THERMODYNAMIC MODELLING OF PHASE EQUILIBRIUM FOR WATER + POLY(ETHYLENE GLYCOL) + SALT AQUEOUS TWO-PHASE SYSTEMS

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Abstract - The NRTL (nonrandom, two-liquid) model, expressed in mass fraction instead of mole fraction, was used to correlate liquid-liquid equilibria for aqueous two-phase polymer-salt solutions. New interaction energy parameters for this model were determined using reported data on the water + poly(ethylene glycol) + salt systems, with different molecular masses for PEG and the salts potassium phosphate, sodium sulfate, sodium carbonate and magnesium sulfate. The correlation of liquid-liquid equilibrium is quite satisfactory.
Keywords: aqueous two-phase systems, liquid-liquid equilibrium, polymers, salts, NRTL model.

INTRODUCTION

The importance of liquid-liquid extraction to biochemical engineering has been increasing as a result of the development of aqueous two-phase systems for purification and isolation of macromolecules, such as proteins or antibiotics. This process costs less than the traditional biomolecule separations due to use of traditional extraction equipment and the small number of stages. According to Kula (1990), aqueous two-phase systems are formed spontaneously when two hydrophilic components are mixed in a solution and a specific concentration is exceeded. Aqueous two-phase systems consist in two polymers [e.g., poly(ethylene glycol) and dextran] or one polymer and one lyotropic salt [poly(ethylene glycol) and phosphates, citrates or sulfates] in water. It is possible to have an extremely selective separation of substances using aqueous two-phase systems; they provide a gentle and protective environment for

biological material, since both phases are composed primarily of water (Albertsson, 1986). Aqueous two-phase systems of the polymer-salt type have several advantages over the polymer-polymer type: the larger relative size of the drops, larger differences in density, greater selectivity, lower viscosity and lower cost; besides, it is more difficult to use systems with two polymers on an industrial scale due to high viscosity and high cost (Franco et al., 1996). However, the thermodynamic behavior of polymer-salt systems is more complicated, due to the size differences between the smaller molecules and the polymer. Several models for the activity coefficient have been proposed, including the combinatorial and free volume effects in one term. In this work, the NRTL (nonrandom, two-liquid) model was used to correlate the liquid-liquid equilibria for aqueous two-phase polymer-salt solutions, expressed in mass fraction instead of mole fraction. New interaction energy parameters for this model were determined using reported data on the water + poly(ethylene

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glycol) + salt systems, with different molecular masses for PEG and the salts potassium phosphate, sodium sulfate, sodium carbonate and magnesium sulfate

THERMODYNAMIC MODEL

There are several models for calculation of activity coefficients. Some, such as those by Margules and Van Laar, are empirical; others, such as Wilson (1964) and NRTL (Renon and Prausnitz, 1968), use the local composition concept; still others, such as UNIQUAC (Abrams and Prausnitz, 1976), have a more theoretical basis; and finally, some, such as ASOG (Derr and Deal, 1969; Kojima and Tochigi, 1979) and UNIFAC (Fredenslund et al., 1975, 1977), use the group contribution method.

The concept of local composition 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 intermolecular forces.

The NRTL (nonrandom, two-liquid) model it is based on the local composition, and it is applicable to partially miscible systems. Mole fractions have been traditionally used in this model, but they are not suitable for polymeric systems because the mole fraction of a polymer, due its large molecular mass, is an extremely small quantity. Instead, mass fraction can be used, as originally proposed by Oishi and Prausnitz (1978), for calculation of the activity coefficient of a solvent in polymeric solutions with the UNIQUAC and the UNIFAC methods. Stragevitch (1997), Velezmoro-Sánchez (1999), Batista et al. (1999), Lintomen (1999) and Lintomen et al. (2000) used this approach with the NRTL model. When mass fractions are used, the model is

$$\ln \gamma_i = \frac{\sum_j \frac{\tau_{ji} G_{ji} w_j}{M_j}}{\sum_j \frac{G_{ji} w_j}{M_j}} + $$

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

where

$$\tau_{ij} = \frac{A_{0ij} + A_{1ij} T}{T} \qquad (2)$$

$$G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right) \qquad (3)$$

where A_{0ij} and A_{1ij} are characteristic parameters of the energy of the i-j interactions, and parameter α_{ij} is related to the nonrandomness of the mixture. This means that the components are distributed in a pattern dictated by the local composition. When the number of points is small or the data are all at the same temperature, there is not enough information and eqn. (2) must be reduced to its original form (Renon and Prausnitz, 1968):

$$\tau_{ij} = \frac{A_{0ij}}{T} \qquad (4)$$

When ionic species are present, the use of a long-range interaction term, such as Debye-Hückel (1923) or Pitzer-Debye-Hückel (Pitzer, 1980) is common; however, in previous works (Santos et al., 2000; Santos et al., 2001) we were able to represent the phase behavior of electrolyte systems with the NRTL model without this long-range term. The same approach is used in this work.

PARAMETER ESTIMATION

The experimental liquid-liquid equilibrium data at several temperatures, reported by Duarte et al. (2000) for the water + PEG 4000 + potassium phosphate system; Snyder et al. (1992) for the water + PEG 1000 + magnesium sulfate, water + PEG 3350 + magnesium sulfate, water + PEG 8000 + sodium sulfate, water + PEG 1000 + potassium phosphate and water + PEG 8000 + potassium phosphate systems; and Voros et al. (1993) for the water + PEG 2000 + sodium carbonate system were used to estimate the molecular interaction and nonrandomness parameters of the NRTL model.

The parameters were estimated using the Fortran code TML-LLE 2.0 (Stragevitch, 1997); the procedure is based on the Simplex method (Nelder and Mead, 1965) and the Maximum Likelihood principle (Anderson et al., 1978; Niesen and Yesavage, 1989; Stragevitch and d'Ávila, 1997) and consists in the minimization of the objective function, S.

$$S = \sum_{k}^{D} \sum_{j}^{N_k} \left\{ \left(\frac{T_{jk}^{calc} - T_{jk}^{exp}}{\sigma_{T_{jk}}} \right)^2 + \sum_{i}^{C_k-1} \left[\left(\frac{w_{ijk}^{I,calc} - w_{ijk}^{I,exp}}{\sigma_{w_{ijk}^I}} \right)^2 + \left(\frac{w_{ijk}^{II,calc} - w_{ijk}^{II,exp}}{\sigma_{w_{ijk}^{II}}} \right)^2 \right] \right\} \quad (5)$$

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

With the molecular energy interaction parameters estimated by this procedure, liquid-liquid equilibrium correlations can be made. Comparisons between experimental and calculated data can be made through mean deviations between the experimental and the calculated composition of each component in both two phases. These mean deviations are given by

$$\Delta w = 100 \sqrt{\frac{\sum_{n}^{N_k} \sum_{i}^{C_k} \left(w_{exp}^I - w_{calc}^I \right)^2 + \left(w_{exp}^{II} - w_{calc}^{II} \right)^2}{2 N_k C_k}} \quad (6)$$

RESULTS AND DISCUSSION

With the procedure above, molecular interaction

energy parameters were obtained, as shown in Table 1, fitting the experimental liquid-liquid equilibrium data at several temperatures, reported by Duarte et al. (2000) for the water + PEG 4000 + potassium phosphate system; Snyder et al. (1992) for the water + PEG 1000 + magnesium sulfate, water + PEG 3350 + magnesium sulfate, water + PEG 8000 + sodium sulfate, water + PEG 1000 + potassium phosphate and water + PEG 8000 + potassium phosphate systems; and Voros et al. (1993) for the water + PEG 2000 + sodium carbonate system.

With these estimated parameters, the experimental data of Duarte et al. (2000), Snyder et al. (1992) and Voros et al. (1993) were correlated. A comparison between the experimental and calculated data is shown numerically in Table 2 and graphically in Figures 1-10.

It can be seen that the representation of liquid-liquid equilibrium for the systems studied is quite good. The NRTL model is able to predict the phase split over the entire range of compositions analyzed. The mean deviations appear in Table 2 and are always below 2.00%.

Table 1: Molecular interaction and nonrandomness parameters

i/j	A_{0ij}	A_{0ji}	A_{1ij}	A_{1ji}	α_{ij}
PEG 1000-MgSO$_4$	1165.7	5999.9	4.7740	74.1322	0.45692
PEG 1000-Water	-1464.5	-5999.9	30.267	-14.993	0.46821
MgSO$_4$-Water	-1766.2	3058.1	-8.4499	2.8745	0.20002
PEG 2000-Na$_2$CO$_3$	2353.7	4774.6	6.2540	-1.1322	0.49763
PEG 2000-Water	-2651.1	3634.7	11.223	7.3008	0.35819
Na$_2$CO$_3$-Water	-2467.1	2618.5	-6.4479	-26.135	0.13863
PEG 8000-Na$_2$SO$_4$	4502.7	-2701.3	0.0	0.0	0.44788
PEG 8000-Water	-4877.6	2361.0	0.0	0.0	0.20000
Na$_2$SO$_4$-Water	-2067.8	3452.0	0.0	0.0	0.20435
PEG 4000-Na$_2$SO$_4$	5946.5	975.64	0.0	0.0	0.43710
PEG 4000-Water	-3001.2	5527.8	0.0	0.0	0.20002
PEG 4000-K$_2$HPO$_4$	1723.9	-3074.7	0.0	0.0	0.31263
K$_2$HPO$_4$-Water	-944.31	1194.7	0.0	0.0	0.46999
PEG 1000-K$_2$HPO$_4$	657.61	4335.7	0.0	0.0	0.20000
PEG 8000-K$_2$HPO$_4$	5999.9	5999.7	0.0	0.0	0.46361

R.A.G.Sé and M.Aznar

Table 2: Experimental and calculated LLE data on PEG + Salt + Water Systems

Top Phase (w/w %)						Bottom Phase (w/w %)						Mean
PEG		Salt		Water		PEG		Salt		Water		Deviation
Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Δw %
PEG 1000 + magnesium sulfate at 25°C (Snyder et al., 1992)												
30.60	31.15	3.30	3.20	66.10	65.65	6.30	5.13	13.20	13.54	80.50	81.33	0.67
33.50	33.61	3.10	2.83	63.40	63.56	3.80	4.31	14.60	14.62	81.60	81.07	0.33
36.10	36.34	3.10	2.46	60.80	61.20	2.60	3.54	15.70	15.86	81.70	80.60	0.68
37.80	38.23	3.10	2.22	59.10	59.55	2.00	3.09	16.50	16.75	81.50	80.16	0.83
PEG 3350 + magnesium sulfate at 25°C (Snyder et al., 1992)												
25.40	25.03	3.10	3.19	71.50	71.78	4.80	4.33	12.20	12.49	83.00	83.18	0.31
29.20	29.39	2.60	2.87	68.20	67.74	4.50	4.54	13.90	13.54	81.60	81.92	0.30
32.80	32.52	2.50	2.67	64.70	64.81	5.10	4.76	14.20	14.29	80.70	80.95	0.23
34.40	34.52	2.40	2.56	63.20	62.92	4.40	4.92	15.20	14.78	80.40	80.30	0.31
PEG 2000 + sodium carbonate at 15°C (Voros et al., 1993)												
49.58	50.04	0.57	0.68	49.85	49.28	0.00	0.01	22.66	22.35	77.34	77.64	0.35
46.82	46.96	0.67	0.81	52.51	52.23	0.00	0.03	20.58	20.37	79.42	79.60	0.18
45.13	44.43	0.78	0.94	54.09	54.63	0.00	0.05	18.77	18.88	81.23	81.07	0.38
40.79	40.65	0.98	1.15	58.23	58.20	0.00	0.11	17.00	16.85	83.00	83.04	0.12
35.92	34.69	1.28	1.55	62.80	63.76	0.00	0.33	13.99	14.05	86.01	85.62	0.68
32.01	31.74	1.83	1.78	66.16	66.48	0.00	0.54	12.87	12.82	87.13	86.64	0.34
29.42	29.69	2.17	1.96	68.41	68.35	0.21	0.74	12.09	12.02	87.70	87.24	0.32
25.32	26.63	2.83	2.26	71.85	71.11	0.99	1.15	10.82	10.89	88.19	87.96	0.67
PEG 2000 + sodium carbonate at 25°C (Voros et al., 1993)												
51.15	51.14	0.49	0.70	48.36	48.16	0.00	0.01	21.55	21.34	78.45	78.65	0.17
48.62	48.54	0.65	0.80	50.73	50.66	0.00	0.03	19.86	19.73	80.14	80.24	0.10
46.57	46.46	0.71	0.89	52.72	52.65	0.00	0.04	18.69	18.53	81.31	81.43	0.12
42.74	42.17	0.93	1.10	56.33	56.73	0.00	0.10	16.28	16.28	83.72	83.62	0.30
37.80	38.10	1.41	1.32	60.79	60.58	0.00	0.21	14.48	14.39	85.52	85.40	0.18
33.77	33.32	1.63	1.63	64.60	65.05	0.00	0.47	12.43	12.42	87.57	87.11	0.37
31.51	31.47	1.96	1.77	66.53	66.76	0.17	0.62	11.66	11.72	88.17	87.66	0.31
27.19	28.09	2.50	2.04	70.31	69.87	0.89	1.00	10.38	10.52	88.73	88.48	0.47
PEG 2000 + sodium carbonate at 35°C (Voros et al., 1993)												
53.63	53.66	0.44	0.59	45.93	45.75	0.00	0.02	20.83	20.67	79.17	79.31	0.13
50.67	50.70	0.54	0.69	48.79	48.61	0.00	0.03	19.04	18.87	80.96	81.10	0.13
48.89	48.93	0.60	0.75	50.51	50.32	0.00	0.05	18.05	17.87	81.95	82.08	0.14
44.87	44.56	0.83	0.93	54.30	54.51	0.00	0.11	15.66	15.63	84.34	84.26	0.17
40.20	39.70	1.09	1.16	58.71	59.14	0.00	0.26	13.45	13.46	86.55	86.28	0.31
36.39	35.96	1.39	1.36	62.22	62.68	0.10	0.47	11.93	11.98	87.97	87.55	0.34
33.87	33.99	1.67	1.48	64.60	64.53	0.18	0.62	11.23	11.26	88.59	88.12	0.28
29.75	30.74	2.12	1.69	68.13	67.57	0.90	0.97	10.02	10.15	89.08	88.88	0.51

Table 2 continuation

Top Phase (w/w %)						Bottom Phase (w/w %)						Mean
PEG		Salt		Water		PEG		Salt		Water		Deviation
Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Δw %
PEG 2000 + sodium carbonate at 45°C (Voros et al., 1993)												
55.47	55.48	0.39	0.54	44.14	43.88	0.00	0.02	20.16	19.96	79.84	80.02	0.17
53.04	53.11	0.48	0.61	46.48	46.28	0.00	0.03	18.63	18.46	81.37	81.51	0.14
51.23	51.10	0.55	0.68	48.22	48.22	0.00	0.05	17.43	17.33	82.57	82.62	0.09
47.34	47.01	0.76	0.81	51.90	52.18	0.00	0.10	15.22	15.24	84.78	84.66	0.19
42.31	41.82	0.98	1.01	56.71	57.17	0.00	0.24	12.90	12.94	87.10	86.82	0.31
38.75	38.66	1.25	1.15	60.00	60.19	0.06	0.38	11.67	11.71	88.27	87.91	0.22
36.58	36.65	1.40	1.24	62.02	62.11	0.10	0.51	10.95	10.98	88.95	88.51	0.26
32.77	33.61	1.74	1.40	65.49	64.99	0.65	0.78	9.86	9.95	89.49	89.27	0.44
PEG 8000 + sodium sulfate at 25°C (Snyder et al., 1992)												
25.80	25.41	4.30	3.78	69.90	70.81	0.50	0.06	11.90	12.72	87.60	87.22	0.61
36.50	36.06	3.20	3.02	60.30	60.92	1.40	0.00	16.00	16.89	82.60	83.11	0.78
38.70	39.04	3.10	2.84	58.20	58.10	1.10	0.00	17.70	18.26	81.20	81.74	0.58
40.40	41.20	2.90	2.72	56.70	56.08	1.10	0.00	19.00	19.30	79.90	80.70	0.70
41.70	43.70	3.20	2.58	55.10	53.71	1.20	0.00	20.30	20.59	78.50	79.41	1.20
PEG 4000 + potassium phosphate at 30°C (Duarte et al., 2000)												
21.73	22.52	5.70	4.76	72.52	72.72	2.40	0.05	14.87	16.66	82.73	83.29	1.33
21.87	22.25	5.61	4.78	72.52	72.95	0.79	0.06	15.53	16.53	83.68	83.41	0.66
30.84	30.98	3.91	3.68	65.25	65.34	4.26	2.54	18.76	18.34	76.98	78.66	0.79
41.16	39.86	2.02	2.80	56.82	57.34	2.75	1.61	25.89	26.63	71.36	72.36	0.54
48.53	50.93	1.56	1.96	49.91	47.11	8.62	6.00	33.80	35.77	57.58	58.23	1.21
50.68	50.48	1.32	1.99	48.00	47.53	4.83	2.30	34.46	35.31	60.71	61.69	1.45
52.61	53.67	1.25	1.79	46.14	44.54	5.34	3.93	38.17	39.74	56.49	56.33	0.89
55.16	55.70	0.99	1.68	43.85	42.62	6.57	4.00	39.28	40.07	54.15	55.93	1.36
57.83	58.32	0.88	1.54	41.29	40.14	6.10	3.41	42.62	43.26	51.28	53.33	1.12
26.79	25.80	4.48	4.31	68.73	69.89	2.65	0.01	16.19	18.34	81.16	81.65	1.54
PEG 1000 + potassium phosphate at 25°C (Snyder et al., 1992)												
22.70	22.71	6.80	5.96	70.50	71.33	5.00	4.77	16.00	16.97	79.00	78.26	0.70
28.90	29.03	5.00	4.51	66.10	66.46	2.80	3.86	18.70	18.52	78.50	77.62	0.62
36.10	35.54	3.50	3.40	60.40	61.06	2.10	2.53	21.60	21.77	76.30	75.70	0.47
39.10	39.46	3.10	2.87	57.80	57.67	1.60	1.94	24.00	23.84	74.40	74.22	0.54
PEG 8000 + potassium phosphate at 25°C (Snyder et al., 1992)												
21.70	21.79	4.40	4.37	73.90	73.84	1.90	2.26	11.50	11.37	86.70	86.37	0.19
24.60	24.62	3.90	3.89	71.50	71.49	1.60	1.40	12.40	12.48	86.10	86.12	0.10
34.60	34.42	2.60	2.54	62.90	63.04	1.60	0.13	16.30	17.06	82.10	82.81	0.75
38.10	38.13	2.20	2.12	59.70	59.75	2.30	0.03	18.30	19.40	79.40	80.57	1.14
41.20	41.52	1.80	1.78	57.00	56.70	3.00	0.01	20.60	21.92	76.40	78.07	1.51
44.40	44.30	1.60	1.52	54.00	54.18	2.00	0.00	23.10	24.26	74.90	75.74	1.01
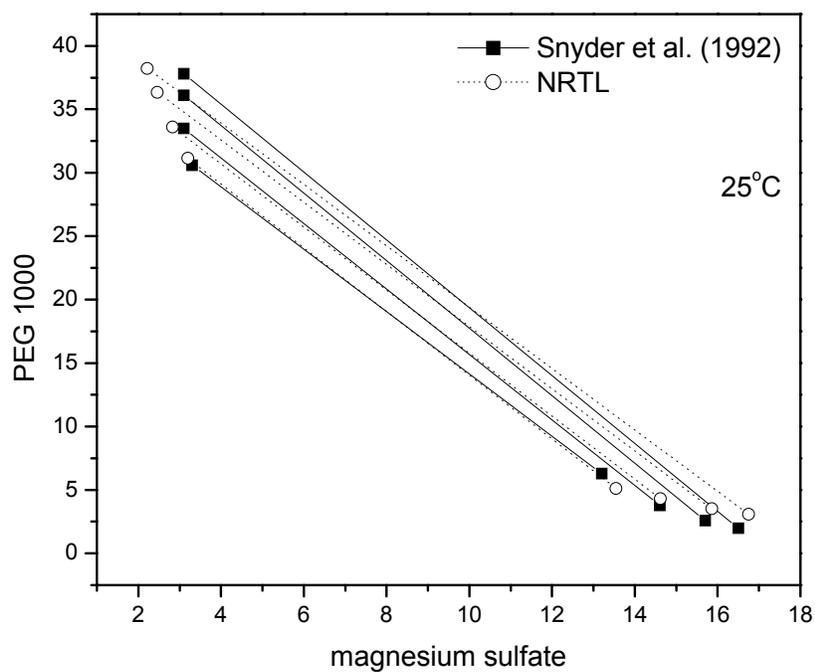
Figure 1: Experimental and calculated LLE data on water + PEG 1000 + MgSO$_4$ at 25°C
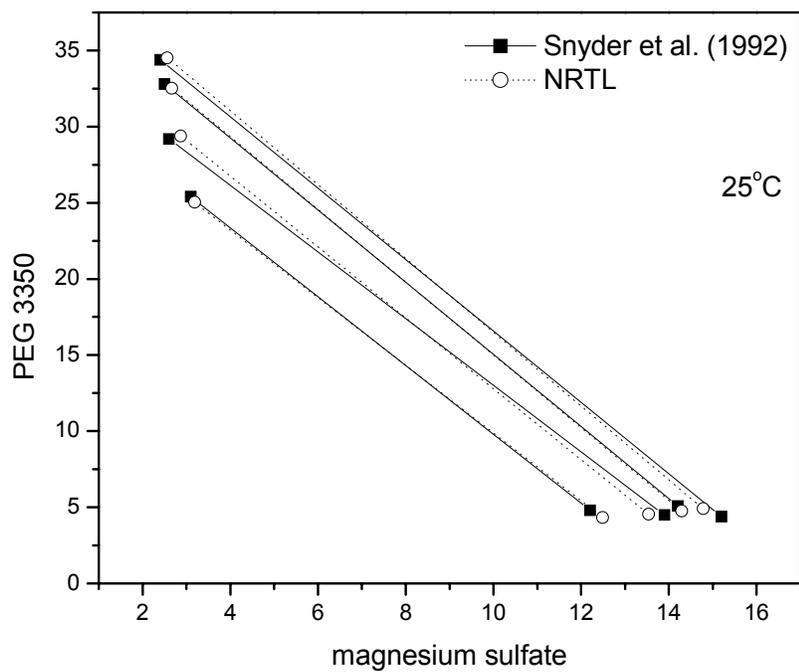
Figure 2: Experimental and calculated LLE data on water + PEG 3350 + MgSO$_4$ at 25°C
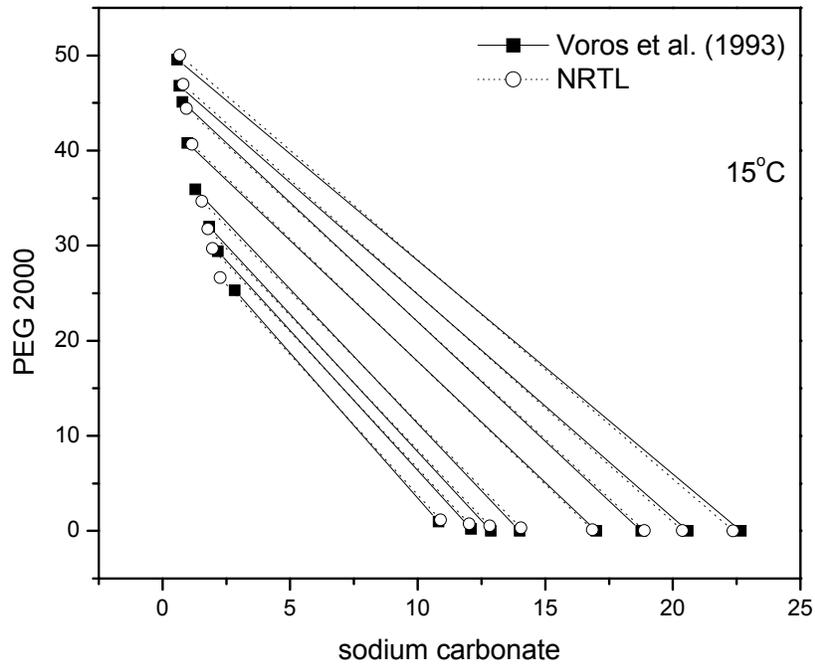
Figure 3: Experimental and calculated LLE data on water + PEG 2000 + Na_2CO_3 at 15°C
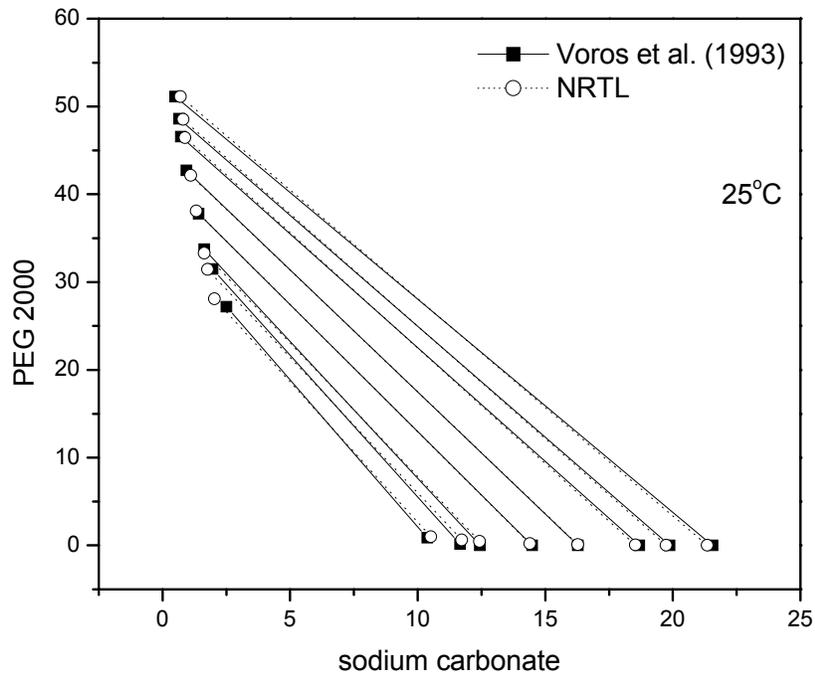
Figure 4: Experimental and calculated LLE data on water + PEG2000 + Na_2CO_3 at 25°C
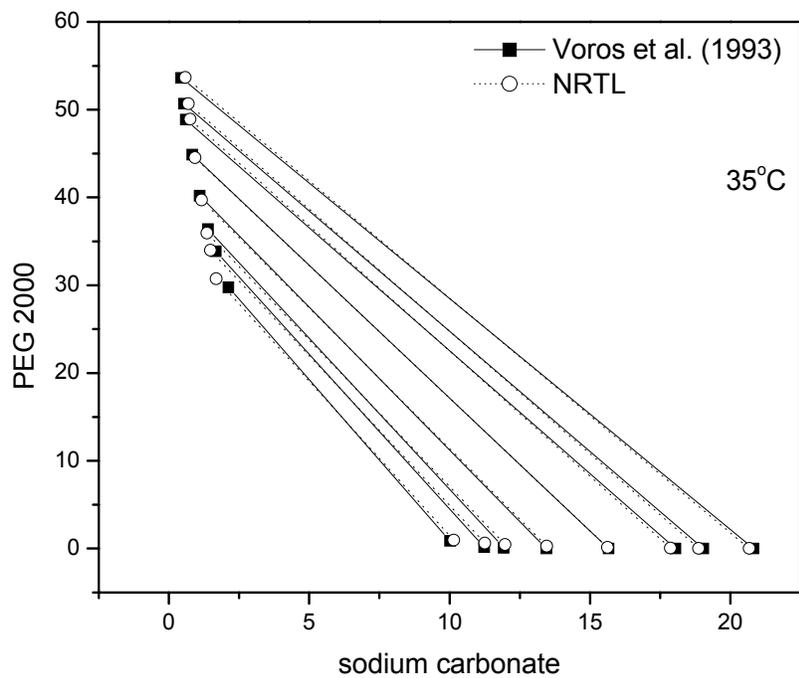
Figure 5: Experimental and calculated LLE data on water + PEG 2000 + Na$_2$CO$_3$ at 35°C
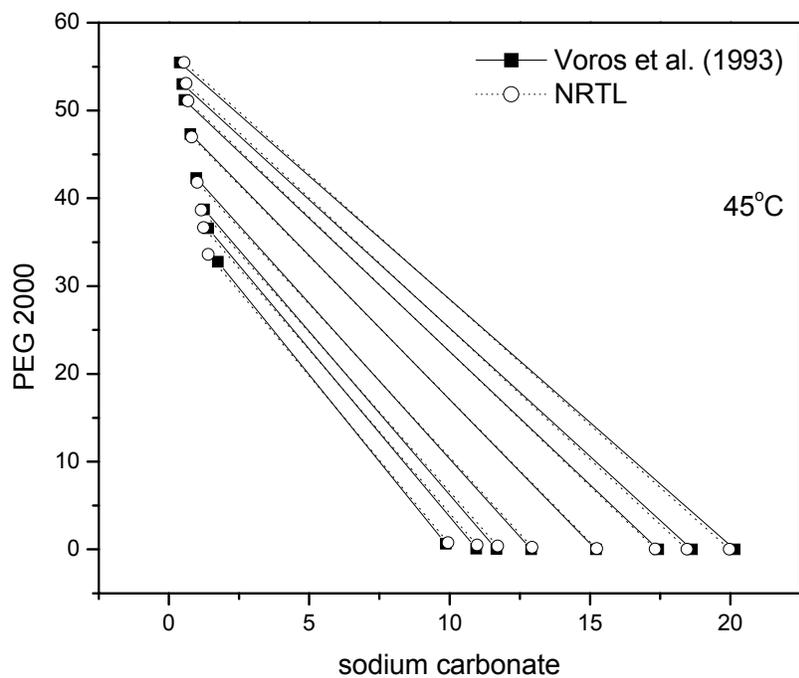
Figure 6: Experimental and calculated LLE data on water + PEG2000 + Na$_2$CO$_3$ at 45°C
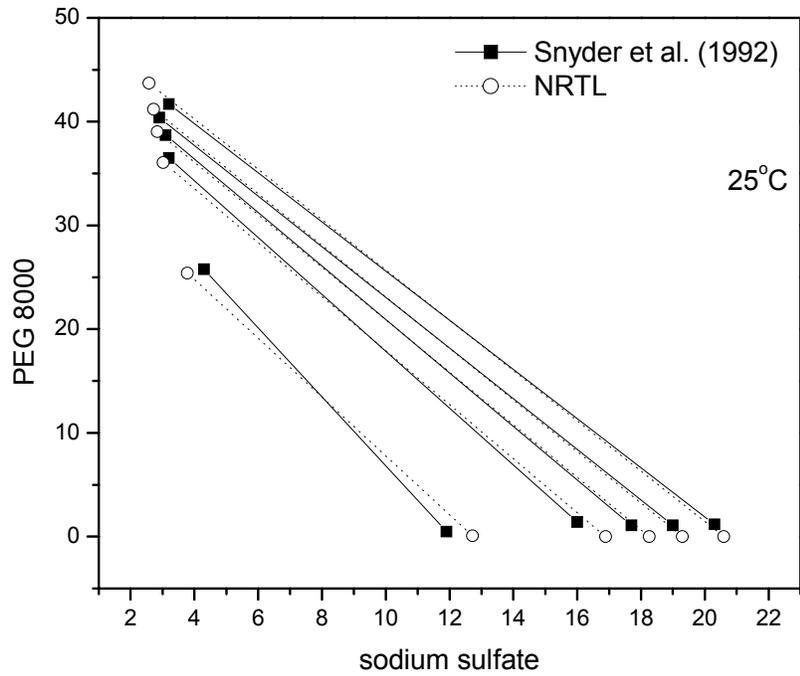
Figure 7: Experimental and calculated LLE data on water + PEG8000 + Na_2SO_4 at 25°C
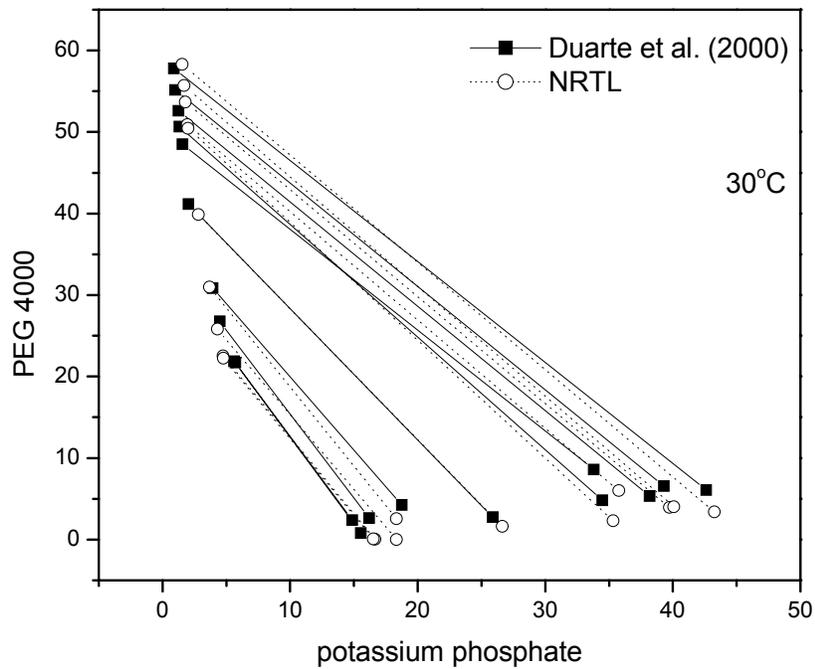
Figure 8: Experimental and calculated LLE data on water + PEG4000 + K_2HPO_4 at 30°C
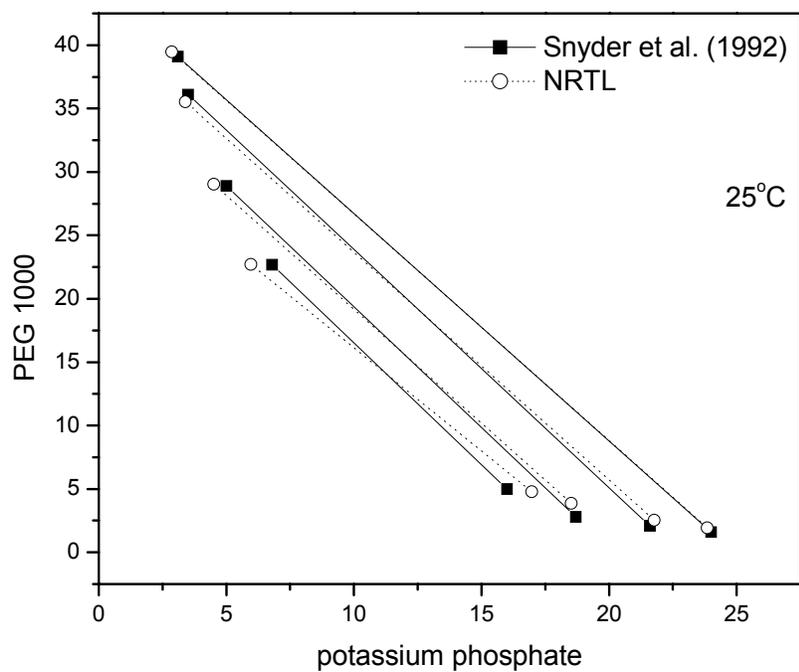
Figure 9: Experimental and calculated LLE data on water + PEG1000 + K$_2$HPO$_4$ at 25°C
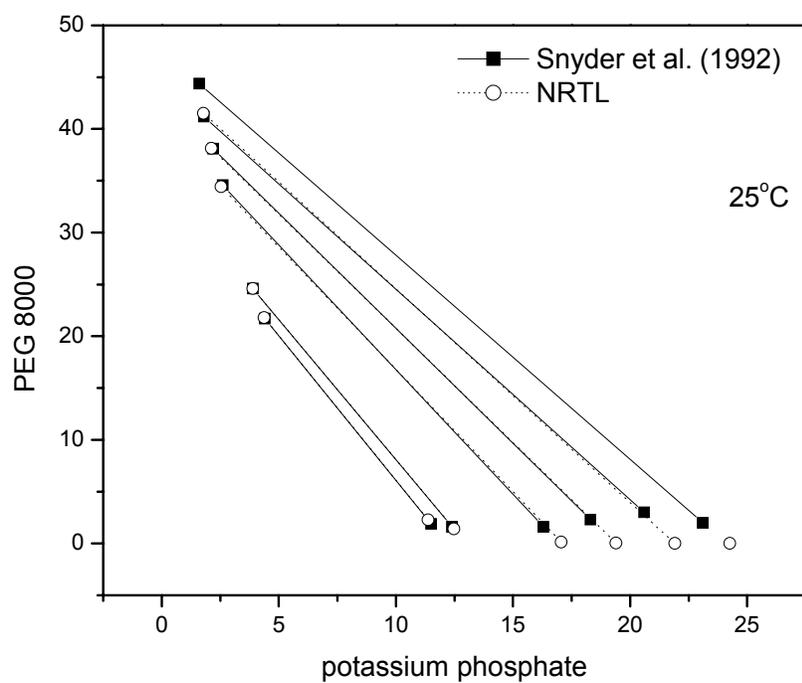
Figure 10: Experimental and calculated LLE data on water + PEG8000 + K$_2$HPO$_4$ at 25°C

CONCLUSION

Experimental liquid-liquid equilibrium data on water + PEG 4000 + potassium phosphate, water + PEG 1000 + potassium phosphate, water + PEG 8000 + potassium phosphate, water + PEG 1000 + magnesium sulfate, water + PEG 3350 + magnesium sulfate, water + PEG 8000 + sodium sulfate and water + PEG 2000 + sodium carbonate aqueous two-phase systems were used to estimate the molecular interaction and nonrandomness parameters of the NRTL model for the activity coefficient. With these new parameters, the experimental data were correlated. The results are very satisfactory, with an overall mean deviation of 0.60%.

ACKNOWLEDGMENTS

NOMENCLATURE

A_{0ij}, A_{1ij}	molecular interaction parameters in the NRTL model for the i-j pair
C_k	number of components in data set k
D	number of data sets
G_{ij}	energy interaction parameters in the Boltzmann form in the NRTL model for the i-j pair
M_k	molecular mass of compound k
N_k	number of data points in data set k
S	objective function to be minimized
T	absolute temperature
w_k	mass fraction of compound k

Greek Letters:

α_{ij}	molecular nonrandomness parameter in the NRTL model
γ_i	activity coefficient of compound i
σ	standard deviation for an independent variable, temperature or composition
τ_{ij}	energy parameters in the NRTL model

Super/subscripts:

exp	experimental
calc	calculated
I, II	liquid phases at equilibrium

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