Liquid−Liquid Equilibrium of Poly(ethylene glycol) 4000 + Diammonium Hydrogen Phosphate + Water at Different Temperatures

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Liquid−liquid equilibrium for an aqueous two-phase system containing poly(ethylene glycol) 4000 + diammonium hydrogen phosphate + water was studied at four different temperatures of (25, 30, 35, and 45) °C. The binodal curve was fitted to three different empirical equations relating the concentrations of PEG 4000 and diammonium hydrogen phosphate, and the coefficients were estimated for the respective temperatures for all three equations. The effective excluded volume values were obtained from the binodal model for the present system, and salting-out ability of the salt was discussed. Tie line compositions were correlated using the Othmer−Tobias and Bancroft equations, and the parameters are also reported. Further, the experimental binodal data of the poly(ethylene glycol) 4000 + diammonium hydrogen phosphate + water system were compared to poly(ethylene glycol) 6000 + diammonium hydrogen phosphate + water for (25, 35, and 45) °C.

Introduction

Adding either two polymers or a polymer and an inorganic salt to water, above a threshold concentration, forms aqueous two-phase systems (ATPS). The primary advantages of ATPS handling of materials are biocompatible environments, economically favorable operation, and easy scale-up. The adjustable factors like operating temperature, viscosity, and density of the system allow for ease of manipulation of the targeted product partitioning. ATPS have been successfully used in the extraction of metallic ions, extractive crystallization of inorganic salts, recovery of nanoparticles, and in the extraction process of sulfide minerals.[1,2] ATPS have advantages over conventional extraction using organic solvents because of their very mild environment for biomolecule separation, they are straightforward, they are efficient toward continuous operation, and their ease of scaling up the process. In recent years, ATPS, especially poly(ethylene glycol) + inorganic salt + water systems, have found widespread applications, mostly because of their use in separation of macromolecules from the mixture of biological materials.[3–5] Aqueous polymer−salt systems have several advantages over the polymer−polymer systems due to the larger differences in density, greater selectivity, lower viscosity, less cost, etc.

Although the aqueous two-phase separation technique is successful, data on the properties and equilibrium of phase systems are necessary for the design of extraction processes and also for the development of models to predict phase partitioning. Several studies have been made on the liquid−liquid equilibrium behavior using PEG with different molecular weights and inorganic salts. Most of the research work on aqueous polymer−salt systems was done using poly(ethylene glycol) with salts consisting of selective cations, namely, ammonium, potassium, or sodium, and anions, namely, phosphate, sulfate, or carbonate. Zaslavsky[5] presented a useful summary of experimental data, including equilibrium phase diagrams for normal systems, involving PEG, inorganic salts, and water. The phase equilibrium diagram for polyethylene glycol 6000 in combination with ammonium dihydrogen phosphate and diammonium hydrogen phosphate systems at different temperatures of (25, 35, and 45)°C was developed by Zafarani−Moattar et al.,[6] and further, the effect of cations in the formation of the aqueous two-phase system was also discussed with the help of the effective excluded volume (EEV) of the systems.[7] Pathak et al.[8] reported phase diagrams for the biphasic liquid zone for systems containing PEG 4000, salt, and water at (25, 30, and 40) °C. Taboada et al.[9] established the equilibrium data and binodal curve for the PEG 4000 + Na_2SO_4 + water system at 25 °C, and further the data were fitted by means of a three-parameter equation. Also the tie line compositions were fitted to both the Othmer−Tobias and Bancroft equations.[10] However, only a very limited amount of research work has been reported using the PEG 4000 + diammonium hydrogen phosphate + water system. In the present work, the binodal and liquid−liquid equilibrium data for PEG 4000 + diammonium hydrogen phosphate + water at four different temperatures, (25, 30, 35, and 45) °C, were measured and correlated with model equations.

Experimental Section

Materials. Analytical grade poly(ethylene glycol) 4000 (Merck-Schuchardt, Germany, cat. no: 8.07490.1000) with a molar mass average of 4000 (3500 to 4500) and diammonium hydrogen phosphate (Merck, India, cat. No: 61757805001730) with a minimum purity of 99 % were used. The polymer and salts were used without further purification. Double distilled, deionized water was used for the present experiments.

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Apparatus and Procedure. The experiments were carried out in an external jacketed glass vessel with a working volume of 200 cm^3 to establish the binodal curve data, representing the minimum concentration needed to form the two phases. In the external jacket, water was circulated at constant temperature using a thermostat (Schott-Gerate CT 52, Germany). The temperature was maintained with an uncertainty of ± 0.05 °C. The binodal curves were obtained by the cloud point method (titration method).[11] PEG 4000 of 50 % (w/w) and diammonium hydrogen phosphate of 30 % (w/w) were prepared. A known amount of the PEG 4000 solution was taken and titrated against diammonium hydrogen phosphate and vise versa. The diammonium hydrogen phosphate solution was added in drops until the appearance of turbidity, which indicates the two-phase formation. Water was then added until the disappearance of turbidity. Yet again, the diammonium hydrogen phosphate solution was added dropwise until the mixture turned turbid, and the above procedure was repeated over a whole range of concentrations starting with PEG 4000 and diammonium hydrogen phosphate. The composition of the mixture was determined by mass using an analytical balance (OHAUS Essae-Teraoka, model AR2140) with a precision of ± 0.1 mg. All the experiments were conducted in duplicate, and the average values were taken for further analysis.

The phase equilibrium studies were carried out in glass separators (100 cm^3). The polymer, salt, and water were mixed together in the vessel with appropriate amounts (50 g basis), which was taken as a feed sample for phase equilibrium studies. The sample was stirred for (3 to 4) h at a desired temperature, and then the mixture was allowed to settle for 24 h at constant temperature using a thermostat. After the individual phases were separated, phase compositions were determined using an Abbe-type refractometer for PEG, and an analytical method was adopted for the phosphate ion. The concentrations of diammonium hydrogen phosphate in the top and bottom phases were determined through an analytical procedure using hydrochloric acid as titrant.[6] The detailed experimental procedure for binodal curves and equilibrium concentration measurement for both PEG and salt are available elsewhere.[6,12,13]

The concentrations of PEG in both phases were determined by refractive index measurements performed at 30 °C using an Abbe-type refractometer. The relationship between the refractive index, n_D, and the mass fraction of polymer, w_p, and salt, w_s, is given by

$$n_D = a_0 + a_1 w_p + a_2 w_s \tag{1}$$

where a_0, a_1, and a_2 are the fitting parameters. For phase analysis, the above equation was originally suggested by Cheluget et al.[14] for the poly(propylene glycol) + NaCl + H_2O system, which was later successfully applied by Zafarani-Moattar and Hamidi[15] for the PEG 6000 + potassium citrate + water system. The calibration plot was drawn for different concentrations of PEG 4000 [(10 to 50) % (w/w)] and diammonium hydrogen phosphate [(1 to 10) % (w/w)]. The values for the fitting parameters of a_0, a_1, and a_2 are obtained through regression analysis, and the values are 1.3303, 0.14789, and 0.2585, respectively, with estimated errors of ± 1.0 %.

Results and Discussion

The phase equilibrium for an aqueous two-phase system can be represented as a binodal curve relating the concentration of the salt and poly(ethylene glycol) in the corresponding phases. For the PEG 4000 + diammonium hydrogen phosphate + water based ATPS, the binodal curve representing the minimum concentration required for the formation of two phases at different temperatures and tie-line data, (25, 30, 35, and 45) °C, are shown in Tables 1 and 2, respectively. The effect of temperature on the binodal curves of the investigated aqueous PEG 4000 + diammonium hydrogen phosphate system is shown in Figure 1, which indicates that an increase in temperature expands the two-phase area of the binodal curve, due to the increase in salt solubility. The experimental results of the present aqueous two-phase systems are in good agreement with the other similar ATPS binodal curves reported in the literature.[6]

Table 1. Binodal Data as Mass Fraction for the PEG 4000 + Diammonium Hydrogen Phosphate + Water System at Different Temperatures

25 °C		30 °C		35 °C		45 °C	
100 w_p	100 w_s	100 w_p	100 w_s	100 w_p	100 w_s	100 w_p	100 w_s
37.13	2.26	37.53	1.96	40.01	1.57	38.33	1.34
35.15	2.45	33.69	2.35	35.86	1.88	34.32	1.80
31.62	2.89	30.43	2.78	32.19	2.39	31.07	2.18
30.04	3.14	27.64	3.25	29.20	2.80	28.27	2.60
28.62	3.36	25.22	3.73	26.61	3.25	23.86	3.34
27.32	3.56	23.19	4.14	24.36	3.72	20.58	3.96
26.03	3.85	21.40	4.56	22.50	4.07	19.21	4.29
24.86	4.11	19.80	5.00	20.83	4.45	16.94	4.82
23.88	4.26	18.43	5.38	19.32	4.89	15.19	5.18
22.89	4.48	17.24	5.70	18.06	5.20	13.68	5.63
21.91	4.76	16.19	5.99	15.93	5.77	12.42	6.03
21.08	4.95	15.23	6.30	15.02	6.06	11.36	6.41
19.53	5.35	14.37	6.57	13.48	6.52	9.72	6.93
18.20	5.70	13.58	6.86	12.21	6.92	8.77	7.25
17.57	5.88	12.87	7.12	10.67	7.49	7.98	7.54
16.99	6.06	11.66	7.56	9.83	7.80	7.31	7.80
16.45	6.22	10.65	7.93	8.82	8.15	6.42	8.12
15.42	6.57	9.42	8.41	8.18	8.52	4.98	8.76
14.97	6.70	8.74	8.67	7.45	8.78	3.35	9.43
14.12	7.00	8.16	8.88	6.49	9.12	2.24	10.03
13.33	7.30	7.89	9.00	4.07	10.25	1.61	10.58
12.67	7.49	6.80	9.41	2.59	11.04	1.02	11.17
12.32	7.66	6.44	9.56				
11.71	7.89	5.82	9.82				
11.43	8.00	5.54	9.94				
10.57	8.27	3.94	10.72				
9.70	8.62	2.48	11.57				
8.75	9.01						
7.63	9.45						
6.48	9.91						
5.50	10.35						
4.63	10.79						
3.69	11.27						
2.88	11.73						
2.12	12.21						
1.55	12.66						
1.20	13.07						

Table 2. Tie Line Data as Mass Fraction for the PEG 4000 + Diammonium Hydrogen Phosphate + Water System at Different Temperatures

polymer-rich phase		salt-rich phase	
100 w_p	100 w_s	100 w_p	100 w_s
30 °C			
28.58	2.94	1.80	16.32
34.66	1.72	0.05	19.18
37.18	1.42	0.25	20.94
35 °C			
29.76	2.63	1.22	16.16
31.77	2.52	1.07	17.14
36.52	2.20	1.09	19.86
45 °C			
26.72	2.85	1.14	15.16
33.10	2.24	0.96	17.00
35.55	1.98	0.88	17.98

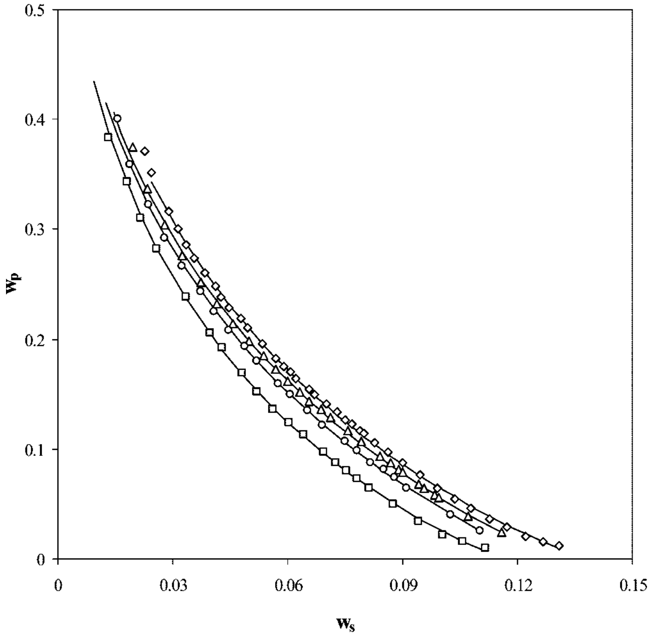

Figure 1. Effect of temperature on the binodal curve for PEG 4000 + diammonium hydrogen phosphate + water. Experimental binodal points for ◇, 25 °C; Δ, 30 °C; ○, 35 °C; and □, 45 °C; —, calcd from eq 3.

Correlation of Binodal Data

An attempt was made to fit the binodal data using different expressions, used previously for ATPS. For representing the binodal data of the present PEG−salt systems, the following nonlinear expression (eq 2) developed by Merchuk[16] was used. Further coefficients *a*, *b*, and *c* along with the corresponding standard deviations for the investigated systems were obtained and are shown in Table 3.

$$w_{\mathrm{p}} = a \exp(b w_{\mathrm{s}}^{0.5} - c w_{\mathrm{s}}^{3}) \tag{2}$$

The following form of the empirical equation (eq 3) used by Malathy et al.[13] was used to correlate the present data on the PEG 4000 + diammonium hydrogen phosphate + water system. The parameters were estimated by regression analysis, and the constants and coefficients are listed in Table 4 for different temperatures along with the corresponding standard deviation

$$w_{\mathrm{p}} = a_1 + b_1 w_{\mathrm{s}}^{0.5} + c_1 w_{\mathrm{s}} \tag{3}$$

where w_{p} and w_{s} are the mass fractions of PEG 4000 and diammonium hydrogen phosphate, respectively.

On the basis of statistical geometry methods, the binodal model developed by Guan et al.[17] for aqueous polymer−polymer systems is extended to correlate the experimental binodal data on the PEG 4000 + diammonium hydrogen phosphate + water system. The effective excluded volume (EEV) can be determined using the model. The binodal equation for the aqueous polymer−salt systems is defined as

$$\ln\left(V_{123}^{*}\frac{w_{\mathrm{p}}}{M_{\mathrm{p}}}\right) + V_{123}^{*}\frac{w_{\mathrm{s}}}{M_{\mathrm{s}}} = 0 \tag{4}$$

where V_{123}^{*} is the effective excluded volume (EEV) and M_{p} and M_s are the molar mass of polymer (4000 g·mol^{-1}) and salt (132.06 g·mol^{-1}), respectively. In the present work, the effective excluded volume along with the corresponding standard deviations were determined (Table 5) for all four temperatures using the present experimental binodal data. The salting-out strength of the salt could be related to V_{123}^{*}, as pointed out by Huddleston et al.[18] Further, the salting-out ability of the anions was analyzed for the salts sharing a common cation but containing different anions (Zafarani-Moattar et al.[7]). The anions follow the order of $\mathrm{HPO_4^{2-}} > \mathrm{SO_4^{2-}} > \mathrm{C_2H_2O_4^{2-}} > \mathrm{H_2PO_4^{-}} > \mathrm{OH^{-}} > \mathrm{CHO_2^{-}}$. It was also observed that the salts having larger values of EEV have a higher salting-out strength.[7]

Table 3. Values of Parameters of Equation 2 for PEG 4000 + Diammonium Hydrogen Phosphate + Water at Different Temperatures

temperature °C	*a*	*b*	*c*	AARD (%)[a]	Sd[b]
25	0.643755	−4.31253	1047.62	3.857793	0.67
30	0.822179	−5.84741	861.7768	3.102386	1.44
35	0.812616	−5.92741	1018.641	2.654593	1.31
45	0.78717	−6.18339	1565.731	3.485718	0.39

[a] AARD $= 1/N\left((100w_{\mathrm{p}}^{\mathrm{exptl}} - w_{\mathrm{p}}^{\mathrm{calcd}})^2/100w_{\mathrm{p}}^{\mathrm{exptl}}\right)^{0.5}$. [b] Sd $= \left(\sum_{i=1}^{N}(w_{\mathrm{p}}^{\mathrm{calcd}} - 100w_{\mathrm{p}}^{\mathrm{exptl}})^2/N\right)^{0.5}$.

Table 4. Values of Parameter for Equation 3 for the PEG 4000 + Diammonium Hydrogen Phosphate + Water System at Different Temperatures

temperature	a_1	b_1	c_1	R^2	Sd
25	0.7502	−3.0103	2.6583	0.9995	0.21
30	0.8462	−3.8993	4.4476	0.9937	1.26
35	0.8160	−3.8009	4.3652	0.9934	1.07
45	0.7205	−3.2552	3.3517	0.9996	1.98

Table 5. Effective Excluded Volumes As Determined by Regression of the Statistical Geometry Model (Equation 4) for the PEG 4000 + Diammonium Hydrogen Phosphate + Water System at Different Temperatures

temp/°C	EEV (g·mol^{-1})	AARD %	Sd
25	37.26781	2.776299	20.16
30	37.57228	2.747705	17.61
35	39.64935	2.981768	17.60
45	43.01212	3.334857	25.15

In the present work, the effect of temperature on EEV was analyzed with four different temperatures, and it was found that the EEV increases with increasing temperature. The salting-out ability can also be related to the Gibbs free energy of hydration of the ions (ΔG_{hyd}). Since the Gibbs energy of hydration value for the $\mathrm{HPO_4^{2-}}$ ion was not available in the literature, the standard partial entropy can be used to explain the hydration energy of the ions. However, Shibukawa et al.[19] pointed out that the standard partial entropy of the aqueous

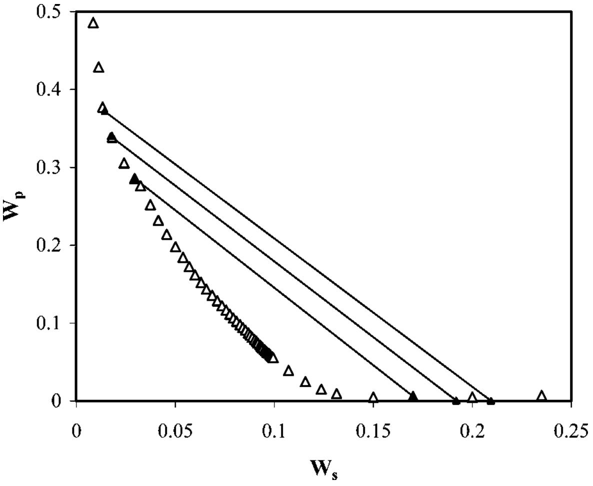

Figure 2. Tie lines for PEG 4000 + diammonium hydrogen phosphate + water at 30 °C: Δ and ▲, experimental; —, calculated from eqs 3 and 4.

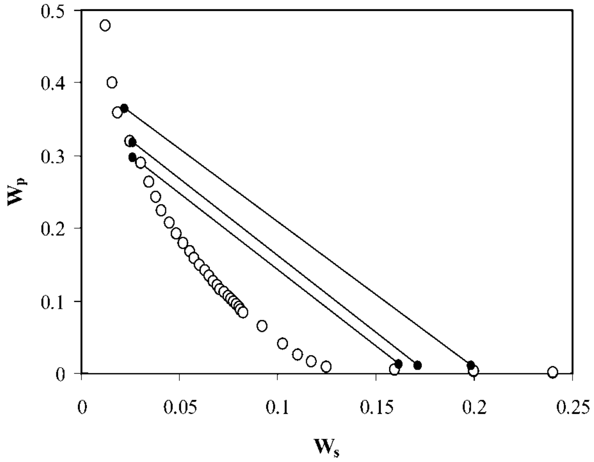

Figure 3. Tie lines for PEG 4000 + diammonium hydrogen phosphate + water at 35 °C: ○ and ●, experimental; —, calculated from eqs 3 and 4.

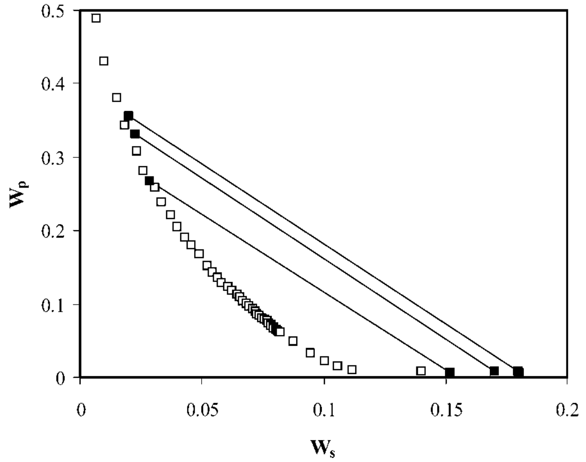

Figure 4. Tie lines for PEG 4000 + diammonium hydrogen phosphate + water at 45 °C: □ and ■, experimental;—, calculated from eqs 3 and 4.

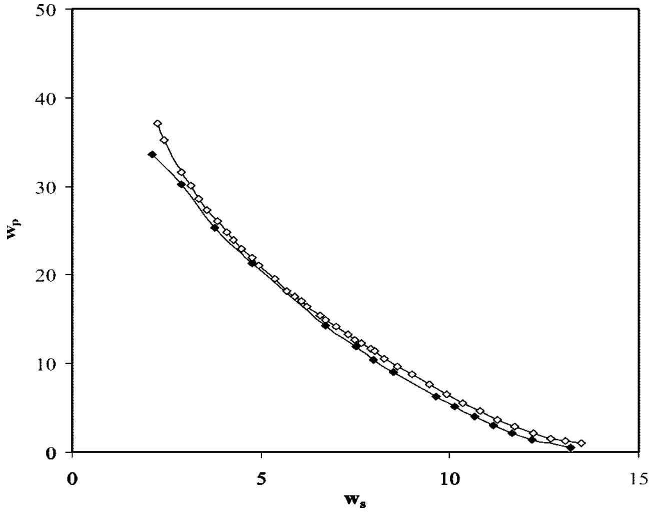

Figure 5. Effect of polymer molecular weight on binodal curve at 25 °C: ◇, PEG 4000 + diammonium hydrogen phosphate + water; ◆, PEG 6000 + diammonium hydrogen phosphate + water.[6]

HPO_4^{2-} ion (10.9 $J\cdot K^{-1}\cdot mol^{-1}$) is smaller, when compared to that of aqueous SO_4^{2-} (64.5 $J\cdot K^{-1}\cdot mol^{-1}$), indicating that the HPO_4^{2-} ion attracts water molecules more strongly than SO_4^{2-}. Similarly for cations, the more negative ΔG_{hyd} value is better at salting-out PEG. For NH_4^+, the ΔG_{hyd} value is −285 $kJ\cdot mol^{-1}$, which shows that the ammonium salts are poor at salting-out when compared to other salts like Zn (−1955 $kJ\cdot mol^{-1}$), Na (−365 $kJ\cdot mol^{-1}$), etc.[19]

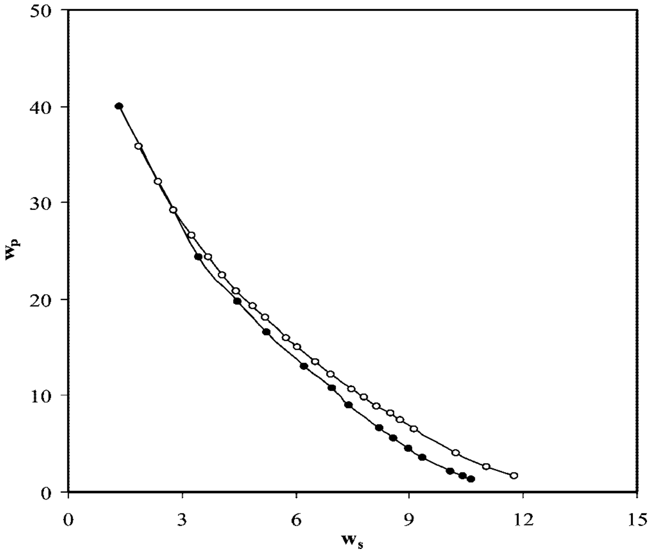

Figure 6. Effect of polymer molecular weight on binodal curve at 35 °C: ○, PEG 4000 + diammonium hydrogen phosphate + water; ●, PEG 6000 + diammonium hydrogen phosphate + water.[6]

It was observed from Tables 3, 4, and 5 that the binodal data of the PEG 4000 + diammonium hydrogen phosphate + water system were well represented by eq 3. Equations 2 and 4 satisfactorily represent the binodal data at lower concentrations of both salt and polymer, and a minor deviation was found at higher concentration which may be due to the interaction effects between the salt and PEG molecules.

The Othmer−Tobias (eq 5) and Bancroft (eq 6)[10] as given below were earlier successfully applied for tie line compositions of other similar polymer−salt systems,[12,13] hence those equations were used to correlate the tie line composition of the PEG 4000 + diammonium hydrogen phosphate + water system.

$$\frac{1 - w_p^t}{w_p^t} = K\left(\frac{1 - w_s^b}{w_s^b}\right)^n \tag{5}$$

$$\left(\frac{w_w^b}{w_s^b}\right) = K_1\left(\frac{w_w^t}{w_p^t}\right)^r \tag{6}$$

where K, n, K_1, and r are the fitting parameters (Table 6). Superscripts t and b represent the polymer-rich phase (top phase) and the salt-rich phase (bottom phase), respectively. Subscripts p, s, and w stand for PEG, salt, and water, respectively. The experimental and correlated tie lines for all the three temperatures (30, 35, and 45) °C are compared and shown in Figures 2 to 4, respectively.

Figures 5 to 7 show the effect of polymer molecular weight on the binodal curve. The reported data of Zafarani-Moattar[6] obtained using the PEG 6000 + diammonium hydrogen phosphate + water system were compared with that of the present system (PEG 4000 + diammonium hydrogen phosphate + water) for three different temperatures, (25, 35, and 45) °C. It was found that as the polymer molecular weight increases the binodal curve shifts down, at lower PEG concentrations, and the effect is less pronounced at higher concentrations of PEG. Further, the effect of PEG molecular weight was more at lower temperatures (25 and 35) °C, and at higher temperature (45 °C), both the binodals approach each other.

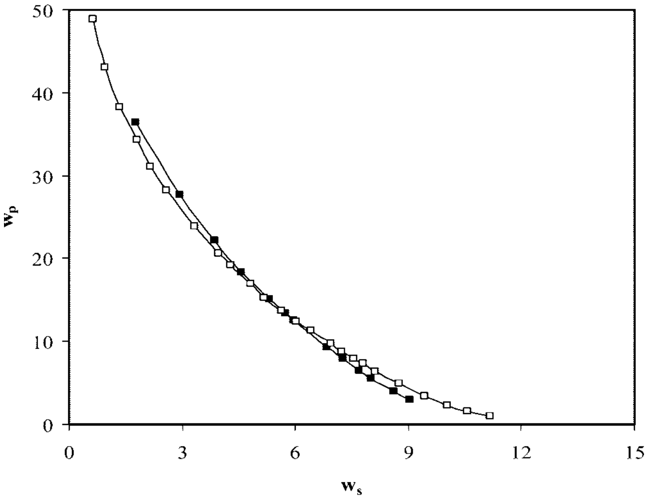

Figure 7. Effect of polymer molecular weight on binodal curve at 45 °C. □, PEG 4000 + diammonium hydrogen phosphate + water; ■, PEG 6000 + diammonium hydrogen phosphate + water.[6]

Table 6. Values of Parameters in Equations 5 and 6 for the PEG 4000 + Diammonium Hydrogen Phosphate + Water System at Different Temperatures

temp/°C	K	n	R^2	K_1	r	R^2
30	0.2975	1.2977	0.9924	2.6197	0.7497	0.9859
35	0.2960	1.2583	0.9914	2.6633	0.7998	0.9911
45	0.0795	2.0519	0.9943	3.4498	0.4879	0.9940

Conclusions

Binodal curves and tie line compositions were measured for the PEG 4000 + diammonium hydrogen phosphate + water based ATPS at four different temperatures, (25, 30, 35, and 45) °C. It was found that as the temperature increases the binodal curve shifts down due to an increase in solubility, resulting in an increase in the two-phase region. The binodal curve and tie line data were correlated using available empirical equations, and the values of the parameters were reported. The effective excluded volume values were estimated from the binodal model for the present system, and salting-out ability of the salt was discussed. In addition, a sample comparison of binodal data for two different polymer molecular weights was made using the PEG 6000 + diammonium hydrogen phosphate + water and PEG 4000 + diammonium hydrogen phosphate + water systems.

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