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Phase Diagram Data for Several PPG + Salt Aqueous Biphasic Systems at 25 °C

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Phase diagrams and liquid−liquid−solid equilibrium (LLSE) data of the aqueous polypropylene glycol (PPG)400 + sodium sulfate, PPG400 + sodium carbonate, and PPG400 + sodium nitrate systems have been determined experimentally at 25 °C. The effect of the type of salt on the binodal and tie lines has been studied, and the salting-out power of the salts in these systems was determined. Furthermore, a three-parameter equation and the Othmer−Tobias−Bancroft equations have been used for the correlation of the binodals and tie lines, respectively.

Introduction

Liquid−liquid extraction utilizing aqueous two-phase systems has been used to separate and purify biological products from the complex mixtures in which they are produced.[1−3] In this respect, it is necessary to know the phase behavior of these systems for the design of extraction processes. Poly(ethylene glycol) (PEG), which is a hydrophilic polymer, is often used in aqueous two-phase partitioning studies. Polypropylene glycol (PPG) is a polymer that is structurally closely related to PEG. Low molecular weights of PPG are completely soluble in water, but high molecular weights are only partially soluble. This polymer can also be used for the separation of biomolecules because its aqueous solutions with a suitable polymer or a salt form two-phase systems. However, liquid−liquid equilibrium (LLE) data of the aqueous PPG−polymer and PPG−salt systems are relatively scarce. With regard to PPG−salt systems, liquid−liquid equilibrium data for PPG425 + NaCl,[4] PPG425 + $MgSO_4$,[5] PPG425 + $(NH_4)_2SO_4$, [6] and PPG425 + Na_2SO_4[6] aqueous two-phase systems have been reported. Recently, Salabat et al.[7] have determined the LLE, density, and viscosity of aqueous PPG + tri-sodium citrate systems at 25 °C.

In this study, we report liquid−liquid−solid equilibrium data for aqueous mixtures of PPG400 + Na_2SO_4, PPG400 + Na_2CO_3, and PPG400 + $NaNO_3$ at 25 °C that have not been previously published.

Experimental Section

Materials. Polypropylene glycol, of molecular weight 400, was obtained from Aldrich. The salts were obtained from Merck (GR, min 99.5% by mass). The polymer and salt were used without further purification. Double-distilled and deionized water was used. The number-average molar mass M_n of this polymer was determined by a cryoscopic osmometer (Osmomat model 030). For this purpose, freezing-point depression measurements on PPG + H_2O were carried out at different concentrations, and $\Delta T/K_s$ versus C curves were plotted (ΔT, C, and K_s are the freezing-point depression, concentration of samples, and cryoscopic constant, respectively). The intercept of this curve is $1/M_n$, from which M_n for this polymer was found to be 403 g·mol^{-1}.

Table 1. Values of Parameters of Equation 1 for PPG400 (1) + Salt (2) + H_2O (3) Systems at 25 °C

PPG + Na_2SO_4 + H_2O			PPG + Na_2CO_3 + H_2O			PPG + $NaNO_3$ + H_2O		
a_0	a_1	a_2	a_0	a_1	a_2	a_0	a	a_2
1.3325	0.1385	0.1576	1.3325	0.1385	0.2200	1.3325	0.1385	0.1236

Table 2. Binodal Data as Mass Fractions of the PPG400 (1) + Salt (2) + H_2O (3) Systems at 25 °C

PPG + Na_2SO_4 + H_2O		PPG + Na_2CO_3 + H_2O		PPG + $NaNO_3$ + H_2O	
$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
10.98	6.85	13.36	4.66	10.45	20.50
12.28	6.34	15.24	4.27	11.47	19.68
13.62	6.10	17.10	4.03	12.68	18.93
15.38	5.68	18.55	3.63	13.66	18.39
16.95	5.35	20.98	3.43	14.94	17.72
18.90	5.00	23.23	3.08	16.86	16.76
20.29	4.76	24.31	3.02	19.75	16.05
20.70	4.66	25.47	2.81	22.47	15.26
20.99	4.56	27.29	2.62	25.37	14.45
24.02	4.06	31.23	2.20	28.10	13.77
27.24	3.52	31.52	2.15	31.04	13.06
30.64	2.97	34.50	1.84	34.13	12.50
34.15	2.40	35.51	1.73	41.42	10.99
37.62	1.94	37.32	1.56	46.70	9.87
41.75	1.49	39.89	1.24	52.83	8.46
45.72	1.12	42.69	1.09	59.16	7.18
49.67	0.83	47.68	0.77	64.43	6.16
52.91	0.63	51.55	0.54	69.10	5.41
55.46	0.50	55.63	0.39	71.73	4.91
65.52	0.19	59.11	0.21	78.17	3.79

Apparatus and Procedure. The experimental apparatus employed is essentially similar to the one used previously.[8−10] A glass vessel, volume 50 cm^3, was used to carry out the phase equilibrium determinations. The glass vessel was provided with an external jacket in which water at constant temperature was circulated using a thermostat. The temperature was controlled to within ±0.05 K. The binodal curves were determined by a titration method. A salt solution of known concentration was titrated with the polymer solution or vice versa until the solution turned turbid. The composition of the mixture was determined by mass using an analytical balance with a precision of $\pm 1 \times 10^{-7}$ kg. For the determination of the tie lines, feed samples (about 20 cm^3) were prepared by mixing appropriate amounts of polymer, salt, and water in the vessel. The thermostat was set at a desired temperature, and the sample was stirred for 1 h. Then the mixture was allowed

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Table 3. Experimental Phase Equilibrium Compositions for the PPG400 (1) + Salt (2) + H_2O (3) Systems at 25 °C[a]

PPG + Na_2SO_4 + H_2O				PPG + Na_2CO_3 + H_2O				PPG + $NaNO_3$ + H_2O			
top phase		bottom phase		top phase		bottom phase		top phase		bottom phase	
$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
42.76	1.44	12.20	7.22	46.26	0.90	13.00	5.11	65.75	5.50	12.00	20.52
53.36	0.52	6.65	9.89	56.25	0.51	6.02	8.11	73.28	4.54	3.96	27.42
62.42	0.25	4.74	12.12	64.79	0.26	3.24	10.17	78.66	4.21	0.00	33.04
69.32	0.19	1.74	15.42	72.84	0.11	2.17	12.87	81.18	4.40	0.00	39.49
75.46	0.09	0.18	19.41	77.12	0.10	0.43	15.76	84.48	4.40	0.00	47.00
88.15	0.00	0.00	34.01	78.86	0.09	0.90	16.64				
				90.10	0.00	0.00	31.71				

[a] For all of the systems, in the last tie line there is the liquid−liquid-solid equilibrium.

Table 4. Values of Parameters of Equation 2 for PPG400 (1) + Salt (2) + H_2O (3) Systems at 25 °C

PPG + Na_2SO_4 + H_2O				PPG + Na_2CO_3 + H_2O				PPG + $NaNO_3$ + H_2O			
a	*b*	*c*	sd[a]	*a*	*b*	*c*	sd[a]	*a*	*b*	*c*	sd[a]
0.7728	−3.1742	2.4750	0.64	0.7294	−2.9759	0.9136	0.44	1.4378	−3.4729	1.0335	1.32

[a] sd = $[\Sigma_i(100w_1^{\text{calcd}} - 100w_1^{\text{exptl}})^2/N]^{0.5}$, where *N* is the number of binodal data.

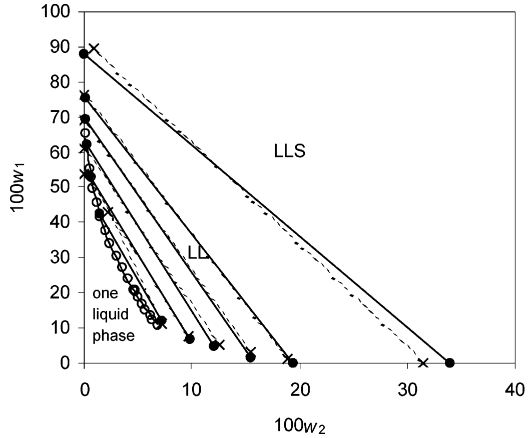

Figure 1. Phase diagram of the PPG 400 (1) + Na_2SO_4 (2) + H_2O (3) two-phase system at 25 °C: ○, experimental binodal; −, calculated binodal; −•−, experimental tie lines; ···×···, calculated tie lines using eq 3.

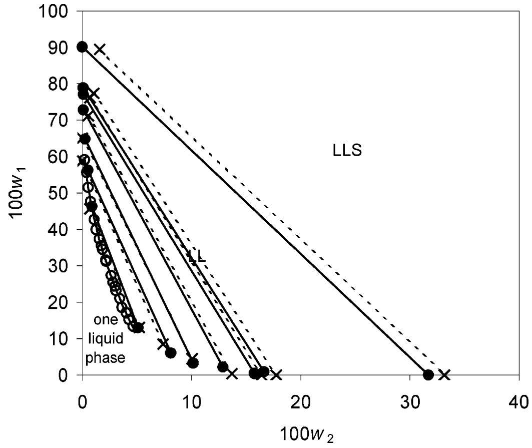

Figure 2. Phase diagram of the PPG 400(1) + Na_2CO_3 (2) + H_2O (3) two-phase system at 25 °C: ○, experimental binodal; −, calculated binodal; −•−, experimental tie lines; ···×···, calculated tie lines using eq 3.

to settle for 24 h. After the separation of the two phases, we determined the concentrations of the salts in the top and bottom phases by flame photometry. The uncertainty in the measurement of the mass fraction of the salts was estimated to be ±0.0002. Following Cheluget et al.,[4] the concentration of PPG in both phases was determined by refractive index measurements performed at 25 °C using a refractometer (Quartz RS-232). The uncertainty in the measurement of the refractive index was found to be ±0.0001. The relation between the refractive index, n_D, and the mass fractions of polymer, w_1, and salt, w_2, is given by[4]

$$n_D = a_0 + a_1 w_1 + a_2 w_2 \tag{1}$$

The values of coefficients a_0, a_1, and a_2 for the applied systems are given in Table 1. However, it was found that this equation is valid only for mass fractions of $w_1 \le 0.1$ and $w_2 \le 0.05$, for which linear calibration plots of the refractive index of the solution against polymer and salt concentration are obtained. Therefore, before refractive index measurements, it was necessary to dilute the samples to the above mass fraction range. The precision of the mass fraction of PPG achieved using eq 1 was better than 0.002.

Results and Discussion

Experimental Results. The equilibrium compositions of all of the studied aqueous two-phase systems are shown in Table 2, and the tie-line data are given in Table 3. The complete phase diagrams of all of the studied systems are shown in Figures 1−3. The effect of salt type on the binodal curves of all three studied systems is given in Figure 4. Figure 4 shows that the higher the valency of the anion,

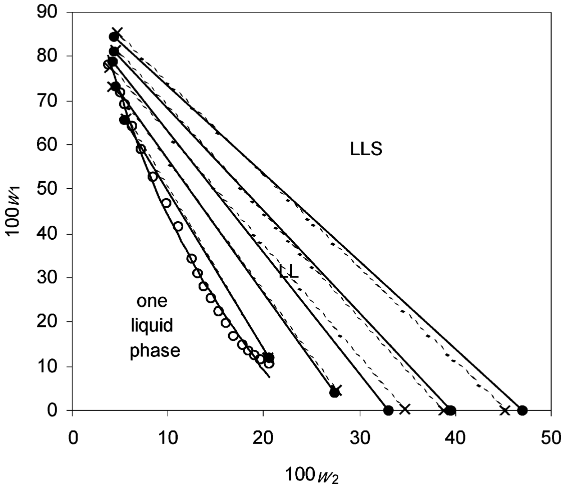

Figure 3. Phase diagram of the PPG 400(1) + $NaNO_3$ (2) + H_2O (3) two-phase system at 25 °C: ○, experimental binodal; −, calculated binodal; −•−, experimental tie lines; ···×···, calculated tie lines using eq 3.

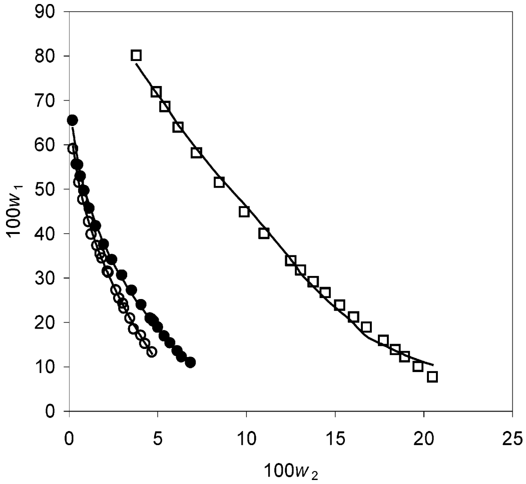

Figure 4. Effect of salt type on the binodal curves for the PPG400 (1) + salt (2) + H_2O (3) two-phase systems at 25 °C: ●, Na_2SO_4; ○, Na_2CO_3; ■, $NaNO_3$.

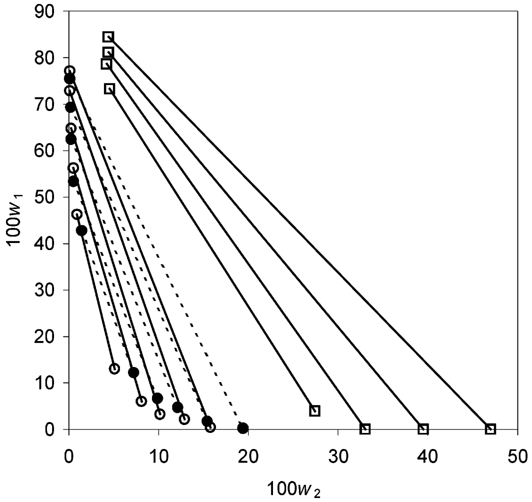

Figure 5. Effect of salt type on the tie lines for the PPG400 (1) + salt (2) + H_2O (3) two-phase systems at 25 °C: ···●···, Na_2SO_4; −○−, Na_2CO_3; −□−, $NaNO_3$.

the lower the concentration required to form a two-phase system. This trend has also been observed for aqueous two-phase systems of PEG with these salts.[11] 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 power of Na_2SO_4 and Na_2CO_3 is not very different, but as shown in Figure 4 the salting-out power of Na_2SO_4 and Na_2CO_3 is greater than of $NaNO_3$. This trend is in agreement with the lyotropic series given by Shaw.[12] The binodals calculated from eq 2 are also shown in Figure 4. Additionally, the slopes of the tie lines for the investigated systems are compared. As can be seen from Figure 5, the slope of tie lines increases with increasing charge on the anion because the anions with a higher valence hydrate more water than the lower-valence anions.

The following empirical equation has been used for the correlation of binodal data of the investigated systems:

$$w_1 = a + bw_2^{0.5} + cw_2 \tag{2}$$

Coefficients a, b, and c of eq 2 along with the corresponding standard deviations for the investigated systems are given in Table 4. On the basis of the obtained standard deviations, it was concluded that eq 2 can be satisfactorily used to correlate the binodal curves of the studied systems. The calculated binodal curves of the investigated systems are also shown in Figures 1−3.

Table 5. Values of the Parameters of Equation 3 for PPG400 (1) + Salt (2) + H_2O (3) Systems at 25 °C

system	k	n	k_1	r	sd_1[a]	sd_2[a]
PPG + Na_2SO_4 + H_2O	0.0494	1.2916	9.3657	0.7036	1.37	0.90
PPG + Na_2CO_3 + H_2O	0.0518	1.0725	14.0645	0.8153	3.24	0.85
PPG + $NaNO_3$ + H_2O	0.1544	0.8902	6.6210	0.8277	0.49	0.66

[a] $sd_j = \{{}^1/_2L\ \sum_{i=1}^{L}[(100w_{i,j,\mathrm{calcd}}^{\mathrm{top}} - 100w_{i,j,\mathrm{exptl}}^{\mathrm{top}})^2 + (100w_{i,j,\mathrm{calcd}}^{\mathrm{bot}} - 100w_{i,j,\mathrm{exptl}}^{\mathrm{bot}})^2]\}^{0.5}$, where L is the number of tie lines and $j = 1$ and 2. sd_1 and sd_2 represent the mass percent standard deviations for PPG and salt, respectively.

The correlation equations[13] given by Othmer−Tabias (eq 3a) and Bancroft (eq 3b) have been used to correlate the tie-line compositions.

$$\left(\frac{1 - w_1^{\mathrm{top}}}{w_1^{\mathrm{top}}}\right) = k\left(\frac{1 - w_2^{\mathrm{bot}}}{w_2^{\mathrm{bot}}}\right)^n \tag{3a}$$

$$\left(\frac{w_3^{\mathrm{bot}}}{w_2^{\mathrm{bot}}}\right) = k_1\left(\frac{w_3^{\mathrm{top}}}{w_1^{\mathrm{top}}}\right)^r \tag{3b}$$

where k, n, k_1, and r represent fit parameters. Superscripts "top" and "bot" represent the top and bottom phases, respectively. The values of the parameters are given in Table 5. On the basis of the obtained standard deviations, sd_1 and sd_2, given in Table 5, we conclude that eq 3 can be satisfactorily used to correlate the tie-line data of the investigated systems. To show the reliability of the model, we also show a comparison between the experimental and correlated tie lines in Figures 1−3.

Conclusions

Liquid−liquid equilibrium data for the systems PPG400 + Na_2SO_4 + H_2O, PPG400 + Na_2CO_3 + H_2O, and PPG400 + $NaNO_3$ + H_2O at 25 °C were obtained. The effect of salt on the binodal curves and tie lines was determined. It was found that the two-phase area and slope of the tie lines increase with increasing charge on the anion. The tie-line data for investigated systems can be satisfactorily described by Othmer−Tobias and Bancroft equations.

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