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Liquid−Liquid Equilibrium in Aqueous Two-Phase (Water + PEG 8000 + Salt): Experimental Determination and Thermodynamic Modeling[†]

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Aqueous two-phase systems have been of increasing importance as a method for separation and purification of biomaterials, such as proteins and enzymes, with economical advantages related to conventional methods. However, the thermodynamic modeling of these systems is not fully developed yet, and the data in the literature are scarce. In this work, liquid−liquid equilibrium data are experimentally determined for aqueous two-phase (water + polyethylene glycol 8000 + sodium sulfate) and (water + polyethylene glycol 8000 + magnesium sulfate), at temperatures of (25 and 50) °C. The experimental data are correlated by the NRTL model for the activity coefficient. New interaction parameters were estimated by the Simplex method.

1. Introduction

Aqueous two-phase systems have been of increasing importance as a method for separation and purification of biomaterials, such as proteins and enzymes, with several advantages compared to conventional methods, such as cost reduction, minimization of the separation stages, high purity products, and high recovery of the materials.

An aqueous two-phase system (ATPS) is traditionally formed when two different polymers (i.e., PEG + dextran) or a polymer and a salt (i.e., PEG + potassium phosphate) (PEG is the acronym for polyethylene glycol) are mixed with water. This ternary system splits in two phases, both of them water-rich, above a certain critical concentration of polymer or salt. A protein and enzyme or any other biomolecule within this kind of system will distribute between the two equilibrium phases. This partition in ATPS is an extremely favorable method to recovery and purification of proteins or enzymes since the conditions are mild, with both phases about (75 to 90) % in water,[1] without degrading the product.[2]

Information about the phase diagram for this kind of system, as well as the thermodynamic modeling of the phase equilibrium, is essential for the development, design, simulation, optimization, and operation of these separation processes.

There is a significant amount of phase equilibrium data for polymer−polymer ATPS; however, these systems are difficult to use in industrial conditions due to their high viscosity and cost. Polymer−salt ATPS are more adequate since they present lower viscosity and higher selectivity.[3] In the recent years, a crescent number of works have been presented for different PEGs and salts, as shown in Table 1.

In this work, experimental liquid−liquid equilibrium data (LLE) for ATPS containing (water + PEG 8000 + sodium sulfate) and (water + PEG 8000 + magnesium sulfate) were obtained. The data were correlated with the NRTL model[24] for the activity coefficient, with estimation of new interaction parameters.

Table 1. Recent Studies of PEG−Salt ATPS

PEG	salt	ref
(1000, 6000)	sodium phosphate	4
6000	ammonium phosphate	5
4000	potassium phosphate	6
6000	potassium citrate	7
4000	cesium sulfate	8
4000	lithium sulfate	9
6000	sodium citrate	10
8000	magnesium sulfate, sodium sulfate	11
6000	sodium succinate, sodium formate	12
2000	sodium citrate	13
(600, 1000, 1450, 3350, 8000)	sodium citrate	14
2000	potassium citrate	15
4000	sodium sulfate, lithium sulfate, potassium phosphate	16
6000	sodium citrate	17
(1500, 4000)	sodium citrate	18
(600, 1000, 2000, 4000, 6000, 8000)	sodium tartrate	19
10 000	magnesium sulfate	20
4000	disodium tartrate	21
4000	zinc sulfate	22
20 000	copper sulfate	23

2. Experimental Section

The chemicals poly(ethylene glycol) 8000 (supplied by Micro Select, Fluka), magnesium sulfate (P.A. Merck, with mass fraction purity > 0.98), sodium sulfate (P.A. Merck, with mass fraction purity > 0.99), and deionized water were used. The chemicals were used as received, without any purification.

2.1. Experimental Procedure. Aqueous two-phase systems were prepared directly inside the liquid−liquid equilibrium cells, jacketed, made of glass, similar to those designed by Stragevitch[25] and described elsewhere.[6,11] The equilibrium cells were sealed with rubber septa and connected to a thermostatic bath (Tecnal TE-184, ± 0.01 °C). The temperatures were measured with J-type thermocouples (Tholz MDH001N), with precision of ± 0.01 °C.

The components were weighted in an analytical balance (Ohaus AS200, ± 0.0001 g) and placed inside the cells. The systems were submitted to agitation for 3 h after the thermal

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Table 2. LLE Data (in wt %) of ATPS Water + PEG 8000 + Magnesium Sulfate at 25 °C

	overall			top phase			bottom phase		
	PEG	salt	water	PEG	salt	water	PEG	salt	water
1	13.99	7.51	78.50	28.521	2.011	69.468	2.805	12.947	84.248
2	15.00	8.00	76.99	31.233	1.526	67.241	3.057	13.858	83.085
3	15.98	8.49	75.53	33.767	1.310	64.923	3.387	14.899	81.714
4	16.94	9.12	73.94	36.274	1.042	62.684	3.489	16.142	80.369
5	17.98	9.56	72.46	38.137	0.994	60.869	2.588	18.372	79.040
6	18.99	10.05	70.96	40.463	0.704	58.833	3.651	18.691	77.658
7	20.01	10.49	69.51	42.463	0.467	57.070	4.400	19.552	76.048
8	20.98	10.99	68.03	45.026	0.145	54.829	3.561	20.578	75.861
9	22.02	11.51	66.47	47.019	0.064	52.917	3.736	21.959	74.305

Table 3. LLE Data (in wt %) of ATPS Water + PEG 8000 + Magnesium Sulfate at 50 °C

	overall			top phase			bottom phase		
	PEG	salt	water	PEG	salt	water	PEG	salt	water
1	14.00	7.50	78.50	34.293	0.819	64.888	2.592	12.395	85.013
2	14.99	8.00	77.01	36.172	0.526	63.302	2.282	13.276	84.442
3	16.01	8.50	75.48	38.834	0.506	60.660	2.405	14.322	83.273
4	16.99	9.01	74.00	40.738	0.314	58.948	2.613	15.441	81.946
5	18.01	9.48	72.51	43.223	0.210	56.567	2.889	16.601	80.510
6	18.97	10.01	71.01	45.347	0.227	54.426	2.911	17.859	79.230
7	20.03	10.50	69.47	47.216	0.173	52.611	3.035	18.786	78.179
8	21.03	11.02	67.95	48.610	0.243	51.147	3.506	19.607	76.887
9	22.00	11.47	66.54	50.260	0.316	49.424	3.910	20.417	75.673

equilibrium, using magnetic stirrers (Tecnal TE-085), and later rested for 24 h to achieve the complete separation of the equilibrium phases. Preliminary tests showed that these times were enough to guarantee the thermodynamic equilibrium for this kind of system. Once the equilibrium was achieved, samples were collected from both equilibrium phases using glass syringes through the rubber septa that sealed the cells.

2.2. Analytical. The method for the determination of compositions in both equilibrium phases was the same as that described by Snyder et al.[26] and Stewart and Todd,[27] using gravimetric techniques. To determine the water content, the lyofilization (freeze-drying) process was applied, by using a Telstar Lioalfa 6 lyofilizator. In this procedure, the samples were previously weighted, frozen in a mixture of acetone and dry ice, sublimated in the lyofilizator, and weighted again. The difference in mass before and after the lyofilization corresponds to the water content in the sample. After the remotion of the water, we had a solid mixture of polymer and salt, which was submitted to calcination in a muffle oven (Quimis Q-318D) at 450 °C for 5 days; in this procedure, the polymer is burned. The difference in mass before and after the calcination corresponds to the polymer content in the sample. Finally, the mass after the entire process corresponds to the salt content in the sample. This procedure was used in previous works[6,11] with excellent results for polymer−salt aqueous two-phase systems. All experiments were performed in triplicate. The estimated uncertainty for mass fractions is ± 0.0005.

3. Thermodynamic Modeling

In a general way, phase equilibrium is represented by the isofugacity condition, given by

$$f_{\mathrm{i}}^{\alpha} = f_{\mathrm{i}}^{\beta} = \ldots = f_{\mathrm{i}}^{\pi} \tag{1}$$

where α, β, and π are the phases in equilibrium. In liquid−liquid equilibrium, the fugacities are represented by the activity coefficients, γ

$$x_{\mathrm{i}}^{\alpha}\gamma_{\mathrm{i}}^{\alpha} = x_{\mathrm{i}}^{\beta}\gamma_{\mathrm{i}}^{\beta} \tag{2}$$

There are several thermodynamic models to describe the activity coefficient dependence of composition. Some are empirical, as those proposed by Margules and Van Laar; others are based on the local composition concept, such as Wilson[28] and NRTL;[24] other equations, such as UNIQUAC,[29] have a more theoretical basis; and some use the group contribution concept, such as ASOG[30,31] and UNIFAC.[32] In this work, the NRTL (nonrandom, two-liquid) model, which is based on local composition and is applicable to partially miscible systems, was used. In previous works,[6,11,33,34] we used NRTL to represent the phase behavior of electrolyte systems as well as polymer−salt aqueous two-phase systems.

Traditionally, mole fractions are used in NRTL calculations, but for polymeric systems, where high molecular weights are involved, it is more convenient to use mass fractions. Stragevitch,[25] Sé and Aznar,[34] and Lintomen et al.[35] used the NRTL model with mass fractions, given by

$$\ln \gamma_{\mathrm{i}} = \frac{\displaystyle\sum_{\mathrm{j}} \frac{\tau_{\mathrm{ji}} G_{\mathrm{ji}} w_{\mathrm{j}}}{M_{\mathrm{j}}}}{\displaystyle\sum_{\mathrm{j}} \frac{G_{\mathrm{ji}} w_{\mathrm{j}}}{M_{\mathrm{j}}}} + \sum_{\mathrm{j}} \left[\frac{w_{\mathrm{j}} G_{\mathrm{ji}}}{M_{\mathrm{j}} \displaystyle\sum_{\mathrm{k}} \frac{G_{\mathrm{kj}} w_{\mathrm{k}}}{M_{\mathrm{k}}}} \left(\tau_{\mathrm{ij}} - \frac{\displaystyle\sum_{\mathrm{k}} \frac{\tau_{\mathrm{kj}} G_{\mathrm{kj}} w_{k}}{M_{\mathrm{k}}}}{\displaystyle\sum_{\mathrm{k}} \frac{G_{\mathrm{kj}} w_{\mathrm{k}}}{M_{\mathrm{k}}}} \right) \right] \tag{3}$$

where M_{j} and w_{j} are the molar mass and mass fraction of component j, and the quantities τ_{ij} and G_{ij} are given by

$$\tau_{\mathrm{ij}} = \frac{\Delta g_{\mathrm{ij}}}{RT} = \frac{A_{\mathrm{ij}}}{T} \tag{4}$$

$$G_{\mathrm{ij}} = \exp(-\alpha_{\mathrm{ij}}\tau_{\mathrm{ij}}) \tag{5}$$

This model has three adjustable parameters for each binary pair (Δg_{ij}, Δg_{ji}, and α_{ij}). The parameters Δg_{ij} and Δg_{ji} are related to the characteristic energy of interaction between the molecules of type i and j, while the parameter α_{ij} is related to the nonrandomness of the mixture. These parameters can be estimated from experimental data by minimizing an objective function through a suitable minimization procedure.

In this work, the estimation was performed using the Fortran code WTML-LLE,[25,36] and the procedure is based on the Simplex method[37] and consists of the minimization of a concentration-based objective function, S[38]

$$S = \sum_{\mathrm{k}}^{D} \sum_{\mathrm{j}}^{N\mathrm{k}} \left\{ \left(\frac{T_{\mathrm{jk}} - T_{\mathrm{jk}}^{\mathrm{m}}}{\sigma_{T\mathrm{jk}}} \right)^2 + \sum_{\mathrm{i}}^{C\mathrm{k}-1} \left[\left(\frac{w_{\mathrm{ijk}}^{\alpha} - w_{\mathrm{ijk}}^{\alpha,\mathrm{m}}}{\sigma_{w\mathrm{ijk}^{\alpha}}} \right)^2 + \left(\frac{w_{\mathrm{ijk}}^{\beta} - w_{\mathrm{ijk}}^{\beta,\mathrm{m}}}{\sigma_{w\mathrm{ijk}^{\beta}}} \right)^2 \right] \right\} \tag{6}$$

Here, D is the number of data sets; N_{k} and C_{k} are the number of tie-lines and components in each data set k; $\sigma_{T\mathrm{jk}}$, $\sigma_{w\mathrm{ijk}}{}^{\alpha}$, and $\sigma_{w\mathrm{ijk}}{}^{\beta}$ are the standard deviations observed in the independent variables temperature, composition of phase α, and composition of phase β; and the superscript m stands for measured.

With the parameters estimated by the procedure above, comparisons between the experimental and calculated composition of each component of two phases were made through root-mean-square (rms) deviation, given by

$$\Delta w = 100\sqrt{\frac{\sum_{i}\{(w_i^{\alpha} - w_i^{\alpha,m})^2 + (w_i^{\beta} - w_i^{\beta,m})^2\}}{2N_k C_k}} \qquad (7)$$

4. Results and Discussion

The experimental liquid−liquid equilibrium data obtained for (water + PEG 8000 + magnesium sulfate) and (water + PEG 8000 + sodium sulfate) at temperatures of (25 and 50) °C are shown in Tables 2 to 5 as a function of the mass fractions. These data were used to estimate the NRTL binary interaction parameters shown in Table 6. The rms deviations between experimental and calculated compositions, according to eq 7, are shown in Table 7.

From these results, the excellent performance of the NRTL model in the correlation of the data, with a global mean deviation of 1.3 %, can be observed. The experimental and calculated equilibrium data are shown in Figures 1 to 4. For the systems including magnesium sulfate (Figures 1 and 2), the model represents better the polymeric phase, while for the systems including sodium sulfate (Figures 3 and 4), the model represents better the saline phase. This can be due to the greater solvation of the magnesium cation, which captures more water and makes the behavior of the saline phase more complicated. On the other hand, the lesser solvation of the sodium cation makes the behavior of the saline phase simpler, since more water is available.

Table 4. LLE Data (in wt %) of ATPS Water + PEG 8000 + Sodium Sulfate at 25 °C

	overall			top phase			bottom phase		
	PEG	salt	water	PEG	salt	water	PEG	salt	water
1	14.02	7.51	78.48	28.623	2.486	68.891	0.420	11.937	87.643
2	15.00	8.03	76.98	31.467	2.176	66.357	0.422	13.253	86.325
3	16.01	8.51	75.49	33.826	1.948	64.226	0.260	14.360	85.380
4	17.00	9.01	73.99	35.872	1.775	62.353	0.156	15.169	84.675
5	18.02	9.49	72.49	37.882	1.560	60.558	0.190	16.300	83.510
6	19.00	10.01	70.99	39.862	1.278	58.860	0.130	17.810	82.060
7	20.04	10.51	69.45	41.818	1.153	57.029	0.229	18.776	80.995
8	21.07	11.06	67.88	43.693	0.945	55.362	0.343	20.202	79.455
9	22.03	11.52	66.45	45.075	0.893	54.032	0.303	21.352	78.345

Table 5. LLE Data (in wt %) of ATPS Water + PEG 8000 + Sodium Sulfate at 50°C

	overall			top phase			bottom phase		
	PEG	salt	water	PEG	salt	water	PEG	salt	water
1	14.00	7.51	78.49	35.490	1.790	62.720	0.080	11.450	88.470
2	15.00	8.00	77.00	37.830	1.540	60.630	0.090	12.340	87.570
3	15.99	8.51	75.49	40.068	1.375	58.557	0.070	13.480	86.450
4	17.01	9.02	73.97	42.230	1.350	56.420	0.164	14.516	85.320
5	18.01	9.50	72.49	43.921	1.168	54.911	0.184	15.519	84.297
6	19.00	10.01	70.99	45.856	0.946	53.198	0.159	16.657	83.184
7	20.00	10.51	69.50	47.826	0.789	51.385	0.169	17.649	82.182
8	21.01	11.01	67.98	49.486	0.756	49.758	0.247	18.569	81.184
9	22.02	11.50	66.48	50.954	0.548	48.498	0.265	19.526	80.209

Table 6. Estimated NRTL Parameters

i−j	A_{ij} (K)	A_{ji} (K)	α_{ij}
PEG 8000−$MgSO_4$	7.8027	6071.4	0.216
PEG 8000−Na_2SO_4	3076.8	3354.4	0.200
PEG 8000−H_2O	−2514.8	6695.3	0.449
$MgSO_4$−H_2O	−2250.2	4083.3	0.166
Na_2SO_4−H_2O	−1054.3	1236.0	0.377

Table 7. Mean Deviations in Composition

System	Δw (%)
PEG 8000 + $MgSO_4$ + H_2O (25 °C)	1.86
PEG 8000 + $MgSO_4$ + H_2O (50 °C)	1.58
PEG 8000 + Na_2SO_4 + H_2O (25 °C)	0.60
PEG 8000 + Na_2SO_4 + H_2O (50 °C)	0.62
global mean deviation	1.30

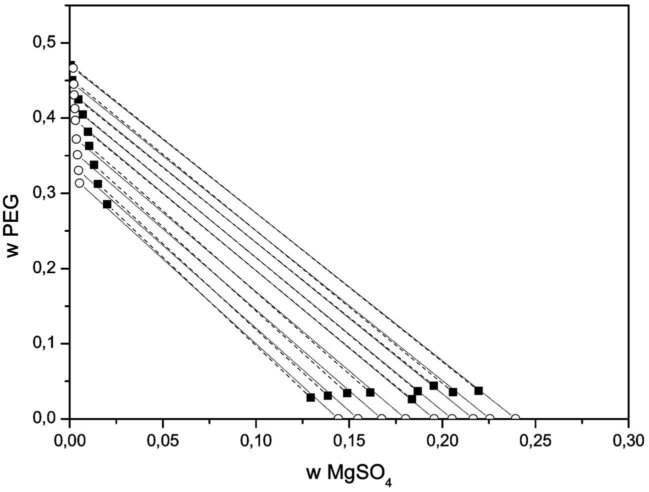

Figure 1. LLE of ATPS water + PEG 8000 + magnesium sulfate at 25 °C (mass fraction). ■, experimental data points; ◇, NRTL calculated data points. Straight lines are tie-lines connecting the equilibrium compositions.

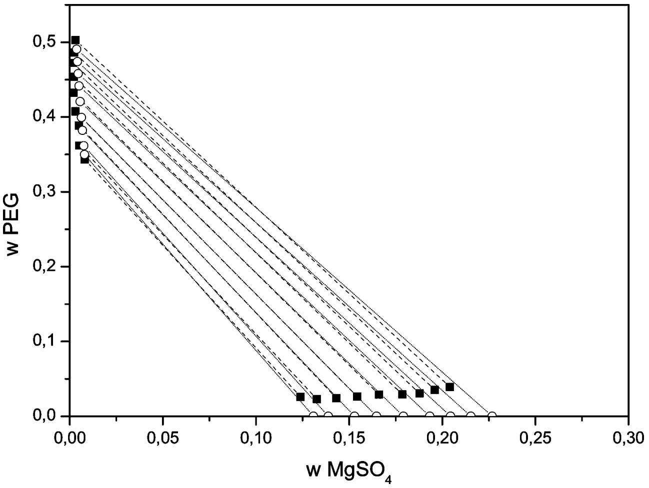

Figure 2. LLE of ATPS water + PEG 8000 + magnesium sulfate at 50 °C (mass fraction). ■, experimental data points; ◇, NRTL calculated data points. Straight lines are tie-lines connecting the equilibrium compositions.

The effect of temperature on LLE is shown in Figures 5 and 6, where the data have been plotted in ternary diagrams at two temperatures. From these figures, it can be concluded that the effect of temperature is very small.

5. Conclusion

Experimental liquid−liquid equilibrium data for the aqueous two-phase (water + PEG 8000 + sodium sulfate) and (water + PEG 8000 + magnesium sulfate) were determined at temperatures of (25 and 50) °C by using a gravimetric technique including lyofilization and calcination steps. Both systems produce a large two-phase region, adequate to be used as separation media for biomolecule purification. The effect of temperature on the liquid−liquid equilibrium seems to be very small.

The data were correlated with the NRTL model for the activity coefficient, with estimation of new interaction param-

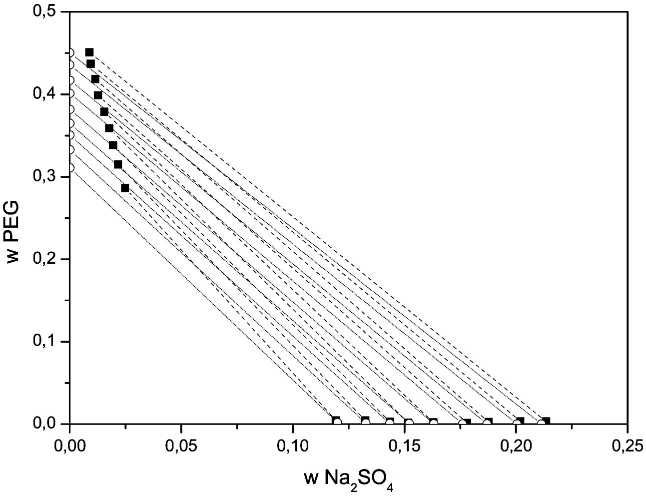

Figure 3. LLE of ATPS water + PEG 8000 + sodium sulfate at 25 °C (mass fraction). ■, experimental data points; ◇, NRTL calculated data points. Straight lines are tie-lines connecting the equilibrium compositions.

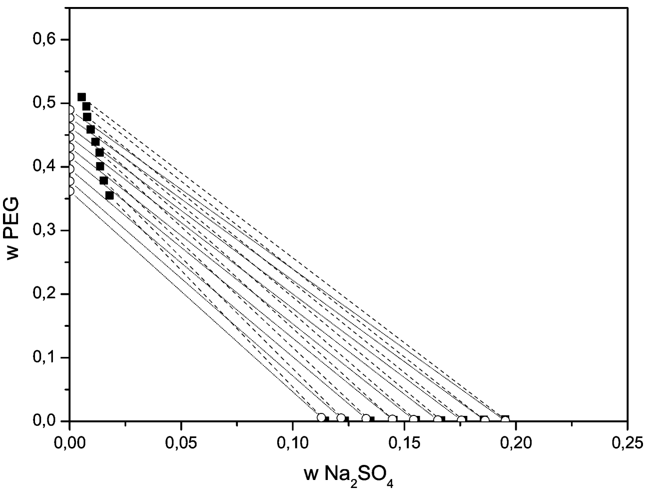

Figure 4. LLE of ATPS water + PEG 8000 + sodium sulfate at 50 °C (mass fraction). ■, experimental data points; ◇, NRTL calculated data points. Straight lines are tie-lines connecting the equilibrium compositions.

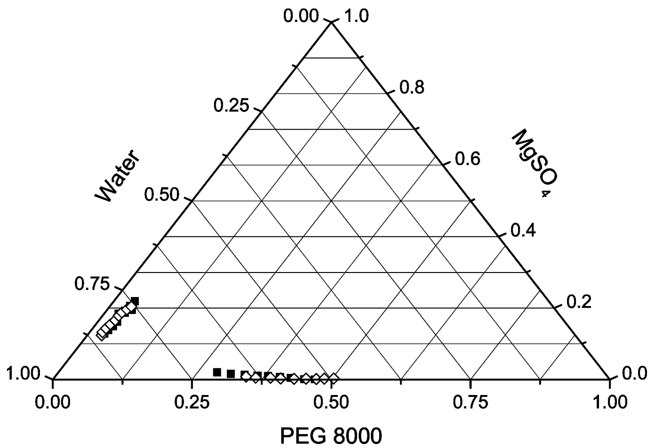

Figure 5. Effect of temperature on LLE of ATPS water + PEG 8000 + magnesium sulfate (mass fraction). ■, 25 °C; ◇, 50 °C.

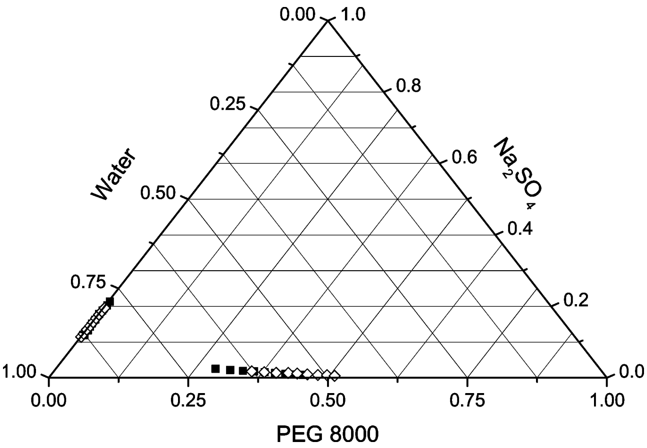

Figure 6. Effect of temperature on LLE of ATPS water + PEG 8000 + sodium sulfate (mass fraction). ■, 25 °C; ◇, 50 °C.

eters. The model was able to correlate the data with good precision, yielding a global mean deviation of 1.3 % between experimental and calculated equilibrium compositions. For the systems including magnesium, the model correlates better the saline phase, while for the systems containing sodium, the model correlates better the polymeric phase. This effect can be due to the greater solvation of magnesium compared to sodium, which makes the behavior of the saline phase more complicated.

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