Isopiestic Determination of the Water Activities of Poly(ethylene glycol) + Salt + Water Systems at 25 °C

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Water activities of poly(ethylene glycol) (PEG) + salt + H_2O systems have been measured using an improved isopiestic method at 25 °C. The salts used were $MgSO_4$, $(NH_4)_2SO_4$, KH_2PO_4, and K_2HPO_4. The water activities were correlated successfully with an empirical equation.

Introduction

Aqueous two-phase extraction has provided a gentle, scalable, and efficient procedure for the separation of various biological materials (Albertsson, 1986; Walter et al., 1985). Recently, there has been interest in utilizing aqueous poly(ethylene glycol) (PEG)/salt two-phase systems for large scale purification because of their relatively low cost and ease of handling. There are some reports on the thermodynamic properties of salt + H_2O (Robinson and Stokes, 1965) and PEG + H_2O binary systems (Herskowitz and Gottlieb, 1985). There are also many phase diagrams of liquid−liquid equilibrium (LLE) of aqueous PEG/salt two-phase systems (Snyder et al., 1992), but the vapor−liquid equilibrium (VLE) data of the ternary (PEG + salt + H_2O) systems are very scarce. For the theoretical research of such systems some LLE data have to be used to correlate the model parameters, so the models based on it seldom have a good predictive capability. The isopiestic method is an accurate and simple experimental technique for measuring the water activities of aqueous solutions (Ochs et al., 1990). However, the time for equilibration is too long for application, especially for highly viscous systems. An improved isopiestic method has been proposed to reduce the time for equilibration to 3 or 4 days, even for polymer solutions, and the average relative error in the observed water activities is 0.01% (Lin et al., 1996).

In this work, the water activities of some PEG + salt + H_2O systems were measured using the improved isopiestic method at 25 °C. The salts used were $MgSO_4$, $(NH_4)_2SO_4$, KH_2PO_4, and K_2HPO_4.

Experimental Section

1. Materials. Poly(ethylene glycol) (PEG) was obtained commercially (Shanghai Chemical Reagent Factory, P. R. China) with three different average molecular weights of 1000 (990−1100, $M_n = 1000$), 4000 (3000−4500, $M_n = 3800$), and 10 000 (9000−10 000, $M_n = 9000$). The salts were analytical reagent grade (Shanghai Chemical Reagent Factory, P. R. China) and were used after twice crystallization. The salts of KCl, $MgSO_4$, $(NH_4)_2SO_4$, KH_2PO_4, and K_2HPO_4 were dried overnight above 100 °C. Double distilled, deionized water was used as the solvent.

2. Apparatus and Procedures. The details of the isopiestic apparatus and procedure have been described elsewhere (Lin et al., 1996). This apparatus consisted of a glass nine-leg manifold attached to round-bottom flasks. The nine flasks were typically used as follows. Three flasks (including the central flask) contained the standard KCl solutions, two flasks contained the salt solutions, one or two for the pure polymer solutions, and three or four for the polymer/salt mixtures. The measurements were performed at (25.00 ± 0.01) °C. The temperature was monitored with a standard thermometer for a readability of 0.01 °C. The manifold rotated around an axis inclined 45°, as the solution in each flask was also stirred during the whole equilibration period. This improvement enhanced the sample mixing and reduced the equilibrium time to 3 or 4 days. For salt solutions, the average relative error in the water activity was about ±0.01%. For polymer solutions, the relative error was on average 0.07% and 0.09% at worst.

Table 1. Water Activities of PEG10000 (1) + Salt (2) + H_2O (3) Systems at 25 °C

system composition			system composition		
PEG10000 $100w_1$	$MgSO_4$ $100w_2$	a_3	PEG10000 $100w_1$	$(NH_4)_2SO_4$ $100w_2$	a_3
11.89	0.0		13.30	0.0	
9.67	0.07		10.30	0.083	
6.92	0.16	0.9987	6.97	0.21	0.9984
4.23	0.31		2.98	0.36	
0.0	0.58		0.0	0.49	
16.00	0.0		17.91	0.0	
13.93	0.10		13.86	0.11	
11.04	0.28	0.9978	10.63	0.28	0.9972
7.31	0.55		4.74	0.55	
0.0	1.22		0.0	0.87	
			29.14	0.0	
			25.96	0.21	
			22.06	0.65	0.9889
			12.95	1.70	
			0.0	3.62	

Results and Discussion

The water activities of PEG1000 + $MgSO_4$ + H_2O, PEG4000 + $MgSO_4$ + H_2O, PEG1000 + $(NH_4)_2SO_4$ + H_2O, and PEG4000 + $(NH_4)_2SO_4$ + H_2O systems have been published elsewhere (Lin et al., 1996). Table 1 reports the water activities of PEG10000 + $MgSO_4$ + H_2O and PEG10000 + $(NH_4)_2SO_4$ + H_2O systems. The water activities of PEG + KH_2PO_4 + H_2O and PEG + K_2HPO_4 + H_2O systems are given in Tables 2 and 3.

As shown in Figure 1, our results for salt + H_2O solutions are in good agreement with the data given by Robinson and Stokes (1965). Likewise, for the PEG + H_2O solutions, our experimental data compare well with those given by Ochs et al. (1990) (see Figure 2). For salt (2) + H_2O (3) systems, the water activities could be correlated

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Table 2. Water Activities of PEG (1) + KH_2PO_4 (2) + H_2O (3) Systems at 25 °C

system composition			system composition		
PEG10000 $100w_1$	KH_2PO_4 $100w_2$	a_3	PEG4000 $100w_1$	KH_2PO_4 $100w_2$	a_3
12.10	0.0		12.97	0.0	
10.01	0.30		10.45	0.25	
7.23	0.67	0.9960	7.45	0.50	0.9972
4.94	1.01		5.26	0.68	
2.33	1.36		2.30	0.89	
0.0	1.72		0.0	1.07	
17.23	0.0		19.13	0.0	
14.55	0.44		15.28	0.36	
11.10	1.02	0.9928	12.33	0.63	0.9950
7.80	1.59		8.21	1.06	
3.92	2.28		3.97	1.53	
0.0	3.03		0.0	2.04	
27.62	0.0		26.16	0.0	
24.42	0.73		22.66	0.54	
19.92	1.84	0.9827	18.71	1.26	0.9896
15.11	3.08		14.85	1.92	
8.47	4.92		8.07	3.11	
0.0	7.66		0.0	4.65	
31.67	0.0		32.12	0.0	
28.44	0.85		28.88	0.68	
23.66	2.18	0.9766	24.77	1.66	0.9820
18.41	3.75		20.43	2.65	
10.77	6.26		12.11	4.66	
0.0	10.59		0.0	8.12	

Table 3. Water Activities of PEG (1) + K_2HPO_4 (2) + H_2O (3) Systems at 25 °C

system composition			system composition		
PEG1000 $100w_1$	K_2HPO_4 $100w_2$	a_3	PEG4000 $100w_1$	K_2HPO_4 $100w_2$	a_3
11.17	0.0		12.45	0.0	
7.91	0.33		9.79	0.20	
6.23	0.61	0.9961	6.49	0.40	0.9974
3.97	0.92		4.32	0.59	
1.96	1.25		1.78	0.82	
0.0	1.57		0.0	0.96	
15.94	0.0		17.13	0.0	
11.62	0.48		13.16	0.29	
8.90	0.87	0.9938	9.06	0.55	0.9962
6.36	1.47		6.25	0.86	
3.01	1.93		2.52	1.27	
0.0	2.57		0.0	1.56	
18.50	0.0		22.18	0.0	
13.49	0.55		18.23	0.37	
10.87	1.03	0.9920	13.56	0.83	0.9930
7.54	1.70		9.77	1.34	
3.93	2.46		4.56	2.11	
0.0	3.34		0.0	2.97	
23.71	0.0		30.46	0.0	
18.89	0.77		26.05	0.54	
15.42	1.46	0.9868	21.39	1.31	0.9848
10.99	2.47		16.53	2.17	
5.98	3.74		7.97	3.76	
0.0	5.58		0.0	6.30	
36.74	0.0				
31.64	1.29				
27.08	2.57	0.9655			
20.79	4.68				
12.50	7.82				
0.0	14.47				

as follows:

$$a_{32} = 1 + C_2 m_2 + C_{22} m_2^{\,2} \tag{1}$$

where a_{32} represents the water activity of salt + H_2O solutions. m_2 is the molality of salt. The coefficients C_2 and C_{22} are empirical parameters and could be correlated from the data of water activities of salt + H_2O binary systems.

For polymer solutions, Grossman et al. (1993) suggested that the molecular−molecular interactions should be replaced by segment−segment interactions. They have successfully used this idea in their virial model. We also incorporate it in our treatment. Therefore for PEG (1) + H_2O (3) systems, the water activities could be correlated as

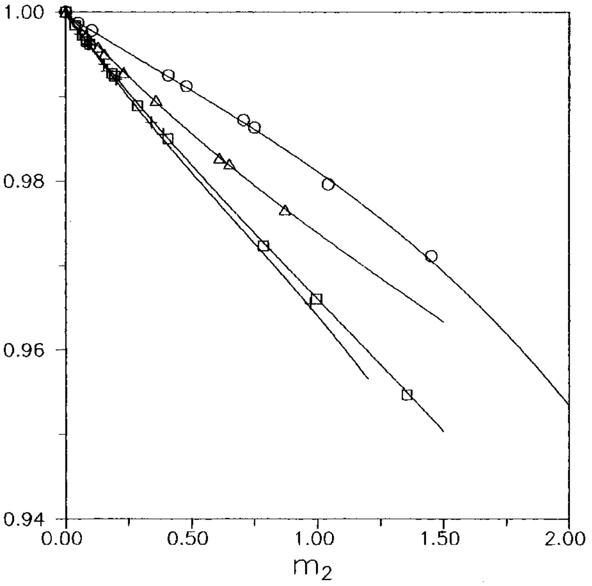

Figure 1. Comparison of experimental water activities of salt + H_2O systems with data (—) from Robinson and Stokes (1965) at 25 °C: (○) $MgSO_4$; (□) $(NH_4)_2SO_4$; (△) KH_2PO_4; (+) KH_2PO_4.

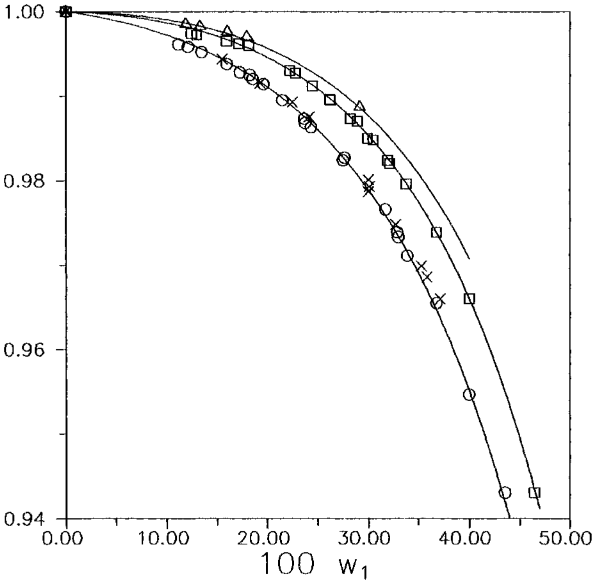

Figure 2. Comparison of experimental water activities of PEG + H_2O systems with data (×) of the PEG1000 + H_2O system from Ochs et al. (1990) and correlation of eq 2 (—) at 25 °C: (○) PEG1000; (□) PEG4000; (△) PEG10000.

$$a_{31} = 1 + C_1 m_1 + C_{11}(r m_1)^2 \tag{2}$$

where a_{31} represents the water activity of PEG + H_2O solutions, m_1 is the molality of PEG, and r is the segment number of polymer and can be calculated from the number average molecular weight of polymer. The coefficients C_1 and C_{11} are empirical parameters and could be correlated from our experimental data of water activities of PEG + H_2O binary systems. Equation 2 could represent the water activities of different molecular weight PEG solutions with an average deviation of 0.04% (see Figure 2).

Furthermore, the water activities for the PEG (1) + salt (2) + H_2O (3) mixtures are correlated by the following

Table 4. Parameters of Different PEG + Salt + H_2O Systems and Average Relative Deviations

	parameter					
system	10^2C_1	10^4C_{11}	10^2C_2	10^3C_{22}	$10C_{12}$	ARD[a] (%)
PEG1000 + $MgSO_4$ + H_2O	−1.6862	−1.5215	−1.7400	−1.7606	−.78456	0.057
PEG4000 + $MgSO_4$ + H_2O					−3.0062	0.058
PEG10000 + $MgSO_4$ + H_2O					−21.070	0.030
PEG1000 + $(NH_4)_2SO_4$ + H_2O	−1.6862	−1.5215	−3.8895	4.1952	−.57109	0.052
PEG4000 + $(NH_4)_2SO_4$ + H_2O					−2.9023	0.050
PEG10000 + $(NH_4)_2SO_4$ + H_2O					−16.957	0.033
PEG1000 + KH_2PO_4 + H_2O	−1.6862	−1.5215	−3.2204	6.3057	−.82070	0.036
PEG4000 + KH_2PO_4 + H_2O					−3.2969	0.059
PEG1000 + K_2HPO_4 + H_2O	−1.6862	−1.5215	−4.1030	5.7489	−1.0448	0.037
PEG4000 + K_2HPO_4 + H_2O					−8.7552	0.035

[a] ARD: average relative deviation of the water activities.

$$\mathrm{ARD} = 100\% \times \left(\sum_{i=1}^{n}\left|\frac{a_{3,\mathrm{cal}} - a_{3,\mathrm{exp}}}{a_{3,\mathrm{exp}}}\right|\right)/n.$$

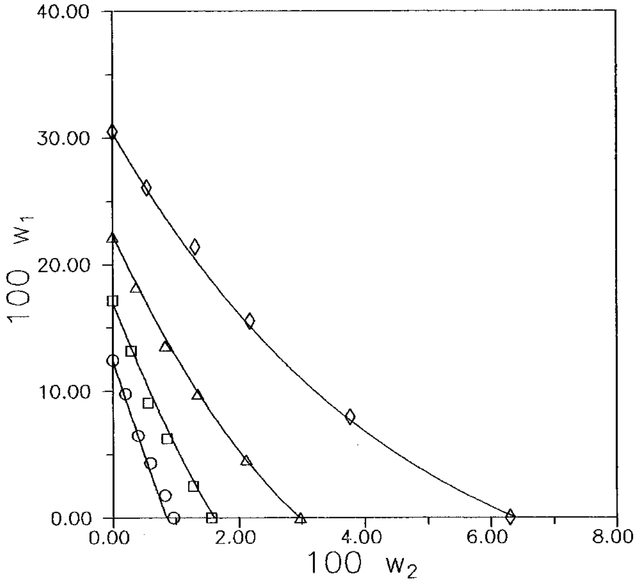

Figure 3. Comparison of experimental water activities of PEG4000 + K_2HPO_4 + H_2O systems with correlation of eq 3 (—) at 25 °C: (○) 0.9974; (□) 0.9962; (△) 0.9930; (◇) 0.9848.

equation:

$$a_3 - 1 = (a_{31} - 1) + (a_{32} - 1) + C_{12}m_1m_2 = C_1m_1 + C_{11}(rm_1)^2 + C_2m_2 + C_{22}m_2^{\,2} + C_{12}m_1m_2 \quad (3)$$

where a_3 is the water activity of aqueous PEG + salt mixtures. All parameters are listed in Table 4. For all ten systems, the parameters C_1 and C_{11} have the same values, and the parameters C_2 and C_{22} vary with the salt type. Only the coefficient C_{12} represents the interaction between PEG and salt and is correlated from the water activity data of ternary PEG + salt + H_2O systems. The parameters correlate the water activities with an average deviation of 0.045%. Figure 3 gives an example of the correlation results.

The above empirical equations have the desirable characteristic of being independent of the chain length of PEG and could represent the water activities of different molecular weight PEG solutions. On the other hand, we have developed a modified virial equation (Wu et al., 1996), which combines the long-range electrostatic contribution from Guggenheim and Fowler with the short-range virial equation. By correlating the parameters only from the corresponding VLE data of binary and ternary systems, the model has a good predictive capability. It shows that the sufficiently accurate data are useful to develop and refine models that describe the solution thermodynamics of aqueous polymer−salt mixtures.

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