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Liquid−Liquid Equilibrium of the Aqueous Two-Phase System Water + PEG 4000 + Potassium Phosphate at Four Temperatures: Experimental Determination and Thermodynamic Modeling

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The effect of temperature on the liquid−liquid equilibrium for the aqueous two-phase system water + poly(ethylene glycol) 4000 + potassium phosphate was studied by determining 29 tie lines at 10 °C, 14 tie lines at 15 °C, 23 tie lines at 20 °C, and 15 tie lines at 30 °C, to give a total of 81 tie lines at four different temperatures. The results show a transition of miscibility: at 10 °C, the pair water + salt is completely miscible and the pair PEG + water is partially miscible, while, at higher temperatures, the pair water + salt becomes partially miscible and the pair PEG + water becomes completely miscible. Experimental results were correlated with a mass fraction-based NRTL activity coefficient model. New interaction parameters were estimated with the Simplex method and the maximum likelihood principle. The mean deviations between the experimental and calculated compositions in both equilibrium phases are below 1.7%.

Introduction

When two different polymers [e.g. dextran and poly(ethylene glycol), PEG] or one polymer and one salt (e.g. PEG and sodium sulfate) 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. This statement, made by Albertsson[1] in the mid-1950s, is the basis for separation processes using aqueous two-phase systems. Liquid−liquid extraction using aqueous two-phase systems is widely recognized today as a highly efficient separation technique,[2] particularly in partitioning and purification of biomolecules, since these systems form a gentle environment for enzymes and other biologically active proteins. This extraction technology offers the advantages of high capacity, high activity yields, and ease of scale-up.

Reliable data on the composition and properties of aqueous two-phase systems are necessary for the design of extraction processes and for the development of both thermodynamics and mass transfer models. Phase diagrams have been reported for a large number of polymer−polymer systems;[1,2] however, experimental data for aqueous polymer−salt mixtures are still relatively scarce. Lei et al.[3] reported liquid−liquid equilibrium data for the systems PEG 400, PEG 600, PEG 1000, PEG 1500, PEG 3400, PEG 8000, and PEG 20000, with potassium phosphate at 4 °C; Gao et al.[4] determined experimental data for systems containing ammonium sulfate and PEG 1000, PEG 1540, PEG 2000, and PEG 4000; Snyder et al.[5] studied systems containing PEG 1000, PEG 3350, and PEG 8000 and magnesium sulfate, sodium sulfate, sodium carbonate, and potassium phosphate as salts at 25 °C; Voros et al.[6] used PEG 1000 and PEG 2000 with ammonium sulfate and sodium carbonate at 15, 25, 35, and 45 °C; Hammer et al.[7] analyzed systems with PEG 1550, PEG 3000, and PEG 6000, using sodium sulfate at 20, 30, and 40 °C; Peng et al.[8] reported data for systems composed by PEG 1000, PEG 2000, PEG 4000, and PEG 6000 with a mixture of potassium hydrogen phosphate and potassium dihydrogen phosphate at 25 °C; Mishima et al.[9] measured liquid−liquid equilibrium for systems containing PEG 7500 and potassium phosphate at 15, 30, and 40 °C; Silva et al.[10] studied the phase behavior of systems containing PEG 1000 and PEG 8000 at 4, 25, and 40 °C and pH 6, 7, and 9; Mishima et al.[11] published data for systems containing PEG 4000 and PEG 20000 with potassium phosphate at 25 °C. In this work, the effect of temperature on the liquid−liquid equilibrium for the aqueous two-phase system water + PEG 4000 + potassium phosphate was studied by determining 81 experimental tie lines at 10, 15, 20, and 30 °C.

Experimental Section

PEG, with a mass average 4000, and potassium hydrogen phosphate were of analytical grade (Merck) and were used without further purification. Experiments were carried out in equilibrium cells, similar to those suggested by Stragevitch[12] and described elsewhere.[13,14] The cell temperature was regulated by a controlled thermostatic bath (Tecnal TE-184, accurate to ±0.01 °C). The overall mixture was prepared directly inside the cell, and the components were weighed on an analytical balance (Ohaus AS200, accurate to ±0.0001 g). The mixture was vigorously agitated with a magnetic stirrer (Tecnal TE-085) for 3 h, to allow an intimate contact between the phases, and the equilibrium was achieved by letting the mixture rest for 12 h. Preliminary tests[15] showed that these times are enough to achieve the equilibrium. The system separated into two liquid phases, that become clear and transparent, with a well-defined interface. Separate samples of both phases were collected and analyzed. Water was determined by gravimetric analysis, using the same analytical balance (Ohaus AS200, accurate to ±0.0001 g), while potassium

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Table 1. Experimental Weight Fractions (*w*) for the Liquid−Liquid Equilibrium of the System Water + PEG 4000 + Potassium Phosphate

overall (100*w*)			top phase (100*w*)			bottom phase (100*w*)			overall (100*w*)			top phase (100*w*)			bottom phase (100*w*)		
PEG	salt	water	PEG	salt	water	PEG	salt	water	PEG	salt	water	PEG	salt	water	PEG	salt	water
10 °C																	
8.09	12.71	79.20	14.06	3.87	82.07	2.11	21.55	76.34	17.90	11.81	70.29	31.22	1.56	67.22	4.59	22.06	73.35
9.95	12.22	77.83	17.12	2.96	79.92	2.78	21.48	75.74	18.40	11.95	69.65	31.81	1.88	66.31	5.00	22.02	72.98
10.67	12.20	77.13	18.37	2.86	78.77	2.97	21.53	75.50	21.73	11.89	66.38	37.58	1.52	60.90	5.88	22.26	71.86
11.71	12.15	76.14	20.17	2.71	77.12	3.24	21.59	75.17	22.20	11.88	65.92	38.40	1.47	60.13	6.00	22.29	71.71
11.98	12.14	75.88	20.65	2.67	76.68	3.31	21.60	75.09	24.33	11.87	63.80	42.09	1.27	56.64	6.58	22.46	70.96
12.15	12.14	75.71	20.95	2.65	76.40	3.36	21.62	75.02	25.09	11.86	63.05	43.39	1.20	55.41	6.79	22.52	70.69
12.40	12.12	75.48	21.37	2.62	76.01	3.42	21.63	74.95	28.18	11.86	59.96	48.69	0.94	50.37	7.67	22.78	69.55
12.42	12.12	75.46	21.41	2.62	75.97	3.43	21.63	74.94	28.33	11.90	59.77	48.96	1.00	50.04	7.71	22.80	69.49
12.67	12.11	75.22	21.85	2.58	75.57	3.49	21.65	74.86	28.50	11.81	59.69	49.53	0.84	49.63	7.47	22.78	69.75
12.70	12.11	75.19	21.90	2.58	75.52	3.50	21.65	74.85	30.40	11.88	57.72	52.48	0.77	46.75	8.32	22.99	68.69
13.55	12.58	73.87	23.37	3.47	73.16	3.72	21.70	74.58	35.63	12.01	52.36	61.25	0.45	38.30	10.00	23.57	66.43
13.57	12.08	74.35	23.41	2.46	74.13	3.73	21.70	74.57	36.78	12.05	51.17	63.16	0.39	36.45	10.40	23.71	65.89
14.10	12.07	73.83	24.33	2.40	73.27	3.87	21.74	74.39	40.39	12.23	47.38	69.00	0.24	30.76	11.77	24.23	64.00
15.08	12.03	72.89	26.03	2.27	71.70	4.12	21.80	74.08	43.25	12.81	43.94	73.98	0.13	25.89	12.51	25.49	62.00
17.46	11.97	70.57	30.17	1.98	67.85	4.75	21.95	73.30									
15 °C																	
9.04	9.59	81.37	17.24	4.00	78.76	0.83	15.18	83.99	13.92	11.00	75.08	27.21	2.99	69.80	0.63	19.01	80.36
9.68	9.82	80.50	18.87	3.87	77.26	0.48	15.78	83.74	14.27	11.11	74.62	27.92	2.94	69.14	0.62	19.28	80.10
10.57	10.25	79.18	20.68	3.59	75.73	0.46	16.92	82.62	15.42	11.48	73.10	30.24	2.78	66.98	0.61	20.17	79.22
12.54	10.58	76.88	24.41	3.22	72.37	0.66	17.95	81.39	19.57	13.25	67.18	38.65	2.45	58.90	0.49	24.05	75.46
12.67	10.63	76.70	24.69	3.20	72.11	0.65	18.06	81.29	20.80	13.68	65.52	41.08	2.24	56.68	0.52	25.11	74.37
12.87	10.68	76.45	25.09	3.16	71.75	0.65	18.21	81.14	20.98	13.26	65.76	41.28	2.27	56.45	0.68	24.26	75.06
13.76	10.95	75.29	26.88	3.01	70.11	0.63	18.89	80.48	24.70	15.02	60.28	48.41	2.11	49.48	0.99	27.93	71.08
20 °C																	
9.34	9.25	81.41	18.55	3.70	77.75	0.13	14.80	85.07	13.86	12.26	73.85	27.70	2.76	69.48	0.02	21.76	78.22
9.55	9.82	80.63	18.87	3.87	77.26	0.23	15.78	83.99	15.68	13.36	70.96	31.28	2.47	66.25	0.08	24.26	75.66
10.41	10.25	79.34	20.68	3.59	75.73	0.13	16.92	82.95	16.09	14.30	69.61	31.78	2.45	65.77	0.41	26.15	73.44
10.90	10.51	78.59	21.69	3.44	74.87	0.10	17.58	82.32	16.13	13.65	70.22	32.16	2.41	65.43	0.10	24.90	75.00
11.73	10.97	77.30	23.39	3.22	73.39	0.06	18.72	81.22	17.60	14.59	67.81	35.01	2.24	62.75	0.19	26.94	72.87
11.83	11.03	77.14	23.60	3.20	73.20	0.06	18.86	81.08	18.52	15.26	66.22	37.03	2.14	60.83	0.01	28.38	71.61
11.98	11.11	76.91	23.90	3.16	72.94	0.05	19.07	80.88	19.99	16.21	63.80	39.86	2.01	58.13	0.12	30.41	69.47
12.55	12.27	75.18	25.02	2.98	72.00	0.08	21.56	78.36	20.19	16.37	63.44	40.34	1.99	57.67	0.05	30.75	69.20
12.90	11.62	75.48	25.30	2.86	71.84	0.50	20.37	79.13	20.80	17.25	61.95	41.06	2.10	56.84	0.54	32.40	67.06
12.82	11.50	75.85	25.60	3.01	71.73	0.03	20.00	79.97	22.93	18.73	58.34	45.63	1.98	52.39	0.24	35.47	64.29
13.04	11.73	75.23	26.04	2.93	71.03	0.03	20.54	79.43	24.12	19.55	56.33	48.11	1.93	49.96	0.12	37.17	62.71
13.44	12.19	74.37	26.85	3.03	70.12	0.03	21.35	78.62									
30 °C																	
11.69	10.20	78.11	21.81	4.45	73.74	1.58	15.95	82.47	17.58	11.66	70.76	34.51	3.01	62.48	0.65	20.32	79.03
12.56	9.91	77.53	23.71	4.01	72.28	1.42	15.81	82.77	18.11	11.97	69.92	35.62	2.64	61.74	0.61	21.30	78.09
12.71	10.41	76.88	24.15	3.96	71.89	1.27	16.87	81.86	19.71	12.63	67.66	38.90	2.69	58.41	0.52	22.58	76.90
13.07	10.45	76.48	24.97	3.69	71.34	1.17	17.22	81.61	21.35	13.10	65.55	42.24	2.30	55.53	0.47	23.91	75.62
13.33	10.52	76.15	25.65	3.56	70.79	1.01	17.48	81.51	21.88	13.39	64.73	43.33	2.43	54.24	0.43	24.36	75.21
15.85	11.39	72.76	30.91	3.30	65.79	0.79	19.48	79.73	22.13	13.33	64.54	43.83	2.11	54.06	0.43	24.55	75.02
16.06	11.12	72.82	31.37	2.95	65.68	0.76	19.28	79.96	22.54	13.62	63.84	44.68	2.34	52.98	0.41	24.90	74.69
16.16	11.31	72.53	31.66	2.84	65.50	0.67	19.78	79.55									

phosphate was determined by titration with potassium hydroxide,[16] using a pH meter (Quimis Q-400A, accurate to ±0.01). Having determined the potassium phosphate and water concentrations, the PEG content is given by the difference. All experiments were performed in triplicate.

Experimental Results and Discussion

The experimental liquid−liquid equilibrium data for the ternary aqueous two-phase system water + PEG 4000 + potassium phosphate at 10, 15, 20, and 30 °C are shown in Table 1 as mass fractions. There were determined 29 tie lines at 10 °C, 14 tie lines at 15 °C, 23 tie lines at 20 °C, and 15 tie lines at 30 °C, to give a total of 81 tie lines at four different temperatures. The same data appear in Figures 1−4.

It can be seen from Figures 1−4 that the experimental data determined at 15, 20, and 30 °C are practically in the same region. However, the data collected at 10 °C are in a different region. It can be concluded that, for this system, there is a decrease in the mutual solubility as the temperature increases. Moreover, the shape of the binodal curve

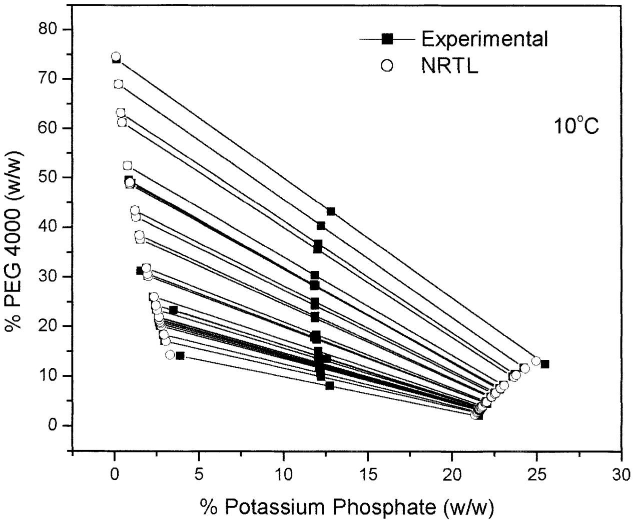


Figure 1. Experimental and calculated liquid−liquid equilibrium for the system water + PEG 4000 + potassium phosphate at 10 °C.

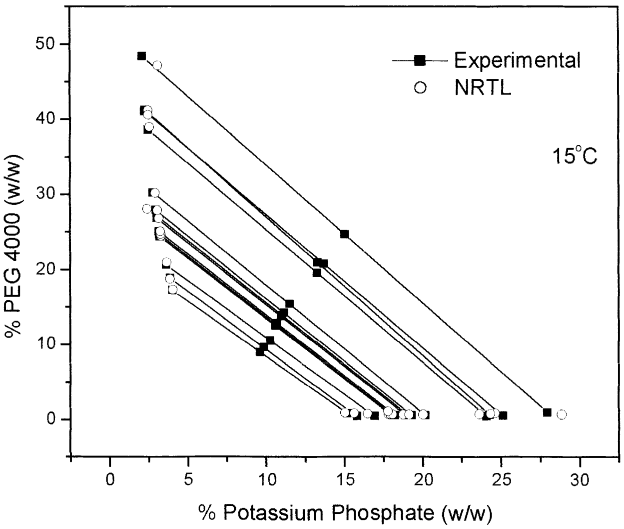


Figure 2. Experimental and calculated liquid−liquid equilibrium for the system water + PEG 4000 + potassium phosphate at 15 °C.

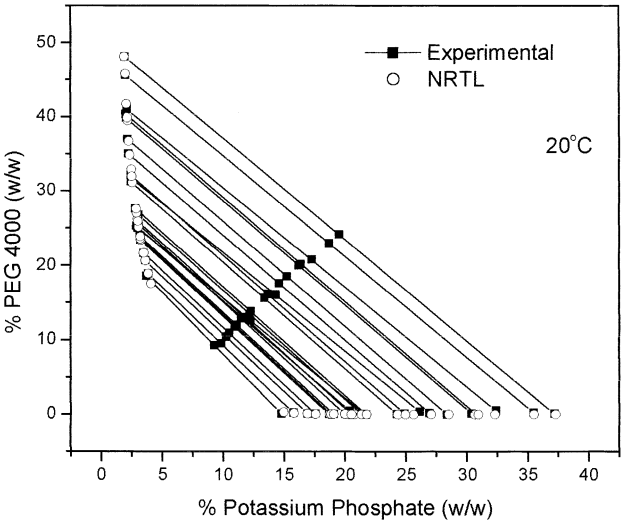


Figure 3. Experimental and calculated liquid−liquid equilibrium for the system water + PEG 4000 + potassium phosphate at 20 °C.

is also modified from 10 °C to 15, 20, and 30 °C. This can be interpreted as a transition of miscibility: at 10 °C, the pair water + salt is completely miscible and the pair PEG + water is partially miscible, while, at 15, 20, and 30 °C, the pair water + salt becomes partially miscible and the pair PEG + water becomes completely miscible (just at extremely small concentrations of salt). This transition is better shown in ternary diagrams, as in Figure 5.

Thermodynamic Model

The concept of the local composition, introduced by Wilson,[17] basically establishes that the composition of the system in the neighborhood of a given molecule is not the same as the "bulk" composition, because of the intermolecular forces. The activity coefficient model NRTL[18] (*non-random, two-liquid*) is based on the local composition concept, and it is applicable for partially miscible systems. Chen et al.[19,20] extended the original NRTL model to electrolyte systems containing small molecules, while Wu et al.[21] proposed a modified NRTL model for a multicomponent salt system, successfully applied to polymer−polymer and polymer−salt ATPSs. In this work, the original NRTL model has been used to describe the LLE of the PEG 4000 + potassium phosphate ATPS. Previous works[22−24] have shown that this model is able to represent electrolyte systems.

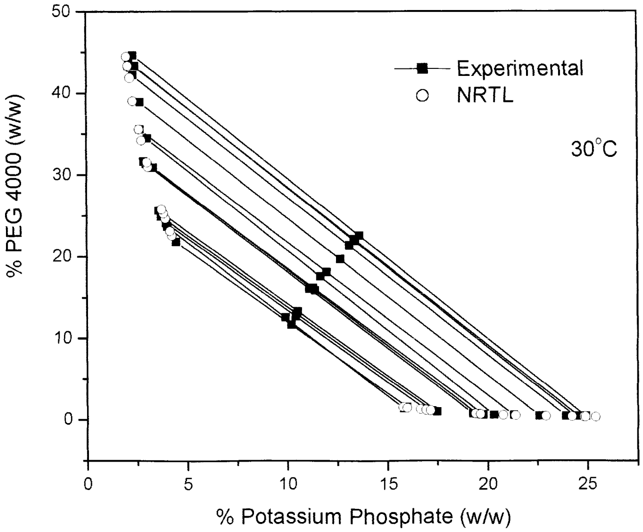


Figure 4. Experimental and calculated liquid−liquid equilibrium for the system water + PEG 4000 + potassium phosphate at 30 °C.

Mole fractions are traditionally used in this model, but they are not suitable for polymeric systems, because the mole fraction of a polymer, due to its large molecular mass, is an extremely small quantity. Instead, mass fraction can be used, as originally proposed by Oishi and Prausnitz[25] for the calculation of the activity coefficient of a solvent in polymeric solutions with the UNIQUAC and the UNIFAC methods. Stragevitch,[12] Sé and Aznar,[24] Velezmoro-Sánchez,[26] Batista et al.,[27] and Lintomen et al.[28] used this approach with the NRTL model. When mass fractions are used, the model is

$$\ln \gamma_i = \frac{\sum_j \frac{\tau_{ji}G_{ji}w_j}{M_j}}{\sum_j \frac{G_{ji}w_j}{M_j}} + \sum_j \left[\frac{w_j G_{ji}}{M_j \sum_k \frac{G_{kj}w_k}{M_k}} \left(\tau_{ij} - \frac{\sum_k \frac{\tau_{kj}G_{kj}w_k}{M_k}}{\sum_k \frac{G_{kj}w_k}{M_k}} \right) \right] \tag{1}$$

where

$$\tau_{ij} = \frac{A_{ij}}{T} \tag{2}$$

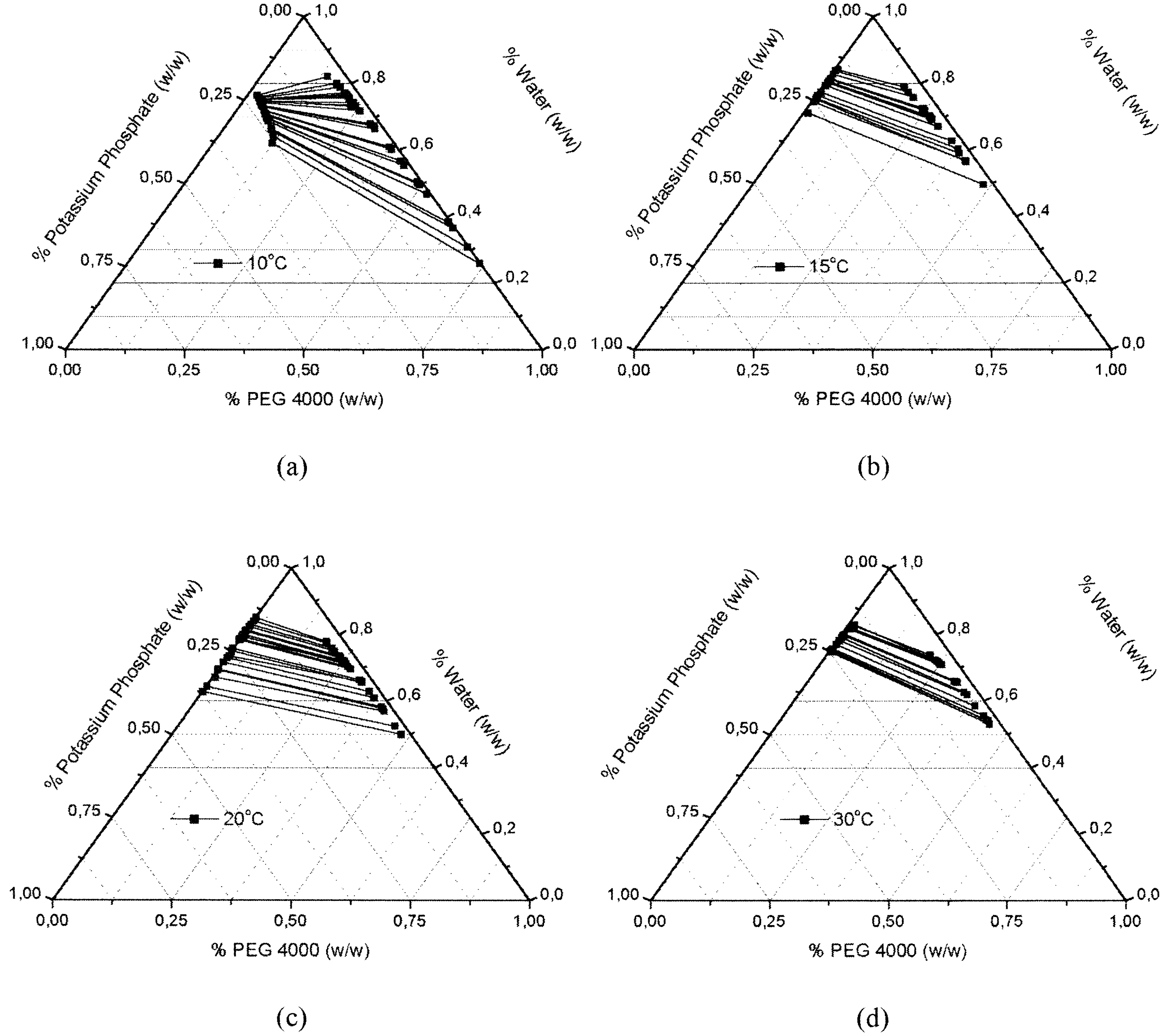
$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{3}$$

where A_{ij} and A_{ji} are characteristic parameters of the energy of the interactions $i-j$, and the parameters α_{ij} are related with the nonrandomness of the mixture. That means that the components are distributed through a pattern dictated by the local composition.

Parameter Estimation

The experimental liquid−liquid equilibrium data were used to estimate the molecular interaction and the nonrandomness parameters of the NRTL model.

The estimation was performed using the Fortran code TML-LLE 2.0;[12] the procedure is based on the Simplex method[29] and maximum likelihood principle,[30−32] and



(a) (b)

(c) (d)

Figure 5. Ternary representation of experimental liquid−liquid equilibrium for the system water + PEG 4000 + potassium phosphate at 10, 15, 20, and 30 °C.

consists of the minimization of the objective function, S.

$$S = \sum_{k}^{D}\sum_{j}^{N_k}\left\{\left(\frac{T_{jk}^{\mathrm{calc}} - T_{jk}^{\mathrm{exp}}}{\sigma_{T_{jk}}}\right)^2 + \sum_{i}^{C_k-1}\left[\left(\frac{w_{ijk}^{\mathrm{I,calc}} - w_{ijk}^{\mathrm{I,exp}}}{\sigma_{w_{ijk}^{\mathrm{I}}}}\right)^2 + \left(\frac{w_{ijk}^{\mathrm{II,calc}} - w_{ijk}^{\mathrm{II,exp}}}{\sigma_{w_{ijk}^{\mathrm{II}}}}\right)^2\right]\right\} \tag{4}$$

Here, D is the number of data sets, N_k and C_k are the number of data points and components in the data set k, $\sigma_{T_{jk}}$ (set equal to 0.1 K) is the standard deviation in temperature, while $\sigma_{w_{ijk}^{\mathrm{I}}}$ and $\sigma_{w_{ijk}^{\mathrm{II}}}$ (set equal to 0.0005) are the standard deviations in the composition of both liquid phases at equilibrium.

The molecular energy interaction parameters estimated by this procedure are shown in Table 2; with these parameters, the experimental liquid−liquid equilibrium data can be correlated. Comparisons between experimental and calculated data can be made through mean deviations between experimental and calculated compositions of each component in both phases. These mean deviations are given by

Table 2. Estimated NRTL Parameters

i−j	A_{ij}	A_{ji}	α_{ij}
PEG 4000/water	−3001.2	5527.8	0.200
PEG 4000/K_2HPO_4	1723.9	−3074.7	0.313
K_2HPO_4/water	−944.31	1194.7	0.470

$$\Delta w = 100\sqrt{\frac{\sum_{n}^{N_k}\sum_{i}^{C_k}(w_{ni}^{\mathrm{I,exp}} - w_{ni}^{\mathrm{I,calc}})^2 + (w_{ni}^{\mathrm{II,exp}} - w_{ni}^{\mathrm{II,calc}})^2}{2N_kC_k}} \tag{5}$$

The results of the correlation, shown in Table 3 and Figures 1-4, are very satisfactory. The mean deviations are below 1.7%, and there is a close agreement between experimental and calculated liquid−liquid equilibrium points.

Table 3. Mean Deviations in Liquid−Liquid Equilibrium Data

system	no. of tie lines	mean deviation, Δw
water + PEG 4000 + K_2HPO_4 at 10 °C	29	0.14
water + PEG 4000 + K_2HPO_4 at 15 °C	14	1.66
water + PEG 4000 + K_2HPO_4 at 20 °C	23	0.44
water + PEG 4000 + K_2HPO_4 at 30 °C	15	0.37

Conclusion

Experimental liquid−liquid equilibrium data for the ternary aqueous two-phase system water + PEG 4000 + potassium phosphate were determined (29 tie lines at 10 °C, 14 tie lines at 15 °C, 23 tie lines at 20 °C, and 15 tie lines at 30 °C), performing a total of 81 tie lines at four different temperatures. As the size of the two-phase region increases, it is concluded that the mutual solubility of the system decreases with the increase of temperature. Also, it seems to be a transition of miscibility between the temperatures 10 and 15 °C.

These experimental liquid−liquid equilibrium data were correlated by a mass fraction NRTL activity coefficient model. Interaction parameters were estimated using the Simplex method and the maximum likelihood principle. The results from the correlation are very satisfactory, as the mean deviations between experimental and calculated liquid compositions of both phases in equilibrium are below 1.7%.

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