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Aqueous Two-Phase Systems of Poly(vinyl pyrrolidone) and Sodium Sulfate: Experimental Results and Correlation/Prediction

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New experimental liquid−liquid-phase equilibrium data are reported for aqueous systems containing poly(vinyl pyrrolidone)—of different molecular mass—and sodium sulfate at (298 and 338) K together with parameters for a semiempirical model for the excess Gibbs energy which is used to describe the experimental data.

Introduction

Aqueous two-phase systems are used, for example, for the separation and purification of biomolecules from complex mixtures in a nondisruptive environment. Quite a large number of experimental results for aqueous two-phase systems containing polymer−polymer and polymer−inorganic salts have been reported in the literature.[1−5] Typical examples of substances used to create an aqueous two-phase system are polymers like, e.g., poly(ethylene glycol) and dextran and salts like, e.g., Na_2SO_4, NaH_2PO_4, and K_2HPO_4. Another polymer which has attracted some attention, as it is also able to form aqueous two-phase systems with suitable salts and polymers, is poly(vinyl pyrrolidone) (PVP). PVP is a synthetic hydrophilic polymer. Its chemical structure is shown in Figure 1. PVP polymers are widely used in many industries as, for example, additives in the food industry, binders in pharmaceutical tablets as well as in paints, and adhesives. It is synthesized by free-radical polymerization of *N*-vinylpyrrolidone in water or alcohols with a suitable initiator. Despite its ability to form aqueous two-phase systems, liquid−liquid equilibrium data of systems containing PVP are relatively scarce in the literature. Liquid−liquid equilibrium data of aqueous solutions of PVP and a single phosphate (sodium dihydrogen phosphate, disodium hydrogen phosphate, and trisodium phosphate) at different temperatures have been reported by Zafarani-Moattar and Sadeghi.[6,7] These authors used an extended form of the Flory−Huggins and the Chen−NRTL equations with an electrostatic term to correlate the liquid−liquid-phase equilibrium. Recently, Sadeghi[8] published a paper on the liquid−liquid equilibrium of aqueous solutions of PVP and a single sodium salt (sodium sulfate, sodium carbonate, and sodium succinate) at 303.15 K. He discussed the influence of the anion on the liquid−liquid-phase behavior and correlated his experimental results applying a method that combines several models (modified Wilson equation, Flory−Huggins model, and modified Debye−Hückel term). The present paper reports experimental results for the phase equilibrium of ternary systems of (PVP + Na_2SO_4 + H_2O) at (298 and 338) K.

Some methods are available in the literature for correlating the liquid−liquid equilibrium in aqueous two-phase systems. One group of models is based on the osmotic virial equation.[9,10] Another group of models is based on lattice theories such as the UNIQUAC model,[11,12] the UNIFAC group contribution model,[13,14] or the NRTL model.[5,15−17] The present work applies the virial equation with relative surface fractions (VERS) model of Grossmann et al.[1,18] The VERS model is a modification of Pitzer's extension of the osmotic virial equation for the excess Gibbs energy of electrolyte solutions. That extension consists of a semiempirical group contribution model for the excess Gibbs energy. The group contribution concept was introduced to account for the influence of the molecular weight of a polymer on that liquid−liquid equilibrium. The VERS model was successfully used in previous works to correlate and predict the liquid−liquid equilibrium in aqueous two-phase systems[1] as well as to correlate the partitioning of some biomolecules[2,10,19−21] to the coexisting phases in such aqueous two-phase systems.

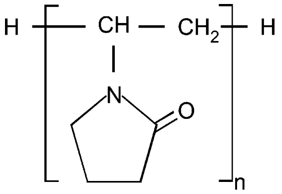

Figure 1. Structure of poly(vinyl pyrrolidone).

Experimental Section

Three poly(vinyl pyrrolidone) samples of different polymer mass (number average molecular mass $M_n/(g\cdot mol^{-1}) = 3882$ (PVPK17); 17 750 (PVPK30); and 138 600 (PVPK90)) were investigated. All samples were provided by BASF AG (Ludwigshafen a. Rh., Germany). Sodium sulfate (water free; purity ≥ 99 mass %) was purchased from MERCK (Darmstadt, Germany). All substances were used without further purification. Double distilled water was used for preparing the solutions.

The phase equilibrium experiments consisted of the determination of the cloud-point curve and the determination of the composition of coexisting liquid phases. The cloud point was investigated by titration where step by step small (and exactly known) amounts of an aqueous solution of sodium sulfate were added to an aqueous polymer solution (or, vice versa, an aqueous polymer solution was added to an aqueous solution of sodium sulfate) under stirring. That mixing occurred in a centrifuge tube, which was immersed in a thermostated water bath. The solution was inspected visually. The titration procedure was ended when

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the turbidity caused by an addition of the titrant did not disappear even after stirring for at least 48 h at constant temperature. The composition at the cloud point was calculated from the amounts of mixed polymer and salt solutions (as the arithmetic average of the compositions before and after the last addition before the mixture remained turbid). In a typical experiment, about (5 to 7) g of an aqueous solution (of either the polymer or the salt) was titrated. The amount of titrant added in a single step was about 0.01 g. That amount was determined gravimetrically with a high-precision analytical balance (AE 240, Mettler-Toledo GmbH, Greifensee, Switzerland) with a precision of ± 10^{-4} g. The experiments were carried out at (298 and 338) K. The uncertainty of the experimental data for the temperature is about ± 0.1 K. The experimental uncertainty of the direct readings for the concentration under cloud-point conditions is about ± 0.15 mass % and about ± 0.11 mass % for the polymer and the salt, respectively. At least 16 cloud points were determined for each aqueous two-phase system at each temperature. An additional uncertainty might arise from the unknown polydispersity of the polymer samples. That statement also holds for the experimental results for the compositions of the coexisting phases. These compositions were determined in separate phase equilibrium investigations. For these experiments, about 8 g of an aqueous feed solution was prepared by mixing stock solutions of the single solutes. The concentrations of the solutes (polymer/salt) in these stock solutions were known from gravimetric preparations. It was aimed to adjust the ratio of both stock solutions in such a way that after phase equilibration and separation nearly equal volumes of a polymer-rich and a salt-rich phase were expected. However, in most experiments, this resulted in feed solutions which were too viscous to achieve an equilibration within a reasonable period of time. Consequently, the ratio of salt-containing to polymer-containing stock solution had to be increased. The feed solutions were equilibrated under stirring in centrifuge tubes in a thermostated water bath for (2 to 3) days. The temperature of that bath was kept at (298 and 338) K, respectively. Afterward, the tubes were centrifuged for about 90 min at 3500 rpm in a centrifuge (model Rotina 48R, Hettich, Tuttlingen, Germany) which was also thermostated to the same temperature. The uncertainty of all temperatures is estimated to about ± 0.1 K. Afterward, the coexisting phases were carefully removed from the centrifuge tube with syringes leaving only a small amount of the two-phase system behind. The amount of mass of the removed samples was determined, and both samples were diluted with (a known amount of) water before they were analyzed.

The water content of a sample was determined by freeze drying using a Lyovac GT 2 freeze dryer (Amsco/Finn-Aqua, Hürth, Germany). For such an analysis, an exactly known amount of a sample (about (1 to 3) g) was poured into a small aluminum pot (diameter, 95 mm; height, 25 mm) and further diluted with about 20 g of water. That dilution was to ensure that the freeze-drying process results in a powder dry sample. The aluminum pots were placed into a refrigerator where the samples were frozen and cooled to about −18 °C. Afterward, they were cooled to about −190 °C with liquid nitrogen. A frozen sample was allowed to dry at 10^{-2} bar for (2 to 3) days. Afterward, the resulting powder was weighted and the water content of the sample was calculated. The dry powder was put into a crucible and burned at 800 °C in a muffle furnace (model Heraeus T 16A, Kendro GmbH, Hanau, Germany). The amount of residue was determined with the precision balance mentioned above. As the residue consisted of dry sodium sulfate, the amount of polymer in a sample could be obtained from a mass balance from the known total amount of mass of the sample and the amounts of mass of water and salt. Typically about three to five liquid−liquid equilibrium points were determined for each aqueous two-phase system at both temperatures. The absolute experimental uncertainty for the salt concentration in the salt-rich (i.e., lower) phase as well as in the salt-lean (i.e., upper) phase is about ± (0.05 to 0.5) mass %. The experimental uncertainty for the polymer concentration in the polymer-rich (i.e., upper) phase is about ± (1.5 to 5) mass % and about ± (0.4 to 0.8) mass % in the salt-rich (i.e., lower) phase. These estimates were confirmed by blind tests where mixtures of known composition (from gravimetric preparations) were analyzed. Some typical examples for such blind tests are given in Table 1.

Table 1. Blind Tests for the Analyzing Procedures of Mixtures of (PVPK90 (p) + Na_2SO_4 (s) + H_2O)

composition of sample (from preparation)		result of analyses		relative deviation		absolute deviation	
ξ_p	ξ_s	ξ_p	ξ_s	$\Delta\xi_p$	$\Delta\xi_s$	ξ_p	ξ_s
$g \cdot g^{-1}$	$g \cdot g^{-1}$	$g \cdot g^{-1}$	$g \cdot g^{-1}$	%	%	$g \cdot g^{-1}$	$g \cdot g^{-1}$
0.1009	0.0151	0.1003	0.0170	0.6	13	0.0006	0.0019
		0.1003	0.0169	0.6	12	0.0006	0.0018
		0.1003	0.0164	0.6	8.6	0.0006	0.0013
0.0106	0.1019	0.0106	0.0995	<0.3	2.4	<0.0001	0.0024
		0.0105	0.0994	1.0	2.5	0.0001	0.0025
		0.0104	0.0984	1.9	3.4	0.0002	0.0035
0.0497	0.1523	0.0494	0.1549	0.6	1.7	0.0003	0.0026
		0.0492	0.1548	1.0	1.6	0.0005	0.0031
		0.0498	0.1572	0.2	3.2	0.0001	0.0049

Table 2. Experimental Results for the Composition of the Cloud-Point Curve of (PVPK*xy* (p) + Na_2SO_4 (s) + H_2O) at 298.2 K

mixtures with PVPK17		mixtures with PVPK30		mixtures with PVPK90	
ξ_p	ξ_s	ξ_p	ξ_s	ξ_p	ξ_s
$g \cdot g^{-1}$	$g \cdot g^{-1}$	$g \cdot g^{-1}$	$g \cdot g^{-1}$	$g \cdot g^{-1}$	$g \cdot g^{-1}$
0.0012	0.1504	0.0003	0.1895	0.0005	0.1987
0.0018	0.1404	0.0004	0.1754	0.0006	0.1706
0.0020	0.1349	0.0005	0.1625	0.0008	0.1514
0.0022	0.1439	0.0008	0.1595	0.0009	0.1220
0.0029	0.1836	0.0012	0.1251	0.0098	0.0778
0.0035	0.1595	0.0012	0.1439	0.0183	0.0683
0.0036	0.1263	0.0013	0.1319	0.0195	0.0615
0.0042	0.1478	0.0018	0.1147	0.0222	0.0611
0.0048	0.1175	0.0022	0.0985	0.0232	0.0651
0.0048	0.1147	0.0637	0.0695	0.0308	0.0599
0.0182	0.1042	0.0772	0.0645	0.0482	0.0595
0.0242	0.0982	0.0918	0.0630	0.0852	0.0576
0.0279	0.0973	0.1296	0.0547	0.0933	0.0568
0.0336	0.0955	0.1503	0.0492	0.1018	0.0561
0.0343	0.0948	0.1778	0.0474	0.1105	0.0550
0.0380	0.0947	0.1946	0.0456	0.1168	0.0538
0.0444	0.0927	0.2147	0.0427		
0.0497	0.0918	0.2414	0.0392		
0.0570	0.0888	0.2725	0.0369		
0.0584	0.0895	0.3255	0.0331		
0.0655	0.0871				
0.0673	0.0872				
0.0712	0.0871				
0.0782	0.0847				
0.0836	0.0863				
0.0878	0.0827				
0.0949	0.0809				
0.1074	0.0758				
0.1302	0.0696				
0.1371	0.0694				
0.1421	0.0676				
0.2531	0.0455				
0.3218	0.0340				

Table 3. Experimental Results for the Composition of the Cloud-Point Curve of (PVPK*xy* (p) + Na_2SO_4 (s) + H_2O) at 338.2 K

mixtures with PVPK17		mixtures with PVPK30		mixtures with PVPK90	
ξ_p	ξ_s	ξ_p	ξ_s	ξ_p	ξ_s
g·g^{-1}	g·g^{-1}	g·g^{-1}	g·g^{-1}	g·g^{-1}	g·g^{-1}
0.0007	0.1886	0.0003	0.1895	0.0001	0.2365
0.0011	0.1498	0.0004	0.1754	0.0001	0.2779
0.0012	0.1676	0.0005	0.1625	0.0001	0.1994
0.0012	0.1392	0.0008	0.1595	0.0001	0.1735
0.0015	0.1573	0.0012	0.1251	0.0001	0.1570
0.0021	0.1107	0.0012	0.1439	0.0002	0.1150
0.0024	0.1205	0.0013	0.1319	0.0140	0.0636
0.0031	0.1190	0.0018	0.1147	0.0363	0.0538
0.0032	0.1485	0.0022	0.0985	0.0413	0.0586
0.0035	0.1001	0.0637	0.0695	0.0421	0.0550
0.0035	0.1001	0.0772	0.0645	0.0500	0.0530
0.0036	0.1177	0.0918	0.0630	0.0597	0.0521
0.0036	0.1011	0.1296	0.0547	0.0599	0.0512
0.0036	0.1011	0.1503	0.0492	0.0738	0.0501
0.0214	0.0906	0.1778	0.0474	0.0866	0.0480
0.0276	0.0891	0.1946	0.0456	0.0940	0.0457
0.0484	0.0819	0.2147	0.0427	0.0998	0.0469
0.0532	0.0854	0.2414	0.0392	0.1007	0.0456
0.0618	0.0752	0.2725	0.0369	0.1118	0.0441
0.0724	0.0751	0.3255	0.0331	0.1231	0.0428
0.0814	0.0749			0.1247	0.0425
0.0858	0.0731			0.1324	0.0427
0.0932	0.0762				
0.0972	0.0752				
0.1086	0.0742				
0.1104	0.0715				
0.1243	0.0707				
0.1329	0.0688				
0.1437	0.0663				
0.1567	0.0630				
0.1591	0.0561				
0.1657	0.0598				
0.1719	0.0601				
0.1917	0.0532				
0.1922	0.0536				
0.2241	0.0503				
0.2298	0.0473				
0.2617	0.0439				
0.2676	0.0428				
0.3131	0.0331				
0.3456	0.0314				

Experimental Results

The experimental results for the cloud points of three aqueous two-phase systems of poly(vinyl pyrrolidone) (PVPK17 or PVPK30 or PVPK90) and sodium sulfate at (298.2 and 338.2) K are given in Tables 2 and 3, respectively. The phase equilibrium data are given in Table 4 (for 298.2 K) and Table 5 (for 338.2 K). The nomenclatures "top" and "bottom" in Tables 4 and 5 designate the polymer-rich upper phase and the salt-rich lower phase, respectively. The experimental results for the cloud points and the liquid−liquid equilibrium are shown in Figures 2 through 6. The influence of temperature on the liquid−liquid equilibrium is very small. Increasing the polymer weight results in a small decrease of the single-phase region. For example, no phase split occurs in the system (PVP + Na_2SO_4 + H_2O) with PVPK17 when the sum of the concentrations of both solutes is below about 13 mass %, but a liquid−liquid-phase split can occur when that sum is higher than about 9 mass % with PVPK90. The polymer-rich phase contains quite a large amount of sodium sulfate (e.g., about 5 mass % of Na_2SO_4 at 20 mass % of PVP), whereas the coexisting salt-rich phase contains very little PVP (e.g., less than 0.5 mass % of PVP when the salt concentration is about 10 mass %). The scattering of the experimental data for the cloud points agrees with the estimated experimental uncertainty with the exception of the near-critical region of the liquid−liquid equilibrium. There the scattering is considerably larger. It is assumed that this larger scattering is caused by experimental problems in the vicinity of the critical point. The experimental results for the composition

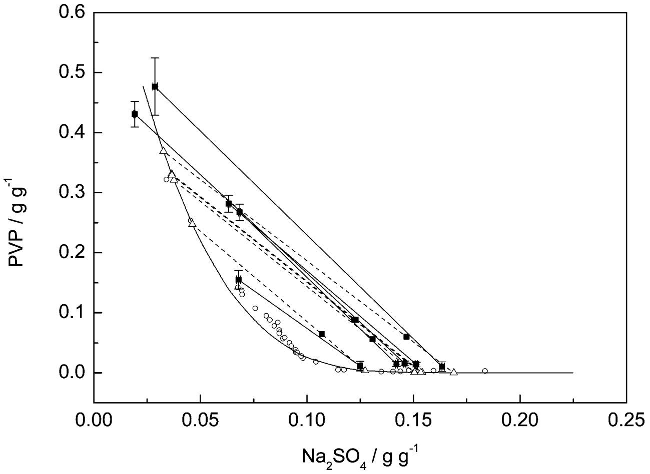

Figure 2. Liquid−liquid equilibrium of the system (PVPK17 + Na_2SO_4 + H_2O) at 298.2 K. Experimental results: −■−, coexisting phases; ○, cloud points. Correlation results from the VERS model: --△--, coexisting phases; ____, cloud-point curve.

Table 4. Experimental Results for the Liquid−Liquid Equilibrium of (PVPK*xy* (p) + Na_2SO_4 (s) + H_2O) at 298.2 K

feed solution		top phase		bottom phase	
ξ_p	ξ_s	ξ_p	ξ_s	ξ_p	ξ_s
g·g^{-1}	g·g^{-1}	g·g^{-1}	g·g^{-1}	g·g^{-1}	g·g^{-1}
		Mixtures with PVPK17			
0.0644	0.1070	0.1551 ± 0.0155	0.0679 ± 0.001	0.0111 ± 0.008	0.1249 ± 0.001
0.0884	0.1228	0.2815 ± 0.0141	0.0633 ± 0.0005	0.0141 ± 0.004	0.1514 ± 0.0005
0.0560	0.1308	0.2672 ± 0.0134	0.0684 ± 0.0005	0.0144 ± 0.004	0.1420 ± 0.0005
0.0884	0.1222	0.4308 ± 0.0215	0.0192 ± 0.0005	0.0156 ± 0.004	0.1459 ± 0.0005
0.0601	0.1468	0.4764 ± 0.0486	0.0287 ± 0.001	0.0102 ± 0.008	0.1634 ± 0.001
		Mixtures with PVPK30			
0.0546	0.0894	0.2936 ± 0.0147	0.0318 ± 0.0005	0.0129 ± 0.004	0.0990 ± 0.0005
0.0487	0.1033	0.3504 ± 0.0350	0.0372 ± 0.0005	0.0102 ± 0.008	0.1143 ± 0.001
0.0614	0.1204	0.3603 ± 0.0180	0.0322 ± 0.0005	0.0044 ± 0.004	0.1352 ± 0.0005
0.0419	0.1197	0.3973 ± 0.0199	0.0344 ± 0.0005	0.0054 ± 0.004	0.1293 ± 0.0005
0.0522	0.1463	0.4186 ± 0.0209	0.0223 ± 0.0005	0.0025 ± 0.004	0.1609 ± 0.0005
		Mixtures with PVPK90			
0.0572	0.0942	0.2954 ± 0.0148	0.0312 ± 0.0005	0.0016 ± 0.004	0.1097 ± 0.0005
0.0398	0.0824	0.2222 ± 0.0222	0.0355 ± 0.001	0.0025 ± 0.008	0.0892 ± 0.001
0.0396	0.1124	0.3258 ± 0.0163	0.0286 ± 0.0005	0.0013 ± 0.004	0.1231 ± 0.0005

Table 5. Experimental Results for the Liquid−Liquid Equilibrium of (PVPK*xy* (p) + Na_2SO_4 (s) + H_2O) at 338.2 K

feed solution		top phase		bottom phase	
ξ_p $\mathrm{g{\cdot}g^{-1}}$	ξ_s $\mathrm{g{\cdot}g^{-1}}$	ξ_p $\mathrm{g{\cdot}g^{-1}}$	ξ_s $\mathrm{g{\cdot}g^{-1}}$	ξ_p $\mathrm{g{\cdot}g^{-1}}$	ξ_s $\mathrm{g{\cdot}g^{-1}}$
Mixtures with PVPK17 (p)					
0.0632	0.1231	0.3748 ± 0.0187	0.0405 ± 0.0005	0.0101 ± 0.004	0.1383 ± 0.0005
0.0768	0.1357	0.3942 ± 0.0394	0.0325 ± 0.001	0.0068 ± 0.008	0.1524 ± 0.001
0.0958	0.1085	0.4035 ± 0.0404	0.0336 ± 0.001	0.0130 ± 0.008	0.1351 ± 0.001
0.0820	0.1303	0.4172 ± 0.0209	0.0301 ± 0.0005	0.0073 ± 0.004	0.1529 ± 0.0005
0.0997	0.1025	0.4325 ± 0.0433	0.0254 ± 0.001	0.0338 ± 0.008	0.1222 ± 0.001
0.0724	0.1715	0.5476 ± 0.0274	0.0105 ± 0.0005	0.0051 ± 0.004	0.1959 ± 0.0005
Mixtures with PVPK30 (p)					
0.0505	0.0998	0.3680 ± 0.0368	0.0285 ± 0.001	0.0055 ± 0.008	0.1071 ± 0.001
0.0395	0.1168	0.3784 ± 0.0189	0.0349 ± 0.0005	0.0060 ± 0.004	0.1262 ± 0.0005
Mixtures with PVPK90 (p)					
0.0547	0.0513	0.0760 ± 0.0038	0.0513 ± 0.0005	0.0166 ± 0.004	0.0588 ± 0.0005
0.0724	0.0599	0.2071 ± 0.0207	0.0392 ± 0.001	0.0070 ± 0.008	0.0752 ± 0.001
0.0392	0.1081	0.2880 ± 0.0288	0.0510 ± 0.001	0.0012 ± 0.008	0.1146 ± 0.001
0.0470	0.1153	0.5163 ± 0.0516	0.0196 ± 0.001	0.0046 ± 0.008	0.1265 ± 0.001

of the polymer-lean (and salt-rich) phase as measured in the phase equilibrium experiments agree within experimental uncertainty with the results from the cloud-point investigations. However, for polymer-rich phases with very high polymer concentrations, the deviations between the experimental data from both types of experiments are beyond the combined (estimated) experimental uncertainty of both investigations. This is mainly due to the high viscosity of such polymer-rich

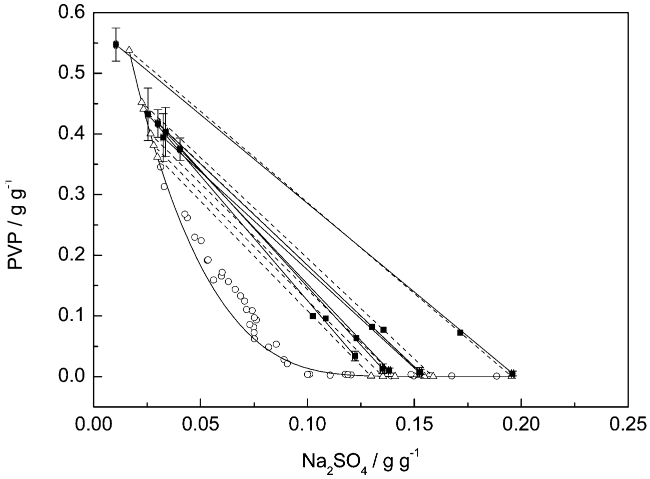

Figure 3. Liquid−liquid equilibrium of the system (PVPK17 + Na_2SO_4 + H_2O) at 338.2 K. Experimental results: −■−, coexisting phases; ○, cloud points. Correlation results from the VERS model: --△--, coexisting phases; ____, cloud-point curve.

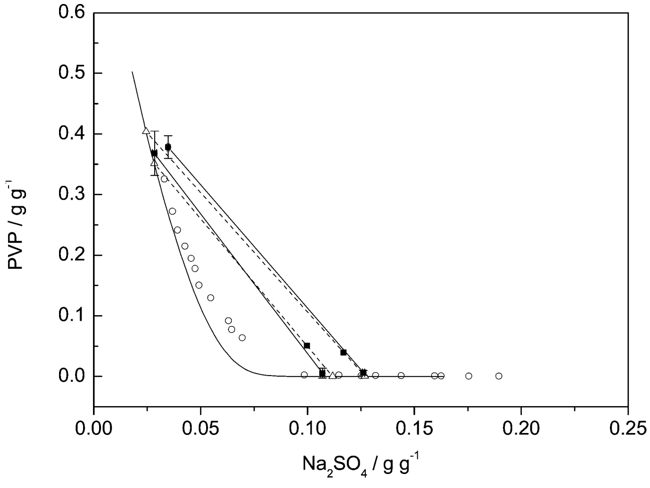

Figure 4. Liquid−liquid equilibrium of the system (PVPK30 + Na_2SO_4 + H_2O) at 338.2 K. Experimental results: −■−, coexisting phases; ○, cloud points. Correlation results from the VERS model: --△--, coexisting phases; ____, cloud-point curve.

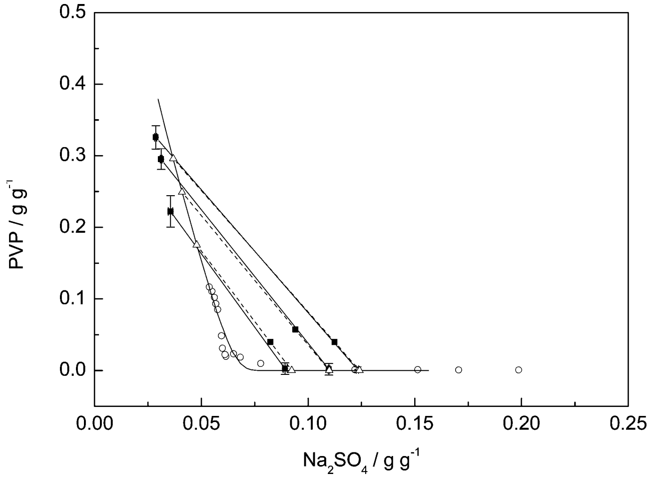

Figure 5. Liquid−liquid equilibrium of the system (PVPK90 + Na_2SO_4 + H_2O) at 298.2 K. Experimental results: −■−, coexisting phases; ○, cloud points. Correlation results from the VERS model: --△--, coexisting phases; ____, cloud-point curve.

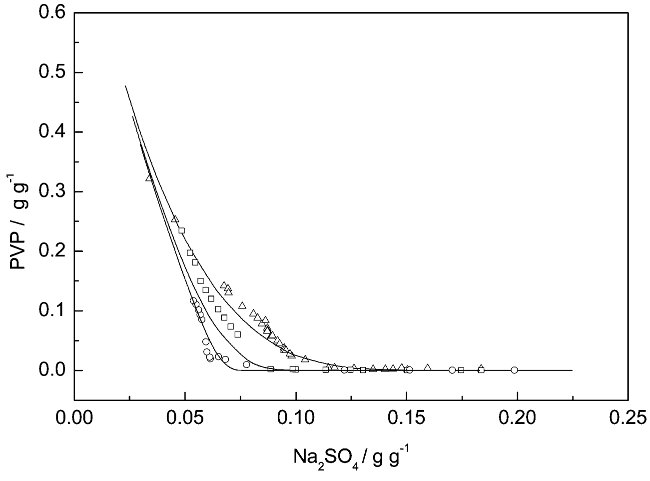

Figure 6. Liquid−liquid equilibrium of the system (PVPK*xy* + Na_2SO_4 + H_2O) at 298.2 K. Comparison of experimental results for the phase boundary for △, *xy* = 17; □, *xy* = 30; and ○, *xy* = 90 with calculation results.

solutions. On one side, the experimental data for the cloud-point curve at such high polymer concentrations are subject to an additional (and unknown) uncertainty due to problems in mixing such solutions. On the other side, the composition results from the phase equilibrium investigations in that region are also subject to some additional uncertainties due to problems in separating that very viscous liquid phase from the salt-rich phase and presumably also from problems in equilibrating such viscous solutions. To further check the consistency of the experimental results for the liquid−liquid equilibrium, the "mass balance test" proposed by Marcilla et al.[22] was performed. In that test, the mass of the feed solution of a phase equilibrium experiment is calculated from the experimental results for the compositions of the coexisting phases and compared with the mass of the feed solution that is known from preparing the feed solution. When all experimental data points are taken into account, the standard deviation in that mass is 0.4 %. That number reduces to 0.3 % when the experiment with the maximum deviation is neglected. We consider these rather small numbers as a confirmation of the quality of the experimental results.

Thermodynamic Modeling

The aqueous two-phase liquid−liquid equilibrium is described here by the VERS (virial equation with relative surface fractions) model.[1] This model is a modification of Pitzer's excess energy equation for aqueous electrolyte solutions.[23] It uses a group contribution approach and replaces the molality scale by a surface-fraction scale for enabling an extension to aqueous polymer solutions. The activity coefficients resulting from the VERS model are normalized according to the asymmetric convention. The reference state for the chemical potential of the solvent (water) is the pure liquid at the system temperature and pressure. The reference state for a solute component is a hypothetical 1 *m* solution of the solute in the pure solvent at the system temperature and pressure. The concentration of a solute in the expression for the activity coefficient is expressed by its "normalized surface fraction", that is, its surface fraction Θ_i divided by the surface fraction of the solvent Θ_w.

The surface fraction of a component *i* is given by

$$\Theta_i = \frac{m_i Q_i}{\sum_{\text{all comp.}j} m_j Q_j} \tag{1}$$

where m_i and Q_i are the molality and surface parameter of component *i*.

As component *i* consists of $\nu_k^{(i)}$ groups, *k*, of surface parameter, q_k

$$Q_i = \sum_{\text{all groups }k} \nu_k^{(i)} q_k \tag{2}$$

The equation for the activity of the solvent (water), a_w, from the VERS model is

$$\ln a_w = -\frac{M_w}{1000}\left[\sum_{j\neq w} m_j - 2A_\varphi \frac{I_m^{1.5}}{1+b\sqrt{I_m}}\right] - \left(\frac{1000}{M_w}\right)\sum_{i\neq w}\sum_{j\neq w}\frac{\Theta_i}{\Theta_w}\frac{\Theta_j}{\Theta_w}[\mathrm{A}_{i,j}^{(0)} + \mathrm{A}_{i,j}^{(1)}\exp\{-\alpha\sqrt{I_m}\}] - 2\left(\frac{1000}{M_w}\right)^2\sum_{i\neq w}\sum_{j\neq w}\sum_{k\neq w}\frac{\Theta_i}{\Theta_w}\frac{\Theta_j}{\Theta_w}\frac{\Theta_k}{\Theta_w}B_{i,j,k} \tag{3}$$

where I_m is the ionic strength (on molality scale) of the solution

$$I_m = \frac{1}{2}\sum_{i=1}^{S} m_i z_i^2 \tag{4}$$

A_φ is the Debye−Hückel constant, and $A_{i,j}^{(0)}$, $A_{i,j}^{(1)}$, and $B_{i,j,k}$ are parameters for interactions between two solutes (*i* and *j*) and three solutes (*i*, *j*, and *k*), respectively. The parameters *b* and α were adopted from Pitzer:[24] $b = 1.2$; $\alpha = 2.0$.

The binary and ternary interaction parameters between solute species are also expressed using a group contribution approach

$$A_{i,j}^{(0)} = \sum_{\text{all groups }k}\ \sum_{\text{all groups }l} \vartheta_k^{(i)}\vartheta_l^{(j)} a_{k,l}^{(0)} \tag{5}$$

$$A_{i,j}^{(1)} = \sum_{\text{all groups }k}\ \sum_{\text{all groups }l} \vartheta_k^{(i)}\vartheta_l^{(j)} a_{k,l}^{(1)} \tag{6}$$

$$B_{i,j,k} = \sum_{\text{all groups }k}\ \sum_{\text{all groups }l}\ \sum_{\text{all groups }m} \vartheta_k^{(i)}\vartheta_l^{(j)}\vartheta_m^{(k)} b_{k,l,m} \tag{7}$$

$$\vartheta_k^{(i)} = \frac{\nu_k^{(i)} q_k}{Q_i} \tag{8}$$

where $\vartheta_k^{(i)}$ is the relative contribution of group *k* to the surface parameter of species *i*, and $a_{k,l}^{(0)}$, $a_{k,l}^{(1)}$, and $b_{k,l,m}$ are binary and ternary interaction parameters between groups, respectively.

The equations for the activity of a solute, $a_{i,m}^*$, from the VERS model is

$$\ln a_{i,m}^* = \ln m_i - A_\varphi z_i^2\left[\frac{\sqrt{I_m}}{1+b\sqrt{I_m}} + \frac{2}{b}\ln(1+b\sqrt{I_m})\right] + 2\left(\frac{1000}{M_w}\right)\frac{q_i}{q_w}\sum_{j\neq w}\frac{\Theta_j}{\Theta_w}[A_{i,j}^{(0)} + A_{i,j}^{(1)} f_2(I_m)] - z_i^2 f_3(I_m)\left(\frac{1000}{M_w}\right)^2\sum_{j\neq w}\sum_{k\neq w}\frac{\Theta_j}{\Theta_w}\frac{\Theta_k}{\Theta_w}A_{j,k}^{(1)} + 3\left(\frac{1000}{M_w}\right)^2\frac{q_i}{q_w}\sum_{j\neq w}\sum_{k\neq w}\frac{\Theta_j}{\Theta_w}\frac{\Theta_k}{\Theta_w}B_{i,j,k} \tag{9}$$

with

$$f_2(I_m) = \frac{2}{\alpha^2 I_m}[1 - (1+\alpha\sqrt{I_m})\exp\{-\alpha\sqrt{I_m}\}] \tag{10}$$

and

$$f_3(I_m) = \frac{1}{\alpha^2 {I_m}^2}\left[1 - \left(1 + \alpha\sqrt{I_m} + \frac{\alpha^2 I_m}{2}\right)\exp\{-\alpha\sqrt{I_m}\}\right] \tag{11}$$

It is worthwhile to mention that all summations in eqs 3 and 9 are over the solute species only (i.e., there is no contribution from the solvent). Instead of considering sodium ions and sulfate ions as different solute species, it is sufficient (due to the condition of electroneutrality of each of the coexisting phases) to consider just sodium sulfate as a single solute. The activity of sodium sulfate is then

$$a^*_{Na_2SO_4,m} = (a^*_{Na^+,m})^2 \cdot a^*_{SO_4^=,m} \tag{12}$$

The calculation of activities requires the Debye−Hückel parameter (A_φ) for water (at 298.15 K, $A_\varphi = 0.39147$, and at 338.15 K, $A_\varphi = 0.42358$),[25] the surface parameter of group k (q_k), and binary ($a^{(0)}_{i,j}$, $a^{(1)}_{i,j}$) as well as ternary ($b_{i,j,k}$) interaction parameters. Poly(vinyl pyrrolidone) was split into monomer units (abbreviated by VP). The number (N_p) of VP groups in a PVP molecule is estimated from the number average molecular mass (M_n) of the polymer and the molecular weight of vinyl pyrrolidone

$$N_p = M_n/111.145 \tag{13}$$

Water is treated as a single group with surface parameter $q_w = 1.4$. Sodium sulfate is considered to be completely dissociated into Na^+ and $SO_4^=$. The surface parameter of water was also used for both ionic species. The surface parameter of vinyl pyrrolidone was estimated from the method of Bondi:[26] $q_{VP} = 3.120$.

Table 6. Interaction Parameters of the VERS Model

		298 K	338 K
$a^{(0)}_{VP,VP}$	set 1	0.004833	0.002767
$b_{VP,VP,VP}$		0.0	0.0
$a^{(0)}_{VP,VP}$	set 2	0.005886	0.003892
$b_{VP,VP,VP}$		$-2.607 \cdot 10^{-5}$	$-2.607 \cdot 10^{-5}$
$a^{(0)}_{Na_2SO_4,VP}$		0.069811	0.069811
$a^{(1)}_{Na_2SO_4,VP}$		−0.188876	−0.188876
$a^{(0)}_{Na^+,SO_4^=}$ (27)		0.01869	0.07983
$a^{(1)}_{Na^+,SO_4^=}$ (27)		1.0994	1.263901
$b^{(27)}_{Na^+,Na^+,SO_4^=}$		0.00131	−0.00152422

The parameters for interactions between sodium ions on one side and sulfate ions on the other side were taken from Rogers and Pitzer[27]—this is no approximation as the VERS model reduces to Pitzer's model for the excess Gibbs energy of an aqueous electrolyte solution when the surface parameter of water is also assigned to all ions. These interaction parameters are given in Table 6. The parameter $a^{(0)}_{VP,VP}$ for interactions between VP groups in water was adjusted to the activity of water in aqueous solutions of PVP at (298.15 and 338.15) K. Kany et al.[28] reported such experimental results. They described the data by the osmotic virial equation and reported second and third osmotic virial coefficients of PVP in water. The osmotic virial equation was used to calculate the activity of water up to the very high polymer concentrations covered in the present work. The resulting "pseudoexperimental" water activity data were used to determine the VERS parameters for interactions between VP groups. In a first approach, the ternary parameter $b_{VP,VP,VP}$ was set to zero and only the binary parameter $a^{(0)}_{VP,VP}$ was fitted. In a second approach, both parameters ($a^{(0)}_{VP,VP}$ and $b_{VP,VP,VP}$) were simultaneously fitted. The resulting numbers for these parameters are given in Table 6. Although $a^{(0)}_{VP,VP}$ slightly depends on temperature, a constant value for $b_{VP,VP,VP}$ proved sufficient to give a good description of the pseudoexperimental data for the activity of water. Figures 7 to 9 show the comparisons between the correlation results from the VERS model (broken curves) and from the osmotic virial equation (full curves) for 298.15 K. The comparisons reveal that the second approach leads to a slightly better agreement between both methods, in particular, for the aqueous solutions of PVP with the higher molecular weights (PVPK30 and PVPK90). However, the VERS results with that set of parameters show a slightly poorer agreement at low polymer concentrations. As that low polymer concentration range is of minor interest in the present work, the second set was adopted for calculating the liquid−liquid equilibrium in the ternary systems (PVPK*xy*−Na_2SO_4−H_2O). The VERS model additionally requires parameters for binary interactions between VP groups on one side and Na^+ as well as $SO_4^=$ ions on the other side and parameters for ternary interactions between VP, Na^+, and $SO_4^=$. A parameter study revealed that all such ternary parameters can be neglected. It also showed that the influence of temperature on the remaining binary parameters can be neglected. The binary parameters for interactions between VP on one side and either Na^+ or $SO_4^=$ on the other side always appear simultaneously (i.e., coupled).

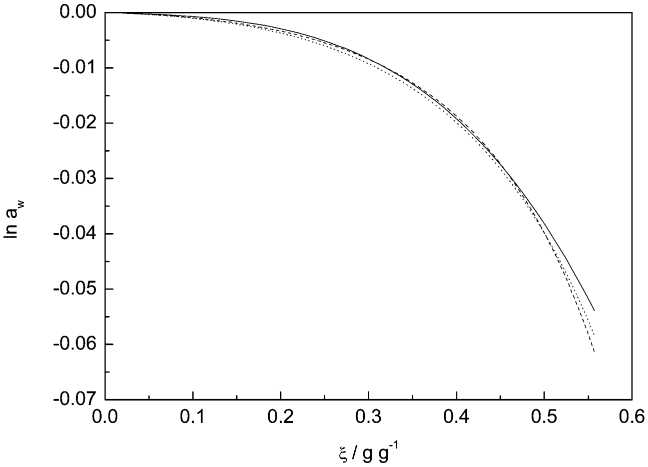

Figure 7. Activity of water in aqueous solutions of PVPK17 at 298.15 K: ____, pseudoexperimental data; and correlation results from the VERS model ------, without; and ...., with a ternary parameter, respectively.

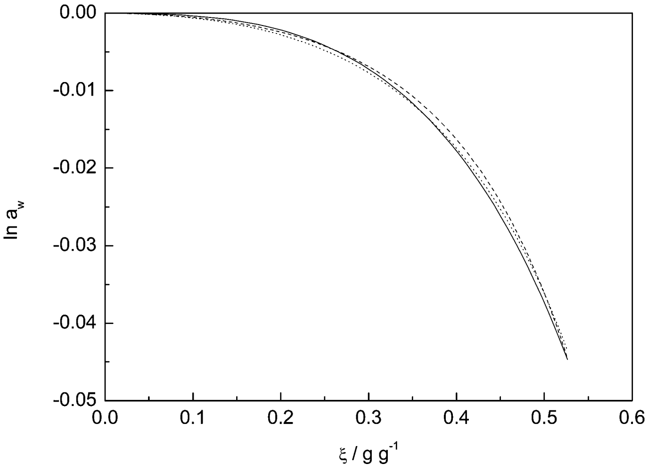

Figure 8. Activity of water in aqueous solutions of PVPK30 at 298.15 K: pseudoexperimental data; and correlation results from the VERS model ------, without; and ...., with a ternary parameter, respectively.

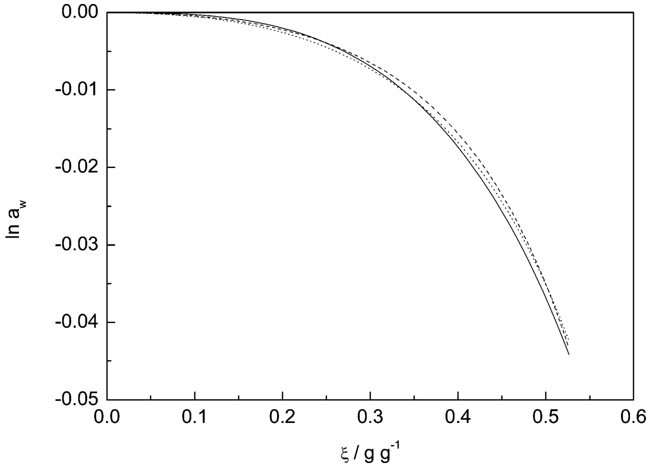

Figure 9. Activity of water in aqueous solutions of PVPK90 at 298.2 K: pseudoexperimental data; and correlation results from the VERS model ------, without; and ...., with a ternary parameter, respectively.

These parameters cannot be determined independently from each other but can be summarized to one single parameter

$$a^{(i)}_{\mathrm{Na_2SO_4,VP}} = a^{(i)}_{\mathrm{Na^+,VP}} + \frac{1}{2}a^{(i)}_{\mathrm{SO_4^=}} \qquad \text{for } i = 0 \text{ and } 1 \tag{14}$$

The remaining, unknown interaction parameters ($a^{(0)}_{\mathrm{Na_2SO_4,VP}}$ and $a^{(1)}_{\mathrm{Na_2SO_4,VP}}$) were adjusted to the new experimental data for the liquid−liquid-phase equilibrium of the system (PVPK17−Na_2SO_4−H_2O) reported in Table 4 for 298.2 K. The parameters were selected by minimizing the following objective function

$$\mathrm{AD} = \sum_{i=1}^{3}\sum_{n=1}^{N}[(\xi^{\mathrm{I}}_{i,\mathrm{exptl}} - \xi^{\mathrm{I}}_{i,\mathrm{calcd}})^2 + (\xi^{\mathrm{II}}_{i,\mathrm{exptl}} - \xi^{\mathrm{II}}_{i,\mathrm{calcd}})^2] \tag{15}$$

ξ^{I}_i and ξ^{II}_i are the mass fractions of component i in the coexisting liquid phases I and II, respectively. N is the number of tie-lines, and the subscripts exptl and calcd designate experimental results and calculated values, respectively. The phase equilibrium calculations started with the experimental results for the feed composition at the experimentally determined temperature and resulted in the compositions of the coexisting liquid phases. The resulting parameters are given in Table 6. Figure 2 shows comparisons between calculation results and experimental data for both the cloud-point line and the liquid−liquid equilibrium for systems containing PVPK17. As already discussed above (due to experimental problems at high polymer concentrations as well as in the vicinity of the critical point), one can only expect a fair agreement between the calculation results and the experimental data. The parameters determined from the correlation of the experimental data for systems with PVPK17 were also used to predict the cloud-point curve and liquid−liquid-phase equilibrium for systems with PVPK17 at 338.2 K as well as with PVPK30 and PVPK90 at (298.2 and 338.2) K. As is shown in Figures 3 to 5, the predictions fairly agree with the experimental data. As already discussed above, the effect of temperature on the two-phase region is very small, but there is an influence of the molecular mass of PVP on the concentration range of the single-phase region. The VERS model correctly predicts that influence (cf. Figure 6).

Comparison with Literature Data. Only a single publication with experimental results for the liquid−liquid equilibrium in aqueous solutions of PVP and sodium sulfate was found in the open literature (Sadeghi[8]). This author reported the binodal curve and the compositions of coexisting phases at 303.15 K for systems with a polymer fraction that was characterized as “PVP10 000”. For comparisons with the prediction results obtained with the VERS model, it was assumed that “10 000” stands for the weight averaged molecular weight of the PVP fraction. The calculations started with a feed solution that was taken as an equimolar mixture of the coexisting liquids as reported by Sadeghi.[8] The prediction results are compared to the experimental data in Figure 10. There is a fair agreement for the binodal curve (which was given by Sadeghi only for polymer mass fractions above about 10 %) but rather large deviations in the polymer concentration of the salt-rich phase. The experimental results for that polymer concentration are considerably larger than the results reported here.

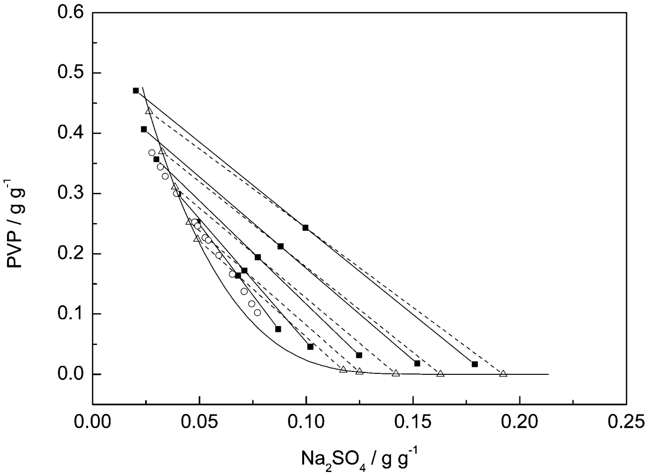

Figure 10. Liquid−liquid equilibrium of the system (PVP + Na_2SO_4 + H_2O) at 303.2 K. Comparison of experimental results from Sadeghi[8] (−■−, coexisting phases; ○, cloud points) with prediction results using the VERS model (--△--, coexisting phases; ____, cloud-point curve).

Conclusions

Cloud-point curves and liquid−liquid equilibrium data for aqueous two-phase systems formed by simultaneously dissolving poly(vinyl pyrrolidone) (three samples with a number averaged molecular weight of about 4000, 18 000, and 140 000, respectively) and sodium sulfate in water are presented for (298.2 and 338.2) K. The experimental results are described using the VERS model for the excess Gibbs energy of the polymer- and salt-containing aqueous solutions. The calculation results fairly agree with the new experimental data (showing some larger deviations at very high polymer concentrations as well as in the vicinity of the critical point of the liquid−liquid equilibrium). The influence of temperature on the liquid−liquid equilibrium is very small. There is an influence of the polymer’s molecular weight on the phase equilibrium: the miscibility gap increases with increasing molecular weight. That influence is qualitatively predicted by the VERS model.

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