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Measurement and Correlation of Water Activities and Refractive Indices for the Systems PPG425 + $(NH_4)_2SO_4$ + H_2O and PPG425 + Na_2SO_4 + H_2O at 298.15 K

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The water activities and refractive indices of the systems polypropylene glycol (PPG425) + $(NH_4)_2SO_4$ + H_2O and PPG425 + Na_2SO_4 + H_2O were measured at 298.15 K. The water activities were obtained using the isopiestic method. The water activities and refractive indices data were correlated with empirical equations. The agreement between the correlation and the experimental data is good.

Introduction

In continuation of our investigations on thermodynamic properties of aqueous salt + polypropylene glycol (PPG425) mixtures,[1,2] the present paper reports the water activities and refractive indices for PPG425 + $(NH_4)_2SO_4$ + H_2O and PPG425 + Na_2SO_4 + H_2O mixtures at 298.15 K. These aqueous two-phase systems, also known as aqueous biphasic systems, can be useful for the separation of various biological materials,[3−5] metal ions, dyes, drug molecules, and small organic species[6,7] using the liquid−liquid extraction method. The liquid−liquid equilibrium (LLE) data for these systems at 298.15 K were obtained by Salabat et al.[1] As far as we know, there is no report on the water activity data and refractive indices of the PPG425 + $(NH_4)_2SO_4$ + H_2O and PPG425 + Na_2SO_4 + H_2O systems.

In this study, the water activities and refractive indices of these systems were measured at 298.15 K. The water activities were measured using the improved isopiestic method.[8] Two empirical equations were used for the correlation of water activities and refractive indices experimental data[2].

Experimental Section

PPG, of molecular weight 425, was obtained from the Aldrich. The number-average molecular weight M_n of this polymer was determined by a cryoscopic osmometer (Osmomat Model 030). For this purpose, freezing point depression measurements on PPG + water were carried out at different concentrations, and the $\Delta T/K_sC$ vs C curve was 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 405 $g \cdot mol^{-1}$. Sodium chloride was obtained from Merck (GR, min 99.5%).

In this study, the isopiestic method is used to obtain the activity of water in aqueous polymer−salt mixtures. It is based on the phenomenon that different solutions, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. The isopiestic apparatus was similar to the one used by Ochs et al.[8] The isopiestic cell consists of a multilegged glass manifold. It has seven female standard 20/14 tapered ground glass fittings and a stopcock. The sample flasks are 10-cm^3 round-bottom flasks with standard 20/14 tapered male ground glass fittings. The seven flasks were typically used as follows: Two flasks contained the standard NaCl solution, one flask contained the $(NH_4)_2SO_4$ or Na_2SO_4 solution, one flask contained the pure polymer solution, two flasks contained the salt/PPG solutions, and the central flask was used as a water reservoir. The center flask was filled with about 0.5 g of water, and the total mass of solution in each flask, at equilibrium, was designed to be about 1 g. The apparatus was held in a constant-temperature bath for at least 3 days for equilibration. The temperature was controlled to within ±0.1K. 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. In all of the isopiestic measurements, aqueous NaCl solutions were used as an isopiestic standard. This technique is capable of giving the water activity with an absolute error of 0.02% or better in the activity. Refractive indices of the solution were measured using a Mettler TOLEDO refractometer with temperature control (RE50). The precision of the refractive index determination is ±0.00001 refractive index units, and uncertainties in refractive index measurement are ±0.00002. The temperature was controlled to within ±0.01 K.

Results and Discussion

At equilibrium, the chemical potentials of the solvent in each of the solutions are identical. The solvent activity is related to the solvent chemical potential by

$$\ln a_w = \frac{\mu_w - \mu_w{}^0}{RT} \tag{1}$$

where a_w is the solvent activity, R is the gas constant, $\mu_w{}^0$

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Table 1. Water Activity Data (a_w) for PPG425 (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) with NaCl (4) as a Reference at 298.15 K

$100w_4$	$100w_2$	$100w_1$	a_w	$100w_4$	$100w_2$	$100w_1$	a_w
2.51	5.08	0.00		6.07	12.59	0.00	
	3.63	5.51	0.9855		9.10	8.15	0.9633
	2.29	10.87			4.76	23.76	
	0.00	23.65			0.00	52.01	
3.36	7.16	0.00		7.08	14.81	0.00	
	5.67	5.50	0.9804		9.47	10.03	0.9564
	3.77	12.30			5.07	27.01	
	0.00	29.75			0.00	56.91	
3.88	7.81	0.00		8.64	18.09	0.00	
	6.52	4.50	0.9773		10.80	12.44	0.9454
	3.58	15.05			7.38	23.52	
	0.00	33.34			0.00	65.05	
4.57	9.58	0.00		9.06	19.33	0.00	
	7.44	6.03	0.9729		12.29	12.74	0.9423
	5.56	12.05			6.76	31.97	
	0.00	38.96			0.00	69.38	
5.44	11.28	0.00					
	6.98	11.03	0.9674				
	5.47	17.05					
	0.00	45.08					

Table 2. Water Activity Data (a_w) for PPG425 (1) + Na_2SO_4 (2) + H_2O (3) with NaCl (4) as a Reference at 298.15 K

$100w_4$	$100w_2$	$100w_1$	a_w	$100w_4$	$100w_2$	$100w_1$	a_w
1.85	3.61	0.00		4.94	10.65	0.00	
	2.38	1.83	0.9895		6.10	9.20	0.9706
	1.36	5.09			2.80	24.10	
	0.00	19.55			0.00	44.27	
2.16	4.46	0.00		5.65	12.44	0.00	
	3.01	2.50	0.9872		7.10	10.04	0.9659
	1.50	9.02			2.80	30.02	
	0.00	21.80			0.00	49.65	
2.71	5.54	0.00		5.74	12.63	0.00	
	3.42	3.86	0.9844		8.32	8.20	0.9655
	1.97	12.16			5.49	18.15	
	0.00	26.61			0.00	52.15	
3.26	6.80	0.00		7.14	15.81	0.00	
	4.34	4.89	0.9810		9.42	11.17	0.9561
	1.23	21.22			6.80	18.97	
	0.00	31.06			0.00	57.53	
3.99	8.47	0.00		7.41	16.41	0.00	
	5.42	7.36	0.9766		10.34	12.05	0.9542
	1.53	24.91			6.94	22.02	
	0.00	37.27			0.00	60.40	

is the standard-state chemical potential of the solvent, and *T* is the absolute temperature. At equilibrium, equality of the solvent chemical potential implies the equality of the solvent activity. Since the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system. The water activity for the standard isopiestic solutions has been calculated from the Pitzer ion interaction parameters for osmotic coefficients with the following equation

$$\ln a_w = -0.001\nu_s m_s M_w \phi_s \qquad (2)$$

Here, ν_s is the salt stoichiometric coefficient, m_s is the salt molality, M_w is solvent molecular weight, and ϕ_s is the practical osmotic coefficient of the standard salt solution.

The water activities for the systems are given in Tables 1 and 2. The lines of constant water activities are plotted in Figures 1 and 2 for these ternary systems. The lines with the lowest water activities are in the neighborhood of the binodal curves where these systems split into two phases.

The water activity results for the mixed PPG + salt solutions correlated by the following empirical equation[2]

$$a_{ps} - a_w = (a_p - a_w) + (a_s - a_w) + (w_s w_p)^{1/2}(b_0 + b_1(w_s w_p)^{1/2}) \qquad (3)$$

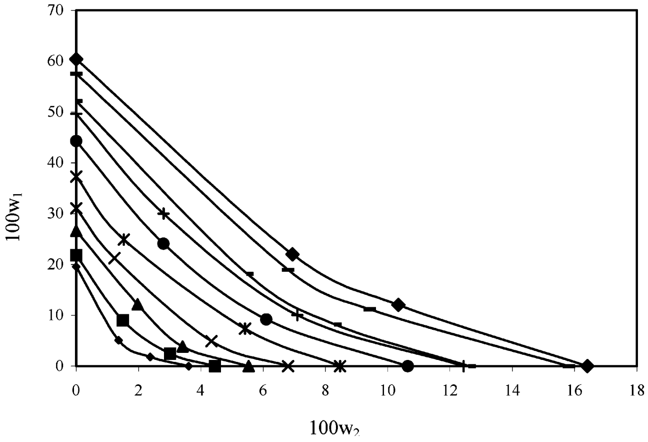

Figure 1. Constant water activity curves for the PPG425 (1) + $(NH_4)_2SO_4$(2) + H_2O (3) system at 298.15 K. ◆, 0.9895; ■, 0.9872; ▲, 0.9844; ×, 0.9810; *, 0.9766; ●, 0.9706; +, 0.9659; −, 0.9655; rectangle, 0.9561; ◆, 0.9542.

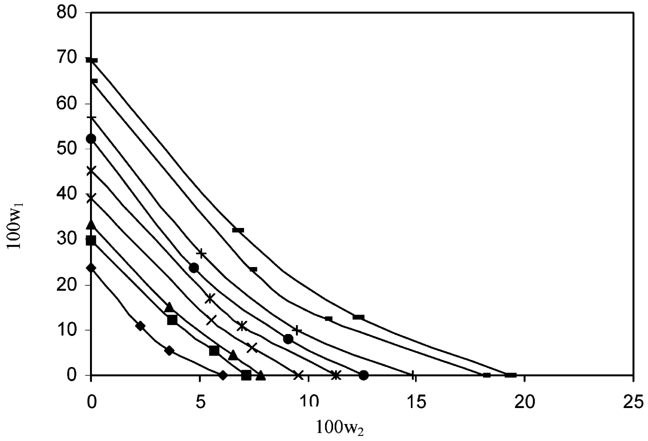

Figure 2. Constant water activity curves for the PPG425 (1) + Na_2SO_4 (2) + H_2O (3) system at 298.15 K. ◆, 0.9855; ■, 0.9804; ▲, 0.9773; ×, 0.9729; *, 0.9674; ●, 0.9633; +, 0.9564; −, 0.9454; rectangle; 0.9423.

where a_{ps}, a_p, a_s, and a_w represent the water activity of aqueous polymer salt (ps), polymer (p), and salt (s) solutions, and pure water ($a_w = 1$). In eq 3, w_s and w_p are the weight percents of the salt and polymer, respectively. The water activities of salt solutions a_s are obtained from eq 2 using the Pitzer osmotic correlation[9]

$$\phi - 1 = f^{\phi} + \left(\frac{2\nu_1\nu_2}{\nu}\right) m B^{\phi} + m^2\left(\frac{2(\nu_1\nu_2)^{1.5}}{\nu}\right)C^{\phi} \qquad (4)$$

where

$$f^{\phi} = -\frac{A_{\phi}|Z_1 Z_2|(I)^{1/2}}{1 + b(I)^{1/2}} \qquad (5)$$

and

$$B^{\phi} = \beta^{(0)} + \beta^{(1)} \exp[-\alpha(1)(I)^{1/2}] \qquad (6)$$

In these equations $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} are Pitzer ionic interaction parameters. These parameters for aqueous sodium sulfate solutions are $\beta^{(0)} = 0.039$, $\beta^{(1)} = 0.6638$, and $C^{\phi} = -0.00083$ and for ammonium sulfate are $\beta^{(0)} = 0.0196$, $\beta^{(1)} = 1.113$, and $C^{\phi} = 0.004974$, which were obtained from ref 9.

The water activity data for the binary PPG + water system up to $W_p = 70\%$ are fitted to a polynomial equation

$$a_w = 1 + A_1 w_p + A_2 {w_p}^2 \qquad (7)$$

with a standard deviation of 5×10^{-4}. The corresponding parameters are $A_1 = -0.0004$ and $A_2 = 6 \times 10^{-6}$.

The parameters of eq 3 (b_0 and b_1) were obtained using experimental water activity data for PPG425 + $(NH_4)_2SO_4$ + H_2O and PPG425 + Na_2SO_4 + H_2O systems and listed in Table 3.

Table 3. Empirical Coefficients of Equation 3 and Average Relative Deviations (ARD)

system	b_0	b_1	ARD[a] (%)
PPG 425 + $(NH_4)_2SO_4$ + H_2O	4.713×10^{-4}	-1.002×10^{-4}	0.09
PPG 425 + Na_2SO_4 + H_2O	-8.321×10^{-4}	1.548×10^{-5}	0.08

[a] ARD of the water activities. ARD = $100(|[a_w(\text{cal}) - a_w(\text{exp})]/[a_w(\text{exp})]|)/n$.

Refractive indices data for the PPG425 + $(NH_4)_2SO_4$ + H_2O, PPG425 + Na_2SO_4 + H_2O, Na_2SO_4 + H_2O, and $(NH_4)_2SO_4$ + H_2O systems at 298.15 K are presented in Tables 4−6. The refractive index of the samples depends on the PPG and salt concentrations. The following empirical equation was used for relating between the refractive index (n_D) and the salt (W_s) and the PPG (W_p) mass fraction

$$n_D = a_0 + a_1 w_s + a_2 w_p \qquad (8)$$

Table 4. Refractive Indices Data (n_D) for the PPG425 (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) System at 298.15 K

	$100w_2$			
$100w_1$	0.5	1.0	1.5	2.0
5.0	1.340 66	1.343 08	1.341 54	1.343 21
10.0	1.347 26	1.348 87	1.348 13	1.349 64
15.0	1.353 81	1.355 31	1.354 67	1.356 02
20.0	1.360 53	1.362 21	1.361 31	1.362 81
25.0	1.367 32	1.369 07	1.367 74	1.370 02
30.0	1.374 12	1.375 67	1.374 72	1.376 26
35.0	1.380 91	1.382 34	1.381 56	1.382 68
40.0	1.387 56	1.388 85	1.388 08	1.389 48

Table 5. Refractive Indices Data (n_D) for the PPG425 (1) + Na_2SO_4 (2) + H_2O (3) System at 298.15 K

	$100w_2$			
$100w_1$	0.5	1.5	1.0	2.0
5.0	1.340 05	1.341 24	1.340 88	1.342 11
10.0	1.346 82	1.348 23	1.347 59	1.348 90
15.0	1.353 54	1.355 11	1.354 24	1.355 82
20.0	1.360 51	1.361 80	1.361 02	1.362 66
25.0	1.367 29	1.368 54	1.367 99	1.369 33
30.0	1.373 91	1.375 41	1.374 65	1.376 20
35.0	1.380 73	1.382 31	1.381 62	1.382 81
40.0	1.387 71	1.389 16	1.388 21	1.389 48

Table 6. Refractive Indices Data (n_D) for the Na_2SO_4 (1) + H_2O (2) and $(NH_4)_2SO_4$ (1) + H_2O(2) Systems at 298.15 K

$100w_1$	$n_D((NH_4)_2SO_4)$	$n_D(Na_2SO_4)$
0.0	1.332 52	1.332 52
0.5	1.333 61	1.334 04
1.0	1.334 42	1.334 82
1.5	1.335 76	1.335 81
2.0	1.336 38	1.336 01
2.5	1.336 98	1.336 91
5.0	1.340 17	1.340 68
10.0	1.347 82	1.347 88
15.0	1.356 41	1.355 07
20.0	1.364 02	1.361 64
25.0	1.371 46	1.369 10
30.0	1.378 93	1.375 40
35.0	1.386 38	1.383 01

Table 7. Parameters of Equation 8 for the Refractive Index Correlation

	a_0	a_1	a_2
Na_2SO_4	1.33252	0.00142	0.00136
$(NH_4)_2SO_4$	1.33252	0.00153	0.00136

The parameters for the two salt fractions are listed in Table 7. The average relative deviation of the refractive index is 0.01%.

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