

# Measurement and Correlation of the Phase Diagram Data for PPG<sub>400</sub> + (K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub>) + H<sub>2</sub>O Aqueous Two-Phase Systems at $T = 298.15$ K

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Experimental liquid–liquid equilibrium (LLE) binodal curves, tie-lines, and plait points were obtained for the PPG<sub>400</sub> + salt (K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub>) + H<sub>2</sub>O systems at  $T = 298.15$  K. The Merchuk equation was used to correlate the binodal data of the investigated systems. Also, the effect of salt on the phase-forming ability has been studied based on the effective excluded volume (EEV) values from fitting the binodal data to the binodal model developed by Guan, and the salting-out abilities of the anions are in the order of PO<sub>4</sub><sup>3-</sup> > HPO<sub>4</sub><sup>2-</sup> > CO<sub>3</sub><sup>2-</sup>, which may be related to the Gibbs free energy of hydration of the ions ( $\Delta_{\text{hyd}}G$ ). Furthermore, tie-line compositions were correlated using the Setschenow-type, Othmer–Tobias, and Bancroft equations, and the parameters are reported.

## Introduction

When two incompatible polymer–polymer or polymer–salt systems are dissolved in water above a certain critical concentration, two immiscible aqueous phases are formed. Since Beijernick<sup>1</sup> introduced aqueous biphasic systems in 1896, aqueous two-phase systems (ATPS's) as an economical and efficient method have been widely used in the separation, preconcentration, and purification of metal ion species,<sup>2</sup> dye molecules,<sup>3</sup> small organic molecules,<sup>4</sup> and nanoparticulates.<sup>5</sup> There are two types of other ATPS's, that is, hydrophilic organic solvent–salt systems and ionic liquid–salt systems. However, the application of those ATPS's are limited because of toxicity for the former ATPS's and high cost for the latter ATPS's.

Poly(ethene glycol) (PEG) is often used in aqueous two-phase partitioning studies,<sup>6–8</sup> and there are extensive data in the literature with this polymer.<sup>9–11</sup> Poly(propene glycol) (PPG) is a polymer that is structurally closely related to PEG. Low molecular masses of PPG are completely water-soluble that can be used in aqueous two-phase partitioning, since its aqueous solutions with a suitable polymer or a salt form a two-phase system. However, the liquid–liquid equilibrium (LLE) data of the aqueous PPG–salt systems are relatively scarce. The LLE data of the PPG<sub>425</sub>/PPG<sub>725</sub> + NaCl,<sup>12</sup> PPG<sub>400</sub> + Na<sub>2</sub>SO<sub>4</sub>/Na<sub>2</sub>CO<sub>3</sub>/NaNO<sub>3</sub>,<sup>13</sup> PPG<sub>425</sub> + Na<sub>2</sub>SO<sub>4</sub>/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>,<sup>14</sup> PPG<sub>400</sub> + Na<sub>2</sub>HPO<sub>4</sub>/Na<sub>3</sub>PO<sub>4</sub>,<sup>15</sup> PPG<sub>425</sub>/PPG<sub>725</sub> + Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>,<sup>16</sup> and PPG<sub>400</sub> + K<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>17</sup> ATPS's have been reported.

Ananthapadmanabhan and Goddard,<sup>18</sup> using the turbidimetric titration technique, have shown that, for a series of sodium salts, two-phase formation occurs with anions such as sulfate which have a marked “salting-out” effect on nonelectrolytes but for large, singly charged ions such as iodide only one phase exists. The formation of the two phases in the polymer–salt system is

due to the “salting-out” effect of salt, that is, a competition between salt and polymer for water molecules exists, and finally, the competition is won by the ions because of their strong affinity for water molecules. In this paper, the salting-out ability of different salts in polymer solution were evaluated by the scaled effective excluded volume (EEV) and salting-out coefficient ( $k_s$ ).

Here, we reported liquid–liquid equilibrium data for the new aqueous PPG<sub>400</sub> + salt (K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub>) + H<sub>2</sub>O systems at  $T = 298.15$  K that have not been previously published. The obtained results are necessary for the design of an extraction process, the understanding of general factors determining the partition of solutes and particles in such ATPS's, and the development and testing of both thermodynamic and mass transfer models of ATPS's. The Merchuk equation<sup>19</sup> was used to correlate the binodal data of the investigated systems. Also, the effect of salt on the phase-forming ability has been studied based on the EEV values from fitting the binodal data to the binodal model developed by Guan.<sup>20</sup> Furthermore, tie-lines were correlated using the Setschenow-type,<sup>21</sup> Othmer–Tobias, and Bancroft equations.<sup>22</sup>

## Experimental Section

**Materials.** PPG with a quoted molar mass of 400 g·mol<sup>-1</sup> was obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). The density and refractive index of the polymer at 298.15 K are 1.004 g·cm<sup>-3</sup> and 1.447. K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub> were analytical grade reagents with a minimum mass fraction purity of 0.99, which were supplied from the Sinopharm Chemical Reagent Co., Ltd. The polymer and salts were used without further purification. Double-distilled, deionized water was used for the present experiments.

**Apparatus and Procedure.** The binodal curves were obtained using a turbidimetric method. From stock, a polymer solution of known concentration was taken into a vessel. A salt solution of known mass fraction was then added dropwise to the vessel until the mixture became turbid; this indicated the formation of

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**Table 1. Binodal Curve Data as the Mass Fraction  $w$  for the PPG<sub>400</sub> (1) + Salt (2) + H<sub>2</sub>O (3) Systems at  $T = 298.15$  K**

PPG <sub>400</sub> + K <sub>3</sub> PO <sub>4</sub>		PPG <sub>400</sub> + K <sub>2</sub> CO <sub>3</sub>		PPG <sub>400</sub> + K <sub>2</sub> HPO <sub>4</sub>	
100 $w_1$	100 $w_2$	100 $w_1$	100 $w_2$	100 $w_1$	100 $w_2$
60.99	0.20	67.21	0.19	67.37	0.14
56.80	0.40	61.52	0.39	60.52	0.34
52.82	0.53	59.04	0.48	57.78	0.41
49.46	0.76	54.73	0.72	53.45	0.67
46.91	1.01	50.89	1.01	50.56	0.88
42.27	1.46	42.59	1.86	47.40	1.15
39.84	1.78	48.35	1.30	43.55	1.58
37.36	2.21	45.86	1.50	36.93	2.58
35.26	2.57	38.70	2.41	34.00	3.16
32.89	2.99	34.77	3.10	31.98	3.59
29.57	3.70	30.81	3.80	29.62	4.16
26.23	4.50	26.93	4.57	26.15	5.09
24.70	4.88	23.32	5.32	22.87	6.10
22.36	5.47	17.04	6.84	18.28	7.59
20.75	5.99	12.21	8.02	14.52	8.90
18.60	6.61	7.95	9.52	11.20	10.15
16.75	7.14	5.44	10.81	8.47	11.37
12.59	8.39	3.52	11.89	6.40	12.34
11.13	8.85	2.71	12.63	4.41	13.96
6.93	10.50	1.66	13.88	2.58	15.43
5.37	11.42	1.02	14.99	1.69	16.73
3.42	12.46	0.84	15.44	1.43	17.24
2.07	13.72			1.22	17.68
1.38	14.76			1.07	18.02
1.02	15.42				

two liquid phases. The starting and added solution masses were measured on an analytical balance with a precision of  $\pm 0.0001$  g. Additional binodal points were obtained by adding a small amount of water to get a clear one-phase system; the salt solution was added to produce turbidity again, and the above procedure was repeated, and so on. The system temperature was maintained constant and controlled to within  $\pm 0.05$  K.

For the determination of the tie-lines, a series of ATPS's of at least three different known total compositions were prepared in 20 mL graduated glass tubes (uncertainty  $\pm 0.05$  mL) and placed in a thermostatic bath for 24 h. The samples of the upper and lower phase were taken out carefully for analysis. 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  $\pm 0.001$ . Following Cheluget et al.,<sup>12</sup> the concentration of PPG in both phases was determined by refractive index measurements performed at 298.15 K using a refractometer. Because the refractive index of the phase samples depends on the polymer and salt concentration and it is an additive property, we obtained the PPG concentration by subtracting the salt concentration from the total solution composition. The uncertainty of the mass fraction of PPG was better than 0.002.

## Results and Discussion

**Binodal Data.** The PPG<sub>400</sub>, a hydrophilic polymer, can be induced to form ATPS's when contacted with solutions of the water-structuring salt. However, at low salt concentrations, the PPG-salt is miscible and coexists in a single phase; above a critical concentration, they will separate into two phases, that is, an upper polymer-rich phase and a lower salt-rich phase. The formation of the two phases in the polymer-salt system is due to the salting-out effect.

The equilibrium compositions of the ATPS's, PPG<sub>400</sub> (1) + salt (K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub>) (2) + H<sub>2</sub>O (3), determined at 298.15 K are shown in Table 1. For the correlation of the binodal data, the following nonlinear expression developed by Merchuk has been successfully used by Huddleston et al.:<sup>23</sup>

$$w_1 = a \exp(bw_2^{0.5} - cw_2^3) \quad (1)$$

where  $w_1$  and  $w_2$  are the mass fractions of PPG<sub>400</sub> and salt, respectively. Using eq 1, the coefficients  $a$ ,  $b$ , and  $c$  along with the corresponding standard deviations for the studied systems were obtained, and the results are shown in Table 2. On the basis of the standard deviations obtained, we conclude that eq 1 can be satisfactorily used to correlate the binodal curves for the investigated systems.

The salts considered share a common cation (K<sup>+</sup>) but contained different anions. EEV values were determined to see the effectiveness of the anions in forming ATPS's with PPG. In this present work, the EEV values of PPG<sub>400</sub> + salt (K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub>) + H<sub>2</sub>O were determined using the model developed by Guan et al.,<sup>19</sup> which was originally used in polymer-polymer systems to correlate the experimental binodal data on the PEG<sub>4000</sub> + diammonium hydrogen phosphate + water system. The binodal equation for the studied aqueous polymer-salt systems can be written as

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

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 salt into the network of the polymer, and the molar mass of polymer and salt, respectively. When there is a great disparity in size between the two components to form an ATPS, the  $f_{213}^*$  value will be very small and consequently can be neglected. For the investigated systems, the  $V_{213}^*$  and  $f_{213}^*$  values obtained from the correlation of the experimental binodal data along with the corresponding correlation coefficients and standard deviations are given in Table 3. As shown in Tables 2 and 3, the standard deviations for PPG<sub>400</sub> + salt (K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub>) + H<sub>2</sub>O systems are 0.34, 0.41, and 0.35 for eq 1 and 1.66, 4.05, and 4.53 for eq 2, respectively. Therefore, we conclude that, in the correlation of the experimental binodal data, eq 2 with two parameters gives rather poor results. As shown in Table 3, the salting-out ability of the anions follows the order of PO<sub>4</sub><sup>3-</sup> > HPO<sub>4</sub><sup>2-</sup> > CO<sub>3</sub><sup>2-</sup>. The salting-out ability may be related to the Gibbs free energy of hydration of the ions ( $\Delta_{\text{hyd}}G$ ),<sup>24,25</sup> and it was found that better salting-out of PPG is observed when the ions of the salt have a more negative Gibbs free energy { $\Delta_{\text{hyd}}G(\text{PO}_4^{3-}) = -2765 \text{ kJ}\cdot\text{mol}^{-126} > \Delta_{\text{hyd}}G(\text{HPO}_4^{2-}) = -1789 \text{ kJ}\cdot\text{mol}^{-127} > \Delta_{\text{hyd}}G(\text{CO}_3^{2-}) = -1315 \text{ kJ}\cdot\text{mol}^{-1}$ }.<sup>26</sup>

**Table 2. Values of  $a$ ,  $b$ ,  $c$ ,  $R^2$ , and the Standard Deviation of Equation 1 for the PPG<sub>400</sub> (1) + Salt (2) + H<sub>2</sub>O (3) Systems at  $T = 298.15$  K**

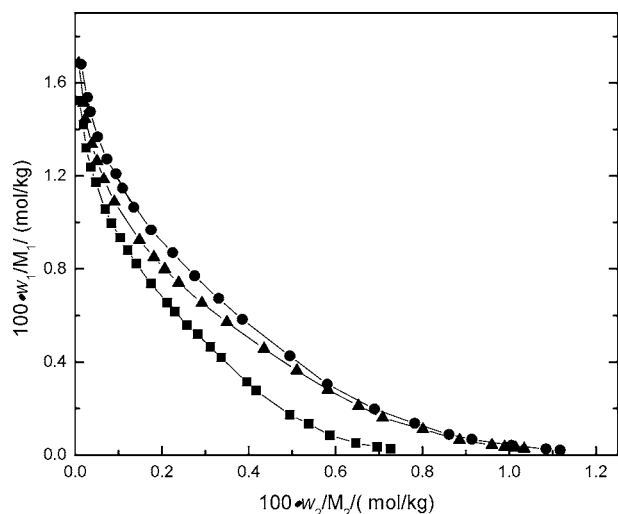
salt	$a$	$b$	$c$	$R^2$	$10^2 \cdot \text{sd}^a$
K <sub>3</sub> PO <sub>4</sub>	74.98	-0.47	0.00072	0.99972	0.34
K <sub>2</sub> CO <sub>3</sub>	83.08	-0.48	0.00094	0.99971	0.41
K <sub>2</sub> HPO <sub>4</sub>	79.17	-0.47	0.00042	0.99970	0.35

<sup>a</sup>  $\text{sd} = (\sum_{i=1}^N ((w_{1,i}^{\text{cal}} - w_{1,i}^{\text{exp}})^2)/N)^{0.5}$ , where  $N$  is the number of binodal data.

**Table 3. Scaled Effective Excluded Volume of Salts for the PPG<sub>400</sub> (1) + Salt (2) + H<sub>2</sub>O (3) Systems at  $T = 298.15$  K**

salt	$V_{213}^*$	$f_{213}^*$	$R^2$	$10^2 \cdot \text{sd}^a$
K <sub>3</sub> PO <sub>4</sub>	1324.50	0.14	0.99141	1.66
K <sub>2</sub> CO <sub>3</sub>	804.89	0.29	0.96474	4.05
K <sub>2</sub> HPO <sub>4</sub>	853.38	0.28	0.95262	4.53

<sup>a</sup>  $\text{sd} = (\sum_{i=1}^N ((w_{1,i}^{\text{cal}} - w_{1,i}^{\text{exp}})^2)/N)^{0.5}$ , where  $N$  is the number of binodal data.



**Figure 1.** Effect of the type of salt on binodal curves for the PPG<sub>400</sub> (1) + salt (2) + H<sub>2</sub>O (3) systems at 298.15 K: ■, K<sub>3</sub>PO<sub>4</sub>; ▲, K<sub>2</sub>HPO<sub>4</sub>; ●, K<sub>2</sub>CO<sub>3</sub>.

**Table 4.** Equilibrium Data as the Mass Fraction for PPG<sub>400</sub> (1) + Salt (2) + H<sub>2</sub>O (3) Systems at *T* = 298.15 K

total composition		top phase		bottom phase	
100 <i>w</i> <sub>1</sub>	100 <i>w</i> <sub>2</sub>	100 <i>w</i> <sub>1</sub>	100 <i>w</i> <sub>2</sub>	100 <i>w</i> <sub>1</sub>	100 <i>w</i> <sub>2</sub>
PPG <sub>400</sub> + K <sub>3</sub> PO <sub>4</sub> + H <sub>2</sub> O					
19.97	8.09	38.65	1.90	1.62	14.25
25.06	7.03	40.04	1.67	1.20	15.29
24.95	7.98	42.37	1.47	0.84	16.82
PPG <sub>400</sub> + K <sub>2</sub> CO <sub>3</sub> + H <sub>2</sub> O					
20.03	7.01	38.28	2.44	7.54	10.06
19.96	8.02	44.52	1.62	4.18	11.78
24.02	7.01	46.05	1.39	3.52	12.29
24.12	8.03	49.82	1.11	2.06	13.61
PPG <sub>400</sub> + K <sub>2</sub> HPO <sub>4</sub> + H <sub>2</sub> O					
20.01	7.99	31.25	3.77	3.00	14.77
24.88	7.03	34.85	3.02	1.50	16.82
24.89	8.15	38.01	2.30	0.71	19.02
29.99	7.05	40.87	1.96	0.36	21.16

To see more closely the relation between the EEV values and the salting-out strength of the salts, the binodals of the investigated systems are plotted in Figure 1. As shown in Figure 1, an increase in EEV is reflected in the phase diagram by a decrease in the concentration of salt required for the formation of ATPS's, which indicates a higher salting-out ability of salt.

**Tie-Lines.** The tie-line compositions for the PPG<sub>400</sub> + salt (K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub>) + H<sub>2</sub>O systems determined at 298.15 K are shown in Table 4. It is observed that in ATPS's an increase in total composition promoted an increase in polymer in polymer-rich phase and salt in salt-rich phases, which is favorable to phase separation. This behavior is in agreement with the reported experimental results for the other ATPS's.<sup>28–30</sup>

For correlation of the liquid–liquid equilibrium data of PPG<sub>400</sub> + salt (K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub>) + H<sub>2</sub>O systems, several models have been developed. However, we decided to use a relatively simple two-parameter equation (Setschenow-type equation), which can be derived from the binodal theory.<sup>21</sup>

$$\ln\left(\frac{C_p^{\text{top}}}{C_p^{\text{bot}}}\right) = k_p(C_p^{\text{bot}} - C_p^{\text{top}}) + k_s(C_s^{\text{bot}} - C_s^{\text{top}}) \quad (3)$$

where  $k_s$ ,  $k_p$ ,  $C_p$ , and  $C_s$  are the salting-out coefficient, the constant related to the activity coefficient, the concentration of the polymer, and the concentration of the salt, respectively.

**Table 5.** Values of  $k_s$  and Intercept from Least-Squares Linear Fits to the Setschenow-Type Equation (eq 3) for PPG<sub>400</sub> (1) + Salt (2) + H<sub>2</sub>O (3) Systems at *T* = 298.15 K

salt	$k_s/(\text{kg} \cdot \text{mol}^{-1})$	intercept	$R^2$	dev <sup>a</sup>
K <sub>3</sub> PO <sub>4</sub>	5.28	0.10	0.99839	0.15
K <sub>2</sub> CO <sub>3</sub>	4.36	−0.81	0.99053	0.85
K <sub>2</sub> HPO <sub>4</sub>	5.06	−0.86	0.99974	0.11

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

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 very small compared with the second term, then a Setschenow-type equation is obtained. This would imply  $k_p \ll k_s$  since the absolute values of  $(C_p^{\text{bot}} - C_p^{\text{top}})$  exceed the  $(C_s^{\text{bot}} - C_s^{\text{top}})$  values. The fitting parameters along with the corresponding standard deviations are presented in Table 5 for the investigated systems. We conclude that the performance of eq 3 is fairly good in correlating the tie-line data of the systems investigated.

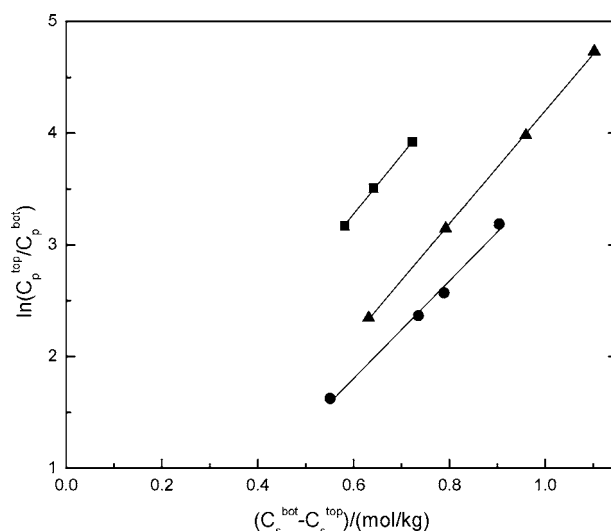
To examine the relation between the Setschenow-type behavior and the phase diagrams more closely, the Setschenow-type plots of the tie-line data for the investigated systems have also been shown in Figure 2. The increase in  $k_s$  is reflected in the phase diagram by a shift in the position of the binodal curve to the top corresponding to a decrease in the area representing the single-phase mixture, as shown in Figure 1, indicating an increasing phase-forming ability. Furthermore, as shown in Table 5 and Figure 2, the values of  $k_s$  are in the order K<sub>3</sub>PO<sub>4</sub> > K<sub>2</sub>HPO<sub>4</sub> > K<sub>2</sub>CO<sub>3</sub>, which is in agreement with the salting-out ability of the anions. For the studied systems, it appears that the  $k_s$  value may have a close relationship with the salting-out ability of salt.

The reliability of the tie line compositions was also ascertained by the Othmer–Tobias (eq 4) and Bancroft (eq 5) equations.<sup>22</sup>

$$[(1 - w_1^t)/w_1^t] = k[(1 - w_2^b)/w_2^b]^n \quad (4)$$

$$(w_3^b/w_2^b) = k_1(w_3^t/w_1^t)^r \quad (5)$$

where  $w_1^t$  is the mass fraction of PPG in the top phase;  $w_2^b$  is the mass fraction of salt in the bottom phase;  $w_3^b$  and  $w_3^t$  are the mass fractions of water in the bottom phase and top phase, respectively.  $k$ ,  $n$ ,  $k_1$ , and  $r$  represent the fitting parameters.



**Figure 2.** Experimental and calculated tie-lines with the Setschenow-type plots of the PPG<sub>400</sub> (1) + salt (2) + H<sub>2</sub>O (3) systems: ■, K<sub>3</sub>PO<sub>4</sub>; ●, K<sub>2</sub>CO<sub>3</sub>; ▲, K<sub>2</sub>HPO<sub>4</sub>.

**Table 6.** Values of  $k$ ,  $n$ ,  $k_1$ , and  $r$  of Equations 4 and 5 for the PPG<sub>400</sub> (1) + Salt (2) + H<sub>2</sub>O (3) Systems at  $T = 298.15$  K

salt	Othmer–Tobias equation			Bancroft equation			dev <sup>a</sup>
	$k$	$n$	$R^2$	$k_1$	$r$	$R^2$	
K <sub>3</sub> PO <sub>4</sub>	0.39	0.79	0.99498	3.44	1.25	0.99460	0.15
K <sub>2</sub> CO <sub>3</sub>	0.078	1.38	0.99800	6.30	0.61	0.99446	0.03
K <sub>2</sub> HPO <sub>4</sub>	0.41	0.95	0.99762	2.64	1.03	0.99509	0.09

<sup>a</sup> Definition is given in Table 5.

**Table 7.** Values of  $f$ ,  $g$ ,  $R^2$ , and Plait Point of Equation 6 for PPG<sub>400</sub> (1) + Salt (2) + H<sub>2</sub>O (3) Systems at  $T = 298.15$  K

salt	$f$	$g$	$R^2$	Plait point 100( $w_1$ , $w_2$ , $w_3$ )
K <sub>3</sub> PO <sub>4</sub>	17.90	1.45	0.99752	(24.82, 4.77, 70.41)
K <sub>2</sub> CO <sub>3</sub>	5.71	3.26	0.99244	(23.39, 5.42, 71.19)
K <sub>2</sub> HPO <sub>4</sub>	9.38	1.50	0.99412	(19.84, 6.97, 73.19)

Equation 4 and 5 are linearized by taking the logarithm on both sides of the equations to determine the fitting parameters. The values of the parameters are given in Table 6, from which we can conclude that eqs 4 and 5 can be satisfactorily used to correlate the tie-line data of the studied systems.

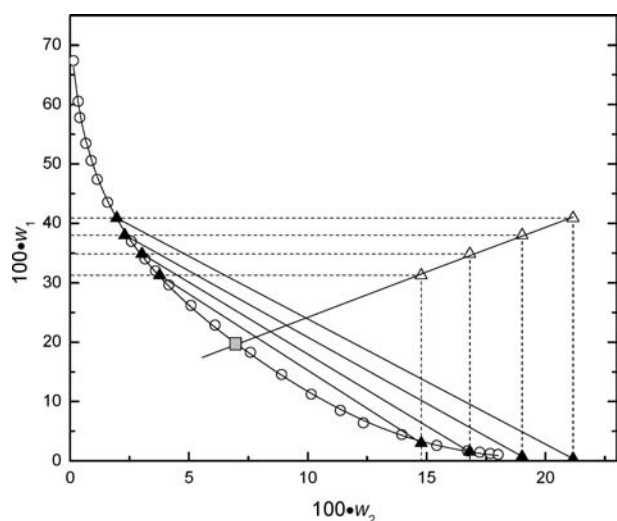
The location of the plait point for the studied systems was also estimated by extrapolation from the auxiliary curve satisfactorily fitted with the following linear equation

$$w_1 = f + gw_2 \quad (6)$$

where  $f$  and  $g$  are the fitting parameters. For the investigated system, the estimated values for the plait points along with the obtained fitting parameters for eq 6 and the corresponding correlation coefficients are shown in Table 7. The locus of the estimated plait point for the PPG<sub>400</sub> + K<sub>2</sub>HPO<sub>4</sub> + H<sub>2</sub>O system along with the used procedure is illustrated in Figure 3, as an example.

## Conclusion

LLE data for the aqueous PPG<sub>400</sub> + salt (K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>HPO<sub>4</sub>) + H<sub>2</sub>O systems at 298.15 K were obtained. The binodal curve was fitted to both the Merchuk equation and the binodal model relating the concentrations of PPG<sub>400</sub> and salt, and it was found that better results were obtained by the Merchuk equation. Furthermore, the salting-out ability of



**Figure 3.** Binodal curve, tie-lines, and plait point for the PPG<sub>400</sub> (1) + K<sub>2</sub>HPO<sub>4</sub> (2) + H<sub>2</sub>O (3) system at 298.15 K: —○—, calculated binodal from eq 1; —▲—, experimental tie-lines; —, tie-lines; △, auxiliary curve data; —, calculated from eq 6; ■, plait point.

different salts were evaluated by the scaled EEV and salting-out coefficient ( $k_s$ ), and both of the results show that the phase-separation abilities of the investigated anions are in the order of PO<sub>4</sub><sup>3-</sup> > HPO<sub>4</sub><sup>2-</sup> > CO<sub>3</sub><sup>2-</sup>. Finally, the tie-line data for the investigated systems can be successfully represented by the Setschenow-type and Othmer–Tobias equations. The plait points were also obtained for the studied systems.

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Received for review April 12, 2010. Accepted June 4, 2010. This work was financially supported by the National Natural Science Foundation of China (No. 20777029 and No. 20976074) and Ph.D. programs of Foundation of Ministry of Education of China (No. 200807100004).

JE100356S