Liquid-Liquid and Vapor-Liquid Equilibria in Water + Poly(ethylene glycol) + Sodium Sulfate

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In this work we have measured liquid-liquid equilibria (LLE) and vapor-liquid equilibria (VLE) in aqueous solutions of poly(ethylene glycol) (PEG) and sodium sulfate. The liquid-liquid equilibria have been determined over a range of polymer molar masses (1550-6000 g/mol), pH values (5.2-8.1), and temperatures (293.15-313.15 K) using a density-sound analyzer. The VLE in the system water + PEG 3000 + sodium sulfate have been measured over the entire homogeneous mixing range at 293.15 and 313.15 K by vapor-pressure osmometry. To demonstrate that the experimental data do not contain any obvious thermodynamic inconsistency, we described VLE and LLE simultaneously using the osmotic virial equation (McMillan, W. G., Jr.; Mayer, J. E. *J. Chem. Phys.* **1945**, *13*, 276) extended with a Debye-Hückel term (Debye, P.; Hückel, E. *Z. Phys.* **1923**, *24*, 195, 305. Pitzer, K. S. *J. Phys. Chem.* **1973**, *77*, 268).

Introduction

If poly(ethylene glycol) (PEG) and sodium sulfate are added to water beyond a certain concentration, two aqueous phases are formed. Such an aqueous polymer + salt two-phase system can be used for the extraction of biomolecules (*4, 5*). For stabilization of the charged biomolecules and to enhance the selectivity of the process, the pH of the system has to be adjusted using buffer salts (*4*).

The design and optimization of the extraction process require knowledge of the liquid-liquid equilibria (LLE) of the system, which can be determined either experimentally or by prediction based on a good process model and a small set of experimental data, e.g., vapor-liquid equilibrium (VLE) data. Several experimental investigations of LLE in aqueous PEG + salt two-phase systems are reported in the literature (*4, 6-9*). These investigations showed that the miscibility gap increases with increasing polymer molar mass (*4, 6-9*), while the effect of temperature on the phase behavior could not be examined significantly (*7*). Investigations on aqueous PEG + potassium phosphate buffer two-phase systems (*6*) showed that the LLE is influenced by variation in the pH which occurs on going from the monobasic to the dibasic potassium phosphate. However, it has not been examined whether it is the pH itself or the change of salt composition which affects the phase behavior of aqueous PEG + salt two-phase systems.

VLE data have been determined for various systems (water + PEG + salt) at 298.15 K using the isopiestic method (*10, 11*). These VLE measurements were performed in the homogeneous mixing range at relatively low concentrations. But for the development of a process model for aqueous two-phase systems, the range of available VLE data has to be extended to the entire homogeneous mixing range including regions in the vicinity of the immiscible region (*12*).

This work is intended to extend the experimental data for the system water + PEG + sodium sulfate into these regions where data are scarce. We measured LLE for various molar masses of PEG (1550, 3000, and 6000 g/mol), temperatures (293.15, 303.15, and 313.15 K), and pH values (5.2, 5.8, and 8.1) adjusted with a sodium phosphate buffer. Small buffer concentrations ensure that only the pH and not the buffer composition influences the phase behavior. Additionally, VLE data were measured over the entire homogeneous mixing range for the system water + PEG 3000 + sodium sulfate at 293.15 and 313.15 K. These results were evaluated with the osmotic virial equation extended by a Debye-Hückel term. The osmotic virial equation describes the short-range interactions between the solutes, while the Debye-Hückel term takes care of the long-range electrostatic forces.

Experimental Section

Materials. PEG (mass-average molar masses 1550, 3000, and 6000 g/mol) was supplied by the Hüls AG, Marl, in the highest purity available and used without further purification. Size-exclusion chromatographic analysis revealed very little polydispersivity and failed to show impurities (*13*). Sodium sulfate, sodium dihydrogen phosphate, and disodium hydrogen phosphate (Merck, Darmstadt) for LLE measurements as well as sodium chloride (Merck, Darmstadt) and D(+)-glucose (monohydrate) (Merck, Darmstadt) for the calibration of the vapor-pressure osmometer were of reference grade. Water used to prepare polymer and salt solutions was triply distilled.

pH Meter. The pH meter (Metrohm Herisau, type E-516) with a glass electrode (Metrohm Herisau, type EA-120) was assembled and calibrated according to the manufacturer's instructions. The accuracy of the measured pH is ±0.05.

Density-Sound Analyzer. The density-sound analyzer (type DSA 48, Heräus Paar, Graz) allows the specific volume, v, and the speed of sound, u, in a solution to be measured simultaneously. The specific-volume determination is based on the period of oscillation of a vibrating U-shaped tube that is filled with the sample (*14*). The sample is simultaneously injected into another cell, in which the speed of sound in the solution can be determined by measuring the residence time of a sound signal in a tube of fixed length.

These values of v and u can be related directly to the solute concentrations of the aqueous PEG + sodium sulfate solutions. Resulting from calibration measurements, the relation between the mass fractions of the solutes and v and u is

$$\begin{pmatrix} v - v_{\text{water}} \\ u - u_{\text{water}} \end{pmatrix} = \begin{pmatrix} v_{\text{PEG}} & v_{\text{Na}_2\text{SO}_4} \\ u_{\text{PEG}} & u_{\text{Na}_2\text{SO}_4} \end{pmatrix} \begin{pmatrix} w_{\text{PEG}} \\ w_{\text{Na}_2\text{SO}_4} \end{pmatrix} \qquad (1)$$

up to an overall solute mass fraction of 0.1. At higher solute concentrations, nonlinear contributions to the solution behavior can no longer be neglected. In the linear range the solute mass fractions of aqueous PEG + sodium sulfate

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Table 1. Specific Volume and Speed of Sound Coefficients of Eq 1 for the System Water (1) + PEG (2) + Sodium Sulfate (3) at 308.15 K

i	v_i (cm^3·g^{-1})	u_i/(m·s^{-1})
1	1.0046	1519.4
2	0.8492	1043.3
3	0.1487	501.1

solutions can be calculated by multiplication of the measured v and u with the inverted coefficient matrix of eq 1. The pure solvent properties v_{water} and u_{water} (*15*) as well as the specific volume and speed of sound parameters in the coefficient matrix are given in Table 1.

The samples were diluted gravimetrically with water to ensure that the measurements are performed in the linear range. Each measurement was repeated twice to ensure reproducibility. After measuring a solution, the DSA was rinsed with triply distilled water and acetone of reference grade and then dried repeatedly until the original specific volume and speed of sound values of air were obtained. The accuracy of the measured v and u were estimated to $\pm 10^{-4}$ cm^3·g^{-1} and $\pm 10^{-1}$ m·s^{-1}, resulting in an accuracy of the solute mass fractions of better than ±0.002 for PEG and ±0.001 for sodium sulfate.

Vapor-Pressure Osmometry. The vapor-pressure osmometer (Gonotec, Berlin) was calibrated using various salt and glucose-solution standards. The calibration measurements showed that the logarithms of the water activities a_1 of the samples are proportional to the measured differences in the resistance of the thermistors, ΔR, with a sample and a pure solvent drop on the thermistors. Since ΔR is proportional to the temperature difference ΔT between the thermistors, the water activities can be evaluated according to the modified Clausius–Clapeyron equation

$$\ln a_1 = -\frac{\Delta H_1^{vap}}{\eta R T^2}\Delta T \qquad (2)$$

where ΔH_1^{vap} is the enthalpy of vaporization of water and the efficiency coefficient η is the calibration constant which corrects for heat losses (*16*).

At least three measurements were made for each sample. After equilibration the sample readings were extrapolated to zero time and averaged. The resulting logarithms of the activities of water have been determined with an accuracy of better than ±1% from their mean values.

Preparation of Solutions for VLE and LLE Measurements. For both VLE and LLE measurements, stock solutions were prepared gravimetrically for each solute (*13*). The solute concentrations were determined by densitometry with an accuracy of better than ±0.0005 in solute mass fraction. The densitometer (type DSA 48, Heräus-Paar, Graz; see above for description) was calibrated with mixtures of water and the dried substances.

For LLE measurements, the stock solutions and water were mixed in a centrifugation tube. The tube was sealed and thermostated, and the phases were then separated as described in a previous publication (*13*). In the samples of the PEG-rich top phase and the sodium sulfate-rich bottom phase the pH was measured. Then the samples were diluted to an overall solute mass fraction between 0.07 and 0.1, slightly degassed in an ultrasound bath (type AK 100-H, Sonorex) for 10 min to avoid the formation of gas bubbles in the DSA, thermostated at 308.15 K, and injected into the DSA for the analysis of the phase compositions. For the measurements of phase systems with buffer salts, the buffer salt concentrations were sufficiently small (0.01 M) as to not influence the measured values.

For VLE measurements, ternary aqueous PEG + salt solutions were generated by mixing different ratios of the two stock solutions in the homogeneous mixing range. The resulting compositions of each of these mixing series do then lie on a straight line in the concentration diagram. The concentrations of the stock solutions for these measurements were chosen such that the mixing lines are approximately parallel to the experimental tie lines near the miscibility gap (*17*). The water activity of each sample was then determined by vapor-pressure osmometry.

Errors in the preparation of solutions were estimated to be well below the instrumental error for both LLE and VLE measurements.

Results and Discussion

The phase compositions and pH values in the coexisting phases of aqueous PEG + sodium sulfate two-phase systems are given in Table 2. Exemplarily, the corresponding phase diagram of the system water + PEG 3000 + sodium sulfate at 293.15 K is shown in Figure 1. The data compare well with those of previous studies (*7, 9*). The phase diagram is not affected by the variation of the phase ratio of the prepared phase system. This indicates that the polydispersity of PEG is too small to influence these measurements (*18*).

A comparison of the system water + PEG 3000 + sodium sulfate without (pH 5.8) and with dilute sodium phosphate buffer solutions (0.01 M, pH 5.2 and 8.1) in Figure 1 shows that the system is essentially not influenced by a variation of pH. However, small pH differences between the coexisting phases have been established in our measurements, as can be seen in Table 2. This experimental finding may be a result of the shortcomings of commercial pH electrodes (*19*). These pH differences depend on the average pH of the system and the tie line length. For a small average pH of the system (pH 5.2 and 5.8) the pH of the PEG-rich top phase is higher, while for a high pH of the system (pH 8.1) the pH of the sodium sulfate-rich bottom phase is slightly higher. For all investigated systems, the pH difference between the coexisting phases decreases with tie line length. The pH in the coexisting phases of unbuffered aqueous two-phase systems does not depend on the temperature and the polymer molar mass.

Figure 2 shows the influence of the polymer molar mass on the phase behavior. As the molar mass of the polymer is increased, the binodal curve shifts to smaller solute concentrations. The slopes of the tie lines are not significantly affected by changes in the polymer molar mass. These dependencies are in agreement with previously reported data (*4, 6, 7, 9*).

Also the temperature has a significant influence on the phase behavior as indicated by a comparison of the system water + PEG 3000 + sodium sulfate at various temperatures in Figure 3. The miscibility gap grows and the slopes of the tie lines are steeper with increasing temperature. Similar temperature effects on the phase behavior of the system water + PEG + sodium sulfate have been studied by Bailey (*20*) and Florin et al. (*21*). They examined a strong lowering of the lower critical solution temperature (LCST) of the system water + PEG by the addition of sodium sulfate. In agreement with our measurements, these examinations indicate an increasing miscibility gap with decreasing temperature. The LCST of the binary system water + PEG occurs at approximately 90–95 °C and thus little above the examined temperature range of this work. As a result, the critical mixing point of the system water + PEG + sodium sulfate shifts toward the LCST on the PEG axis and the tie lines near the critical mixing point become more parallel to the PEG axis as the temperature is increased in the experiments.

In the second step of our investigations, we have measured water activities for the entire homogeneous mixing range of

Table 2. Tie Lines for Water + PEG + Sodium Sulfate

		top phase			bottom phase			overall	
$M_{PEG}/(g \cdot mol^{-1})$	T/K	w_{PEG}	w_{salt}	pH	w_{PEG}	w_{salt}	pH	w_{PEG}	w_{salt}
1550 (pH 5.8)	293.15	0.4101	0.0189		0.0000	0.1911		0.1976	0.1081
		0.3834	0.0199	5.95	0.0000	0.1804	5.75	0.1835	0.1008
		0.3316	0.0259		0.0020	0.1631		0.1601	0.0960
		0.2889	0.0327		0.0178	0.1452		0.1498	0.0901
		0.2064	0.0564		0.0401	0.1261		0.1312	0.0869
3000 (pH 5.2)	293.15	0.3943	0.0115	5.35	0.0007	0.1804	5.15	0.1830	0.1022
		0.3482	0.0174	5.30	0.0011	0.1611	5.05	0.1611	0.0900
		0.2743	0.0299	5.20	0.0161	0.1354	5.05	0.1354	0.0798
		0.2357	0.0368	5.15	0.0396	0.1180	5.00	0.1180	0.0774
3000 (pH 5.8)	293.15	0.4007	0.0100	6.05	0.0057	0.1791	5.75	0.3246	0.0415
		0.3764	0.0137	5.95	0.0000	0.1704	5.75	0.2034	0.0847
		0.3770	0.0134	5.95	0.0000	0.1691	5.80	0.2084	0.0829
		0.3778	0.0132	5.95	0.0162	0.1689	5.75	0.2016	0.0854
		0.3578	0.0153	6.00	0.0239	0.1617	5.75	0.1004	0.1215
		0.3420	0.0183	5.90	0.0170	0.1586	5.75	0.2002	0.0764
		0.3007	0.0248	5.85	0.0082	0.1458	5.70	0.1832	0.0736
		0.2624	0.0293	5.85	0.0218	0.1354	5.75	0.1653	0.0734
		0.2357	0.0369	5.85	0.0380	0.1174	5.70	0.1660	0.0651
		0.1890	0.0482	5.80	0.0899	0.0875	5.70	0.1538	0.0617
		0.1424	0.0591		0.1424	0.0591		0.1424	0.0591
3000 (pH 8.1)	293.15	0.4057	0.0108	7.80	0.0011	0.1833	7.95	0.1724	0.1105
		0.3424	0.0188	7.90	0.0041	0.1582	8.05	0.1603	0.0933
		0.2782	0.0298	8.10	0.0108	0.1395	8.15	0.1447	0.0839
		0.2368	0.0375	8.15	0.0335	0.1196	8.20	0.1378	0.0774
3000 (pH 5.8)	303.15	0.3912	0.0098		0.0000	0.1623		0.1929	0.0875
		0.3552	0.0138		0.0079	0.1440		0.1746	0.0819
		0.3073	0.0199		0.0230	0.1254		0.1543	0.0764
		0.2438	0.0329		0.0501	0.1040		0.1446	0.0694
		0.1903	0.0464		0.0796	0.0854		0.1339	0.0660
3000 (pH 5.8)	313.15	0.4136	0.0063		0.0006	0.1587		0.1832	0.0911
		0.4004	0.0070	5.90	0.0030	0.1487	5.75	0.1725	0.0875
		0.3716	0.0092		0.0063	0.1376		0.1554	0.0847
		0.3335	0.0119		0.0117	0.1277		0.1501	0.0784
		0.2843	0.0216		0.0226	0.1114		0.1382	0.0722
		0.2212	0.0367		0.0474	0.0937		0.1242	0.0681
6000 (pH 5.8)	293.15	0.3730	0.0118	5.95	0.0013	0.1535	5.70	0.1779	0.0868
		0.3640	0.0121		0.0000	0.1520		0.1832	0.0815
		0.3221	0.0177		0.0022	0.1381		0.1575	0.0802
		0.2853	0.0232		0.0067	0.1244		0.1492	0.0721
		0.2455	0.0298		0.0112	0.1101		0.1160	0.0743
		0.2120	0.0362		0.0184	0.1033		0.1157	0.0694
		0.1613	0.0492		0.0372	0.0907		0.1148	0.0645

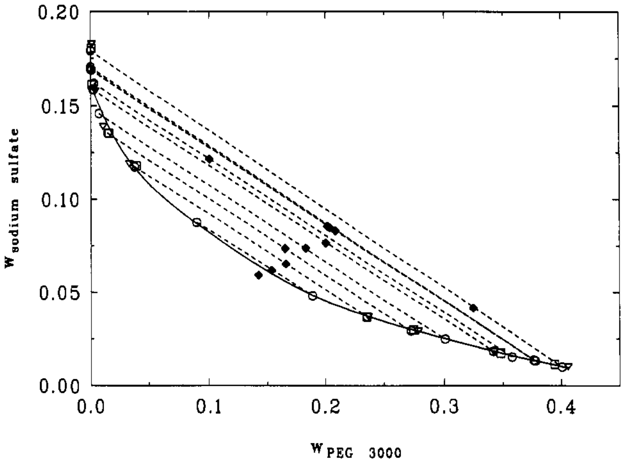

Figure 1. Phase diagram of the system water + PEG 3000 + sodium sulfate at 293.15 K: (---) tie lines, (◆) total composition, (□) coexisting phases (pH 5.2), (○) coexisting phases (pH 5.8), (▽) coexisting phases (pH 8.1).

aqueous PEG 3000 + sodium sulfate two-phase systems. The data are reported in Table 3, and the water activities measured for four mixing series of the system at 293.15 K are illustrated in Figure 4. It can be seen that the measurements were extended to concentrations close to the two-phase region.

The water activity data were evaluated using a model for the molar Gibbs free energy of mixing, G^M, combined with the osmotic virial equation (*12*) and the Debye–Hückel theory as suggested previously (*3*, *22*):

$$\frac{G^M}{RT} = \sum_{i=2}^{N} x_i \ln \frac{x_i M_i V_i}{V} + \sum_{i=2}^{N}\sum_{j=2}^{N} A_{ij}\frac{x_i x_j}{V} + \frac{1}{2}\sum_{i=2}^{N}\sum_{j=2}^{N}\sum_{k=2}^{N} A_{ijk}\frac{x_i x_j x_k}{V^2} - \sum_{i=2}^{N} A_{ii}\frac{x_i}{V_i M_i} - \frac{1}{2}\sum_{i=1}^{N} A_{iii}\frac{x_i}{V_i^2 M_i^2} - \frac{e^2 x_i (\sum_{j=1}^{n_i} \nu_{j,i} z_{j,i}^2)/(\sum_{j=1}^{n_i} \nu_{j,i})}{3RT\epsilon_0\epsilon_r}\kappa\tau(\kappa a) \quad (3)$$

with

$$\tau(\kappa a) = \frac{3}{(\kappa a)^2}\left(\ln(1 + (\kappa a)) - (\kappa a) + \frac{1}{2}(\kappa a)^2\right) \quad (4)$$

and

$$k^2 = \frac{4\pi e^2 x_i (\sum_{j=1}^{n_i} \nu_{j,i} z_{j,i}^2)/(\sum_{j=1}^{n_i} \nu_{j,i})}{\epsilon_0\epsilon_r RTV} \quad (5)$$

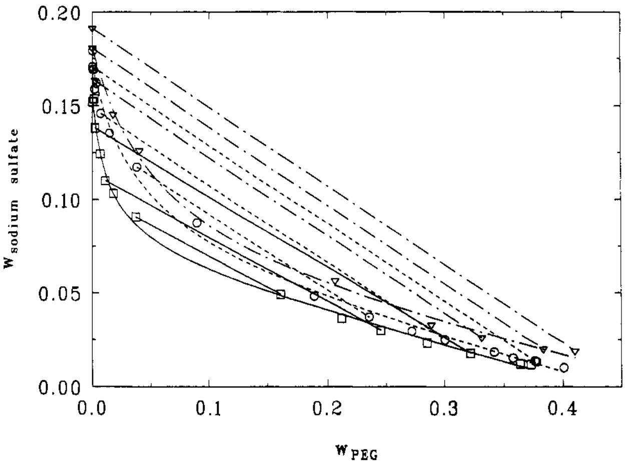

Figure 2. Phase diagram of the system water + PEG + sodium sulfate at 293.15 K for various polymer molar masses at pH 5.8: (▽) water + PEG 1550 + sodium sulfate, (○) water + PEG 3000 + sodium sulfate, (□) water + PEG 6000 + sodium sulfate.

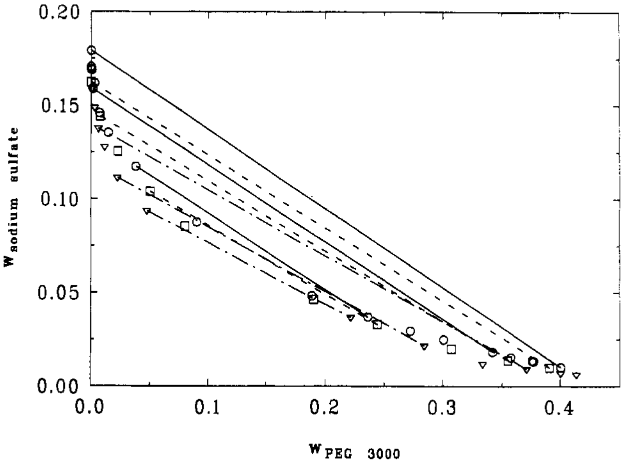

Figure 3. Phase diagram of the system water + PEG 3000 + sodium sulfate at various temperatures and pH 5.8: (○) T = 293.15 K, (□) T = 303.15 K, (▽) T = 313.15 K.

where component 1 is water, 2 is PEG, and 3 is sodium sulfate. x_i is the mole fraction of component i, M_i the number-average molar mass of component i, e the charge of a proton, $\nu_{j,i}$ the stoichiometric coefficient of ion j of component i, $z_{j,i}$ the charge of this ion, n_i the number of ions of component i, ϵ_0 the dielectric constant of a vacuum, and k the inverse Debye length. The model parameters in eq 3 are the osmotic virial coefficients A_{ij} and A_{ijk} as well as the closest distance between an ion pair a. V is the molar volume of the solution, calculated from $V = \sum_{i=1}^{N} x_i M_i V_i$, where V_i is the partial molar volume of component i. Significant deviations from this linear relation for the calculation of V only occur at high salt concentrations. The relative dielectric constant of the continuum, ϵ_r, has been set equal to the ϵ_r of pure water (*8*).

Table 3. Water Activities for the System Water + PEG 3000 + Sodium Sulfate for Different Mixing Series

T = 293.15 K			T = 313.15 K		
a_1	w_{PEG}	$w_{Na_2SO_4}$	a_1	w_{PEG}	$w_{Na_2SO_4}$
0.999 029	0.000 00	0.002 83	0.999 004	0.000 00	0.002 73
0.999 109	0.010 16	0.002 26	0.999 093	0.009 72	0.002 18
0.999 189	0.020 22	0.001 69	0.999 198	0.019 50	0.001 62
0.999 269	0.030 25	0.001 12	0.999 293	0.028 97	0.001 08
0.999 335	0.039 88	0.000 57	0.999 390	0.038 50	0.000 54
0.999 415	0.050 02	0.000 00	0.999 500	0.047 96	0.000 00
0.995 774	0.000 00	0.013 99	0.995 605	0.000 00	0.014 20
0.996 119	0.019 96	0.011 18	0.996 009	0.020 08	0.011 33
0.996 518	0.039 89	0.008 37	0.996 576	0.040 11	0.008 47
0.997 661	0.079 55	0.002 78	0.997 167	0.058 94	0.005 78
0.998 458	0.099 34	0.000 00	0.997 901	0.079 87	0.002 79
			0.998 737	0.099 47	0.000 00
0.981 175	0.000 00	0.066 62	0.981 085	0.000 00	0.066 48
0.982 825	0.032 61	0.053 56	0.982 302	0.032 56	0.053 43
0.984 739	0.065 51	0.040 38	0.984 285	0.065 27	0.040 33
0.987 290	0.098 95	0.026 99	0.987 217	0.098 68	0.026 94
0.990 692	0.131 84	0.013 81	0.991 097	0.132 16	0.013 53
0.996 008	0.166 34	0.000 00	0.996 711	0.165 93	0.000 00
0.956 298	0.000 00	0.161 02	0.975 131	0.000 00	0.089 90
0.970 701	0.171 02	0.045 78	0.974 551	0.026 40	0.080 20
0.974 485	0.189 95	0.033 03	0.974 182	0.060 00	0.067 90
0.981 077	0.214 33	0.016 60	0.978 684	0.150 80	0.034 60
0.990 638	0.238 97	0.000 00	0.984 588	0.203 40	0.015 30
			0.992 702	0.245 10	0.000 00
			0.967 898	0.000 00	0.117 30
			0.965 922	0.018 10	0.110 90
			0.969 020	0.261 50	0.024 70
			0.972 122	0.280 70	0.017 90
			0.977 797	0.301 90	0.010 40
			0.985 312	0.331 30	0.000 00

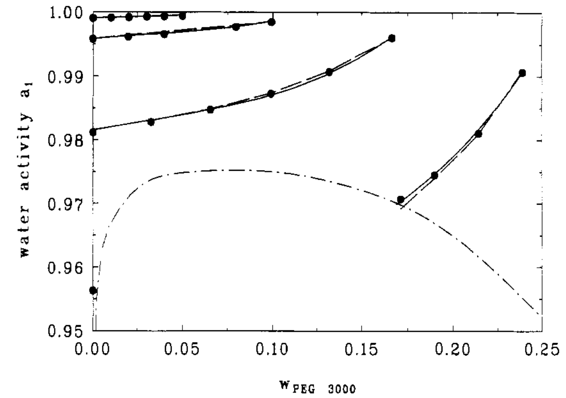

Figure 4. Water activity as a function of the polymer mass fraction in the system water + PEG 3000 + sodium sulfate at 293.15 K for the mixing series given in Table 3: (●) water activity data, (—) fit of VLE alone, (- - -) fit of VLE and LLE, (- · -) binodal curve.

Table 4. Model Parameters for the System Water (1) + PEG 3000 (2) + Sodium Sulfate (3)

parameter		fit procedure	T/K = 293.15	T/K = 313.15
a	10^{-10} m	VLE	8.93	8.93
A_{22}/M_2^2	10^{-3} (cm^3 mol)/g^2	VLE	2.72	2.37
A_{23}/M_2M_3	10^{-2} (cm^3 mol)/g^2	VLE + LLE	0.66	1.17
A_{33}/M_3^2	10^{-2} (cm^3 mol)/g^2	VLE	−2.32	−2.32
A_{222}/M_2^3	10^{-2} (cm^6 mol^2)/g^3	VLE	1.63	1.00
$A_{223}/M_2^2M_3$	10^{-1} (cm^6 mol^2)/g^3	VLE + LLE	1.45	0.99
$A_{233}/M_2M_3^2$	10^{-1} (cm^6 mol^2)/g^3	VLE + LLE	1.79	1.42
A_{333}/M_3^3	10^{-2} (cm^6 mol^2)/g^3	VLE	5.24	5.24

The model parameters for the binary PEG solution, A_{22} and A_{222}, have been determined previously (*17*). The model parameters for the system water + sodium sulfate, a, A_{33}, and A_{333}, were evaluated from literature data (*23*) at 298.15 K. Experimental investigations at 293.15 and 313.15 K showed that these parameters of the binary water + sodium sulfate system are not significantly affected by temperature. On the basis of the binary solution parameters, the cross osmotic virial coefficients A_{23}, A_{223}, and A_{233} have been determined by a simultaneous fit of LLE and VLE in the ternary water + PEG 3000 + sodium sulfate system using a least-squares method. The fitted parameters are given in Table 4. Using these parameters, we can calculate VLE and LLE in good agreement with our experimental results, as can be seen in Figures 4 and 5. This shows that no obvious thermodynamic inconsistencies are contained in both sets of experimental data.

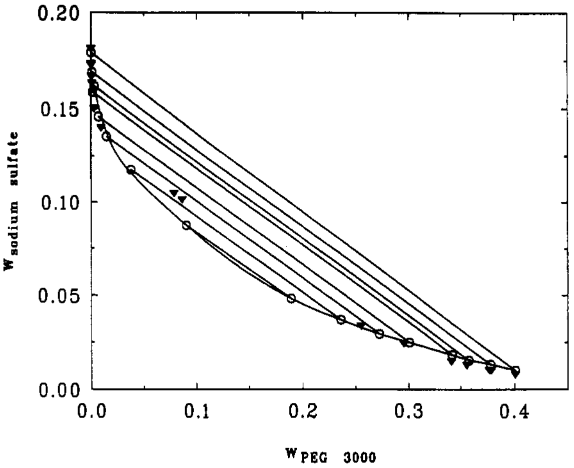

Figure 5. Prediction of the phase diagram of the system water + PEG 3000 + sodium sulfate at 293.15 K and pH 5.8: (○) experimental phase compositions, (▼) calculated phase compositions.

Registry Numbers Supplied by Author. Poly(ethylene glycol), 25322-68-3; sodium sulfate, 7757-82-6; disodium hydrogen phosphate, 7558-79-4; sodium dihydrogen phosphate, 7558-79-4.

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