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Isopiestic Determination of Water Activity in the Poly(vinylpyrrolidone) + NaCl + H_2O System at Different Temperatures

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Water activities of the poly(vinylpyrrolidone) (PVP) + NaCl + H_2O system have been determined experimentally using the improved isopiestic method at (298.15, 308.15, and 318.15) K. The effect of temperature on the constant water activity lines has been studied. It was found that the slope of all constant water activity lines increased with increasing temperature. Furthermore, the extended Flory−Huggins theory has been used for the correlation of the experimental water activity data. The agreement between the correlation and the experimental data is good.

Introduction

Aqueous two-phase systems (ATPS) can be useful for the separation of various biological materials,[1−3] metal ions, dyes, drug molecules, and small organic species[4,5] using the liquid−liquid extraction method. There are two kinds of ATPS: polymer−polymer ATPS and polymer−salt ATPS. It has been found that the latter have more advantages. Liquid−liquid equilibrium data for some aqueous PVP−salt two-phase systems have been reported in the literature.[6−9]

In an ATPS, water is a special and key component and is closely related to the other two-phase-forming components. Thus, the thermodynamic properties of water in these systems should be given great attention. Also, the activity is an important and key thermodynamic property because it is closely related to the other thermodynamic properties. There are some reports on the water activity data of NaCl + H_2O[10,11] and the PVP + H_2O[12] binary systems at different temperatures. But as far as we know, there is no report on the water activity data of the PVP + NaCl + H_2O system.

The isopiestic method is the most accurate, simple experimental technique available for measuring the solvent activity of solutions that contain nonvolatile solutes. This technique has been used extensively for the determination of the water activities for the systems PEG + salt + water[13−15] and PPG + salt + water[16,17] at 298.15 K.

In this study, the water activities of the PVP + NaCl + H_2O system have been determined experimentally using an improved isopiestic method[13] at (298.15, 308.15, and 318.15) K. The effect of temperature on the constant water activity lines has been studied. Furthermore, the extended Flory−Huggins[6,7] theory with temperature-dependent parameters has been used for the correlation of the experimental water activity data.

Experimental Section

Chemicals. PVP (K15, molecular weight 10 000) was obtained from Aldrich. Sodium chloride was obtained from Merck (GR, minimum purity 99.5%). The salt was dried in an oven at about $T = 393.15$ K for 24 h prior to use. Double-distilled, deionized water was used.

Apparatus and Procedures. In this study, the isopiestic method is used to obtain the activity of water in aqueous PVP−NaCl mixtures. It is based on the phenomenon that different solutions, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. Equilibrium has been established once the temperature and pressure are uniform throughout the system, provided that no concentration gradients exist in the liquid phase. At equilibrium, the chemical potentials of the solvent in each of the solutions in the closed system are identical. Equality of the solvent chemical potential implies the equality of the solvent activity. Because the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system. The isopiestic apparatus used in this work was similar to the one used by Ochs et al. [13] This apparatus consisted of an eight-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions, two flasks contained the pure PVP solutions, three flasks contained the PVP/NaCl solutions, and the central flask was used as a water reservoir. The apparatus was held in a constant-temperature bath for at least 120 h for equilibrium. The temperature was controlled to within ±0.1 K. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance with a precision of $\pm 1 \times 10^{-7}$ kg. From the weight of each flask after equilibrium and the initial weight of salt and polymer, the mass fraction of each solution was calculated. The water activity for the standard aqueous NaCl solutions at different concentrations and temperatures has been calculated from the correlation of Colin et al.[11] It was assumed that the equilibrium condition was reached when the differences between the mass fractions of two standard solutions were less than 1%. In all cases, averages of the mass fractions of two standard solutions are reported. The accuracy of the method depends on the standard solutions, sample mixing during the equilibrium period, temperature stability, and time allowed for the equilibrium process. The uncertainty

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Table 1. Water Activity (a_3) and Vapor Pressure (p) for PVP (1) + NaCl (2) + H_2O (3) at 298.15 K

$100w_1$	$100w_2$	a_3	p/kPa	$100w_1$	$100w_2$	a_3	p/kPa
28.21	0.00			48.50	0.00		
18.33	0.70			35.34	1.92		
10.00	1.21	0.9890	3.134	20.60	3.98	0.9588	3.038
3.18	1.69			10.83	5.22		
0.00	1.90			0.00	6.69		
29.10	0.00			49.44	0.00		
19.28	0.74			40.10	1.47		
10.33	1.32	0.9884	3.132	26.7	3.48	0.9543	3.024
3.36	1.78			17.13	4.93		
0.00	2.01			0.00	7.34		
38.58	0.00			53.50	0.00		
13.38	2.44			41.72	2.00		
13.21	2.50	0.9794	3.103	28.69	4.21	0.9417	2.984
3.02	3.46			12.90	6.89		
0.00	3.63			0.00	9.08		
43.62	0.00			59.41	0.00		
21.92	2.66			47.16	2.24		
7.33	4.33	0.9685	3.069	34.12	4.78	0.9259	2.934
3.46	4.82			19.33	7.51		
0.00	5.27			0.00	11.10		
45.30	0.00						
35.35	1.30						
23.33	2.79	0.9669	3.064				
13.60	3.91						
0.00	5.48						

Table 2. Water Activity (a_3) and Vapor Pressure (p) for PVP (1) + NaCl (2) + H_2O (3) at 308.15 K

$100w_1$	$100w_2$	a_3	p/kPa	$100w_1$	$100w_2$	a_3	p/kPa
32.45	0.00			52.97	0.00		
18.39	1.02			40.55	2.02		
11.09	1.54	0.9865	5.550	25.05	4.25	0.9496	5.342
4.42	1.99			12.24	6.21		
0.00	2.34			0.00	8.03		
39.85	0.00			57.02	0.00		
25.26	1.41			43.13	2.50		
15.5	2.33	0.9774	5.499	35.44	3.95	0.9329	5.248
6.97	3.13			17.45	7.12		
0.00	3.85			0.00	10.26		
48.38	0.00			58.37	0.00		
32.05	2.02			46.92	2.33		
25.65	2.86	0.9640	5.423	31.91	5.08	0.9273	5.216
10.16	4.69			15.91	8.08		
0.00	5.94			0.00	10.96		
49.77	0.00			62.73	0.00		
36.53	1.82			41.83	4.67		
27.82	2.90	0.9603	5.402	30.40	7.12	0.9051	5.091
10.24	5.20			20.11	9.29		
0.00	6.49			0.00	13.57		

Table 3. Water Activity (a_3) and Vapor Pressure (p) for PVP (1) + NaCl (2) + H_2O (3) at 318.15 K

$100w_1$	$100w_2$	a_3	p/kPa	$100w_1$	$100w_2$	a_3	p/kPa
37.05	0.00			53.10	0.00		
21.91	1.06			41.50	1.55		
11.89	1.86	0.9830	9.426	21.34	4.18	0.9563	9.169
3.65	2.66			8.94	5.79		
0.00	2.93			0.00	7.10		
44.75	0.00			59.08	0.00		
25.84	1.67			41.10	3.17		
15.79	2.78	0.9733	9.333	27.27	5.48	0.9336	8.951
6.78	3.82			11.95	8.05		
0.00	4.52			0.00	10.20		
46.04	0.00			60.95	0.00		
24.92	2.29			52.25	1.67		
15.27	3.27	0.9713	9.314	32.17	5.46	0.9243	8.862
4.01	4.45			17.35	8.25		
0.00	4.83			0.00	11.37		
52.28	0.00			61.65	0.00		
32.72	2.52			43.56	3.46		
20.36	4.09	0.9589	9.194	33.13	5.48	0.9214	8.834
8.31	5.60			14.27	8.96		
0.00	6.73			0.00	11.72		

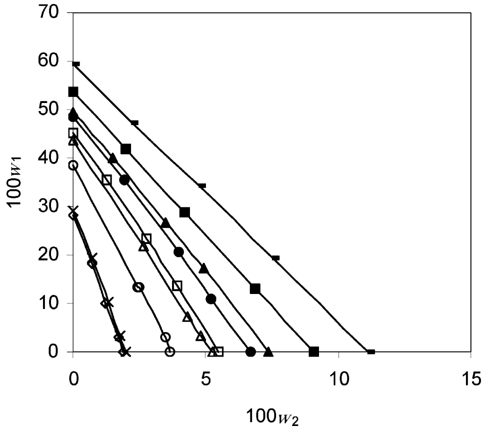

Figure 1. Constant water activity curves for the PVP (1) + NaCl (2) + H_2O (3) system at 298.15 K: ◇, 0.9890; ×, 0.9884; ○, 0.9794; △, 0.9685; □, 0.9669; ●, 0.9588; ▲, 0.9543; ■, 0.9417; solid rectangle, 0.9259.

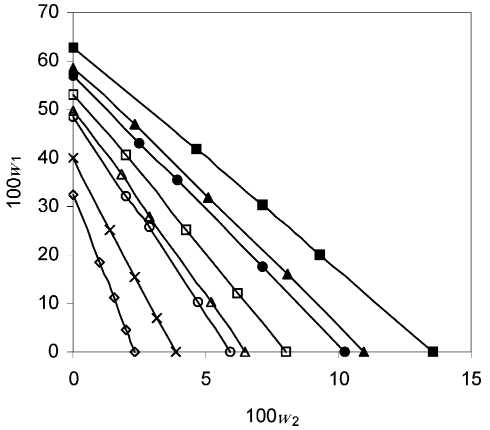

Figure 2. Constant water activity curves for the PVP (1) + NaCl (2) + H_2O (3) system at 308.15 K: ◇, 0.9865; ×, 0.9774; ○, 0.9640; △, 0.9603; □, 0.9496; ●, 0.9329; ▲, 0.9273; ■, 0.9051.

in the measurement of solvent activity was estimated to be ±0.0002.

Results and Discussion

Tables 1 to 3 report the water activities of the PVP (1) + NaCl (2) + H_2O (3) system at (298.15, 308.15, and 318.15) K, respectively. In these Tables, w_i is the mass fraction of species i. The lines of constant water activity are plotted in Figures 1 to 3. The vapor pressures (p) of various PVP−NaCl aqueous solutions at each temperature were computed from the water activity measurements by using the following equation:

$$\ln a_3 = \ln\left(\frac{p}{p^\circ}\right) + \frac{(B - V_3^\circ)(p - p^\circ)}{RT} \qquad (1)$$

where B is the second virial coefficient of water vapor, V_3° is the molar volume of liquid water, and p° is the vapor pressure of pure water, respectively. The second virial coefficients of water vapor were calculated by using the equation provided by Rard and Platford.[18] Molar volumes of liquid water were calculated using the density of water at different temperatures.[19] The vapor pressures of pure water were calculated using the equation of state of Saul

Table 4. Parameters of the Extended Flory−Huggins Equation along with the Corresponding Absolute Relative Percentage Deviations for PVP (1) + NaCl (2) + H_2O (3) at (298.15, 308.15, and 318.15) K

T/K	a_{12}	$b_{12} \times 10^{-3}$	$c_{12} \times 10^4$	a_{13}	$b_{13} \times 10^3$	c_{13}	a_{23}	b_{23}	$c_{23} \times 10^4$	ARD/%[a]
298.15	6.081	−2.115	−6.330	−7.148	−4.272	1.341	−3.101	−0.146	−1.328	0.24
308.15										0.34
318.15										0.41

[a] $$\mathrm{ARD} = \frac{100}{n}\sum_{l=1}^{n}\frac{|a_3^{\mathrm{calcd}} - a_3^{\mathrm{exptl}}|}{a_3^{\mathrm{exptl}}}$$, where n is the number of experimental data points.

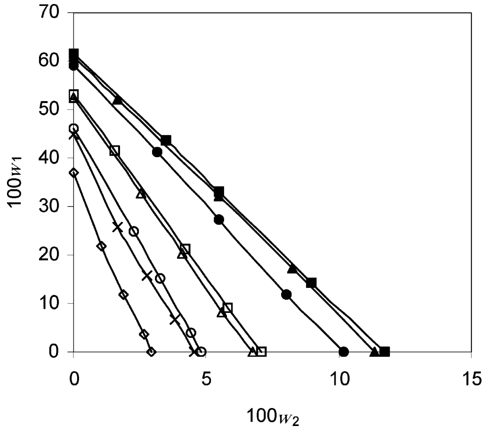

Figure 3. Constant water activity curves for the PVP (1) + NaCl (2) + H_2O (3) system at 318.15 K: ◇, 0.9830; ×, 0.9733; ○, 0.9713; △, 0.9589; □, 0.9563; ●, 0.9336; ▲, 0.9243; ■, 0.9214.

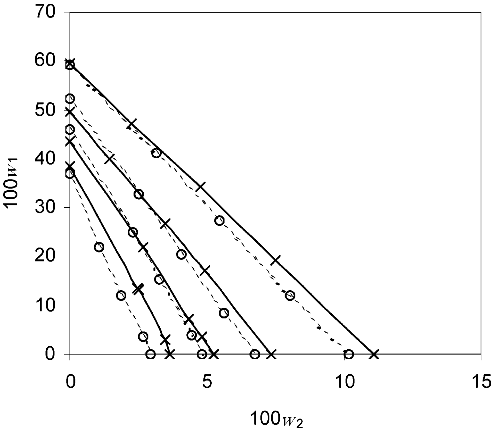

Figure 4. Effect of temperature on the constant water activity lines for the PVP (1) + NaCl (2) + H_2O (3) system: ×, 298.15 K; ○, 318.15 K.

and Wagner.[20] The calculated values of p have also been given in Tables 1 to 3. As can be seen in Tables 1 to 3, in fact five points on each line in Figures 1 to 3 have a constant water activity or vapor pressure, and thus these points are in equilibrium. As shown in Figure 4, the slope of the constant water activity lines increases with increasing temperature. This is because the composition of the systems in equilibrium changes with varying temperature. It was found that the PVP becomes more hydrophobic with increasing temperature.[12] Thus, by increasing the temperature of these five systems in equilibrium, the increase in concentration for the system with higher PVP concentration is larger than for the systems with lower PVP concentration. This behavior is in agreement with our previous observations in which increasing the temperature of the aqueous PVP−salt two-phase system causes an increase in the concentration in the PVP-rich phase and a decrease in the concentration of the salt-rich phase.[6,7]

In our previous papers,[6,7] we represented an extended Flory−Huggins model for polymer (1) + ion (2) + H_2O (3) systems. In this model, the relation for the activity of water (3) is given by

$$\ln a_3 = \frac{2A_x I_x^{3/2}}{1 + \rho I_x^{1/2}} + \ln \phi_3 + \phi_1 - \frac{\phi_1}{r_1} + (1 - \phi_3)(\chi_{13}\phi_1 + \chi_{23}\phi_2) - \chi_{12}\phi_1\phi_2 \quad (2)$$

where

$$A_x = \frac{1}{3}\left(\frac{2\pi N_A}{V_s}\right)^{1/2}\left(\frac{e^2}{4\pi\epsilon D_s k T}\right)^{3/2} \quad (3)$$

$$\phi_i = \frac{r_i x_i}{\sum_i r_i x_i} \quad (4)$$

$$I_x = 0.5\sum_k x_k z_{k^2} \quad (5)$$

In the above relations, x_i is the mole fraction of component i (polymer, ion, and water); z_k is the charge number of ion k; and ρ is the closest-distance parameter. The value of $\rho = 14.9$ has been frequently used for aqueous electrolyte solutions;[21] therefore, this value was also used in this work. N_A, k, ϵ and e are Avogadro's number, the Boltzmann constant, the permittivity of vacuum, and the electronic charge, respectively. r_i is the number of segments of component i ($r_1 = V_1/V_3$, $r_2 = 1$, and $r_3 = 1$). V_s and D_s are the molar volume and dielectric constant of the mixed solvent (here, the polymer is the pseudosolvent), respectively. The values of V_s and D_s are empirically calculated using the following relations:

$$V_s = \phi'_1 V_1 + \phi'_3 V_3 \quad (6)$$

$$D_s = \phi'_1 D_1 + \phi'_3 D_3 \quad (7)$$

where ϕ'_j is the salt-free segment fraction of nonionic species j and is defined as

$$\phi'_j = \frac{r_j x_j}{r_1 x_1 + r_3 x_3} \quad (8)$$

In the above relations, V_1 and V_3 are the molar volumes of the polymer and water, respectively, and D_1 and D_3 are the dielectric constants of the polymer and water, respectively. The infinite dilution apparent molal volume of the polymer at each temperature calculated from the density data of aqueous solutions of PVP[12] is considered to be the V_1 value. The molar volumes of water were calculated using the density of water at different temperature.[19] For PVP, a dielectric constant of $D_1 = 2.2$ was calculated, according to the method proposed by van Krevelen et al.[22] This value was used for all three temperatures. The dielectric constants of water at (298.15, 308.15, and 318.15) K are 78.30, 74.82, and 71.51, respectively.[10] For temperature-dependent of parameters χ_{ij}, the following simple relation was used

$$\chi_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T \tag{9}$$

where a_{ij}, b_{ij}, and c_{ij} are the adjustable parameters that were estimated by the simultaneous fitting of the experimental water activity data for binary and ternary PVP + H_2O,[12] NaCl + H_2O,[11] and PVP + NaCl + H_2O systems at (298.15, 308.15, and 318.15) K. The evaluated parameters along with the corresponding deviations are given in Table 4.

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