J. Chem. Eng. Data **2010,** *55,* 2857–2861

Liquid−Liquid Equilibrium of Aqueous Two-Phase Systems of PPG_{400} and Biodegradable Salts at Temperatures of (298.15, 308.15, and 318.15) K

Xueqiao Xie,[†] Yongsheng Yan,*[,†] Juan Han,[†] Yun Wang,[†] Guowu Yin,[‡] and Weisheng Guan[§]

School of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang, 212013, People's Republic of China, The Fourth Military Medical University, Tangdu Hospital, Changle West Road, Xi'an, 710032, People's Republic of China, and School of Environmental Science and Engineering, Chang'an University, South Second Ring Road, Xi'an, 710064, People's Republic of China

---

Liquid−liquid equilibrium data for the PPG_{400} (poly(propylene glycol)) + salt (potassium citrate, potassium tartarate, potassium oxalate) + water systems have been determined experimentally at T = (298.15, 308.15, and 318.15) K. The effects of temperature on the binodal curves and tie-lines were studied, and it was observed that an increase of the temperature generally led to an increase of the biphasic area. Furthermore, the binodal curves were fitted to a five-parameter equation relating the concentrations of PPG_{400} and salt. The effective excluded volume (EEV) values obtained from the binodal model were determined, and the salting-out ability of the anions follows the ordering citrate^{3-} > tartarate^{2-} ≈ oxalate^{2-}. Finally, the Setschenow-type and Othmer−Tobias and Bancroft equations have been successfully used to correlate the tie-line compositions.

Introduction

Liquid−liquid extraction utilizing aqueous two-phase systems (ATPS's) as an economical and efficient method has attracted considerable attention for separation of biomolecules,[1,2] metal ions,[3] and drug molecules.[4] ATPS's can be formed with combinations of two hydrophilic polymers or of a polymer and a salt in aqueous solution above a certain critical concentration. Recently, several new types of ATPS's have been reported, such as those containing hydrophilic organic solvent−salt systems[5] or ionic liquid−salt systems.[6−8] The ATPS has several advantages over the conventional extraction methods due to the lower cost, nontoxicicty, and the possibility of application on a large scale.[9]

Low molecular weights of poly(propylene glycol) (PPG) are completely water-soluble, so it can be used for the separation of biomolecules, since its aqueous solutions with a suitable polymer or a salt forms a two-phase system. Liquid−liquid equilibrium (LLE) data for some aqueous PPG + inorganic salt two-phase systems have been reported in the literature.[10−12] In these studies, the salting-out of PPG has been accomplished by the use of phosphate, sulfate, or carbonates. These salts, however, lead to high salt concentrations in effluent streams, and therefore they are of environmental concern. To avoid this problem, biodegradable salts such as citrates can be used to substitute these inorganic salts. However, only a limited amount of experimental work has been devoted to PPG/organic salt ATPS's.

Salabat et al.[13] determined the LLE, density, and viscosity for the aqueous PPG + trisodium citrate system at 298.15 K. The effect of aqueous solution of tripotassium citrate on the volumetric behavior of PPG_{400} at T = (288.15 to 313.15) K was developed by Sadeghi and Ziamajidi.[14] Zafarani-Moattar et al.[15] studied the effect of temperature on the phase equilibrium of the aqueous two-phase PPG + tripotassium citrate system; however, only a small part of binodal data was determined, so we added a portion of binodal data, which provided a basis for selecting an appropriate salting-out agent in different salt concentrations. However, the LLE data for PPG_{400} + potassium tartarate + water and PPG_{400} + potassium oxalate + water systems were not reported.

This work is devoted to the systematic study of the phase behaviors of LLE for PPG_{400} and biodegradable salts (potassium citrate, potassium tartarate, potassium oxalate) aqueous biphasic systems, which are scarce in the literature. A nonlinear equation was proposed to correlate the binodal data, and the effective excluded volume (EEV) values were used to evaluate the phase-separation abilities of the investigated systems. The tie-line compositions at different temperatures were fitted to the Setschenow-type[16] and Othmer−Tobias and Bancroft equations.[17] The obtained results are necessary for the design of an extraction process, understanding of general factors determining partition of solutes and particles in such ATPS's, and the development and testing of both thermodynamic and mass transfer models of ATPS's.

Experimental Section

Materials. PPG with a quoted molar mass of 400 $g \cdot mol^{-1}$ was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Potassium citrate, potassium tartarate, and potassium oxalate were supplied by the Sinopharm Chemical Reagent Co., Ltd. with a minimum mass fraction purity of 0.995, 0.990, and 0.998, respectively. All chemicals were used without further purification. Double-distilled deionized water was used in the experiments.

Apparatus and Procedure. The phase diagram includes the binodal curves and the tie-lines. The experimental apparatus employed is essentially similar to the one used previously.[18−20]

---

* Corresponding author. Tel.: +086051188790683. Fax: +086051188791800. E-mail: yys@ujs.edu.cn; qiao_84122@163.com.

[†] Jiangsu University.

[‡] The Fourth Military Medical University.

[§] Chang'an University.

10.1021/je901019t

Table 1. Binodal Data as the Mass Fraction for the PPG_{400} (1) + Potassium Citrate (2) + Water (3) System at T = (298.15, 308.15, and 318.15) K

T = 298.15 K		T = 308.15 K		T = 318.15 K	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
77.79	0.04	66.32	0.15	64.37	0.07
69.38	0.15	60.03	0.37	57.85	0.24
64.25	0.31	56.19	0.61	50.41	0.56
55.48	1.08	52.30	0.90	44.41	0.89
52.72	1.32	47.51	1.42	38.43	1.34
49.59	1.75	42.61	2.02	33.64	1.63
43.07	2.93	39.06	2.45	30.04	1.89
37.48	4.08	35.03	3.11	23.68	2.46
27.01	6.39	32.86	3.43	20.77	2.84
23.67	7.39	31.26	3.74	13.39	4.12
20.65	8.22	20.10	5.91	10.69	4.89
16.05	10.06	13.64	7.54	8.64	5.52
14.27	10.62	12.98	7.91	7.73	5.96
11.87	11.68	10.78	8.82	7.10	6.21
10.16	12.49	9.28	9.34	6.44	6.80
7.82	13.98	6.92	10.70	4.71	8.04
7.01	14.48	5.77	11.31	3.97	9.27
5.55	15.70	4.63	12.49	3.23	10.24
4.64	16.67	3.74	13.31	2.38	11.05
3.65	17.67	2.97	14.84	2.26	11.78
3.01	18.44	2.11	15.95	1.92	12.48
2.49	19.52	1.58	17.28	1.69	13.29
2.11	20.05	1.28	18.23	1.51	13.78
1.59	21.37	0.99	19.34	1.31	14.46
1.07	22.30				

The binodal curves were carried out by a turbidimetric titration method. From the stock, a PPG_{400} solution of known mass fraction was taken into the vessel. A salt solution of known concentration was then added to the vessel until the mixture became turbid or cloudy, which indicates the two-phase formation. Then, water was added until the turbidity disappeared, and the procedure was repeated, and so on. The composition of the mixture was determined by mass using an analytical balance (BS124S, Beijing Sartorius Instrument Co., China) with an uncertainty of $\pm 1.0 \cdot 10^{-7}$ kg. The temperature of the working vessel was maintained by circulating water through an external jacket using a thermostat (Shanghai Hengping Instrument Factory, China). The temperature was maintained with an uncertainty of ± 0.05 K.

For determination of the tie-lines, feed samples (about $2 \cdot 10^{-5}$ m^3) were prepared by mixing appropriate amounts of PPG_{400}, salt, and water in the vessel. The samples were stirred for 1 h at a desired temperature, and then the mixture was allowed to settle for at least 72 h at constant temperature using a thermostat. When phases were separated, they were properly diluted to determine PPG_{400} and salt equilibrium concentrations. The concentrations of salts in the top and bottom phases were determined by flame photometry. The uncertainty in the measurement of the mass fraction of the salts was estimated to be ± 0.001. Following Cheluget et al.,[19] the concentrations of PPG_{400} in phases were determined by refractive index measurements performed at 298.15 K using an Abbe-type refractometer with a precision of ± 0.0001. The uncertainty of the mass fraction of PPG was better than 0.002.

Results and Discussion

Correlation of Binodal Data. The binodal experimental data for the PPG_{400} + salt (potassium citrate, potassium tartarate, potassium oxalate) + water systems obtained at T = (298.15, 308.15, and 318.15) K are shown in Tables 1, 2, and 3, respectively. Several expressions have been developed to correlate the binodal data; however, better results were obtained with the following equation

$$w_1 = a_1 \exp\left(-\frac{w_2}{b_1}\right) + a_2 \exp\left(-\frac{w_2}{b_2}\right) + c \qquad (1)$$

where w_1 and w_2 are the mass fractions of PPG_{400} and salt, respectively. This equation has been used to fit the results of ATPS's based on hydrophilic organic solvents.[21] The coefficients a_1, a_2, b_1, b_2, and c along with the corresponding standard deviations for the investigated systems were obtained, and the results are collected in Table 4. On the basis of the obtained standard deviations, we conclude that eq 1 can be satisfactorily used to correlate the binodal curves of the investigated systems.

Effect of Salt on Binodal Curves and Tie-Lines. The binodal curves determined at 298.15 K for PPG_{400} + salt (potassium citrate, potassium tartarate, potassium oxalate) are plotted in Figure 1. Considering that the salts shared a common cation (K^+) but contained different anions, it can be see that three anions promote the formation of the ATPS's in the following order: $\text{citrate}^{3-} > \text{tartarate}^{2-} \approx \text{oxalate}^{2-}$. The salting-out powers

Table 2. Binodal Data as the Mass Fraction for the PPG_{400} (1) + Potassium Tartarate (2) + Water (3) System at T = (298.15, 308.15, and 318.15) K

T = 298.15 K		T = 308.15 K		T = 318.15 K	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
73.50	0.18	78.07	0.11	67.64	0.11
66.27	0.39	66.01	0.33	64.95	0.16
58.90	0.90	55.34	0.96	62.53	0.20
55.40	1.28	44.68	2.12	59.69	0.27
51.35	1.77	39.80	2.79	56.71	0.36
47.50	2.35	31.04	3.98	52.73	0.53
42.56	3.27	23.53	5.30	47.84	0.82
35.62	4.78	20.03	6.07	42.57	1.17
20.00	9.01	15.27	7.41	32.72	1.88
13.74	11.65	13.43	7.99	26.41	2.48
10.40	13.08	11.79	8.64	20.93	3.40
8.56	13.97	9.96	9.71	14.72	4.56
6.48	15.42	8.45	10.20	10.94	5.82
5.95	15.97	6.57	11.66	7.89	6.91
5.03	16.72	5.88	12.24	6.61	7.74
4.03	17.49	4.91	13.04	5.21	8.74
3.00	18.86	4.12	14.01	4.66	9.32
2.37	19.73	3.19	15.58	3.48	10.66
1.80	20.89	2.43	16.37	2.68	11.86
1.38	22.51	1.71	18.12	2.03	13.44
1.05	23.41	1.12	20.13		

Table 3. Binodal Data as the Mass Fraction for the PPG_{400} (1) + Potassium Oxalate (2) + Water (3) System at T = (298.15, 308.15, and 318.15) K

T = 298.15 K		T = 308.15 K		T = 318.15 K	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
67.60	0.26	73.88	0.06	64.97	0.15
59.39	0.63	65.31	0.21	60.50	0.25
54.59	0.99	59.00	0.44	54.51	0.40
52.91	1.15	53.88	0.77	43.71	0.72
49.29	1.55	47.60	1.26	38.00	0.91
46.80	1.86	41.71	1.74	33.63	1.07
44.08	2.21	35.99	2.34	21.92	1.88
40.10	2.85	31.59	2.79	19.42	2.14
37.47	3.33	29.05	3.07	11.81	3.44
30.04	4.68	24.40	3.74	9.03	4.41
23.15	6.10	17.59	4.88	8.01	4.80
18.48	7.22	13.92	5.71	6.02	5.65
14.06	8.56	12.80	6.08	4.84	6.60
10.74	9.80	10.62	6.79	3.84	7.30
8.13	10.91	8.38	7.69	3.01	8.26
5.59	12.42	5.67	8.99	2.69	8.96
4.14	13.43	4.46	9.86	2.15	9.85
3.19	14.37	3.57	10.74	1.72	10.71
2.39	15.24	2.28	12.30	1.41	11.41
1.60	16.94	1.48	13.89	1.18	12.10
		1.26	14.33		

Table 4. Values of a_1, a_2, b_1, b_2, and c of Equation 1 for PPG_{400} (1) + Salt (2) + Water (3) Systems at T = (298.15, 308.15, and 318.15) K

T/K	a_1	a_2	b_1	b_2	c	SD[a]
		PPG_{400} + Potassium Citrate + Water				
298.15	67.08	18.49	8.09	0.17	−3.69	0.39
308.15	13.20	64.07	0.16	5.28	−1.14	0.41
318.15	14.97	59.71	0.18	2.93	2.02	0.47
		PPG_{400} + Potassium Tartarate + Water				
298.15	19.20	68.76	0.28	8.37	−3.93	0.43
308.15	25.45	67.95	0.14	5.06	−0.23	0.31
318.15	16.10	59.88	0.16	2.91	2.05	0.45
		PPG_{400} + Potassium Oxalate + Water				
298.15	16.70	68.37	0.29	6.75	−4.91	0.39
308.15	14.24	66.72	0.12	3.76	−0.34	0.20
318.15	24.47	49.21	4.17	0.93	−0.21	0.27

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

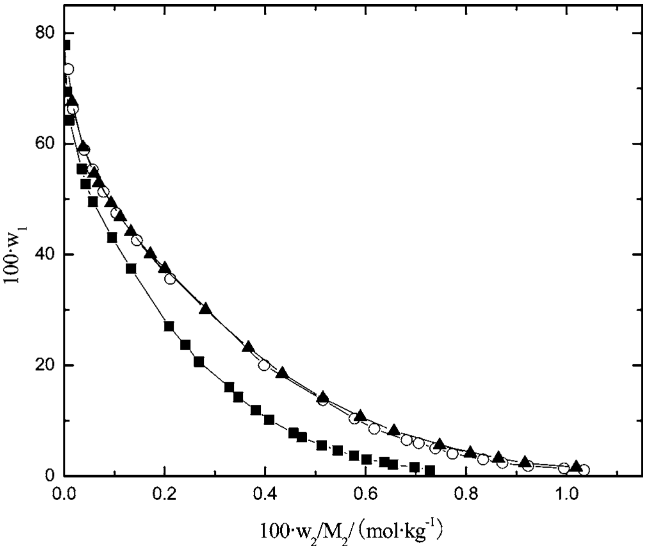

Figure 1. Effect of the type of salt on the binodal curves for the PPG_{400} (1) + salt (2) + water (3) ATPS's at T = 298.15 K: ▲, potassium oxalate; ○, potassium tartarate; ■, potassium citrate.

Table 5. Scaled EEV of Equation 2 for the PPG_{400} (1) + Salt (2) + Water (3) Systems at T = (298.15, 308.15, and 318.15) K

T/K	$10^3\ V^*_{213}$/(g·mol^{-1})	f_{213}	SD
	PPG_{400} + Potassium Citrate + Water		
298.15	1.46	0.07	2.16
308.15	1.78	0.04	1.98
318.15	2.47	0.01	2.87
	PPG_{400} + Potassium Tartarate + Water		
298.15	0.95	0.20	3.68
308.15	1.44	0.06	3.48
318.15	1.99	0.03	2.01
	PPG_{400} + Potassium Oxalate + Water		
298.15	0.91	0.23	2.99
308.15	1.42	0.08	3.29
318.15	2.09	0.01	4.41

Table 6. Experimental Phase Equilibrium Data as Mass Fraction for PPG_{400} (1) + Salt (2) + Water (3) Systems at T = (298.15, 308.15, and 318.15) K

	total compositions		top phase		bottom phase	
T/K	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
			PPG_{400} + Potassium Citrate + Water			
298.15	27.91	7.55	51.79	1.56	14.83	10.85
	30.83	7.71	55.09	1.17	11.07	12.48
	34.92	7.56	60.90	0.70	7.11	14.93
308.15	24.02	8.01	56.09	0.72	5.57	12.02
	30.95	8.97	62.87	0.36	1.80	16.94
	33.44	9.98	66.39	0.16	1.00	19.23
318.15	18.11	3.63	52.44	0.55	13.25	4.10
	22.91	4.08	59.61	0.22	7.93	5.80
	25.08	4.30	61.03	0.21	6.83	6.51
			PPG_{400} + Potassium Tartarate + Water			
298.15	15.46	14.04	60.65	0.77	3.99	17.60
	18.05	14.49	63.93	0.47	2.88	18.76
	23.90	15.08	71.70	0.17	1.05	22.11
308.15	25.60	8.06	60.58	0.65	5.58	12.42
	31.55	8.95	63.27	0.50	2.70	15.76
	35.13	10.00	67.89	0.29	1.23	19.79
318.15	20.17	4.10	61.04	0.23	13.24	4.64
	23.17	4.99	62.75	0.19	8.03	6.73
	26.06	5.50	63.91	0.18	6.20	8.17
			PPG_{400} + Potassium Oxalate + Water			
298.15	10.22	12.44	65.73	0.29	3.82	13.76
	14.07	12.97	69.02	0.23	2.19	15.64
	14.06	13.47	70.12	0.21	1.90	16.18
308.15	29.93	6.48	58.69	0.41	2.51	12.11
	33.06	6.98	62.55	0.27	1.51	13.82
	34.90	7.54	66.53	0.19	0.99	15.38
318.15	20.38	2.57	52.16	0.42	13.46	3.04
	22.50	2.57	54.01	0.39	13.23	3.26
	25.06	3.10	63.53	0.21	9.53	4.32

of tartarate^{2-} and oxalate^{2-} are not very different, but the salting-out power of citrate^{3-} is greater than of tartarate^{2-} and oxalate^{2-}; namely, anions with a higher valence are better salting-out agents than anions with a lower valence, because higher-valence anions hydrate more water than lower-valence anions, thus decreasing the amount of water available to hydrate PPG.

The salting-out strength of the salt could be related to the EEV, as proposed by Huddleston et al.[22] In this paper, the EEV for the studied systems was calculated using the binodal model developed by Guan et al.[23] This model was originally used in polymer−polymer systems, while we extended the application of this model to the studied systems. The binodal equation can be written as

$$\ln\left(V^*_{213}\frac{w_2}{M_2} + f_{213}\right) + V^*_{213}\frac{w_1}{M_1} = 0 \qquad (2)$$

where V^*_{213}, f_{213}, M_1, and M_2 are the EEV of salt, the volume fraction of unfilled effective available volume after tight packing of the salt into the network of the polymer, and the molar mass of polymer and salt, respectively. The V^*_{213} and f_{213} values obtained from the correlation of binodal data along with the corresponding standard deviations are given in Table 5. It can be seen that at a constant temperature, the salting-out ability of the anions follows the order of citrate^{3-} > tartarate^{2-} ≈ oxalate^{2-}, which was in agreement with the phase separation order mentioned previously.

Additionally, Table 6 shows that, at constant temperature, the polymer concentration in the top phase increases when the salt concentration in the total phase increases and consequently in the tie-line length, which is beneficial to phase separation. This behavior is in agreement with the reported results for other ATPS's.[6,8,12] Figure 2 presents the effect of the salt type on the phase compositions. The slopes of tie-lines increase with increasing charge on the anion. That is because the anions with a higher charge hydrate more water than the lower charged anions, thus decreasing the amount of water available to hydrate PPG.

Effect of Temperature on Binodal Curves and Tie-Lines. As an example, the effect of temperature on the phase-forming ability of the PPG_{400} + potassium tartarate + water system is illustrated in Figure 3. The locus for the experimental binodal

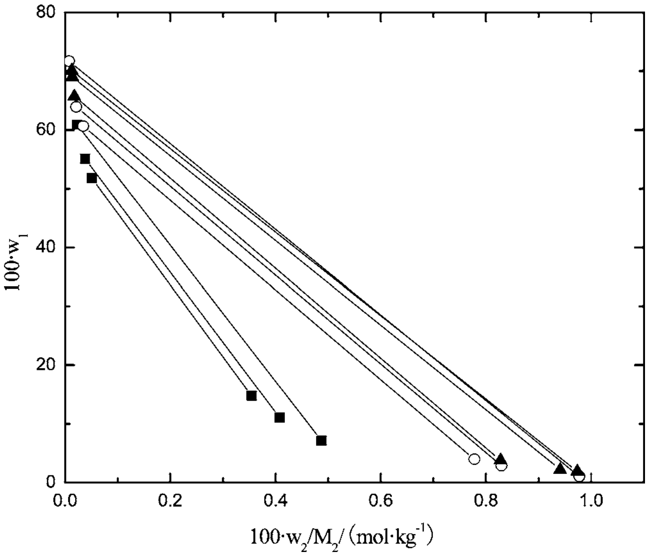

Figure 2. Effect of the type of salt on the tie-lines for the PPG_{400} (1) + salt (2) + water (3) ATPS's at $T = 298.15$ K: -▲-, potassium oxalate; -○-, potassium tartarate; -■-, potassium citrate.

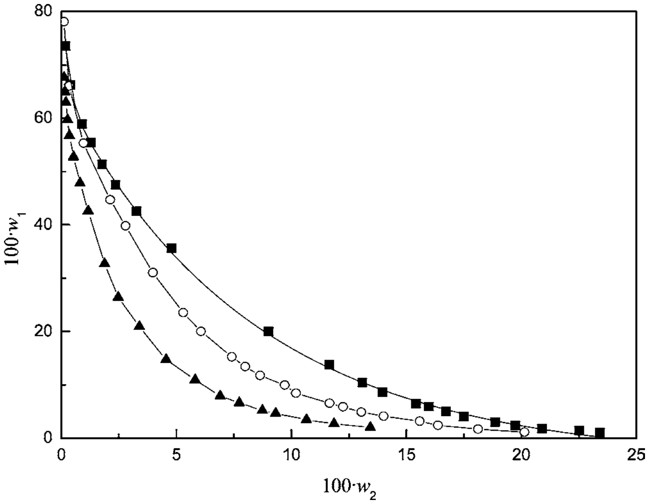

Figure 3. Effect of temperature on the binodal curves for the PPG_{400} + potassium tartarate + water system. Experimental binodal points for ■, 298.15 K; ○, 308.15 K; ▲, 318.15 K.

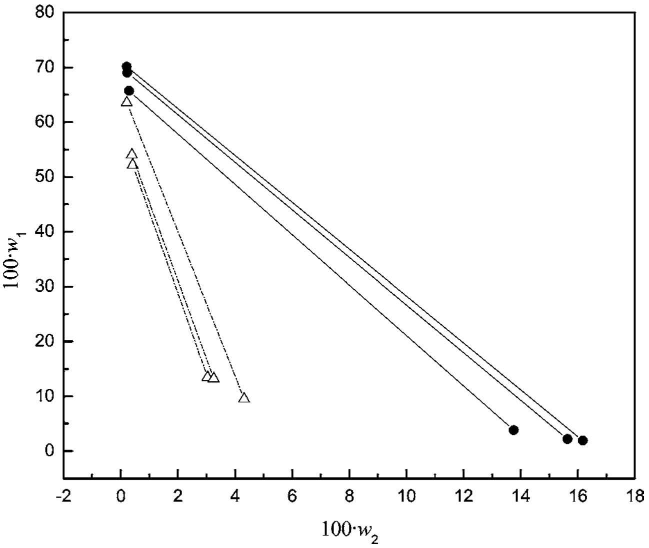

Figure 4. Effect of temperature on the phase equilibrium compositions for the PPG_{400} (1) + potassium oxalate (2) + water (3) system: -●-, tie-lines at 298.15 K; ---△---, tie-lines at 318.15 K. These tie-lines were obtained by connecting the experimental equilibrium phase composition data.

Table 7. Values of k_s and Intercept of Setschenow-Type Equation (eq 3) for the PPG_{400} (1) + Salt (2) + Water (3) Systems at T = (298.15, 308.15, and 318.15) K

T/K	k_s/(kg·mol^{-1})	intercept	R^2	dev[a]
	PPG_{400} + Potassium Citrate + Water			
298.15	5.57	−0.44	0.9999	0.04
308.15	7.40	−0.43	0.9997	0.72
318.15	9.21	0.32	0.9986	0.52
	PPG_{400} + Potassium Tartarate + Water			
298.15	6.71	−2.29	0.9993	0.73
308.15	4.80	−0.12	0.9997	0.40
318.15	5.12	0.54	0.9976	0.76
	PPG_{400} + Potassium Oxalate + Water			
298.15	5.10	−1.29	0.9998	0.06
308.15	5.03	−0.39	0.9999	0.02
318.15	6.32	0.33	0.9980	0.34

[a] dev = $(\sum_p\sum_l\sum_j(100w_{p,l,j}^{\mathrm{cal}} - 100w_{p,l,j}^{\mathrm{exp}})^2/6N)$, where $w_{p,l,j}$ is the mass fraction of the component j (i.e., polymer, salt, or water) in the phase p for lth tie-line. N is the number of tie-line data.

data shown in Figure 3 indicates that an increase in temperature expands the two-phase area of the binodal curve. In other words, the critical concentration of a salt required to form an ATPS is decreased with increasing the temperature. That is because the PPG−solvent interaction decreased with an increase in temperature and then resulted in a decrease in the solubility of PPG in water.[24] Moreover, to show the effect of temperature on the phase equilibrium compositions for the investigated systems, the experimental tie-lines for the PPG_{400} + potassium oxalate + water system are compared in Figure 4 with the temperatures (293.15 and 318.15) K, as an example. As shown in Figure 4, an increase in temperature promotes an increase in the slope of the tie-line (STL) (STL = $\Delta_{\mathrm{polymer}}/\Delta_{\mathrm{salt}}$). It is possible that the STL change was due to the transfer of water from the top to the bottom phase. Therefore, the polymer concentration increases in the upper phase, and the salt content decreases in the lower. Similar results were reported in other ATPS's.[15,25]

Tie-Lines. The tie-line compositions for the investigated systems are also given in Table 6. Several models have been developed to correlate the LLE data of ATPS. However, we decided to use a relatively simple two-parameter equation (Setschenow-type) to examine the reliability of the tie-line compositions, which can be derived from the binodal theory.[16] The equation used has the following form:

$$\ln\left(\frac{C_{\mathrm{p}}^{\mathrm{top}}}{C_{\mathrm{p}}^{\mathrm{bot}}}\right) = k_{\mathrm{p}}(C_{\mathrm{p}}^{\mathrm{bot}} - C_{\mathrm{p}}^{\mathrm{top}}) + k_{\mathrm{s}}(C_{\mathrm{s}}^{\mathrm{bot}} - C_{\mathrm{s}}^{\mathrm{top}}) \qquad (3)$$

where C_p, C_s, k_p, and k_s represent the concentration of the polymer, the concentration of the salt, a parameter relating the activity coefficient of polymer to its concentration, and the salting-out coefficient, respectively. Superscripts "top" and "bot" stand for the polymer-rich phase and salt-rich phase, respectively. If the first term on the right-hand side of eq 3 is small compared with the second term, then a Setschenow-type equation is obtained. Recently, eq 3 has been successfully applied for correlating the tie-line data of polymer−salt systems[15,25] and ionic liquid−salt systems.[6] The fitting parameters of eq 3 along with the corresponding standard deviations are presented in Table 7 for the studied systems. It is clear that the tie-line data can be presented adequately by eq 3.

The Othmer−Tobias (eq 4) and Bancroft (eq 5) equations have also been used to correlate the tie-line compositions of

Table 8. Values of *k*, *n*, k_1, and *r* of Equations 4 and 5 for the PPG$_{400}$ (1) + Salt (2) + Water (3) Systems at T = (298.15, 308.15, and 318.15) K

T/K	k	n	R^2	k_1	r	R^2	dev[a]
			PPG$_{400}$ + Potassium Citrate + Water				
298.15	0.11	1.02	0.9963	7.36	0.75	0.9979	0.13
308.15	0.17	0.77	0.9966	9.31	1.20	0.9976	0.44
318.15	0.09	0.74	0.9963	22.97	1.16	0.9950	0.80
			PPG$_{400}$ + Potassium Tartarate + Water				
298.15	0.04	1.74	0.9999	5.64	0.52	0.9999	0.01
308.15	0.21	0.58	0.9867	13.00	1.58	0.9894	1.82
318.15	0.35	0.20	0.9976	126.31	4.34	0.9985	0.32
			PPG$_{400}$ + Potassium Oxalate + Water				
298.15	0.08	1.04	0.9988	10.48	0.85	0.9992	0.31
308.15	0.06	1.21	0.9971	9.30	0.78	0.9975	0.15
318.15	0.01	1.30	0.9992	29.02	0.67	0.9982	0.24

[a] Definition is given in Table 7.

the PPG$_{400}$ (1) + salt (2) + water (3) systems, which have been successfully used in the correlation of LLE compositions of other ATPS's.[20,21]

$$\left(\frac{1-w_1^{\mathrm{top}}}{w_1^{\mathrm{top}}}\right) = k\left(\frac{1-w_2^{\mathrm{bot}}}{w_2^{\mathrm{bot}}}\right)^n \qquad (4)$$

$$\left(\frac{w_3^{\mathrm{bot}}}{w_2^{\mathrm{bot}}}\right) = k_1\left(\frac{w_3^{\mathrm{top}}}{w_1^{\mathrm{top}}}\right)^r \qquad (5)$$

where k, n, k_1, and r are the fitting parameters; w_1, w_2, and w_3 are the mass fractions of polymer, salt, and water, respectively. A linear dependency of the plots $\log((1 - w_1^{\mathrm{top}})/w_1^{\mathrm{top}})$ against $\log((1 - w_2^{\mathrm{bot}})/w_2^{\mathrm{bot}})$ and $\log(w_3^{\mathrm{bot}}/w_2^{\mathrm{bot}})$ against $\log(w_3^{\mathrm{top}}/w_1^{\mathrm{top}})$ indicated an acceptable consistency of the results. The values of the parameters k, n, k_1, and r of equations with the standard deviations are given in Table 8. On the basis of standard deviations, we conclude that eq 4 and 5 can be satisfactorily used to correlate the tie-line data of the investigated systems.

Conclusion

LLE of ATPS's composed of PPG$_{400}$ + salt (potassium citrate, potassium tartarate, potassium oxalate) + water were studied at T = (298.15, 308.15, and 318.15) K. The effect of temperature and salt on the binodal curves and tie-line compositions were studied. Additionally, the EEV values of salts were calculated for the investigated systems, and it was found that anions with a higher valence are better salting-out agents than anions with a lower valence. Finally, the tie-line compositions for the studied systems were satisfactorily correlated with the Setschenow-type and Othmer−Tobias and Bancroft equations.

Literature Cited

(1) Riedl, W.; Raiser, T. Membrane-supported extraction of biomolecules with aqueous two-phase systems. *Desalination* **2008**, *224*, 160–167.
(2) Luechau, F.; Ling, T. C.; Lyddiatt, A. Partition of plasmid DNA in polymer-salt aqueous two-phase systems. *Sep. Purif. Technol.* **2009**, *66*, 397–404.
(3) Bulgariu, L.; Bulgariu, D. Extraction of metal ions in aqueous polyethylene glycol-inorganic salt two-phase systems in the presence of inorganic extractants:Correlation between extraction behaviour and stability constants of extracted species. *J. Chromatogr., A* **2008**, *1196*−*1197*, 117–124.
(4) Mokhtarani, B.; Karimzadeh, R.; Amini, M. H. Partitioning of Ciprofloxacin in aqueous two-phase system of poly(ethylene glycol) and sodium sulphate. *Biochem. Eng. J.* **2008**, *38*, 241–247.
(5) Li, S. N.; Guo, H. Y.; Zha, Q. Q. (Liquid + Solid) Equilibrium, Density, and Refractive Index for (Methanol + Sodium Chloride + Rubidium Chloride + Water) and (Ethanol + Sodium Chloride + Rubidium Chloride + Water) at Temperatures of (288, 298, and 308) K. *J. Chem. Eng. Data* **2009**, *54*, 3108–3111.
(6) Zafarani-Moattar, M. T.; Hamzehzadeh, S. Phase Diagrams for the Aqueous Two-Phase Ternary System Containing the Ionic Liquid 1-Butyl-3-methylimidazolium Bromide and Tri-potassium Citrate at T = (278.15, 298.15, and 318.15) K. *J. Chem. Eng. Data* **2009**, *54*, 833–841.
(7) Pei, Y. C.; Wang, J. J.; Liu, L. Liquid-Liquid Equilibria of Aqueous Biphasic Systems Containing Selected Imidazolium Ionic Liquids and Salts. *J. Chem. Eng. Data* **2007**, *52*, 2026–2031.
(8) Zafarani-Moattar, M. T.; Hamzehzadeh, S. Liquid-Liquid Equilibria of Aqueous Two-Phase Systems Containing 1-Butyl-3-methylimidazolium Bromide and Potassium Phosphate or Dipotassium Hydrogen Phosphate at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 1686–1692.
(9) Boaglio, A.; Bassani, G.; Picó, G.; et al. Features of the milk whey protein partitioning in polyethyleneglycol-sodium citrate aqueous two-phase systems with the goal of isolating human α-1 antitrypsin expressed in bovine milk. *J. Chromatogr., B* **2006**, *837*, 18–23.
(10) Zafarani-Moattar, M. T.; Sadeghi, R. Phase Diagram Data for Several PPG Salt Aqueous Biphasic Systems at 25 °C. *J. Chem. Eng. Data* **2005**, *50*, 947–950.
(11) Salabat, A.; Dashti, H. Measurement and Correlation of Water Activities and Refractive Indices for the Systems PPG$_{425}$ + $(NH_4)_2SO_4$ + H_2O and PPG$_{425}$ + Na_2SO_4 + H_2O at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 980–982.
(12) Sadeghi, R.; Jamehbozorg, B. The salting-out effect and phase separation in aqueous solutions of sodium phosphate salts and Poly(propylene glycol). *Fluid Phase Equilib.* **2009**, *280*, 68–75.
(13) Salabat, A.; Shamshiri, L.; Sardrodi, J. J. Liquid-Liquid Equilibrium Data, Viscosities, and Densities of Aqueous Mixtures of Poly(propylene glycol) with Tri-sodium Citrate at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 154–156.
(14) Sadeghi, R.; Ziamajidi, F. Effect of Aqueous Solution of Tri-potassium Citrate on the Volumetric Behavior of Poly(propylene glycol) 400 at T = (288.15 to 313.15) K. *J. Chem. Eng. Data* **2007**, *52*, 1268–1272.
(15) Zafarani-Moattar, M. T.; Emamian, S.; Hamzehzadeh, S. Effect of Temperature on the Phase Equilibrium of the Aqueous Two-Phase Poly(propylene glycol) + Tripotassium Citrate System. *J. Chem. Eng. Data* **2008**, *53*, 456–461.
(16) Hey, M. J.; Jackson, D. P.; Yan, H. The Salting-Out Effect and Phase Separation in Aqueous Solutions of Electrolytes and Poly(ethylene glycol). *Polymer* **2005**, *46*, 2567–2572.
(17) Othmer, D. F.; Tobias, P. E. Liquid-liquid extraction data-toluene and acetaldehyde systems. *Ind. Eng. Chem.* **1942**, *34*, 690–692.
(18) Ting, A. M.; Lynn, S.; Prausnitz, J. M. Liquid-liquid equilibria for aqueous systems containing *N*,*N*-diethylmethylamine and sodium chloride or sodium sulfate. *J. Chem. Eng. Data* **1992**, *37*, 252.
(19) Cheluget, E. L.; Gelinas, S.; Vera, J. H.; et al. Liquid-liquid equilibrium of aqueous mixtures poly(propylene glycol) with NaCl. *J. Chem. Eng. Data* **1994**, *39*, 127–130.
(20) Zafarani-Moattar, M. T.; Hamidi, A. A. Liquid-Liquid Equilibria of Aqueous Two-Phase Poly(ethylene glycol)-Potassium Citrate System. *J. Chem. Eng. Data* **2003**, *48*, 262–265.
(21) Wang, Y.; Yan, Y. S.; Hu, S. P. Phase Diagrams of Ammonium Sulfate Ethanol/1-Propanol/2-Propanol + Water Aqueous Two-Phase Systems at 298.15 K and Correlation. *J. Chem. Eng. Data* **2010**, *55*, 876–881.
(22) Huddleston, J. G.; Willauer, H. D.; Rogers, R. D. Phase Diagram Data for Several PEG + Salt Aqueous Biphasic Systems at 25 °C. *J. Chem. Eng. Data* **2003**, *48*, 1230–1236.
(23) Guan, Y.; Lilley, T. H.; Treffry, T. E. A new excluded volume theory and its application to the coexistence curves of aqueous polymer two-phase systems. *Macromolecules* **1993**, *26*, 3971–3979.
(24) Sadeghi, R.; Ziamajidi, F. Effect of Aqueous Solution of Tri-potassium Citrate on the Volumetric Behavior of Poly(propylene glycol) 400 at T = (288.15 to 313.15) K. *J. Chem. Eng. Data* **2007**, *52*, 1268–1272.
(25) Zafarani-Moattar, M. T.; Nikjoo, D. Liquid-Liquid and Liquid-Liquid-Solid Equilibrium of the Poly(ethylene glycol) Dimethyl Ether 2000 + Sodium Sulfate + Water System. *J. Chem. Eng. Data* **2008**, *53*, 2666–2670.

Received for review December 2, 2009. Accepted April 27, 2010. This work was financially supported by the National Natural Science Foundation of China (Nos. 20777029 and 20976074) and Ph.D. programs of Foundation of Ministry of Education of China (No. 200807100004).

JE901019T