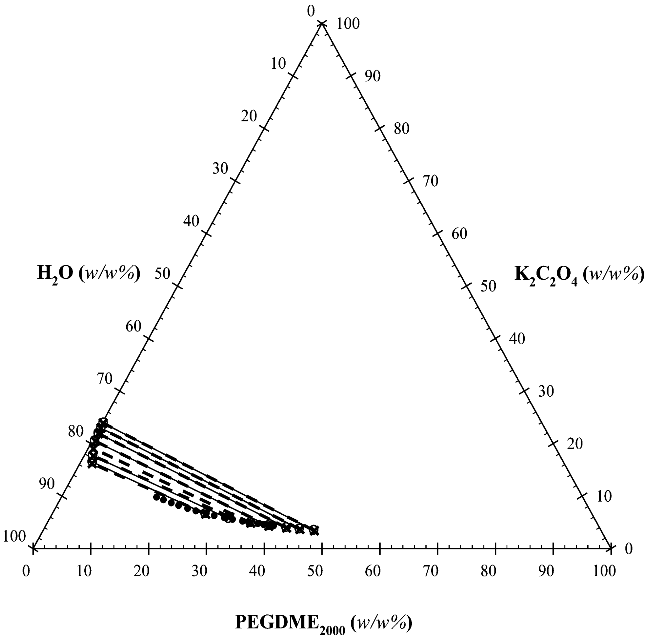

Figure 5. Experimental and calculated tie-line data and experimental binodal data at T = 303.15 K. −○−, experimental tie-lines; ---×---, calculated tie-lines from eq 9; ●, experimental binodal data.

3.3. Estimated Plait Point, Slope, and the Length of Tie-Lines.

Somewhere in the binodal curve, we have a plait point where the length of tie-line has shrunk to zero, that is, when the two liquid phases become identical.[20] The location of the plait point for the studied system was also estimated by extrapolation from the auxiliary curve satisfactorily fitted with the following linear equation:

$$w_p = f + g w_s \tag{10}$$

where f and g represent fit parameters. For the studied system, the estimated values for the plait points along with the obtained fitting parameters for eq 10 and the corresponding correlation coefficients, R^2, are listed in Table 9. As an example, the locus of estimated plait point for this system along with the used procedure is illustrated in Figure 6 at T = 303.15 K.

Table 9. Values of Parameters of Equation 10 and the Plait Points, (f, g), for the PEGDME2000 (p) + $K_2C_2O_4$ (s) + H_2O (w) System at T = (298.15, 303.15, 308.15, and 318.15) K

T/K	f	g	R^2	plait point (w_p%, w_s%, w_w%)[a]
298.15	−14.7686	2.5062	0.9909	(13.42, 11.25, 75.33)
303.15	−16.2982	2.6657	0.9941	(12.47, 10.79, 76.74)
308.15	−11.9220	2.4280	0.9927	(12.71, 10.14, 77.15)
318.15	−3.0248	2.1945	0.9876	(15.59, 8.48, 75.93)

[a] w_i % represents the mass percent of component i.

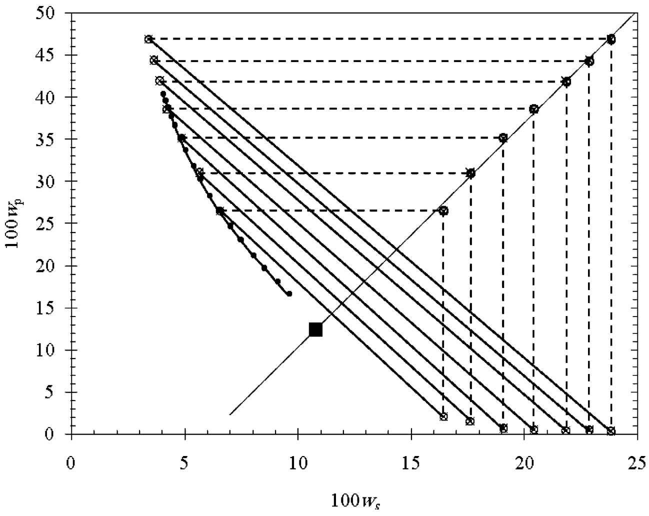

Figure 6. Binodal curve, tie-lines, and plait point for the PEGDME2000 (p) + $K_2C_2O_4$ (s) + H_2O (w) system at T = 303.15 K; ●, experimental binodal data; —, calculated binodal from eq 5; ○, tie-line data; ---×---, calculated auxiliary and ■, plait point.

The tie-line length, TLL, and the slope of the tie-line, S, at different compositions and temperatures were also calculated respectively using eqs 11 and 12 as follows:

$$\mathrm{TLL} = [(w_1^{\mathrm{top}} - w_1^{\mathrm{bot}})^2 + (w_2^{\mathrm{top}} - w_2^{\mathrm{bot}})]^{0.5} \tag{11}$$

$$S = (w_1^{\mathrm{top}} - w_1^{\mathrm{bot}})/(w_2^{\mathrm{top}} - w_2^{\mathrm{bot}}) \tag{12}$$

Results are also collected in Table 3.

3.4. Free Energies of the Cloud Point (CP).

The free energy of phase separation (ΔG_c) can be calculated from the relation[21]

$$\Delta G_c = RT \ln X_p \tag{13}$$

X_p is the mole fraction concentration of PEGDME at cloud point. In Table 10, the values of ΔG_c are presented. The enthalpy values of phase separation (ΔH_c) were calculated by the relation,

$$\Delta H_c = \frac{d(\Delta G_c/T)}{d(1/T)} \tag{14}$$

The calculated ΔH_c values are presented in the Table 10 which are positive and show that the aqueous two-phase formation processes are endothermic.

The following Gibbs−Helmoltz equation was used to calculate the entropy of phase separation (ΔS_c),

$$\Delta S_c = \frac{\Delta H_c - \Delta G_c}{T} \tag{15}$$

Table 10. Free Energy Changes, ΔG_c (kJ·mol^{-1}), Entropy Changes, ΔS_c (J·K^{-1}·mol^{-1}), and Enthalpy Changes, ΔH_c (kJ·mol^{-1}), for Clouding Point of PEGDME2000 (p) + $K_2C_2O_4$ (s) + Water (w) for Different Salt Mass Fractions, w_s, at T = (298.15, 308.15, and 318.15) K

		T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 318.15	
w_s	ΔH_c	ΔG_c	ΔS_c	ΔG_c	ΔS_c	ΔG_c	ΔS_c	ΔG_c	ΔS_c
0.04	10.718	−12.294	77	−12.666	77	−13.040	77	−13.837	77
0.06	10.738	−13.558	81	−13.943	81	−14.301	81	−15.189	81
0.08	12.409	−14.525	90	−14.930	90	−15.318	90	−16.333	90
0.10	15.796	−15.351	105	−15.784	104	−16.247	105	−17.443	105

The calculated ΔS_c values are all positive, and they are also collected in Table 10. This shows that the increase of entropy is the driving force for the aqueous two-phase formation processes in the studied system at T = (298.15, 308.15, and 318.15) K.

4. CONCLUSION

Liquid−liquid data for the {PEGDME2000 + $K_2C_2O_4$ + H_2O} system were determined at T = (298.15, 303.15, 308.15, and 318.15) K. A comparison between the experimental data shows that the phase-separation ability of the studied systems increased with increasing the temperature.

Also, from the comparison of the obtained binodal data for the {PEGDME2000 + $K_2C_2O_4$ + H_2O} and {PEG2000 + $K_2C_2O_4$ + H_2O} systems, we found that, for $K_2C_2O_4$, the phase-separation ability of PEGDME2000 is better than PEG2000. Using the Gibbs free energies of hydration of ions, the effect of type of salt on the binodals of PEGDME2000 has also been discussed.

Moreover, the experimental binodal data were satisfactorily correlated using an empirical equation and the Merchuk and the Graber et al. equations as a function of temperature with a linear temperature dependency in the form of $(T - T_0)$ K as a variable. We found that the Graber et al. equation gives better results than the two other equations in the correlation and prediction of binodal data.

Additionally, the Othmer−Tobias and Bancroft and Setschenow-type equations were satisfactorily used for the correlation and prediction of the liquid−liquid phase behavior of the studied system. On the basis of the obtained results, it can be concluded that the Seteschenow- type equation with only two parameters has a good performance in the correlation and prediction of the tie-line compositions of the studied system.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +98 411 3340191. E-mail address: zafarani47@yahoo.com.

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