Thermodynamics of Phase Equilibria of Aqueous Poly(ethylene glycol) + Sodium Tungstate Two-Phase Systems

Rahmat Sadeghi* and Roonak Golabiazar

Department of Chemistry, University of Kurdistan, Sanandaj, Iran

Phase diagrams and liquid−liquid equilibrium (LLE) data of the aqueous poly(ethylene glycol) (PEG) + sodium tungstate two-phase system have been determined experimentally at (298.15, 303.15, 308.15, 313.15, and 318.15) K. The effects of temperature on the binodal curves and tie-lines have been studied. It was found that an increase in temperature caused the expansion of the two-phase region. It was also found that the concentration of salt which is in equilibrium with a certain concentration of PEG decreases by increasing temperature. The effect of temperature on the phase-forming ability in the investigated system has been studied based on a salting-out coefficient obtained from fitting the binodal data to a Setschenow-type equation for each temperature. On the basis of cloud point values, the energetics of the clouding process have been estimated, and it was found that entropy increase is the driving force for biphasic formation.

Introduction

When two different polymers [e.g., dextran and poly(ethylene glycol) (PEG)] or one polymer and one salt (e.g., PEG and sodium tungstate) are mixed at certain concentrations in an aqueous solution, the solution separates into two immiscible phases, one rich in one polymer and the other rich in the other polymer (or salt), with water as solvent in both phases. Liquid−liquid extraction utilizing these aqueous two-phase systems (ATPS) has been used to separate and purify biological products from the complex mixtures in which they are produced.[1−3]

Data on the composition and properties of phase systems are necessary for design and optimization of extraction processes, understanding of general factors determining partition of solutes and particles in such ATPS, and development and testing of both thermodynamic and mass transfer models of aqueous two-phase systems. Zaslavsky[3] presented a useful summary of experimental liquid−liquid data and equilibrium diagrams for systems formed by PEG, inorganic salts, and water. The principal inorganic salts discussed included ammonium phosphate, ammonium, sodium, and magnesium sulfates, potassium and sodium carbonates, and sodium and potassium hydroxides. Equilibrium diagrams for two-phase systems containing PEG and some organic and inorganic salts have also been recently reported.[4−31]

Here, we report liquid−liquid equilibrium data for the new aqueous $PEG_{6000} + Na_2WO_4 + H_2O$ system at $T = (298.15, 303.15, 308.15, 313.15, \text{and } 318.15)$ K that have not been previously published. The effect of temperature on the binodal and tie-lines was studied. The salting-out effect of the Na_2WO_4 on the polymer was obtained by fitting a Setschenow-type equation to the binodal data to derive a salting-out coefficient of the salt at each temperature.

Experimental Section

Materials. Poly(ethylene) glycol with a quoted molar mass of 6000 $g\cdot mol^{-1}$ was obtained from Merck. The manufacturer has characterized this polymer with charge/lot number S35317 203. Sodium tungstate ($Na_2WO_4\cdot 2H_2O$) (> 99 %) was obtained from Merck. The polymer and salt were used without further purification. Double distilled and deionized water was used.

Apparatus and Procedure. The experimental apparatus employed is essentially similar to the one used previously.[9] 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 on a Sartorius CP124S analytical balance with a precision of $\pm 1\cdot 10^{-4}$ g. For the determination of the tie-lines, feed samples (about 10 cm^3) were prepared by mixing appropriate amounts of polymer, salt, and water in the vessel and brought into a thermostatic bath to maintain appropriate temperature. The systems were stirred and well mixed and allowed to settle, to ensure the proper phase separation at a desired temperature, as indicated by the absence of turbidity in each phase. Once the equilibrium was achieved, samples were collected from both equilibrium phases using glass syringes through the rubber septa that sealed the cells. The concentrations of the salts in the top and bottom phases were determined by flame photometry. The uncertainty in the measurement of the mass fraction of the salts was estimated to be ± 0.001. The concentration of PEG in both phases was determined by refractive index measurements performed at 298.15 K using a refractometer (QUARTZ RS-232, Ceti, Belgium) with a precision of ± 0.0001. The precision of the mass fraction of PEG was better than 0.002.

Results and Discussion

The binodal data of the aqueous $PEG_{6000}(p) + Na_2WO_4(ca)$ two-phase system obtained at $T = (298.15, 303.15, 308.15, 313.15, \text{and } 318.15)$ K are shown in Table 1, and the tie-line data obtained at $T = (303.15, 308.15, 313.15, \text{and } 318.15)$ K are given in Table 2. The complete phase diagrams of the studied

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* Corresponding author. Tel.: +98 871 6624133. Fax: +98 871 6660075. E-mail: rahsadeghi@yahoo.com; rsadeghi@uok.ac.ir.

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Table 1. Binodal Data as Mass Fraction, w, for the $PEG_{6000}(p) + Na_2WO_4(ca) + H_2O(w)$ System at Different Temperatures

T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}
0.4532	0.0518	0.4612	0.0460	0.4854	0.0410	0.4430	0.0469	0.4366	0.0432
0.4208	0.0590	0.4327	0.0514	0.4602	0.0452	0.4204	0.0512	0.4057	0.0489
0.3797	0.069	0.4079	0.0566	0.4298	0.0507	0.4053	0.0542	0.3809	0.0539
0.3444	0.0787	0.3795	0.0630	0.3925	0.0583	0.3781	0.0600	0.3646	0.0574
0.3354	0.0812	0.3503	0.0702	0.3582	0.0660	0.3476	0.0671	0.3360	0.0639
0.3306	0.0827	0.3246	0.0771	0.3227	0.0749	0.3172	0.0746	0.3091	0.0705
0.3028	0.0911	0.3013	0.0837	0.2949	0.0825	0.2866	0.0828	0.2744	0.0796
0.2972	0.0929	0.2722	0.0926	0.2653	0.0912	0.2588	0.0908	0.2481	0.0871
0.2741	0.1005	0.2481	0.1006	0.2435	0.0981	0.2333	0.0985	0.2235	0.0945
0.2549	0.1071	0.2273	0.1078	0.2179	0.1066	0.2119	0.1054	0.2004	0.1019
0.2441	0.1109	0.2093	0.1144	0.1960	0.1145	0.1896	0.1129	0.1809	0.1085
0.2214	0.1193	0.1923	0.1209	0.1774	0.1215	0.1714	0.1195	0.1641	0.1145
0.2162	0.1212	0.1770	0.1270	0.1593	0.1287	0.1564	0.1251	0.1479	0.1205
0.1899	0.1317	0.1630	0.1329	0.1444	0.1350	0.1409	0.1312	0.1326	0.1266
0.1662	0.1416	0.1527	0.1374	0.1307	0.1412	0.1277	0.1367	0.1202	0.1317
0.1456	0.1510	0.1388	0.1438	0.1197	0.1464	0.1155	0.1421	0.1089	0.1367
0.1288	0.1591	0.1371	0.1446	0.1106	0.1509	0.1084	0.1454	0.0992	0.1413
0.1258	0.1606	0.1268	0.1496	0.1006	0.1561	0.0981	0.1504	0.0961	0.1428
0.1112	0.1683	0.1211	0.1524	0.0929	0.1603	0.0941	0.1524	0.0866	0.1476
0.1063	0.1709	0.1073	0.1596	0.0756	0.1707	0.0853	0.1570	0.0728	0.1552
0.0974	0.1760	0.1023	0.1624	0.0625	0.1796	0.0707	0.1654	0.0621	0.1617
0.0893	0.1809	0.0969	0.1654	0.0519	0.1877	0.0566	0.1747	0.0518	0.1687
0.0868	0.1824	0.0828	0.1740	0.0433	0.1953	0.0466	0.1822	0.0444	0.1743
0.0782	0.1880	0.0694	0.1830	0.0343	0.2043	0.0376	0.1900	0.0364	0.1812
0.0722	0.1921	0.0565	0.1927	0.0281	0.2116	0.0309	0.1968	0.0248	0.1936
0.0712	0.1929	0.0444	0.2034			0.0267	0.2016	0.0203	0.1994
0.0653	0.1971	0.0359	0.2121			0.0229	0.2064		
0.0609	0.2005	0.0289	0.2206						
0.0566	0.2040	0.0226	0.2295						
0.0565	0.2041	0.0179	0.2377						
0.0527	0.2073	0.0142	0.2451						
0.0451	0.2142								
0.0376	0.2219								
0.0332	0.2270								
0.0282	0.2334								

Table 2. Experimental Phase Equilibrium Compositions as Mass Fraction, w, for the $PEG_{6000}(p) + Na_2WO_4(ca) + H_2O(w)$ System at Different Temperatures

overall composition		top phase		bottom phase	
w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}
		T = 303.15 K			
0.1528	0.1629	0.3080	0.0791	0.0117	0.2452
0.1631	0.1792	0.3493	0.0695	0.0158	0.2607
0.1734	0.1978	0.4186	0.0545	0.0173	0.2873
0.1816	0.2063	0.4377	0.0514	0.0194	0.3008
0.1917	0.2191	0.4687	0.0461	0.0182	0.3219
0.2064	0.2241	0.5124	0.0388	0.0203	0.3368
0.2318	0.2379	0.5579	0.0370	0.0184	0.3769
		T = 308.15 K			
0.1731	0.1398	0.2719	0.0872	0.0177	0.2356
0.1882	0.1528	0.3277	0.0721	0.0170	0.2564
0.1972	0.1605	0.3613	0.0697	0.0171	0.2723
0.2099	0.1741	0.4042	0.0637	0.0176	0.2948
0.2224	0.1834	0.4715	0.0402	0.0136	0.3157
0.2373	0.1961	0.4879	0.0463	0.0146	0.3319
		T = 313.15 K			
0.1337	0.1457	0.2669	0.0867	0.0349	0.1925
0.1420	0.1532	0.2942	0.0786	0.0215	0.2169
0.1586	0.1594	0.3377	0.0688	0.0132	0.2379
0.1682	0.1692	0.3813	0.0589	0.0146	0.2535
0.1797	0.1782	0.4132	0.0534	0.0129	0.2711
0.1987	0.1851	0.4358	0.0513	0.0159	0.2914
0.2178	0.1908	0.4654	0.0455	0.0182	0.3078
		T = 318.15 K			
0.1716	0.1309	0.2988	0.0697	0.0155	0.1986
0.1780	0.1360	0.3291	0.0658	0.0200	0.2108
0.1856	0.1454	0.3853	0.0528	0.0231	0.2230
0.1983	0.1655	0.4229	0.0494	0.0206	0.2557
0.1968	0.1831	0.4501	0.0482	0.0304	0.2712
0.2160	0.1875	0.4907	0.0391	0.0191	0.2941
0.2334	0.1992	0.5369	0.0337	0.0168	0.3159

system at (303.15 and 313.15) K are shown in Figures 1 and 2, respectively. Figure 3 shows the binodal boundaries obtained from turbidimetric titrations at different temperatures. The region below the indicated curves at each temperature in Figure 3 represents homogeneous solutions, and above, a two-phase region. Figure 3 shows that an increase in the temperature caused an expansion of two-phase area. In other words, if one takes a sample on the binodal with a known composition, this mixture becomes a two-phase system by increasing the temperature as we observed experimentally. The solubility,[32] n.m.r.,[33] volumetric,[34] and vapor−liquid equilibria[35] properties of PEG in

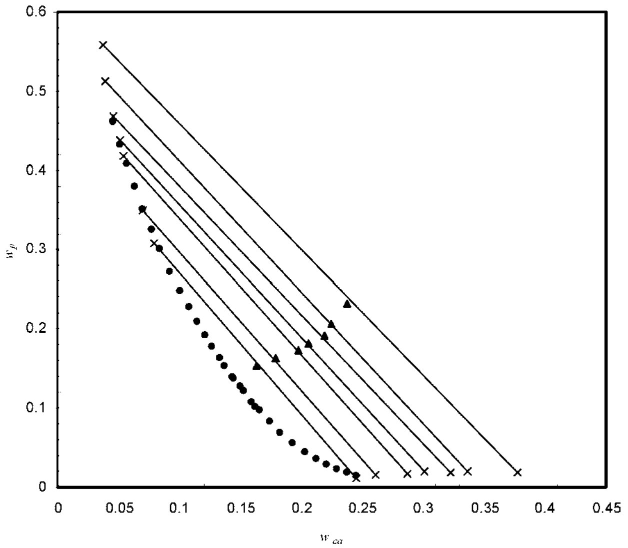

Figure 1. Phase diagram (as polymer mass fraction, w_p, against salt mass fraction w_{ca}) for the $PEG_{6000}(p) + Na_2WO_4(ca)$ aqueous two-phase system at 303.15 K: ●, experimental binodal; ▲, feed compositions; —×—, experimental tie-lines.

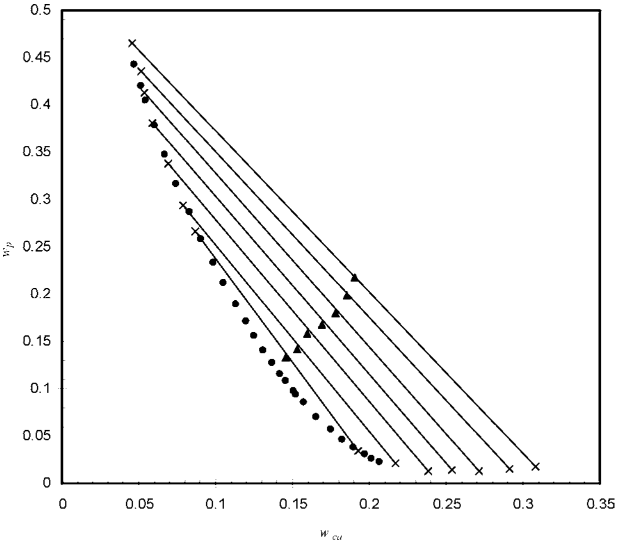

Figure 2. Phase diagram (as polymer mass fraction, w_p, against salt mass fraction w_{ca}) for the PEG_{6000}(p) + Na_2WO_4(ca) aqueous two-phase system at 313.15 K: ●, experimental binodal; ▲, feed compositions; —×—, experimental tie-lines.

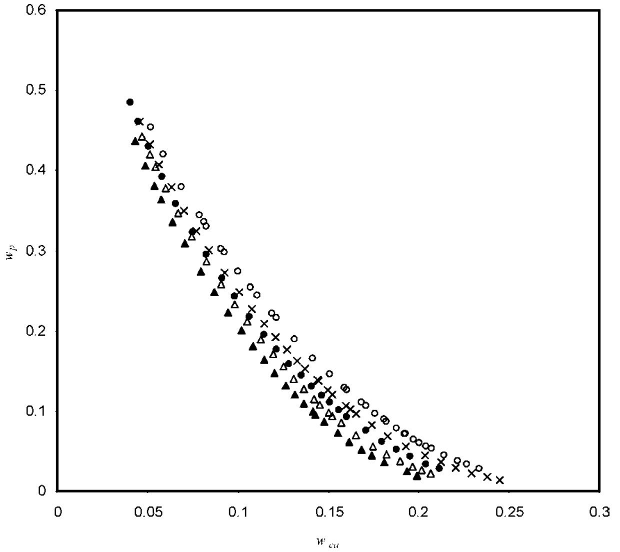

Figure 3. Binodal curves (as polymer mass fraction, w_p, against salt mass fraction w_{ca}) for the aqueous PEG_{6000}(p) + Na_2WO_4(ca) two-phase system at different temperatures: ○, T = 298.15 K; ×, T = 303.15 K; ●, T = 308.15 K; △, T = 313.15 K; ▲, T = 318.15 K.

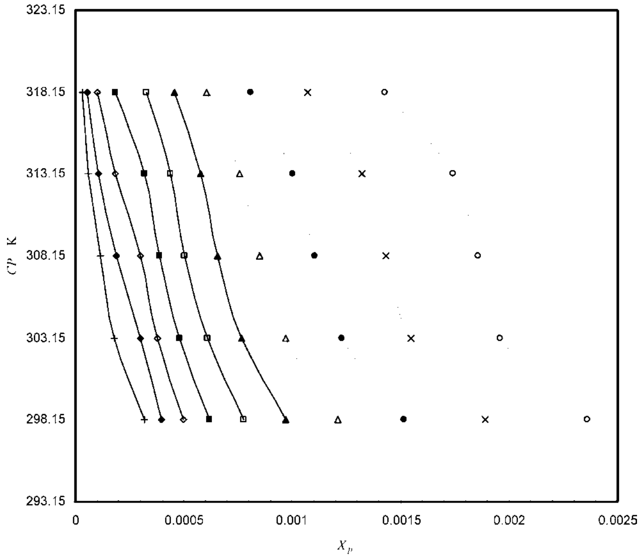

Figure 4. Dependence of cloud point, CP, on PEG mole fraction, X_p, in the presence of Na_2WO_4: ○, X_{ca} = 0.0063; ×, X_{ca} = 0.0071; ●, X_{ca} = 0.0080; △, X_{ca} = 0.0089; ▲, X_{ca} = 0.0098; □, X_{ca} = 0.0107; ■, X_{ca} = 0.0116; ◇, X_{ca} = 0.0124; ◆, X_{ca} = 0.0133; +, X_{ca} = 0.0142.

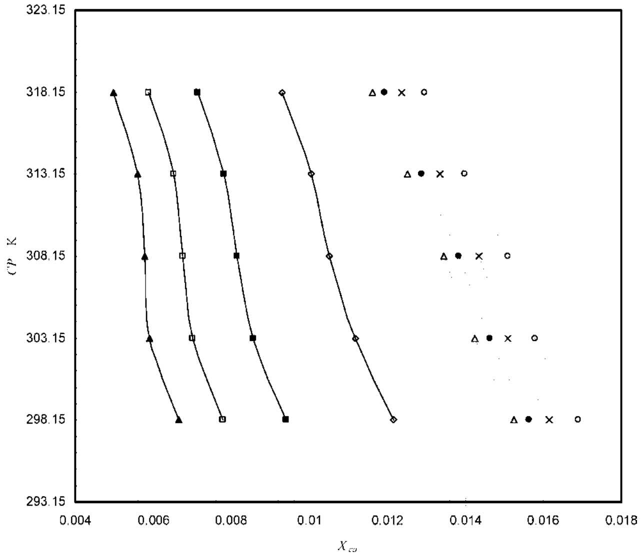

Figure 5. Dependence of cloud point, CP, on Na_2WO_4 mole fraction, X_{ca}, in the presence of PEG: ○, % X_p = 0.0071; ×, % X_p = 0.0106; ●, % X_p = 0.0142; △, % X_p = 0.0178; ▲, % X_p = 0.0534; □, % X_p = 0.1071; ■, % X_p = 0.1608; ◇, % X_p = 0.2145.

water as a function of temperature indicate that the PEG becomes more hydrophobic with increasing temperature. Depression of the cloud point by increasing temperature is related to the salting-out phenomenon since water becomes a poorer solvent for PEG as the temperature is raised. In other words, a decrease in the solubility of PEG in water with an increase in temperature is reflected by a decrease in the critical concentration of a salt required to form a two-phase system, which in turn indicates the effectiveness of the salt in inducing the formation of two phases. In fact, the salt competes with PEG for hydration, and the temperature reduces it further to make PEG behave as a clouding compound. The temperature behavior of the investigated aqueous two-phase systems can be further illustrated by considering the diagram of cloud-point temperature as a function of PEG and salt molalities. Figures 4 and 5, respectively, show the PEG and salt concentration dependence of cloud points (CP). In Figure 4, the diagram of cloud-point temperature as a function of PEG mole fraction has been shown for different salt concentrations. Similarly, Figure 5 shows the cloud-point temperature as a function of salt mole fraction at different PEG concentrations. Ionic species, which hydrate strongly, along with increasing the temperature, induce the dehydration of PEG acting concertedly toward the instability of the polymer to result in clouding. With consideration of clouding as the point of phase separation (or the solubility limit), following Dan et al.,[36] the free energy of phase separation or clouding (ΔG_C) can be calculated from the relation

$$\Delta G_C = RT \ln X_{p(ca)} \tag{1}$$

where $X_{p(ca)}$ is the concentration expressed as mole fraction of PEG (in the case of Figure 4) or salt (in the case of Figure 5). The calculated values of ΔG_C are shown in Figure 6 with reference to clouding temperatures. The values of ΔG_C at different temperatures were processed according to the following Gibbs−Helmholtz equation to get ΔH_C from the slope of the linear (least-squares) plot between ($\Delta G_C/T$) and ($1/T$)

$$\frac{d(\Delta G_C/T)}{d(1/T)} = \Delta H_C \qquad (2)$$

The calculated ΔH_C values are shown in Figure 7. As can be seen from Figure 7, the values of ΔH_C for clouding of PEG in the presence of Na_2WO_4 are larger than those for clouding of Na_2WO_4 in the presence of PEG. The following equation was also used to calculate the entropy changes

$$\Delta S_C = \frac{\Delta H_C - \Delta G_C}{T} \qquad (3)$$

The ΔS_C values are shown in Figure 8, which were all large and positive so that although the calculated ΔH_C values are positive, as can be seen from Figure 6 the calculated free energies of clouding (ΔG_C) have negative values. The calculated data show that the aqueous two-phase formation processes are endothermic. Therefore, these processes must be driven by entropy increase. The high positive entropy has suggested loose, disorderly, and desolvated PEG assemblies in solution; desolvation of the polymer made a major contribution to the positive entropy change. Similar behaviors were obtained for poly(vinylpyrrolidone) (PVP)−salt aqueous two-phase systems.[36] The formation of polymer−salt aqueous two-phase systems clearly indicates the mutual exclusion of the ions and the polymer and their high affinity for the solvent. Exclusion of ions from the polymer molecule−water interface itself can occur for a number of reasons. Both the polymer and the ion are strongly hydrated in solution. Because of the hydration sheath, the near-surface region of the polymer may not be accessible to structure-making ions. Exclusion can occur also by repulsive interaction between the anions and the anionic-like polyether group of PEG especially in the presence of nonbonding cations like K^+, NH_4^+, and Na^+. Ananthapadmanabhan and Goddard,[37] using the turbidimetric titration technique, have shown that for a series of sodium salts two-phase formation occurs with anions such as sulfate which have a marked salting-out effect on nonelectrolytes but that for large, singly charged ions such as iodide only one phase exists. The same authors also found that for a series of sulfates the salting-out effects of the anions are offset by di- and trivalent cations which are believed to coordinate to the ether oxygens to produce a salting-in effect. Hey et al.[18] also obtained the same results for aqueous solutions of electrolytes and PEG. Silva and Loh[38] from the calorimetric measurement of enthalpy of solution of electrolytes in pure water and in aqueous PEG solutions showed that for aqueous PEG + salt solutions phase separation was accompanied by an enthalpy increase, indicating that entropy increase is the driving force for aqueous two-phase system formation. Experimental evidence for the entropic origin of the salting-out of PVP by salt was also obtained by Garvey and Robb[39] from measurements of heats of dilution.

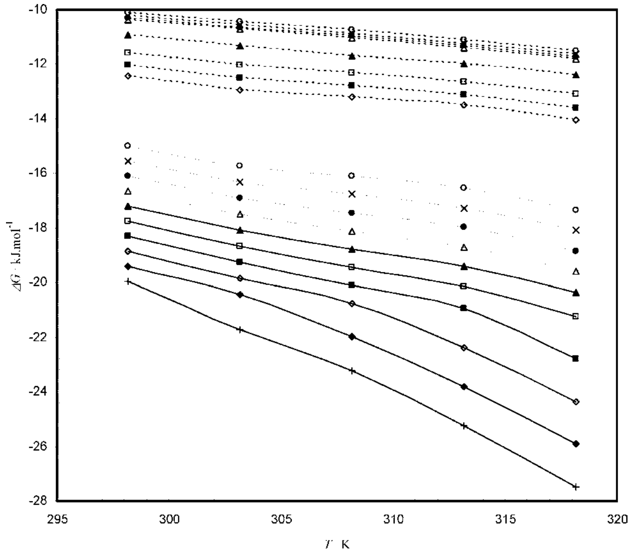

Figure 6. Temperature, *T*, dependence of Gibbs energy change, ΔG, for clouding of PEG in the presence of Na_2WO_4 (solid line): ○, $X_{ca} = 0.0063$; ×, $X_{ca} = 0.0071$; ●, $X_{ca} = 0.0080$; △, $X_{ca} = 0.0089$; ▲, $X_{ca} = 0.0098$; □, $X_{ca} = 0.0107$; ■, $X_{ca} = 0.0116$; ◇, $X_{ca} = 0.0124$; ◆, $X_{ca} = 0.0133$; +, $X_{ca} = 0.0142$; and for clouding of Na_2WO_4 in the presence of PEG (dotted line): ○, % $X_p = 0.0071$; ×, % $X_p = 0.0106$; ●, % $X_p = 0.0142$; △, % $X_p = 0.0178$; ▲, % $X_p = 0.0534$; □, % $X_p = 0.1071$; ■, % $X_p = 0.1608$; ◇, % $X_p = 0.2145$.

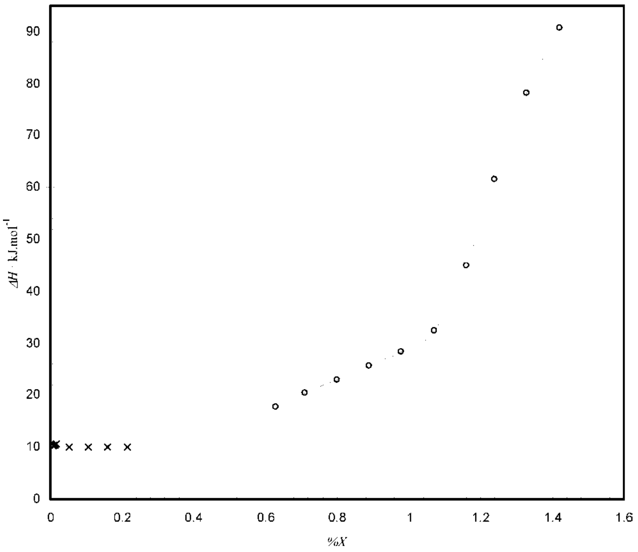

Figure 7. Concentration dependence of the enthalpy changes, ΔH_C: ○, for clouding of PEG in the presence of Na_2WO_4; ×, for clouding of Na_2WO_4 in the presence of PEG.

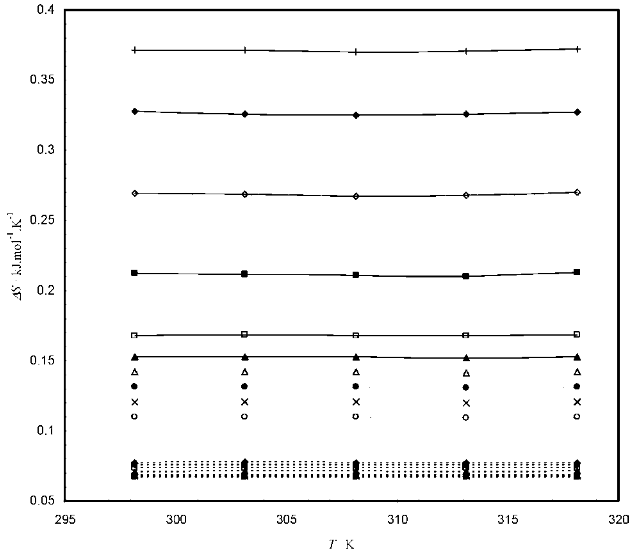

Figure 8. Temperature, *T*, dependence of entropy change, ΔS, for clouding of PEG in the presence of Na_2WO_4 (solid line): ○, $X_{ca} = 0.0063$; ×, $X_{ca} = 0.0071$; ●, $X_{ca} = 0.0080$; △, $X_{ca} = 0.0089$; ▲, $X_{ca} = 0.0098$; □, $X_{ca} = 0.0107$; ■, $X_{ca} = 0.0116$; ◇, $X_{ca} = 0.0124$; ◆, $X_{ca} = 0.0133$; +, $X_{ca} = 0.0142$; and for clouding of Na_2WO_4 in the presence of PEG (dotted line): ○, % $X_p = 0.0071$; ×, % $X_p = 0.0106$; ●, % $X_p = 0.0142$; △, % $X_p = 0.0178$; ▲, % $X_p = 0.0534$; □, % $X_p = 0.1071$; ■, % $X_p = 0.1608$; ◇, % $X_p = 0.2145$.

Since the formation of aqueous two-phase systems is essentially due to the effect of an electrolyte on the solubility of

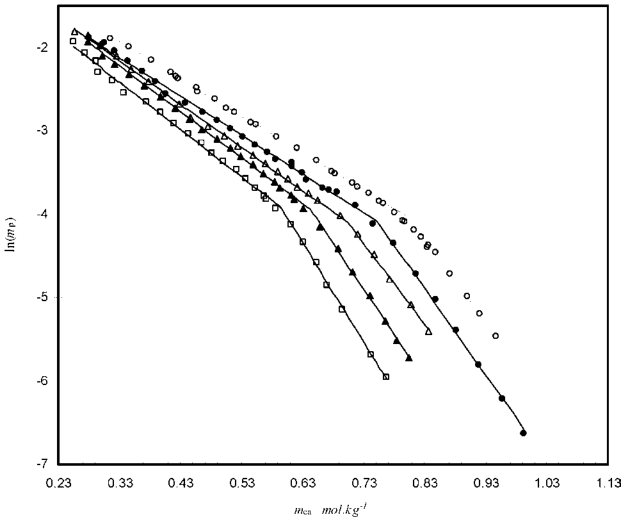

Figure 9. Setschenow plots for binodal curves of the PEG_{6000}(p) + Na_2WO_4(ca) aqueous two-phase system at different temperatures: ○, T = 298.15 K; ●, T = 303.15 K; △, T = 308.15 K; ▲, T = 313.15 K; □, T = 318.15 K, —, calculated by eq 4.

Table 3. Values of Parameters from Least-Squares Linear Fits to the Setschenow-Type Equation (Equation 4) for the PEG_{6000}(p) + Na_2WO_4(ca) + H_2O(w) System at Different Temperatures for Two Salt Concentration Regions

T	low salt concentration		high salt concentration	
	k_{ca}	m_{p0}	k_{ca}	m_{p0}
K	(kg·mol^{-1})	(mol·kg^{-1})	(kg·mol^{-1})	(mol·kg^{-1})
298.15	4.4428	0.6263	9.6776	40.7668
303.15	4.6673	0.5614	10.3758	41.1482
308.15	5.1905	0.6399	9.7548	15.9621
313.15	5.5200	0.6730	10.9586	22.2687
318.15	5.6932	0.5855	11.8950	23.3689

a nonelectrolyte, the the possibility of using Setschenow's equation[37,40] to characterize the phase boundary can be examined. This equation was originally proposed as an empirical equation to describe the solubility of nonelectrolyte in the presence (m_p) and absence (m_{p0}) of salt to the electrolyte concentration (m_{ca}) as

$$\ln \frac{m_{p0}}{m_p} = k_{ca}m_{ca} \tag{4}$$

where k_{ca} is the salting-out coefficient (electrolyte−nonelectrolyte interaction parameter) which is specific for a particular nonelectrolyte/salt pair. Results given in Figure 9 show that the logarithm of the PEG molality required to achieve phase separations against the salt molality may be divided into two linear parts related to the PEG-rich phase and to the salt-rich phase. The values of coefficients of eq 4 for two concentration regions are given in Table 3. As can be seen from Table 3, the values of salting-out coefficients increase by increasing temperature. Increasing of the salting-out coefficient by increasing temperature is in agreement with our experimental observations in which, at higher temperatures, aqueous two-phase formation occurs at lower levels of the polymer and salt.

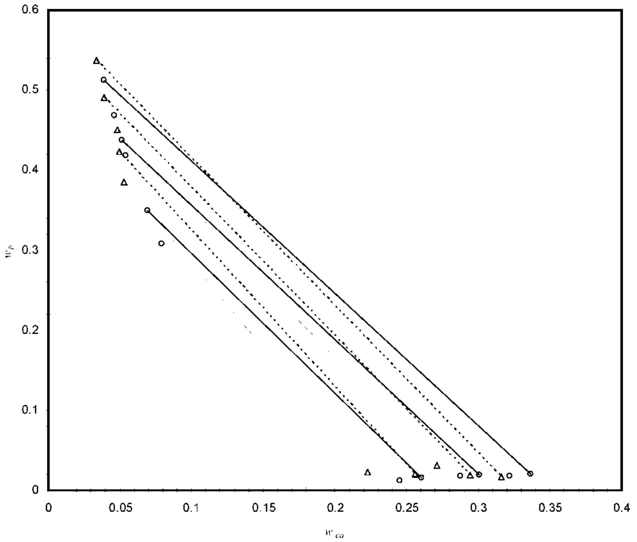

Figure 10. Effect of temperature on the equilibrium phase compositions (as polymer mass fraction, w_p, against salt mass fraction w_{ca}) for the PEG_{6000}(p) + Na_2WO_4(ca) aqueous two-phase system at different temperatures: ○, T = 303.15 K; △, T = 318.15 K.

As shown in Figure 10, the slope of the equilibrium tie-lines increases with increasing temperature. In other words, the concentration of salt which is in equilibrium with a certain concentration of PEG decreases by increasing temperature. Also, by increasing temperature the volume of the salt-rich phase increases at the expense of the PEG-rich phase. This is because the compositions of the phases in equilibrium change with varying temperature. In fact, for aqueous two-phase systems composed of PEG and salt, the concentrations of the salt in the top phase are very small (as shown in Table 2). Thus, it may be assumed that the top phase is aqueous solutions containing mainly PEG. Although thermodynamic studies of aqueous electrolyte solutions show that the temperature has a very slight effect on the thermodynamic properties of aqueous electrolyte solutions, however, the thermodynamic properties of aqueous polymer solutions are very sensitive to the temperature. As mentioned above, the attraction between PEG and water will decrease with an increase in temperature, and therefore by increasing temperature of the aqueous PEG−salt two-phase system, water is driven from the PEG-rich phase to the salt-rich phase. The PEG concentration of the PEG-rich phase increases, while the salt-rich phase will be somewhat more diluted (i.e., the salt concentration will be decreased) and the volume of the salt-rich phase increases at the expense of the PEG-rich phase. That is to say, at a constant temperature, all of the samples with feed compositions on a tie-line have the same coexisting phases. Therefore, if one takes a sample with a feed composition on the crossing point of two tie-lines at different temperature, the compositions of coexisting phases at each temperature will be the same as those of these two tie-lines at the corresponding temperatures. On the basis of the lever rule, the relative amounts of the phases are in inverse proportion to the distances of the respective phase boundary lines from the point of overall composition. Therefore, as can be seen from Figure 10, by increasing temperature, variation of concentration for the phase with less volume is larger than the other phase with higher volume. This is because by driving a fixed amount of water from the PEG-rich phase to the salt-rich phase (because of increasing temperature) it should be expected that the variation of concentration for the phase with less volume will be larger than the other phase with higher volume.

Conclusions

Phase diagrams and LLE data of the aqueous PEG_{6000} + Na_2WO_4 two-phase system have been determined experimentally at T = (298.15, 303.15, 308.15, 313.15, and 318.15) K. The results show that at higher temperatures the salt and polymer concentration required for phase separation is lower. Increasing the temperature produces an increase in PEG concentration in the top phase and a decrease of salt concentration in the lower phase. The effect of temperature on the phase-forming ability for the studied system was also successfully discussed on the basis of the salting-out coefficient of the salt, k_{ca}, obtained from fitting the binodal data to a Setschenow-type equation. It was shown that the value of k_{ca} increases with increasing temperature. Furthermore, based on the calculated values of Gibbs free energy, enthalpy, and entropy of the clouding process, we conclude that the entropy increase is the driving force for biphasic formation.

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