Liquid−Liquid Equilibrium of the Aqueous Two-Phase System Water + PEG 4000 + Lithium Sulfate at Different Temperatures. Experimental Determination and Correlation

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A study was made of the effect of temperature on the liquid−liquid equilibrium (LLE) in the aqueous biphasic system formed by lithium sulfate + polyethylene glycol 4000 + water at 5, 25, and 45 °C. The tie lines and binodal curves as well as the densities and refractive indexes were determined on solutions in equilibrium at each temperature. The LLE experimental data obtained were well correlated to the nonrandom two-liquid thermodynamic model for activity coefficients. When using data from seven equilibrium lines for each temperature, a mean deviation of 1.07% was obtained between experimental compositions and compositions calculated using the model.

Introduction

Aqueous two-phase systems (ATPSs) are formed by soluble polymers in water by using two polymers or even an inorganic salt and a polymer.[1] ATPSs have been used for over 30 years for the extraction of biological materials such as cells and proteins.[2] In the past decade, ATPSs have been also used in the extraction of metallic ions,[3] in the extractive crystallization of inorganic salts,[4] in the recovery of nanoparticles,[5] and in extraction process of sulfide minerals.[6]

One of the ATPSs of major practical interest is formed by aqueous solutions of polyethylene glycol (PEG) and inorganic salts, given that this polymer is low in cost, is nontoxic, is noninflammable, and is easy to handle. Zaslavsky[7] presented a useful summary of experimental data and phase equilibrium diagrams for ATPSs formed by polymers and water. The main inorganic salts described include $(NH_4)_3PO_4$, Na_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$, NaOH, KOH, Na_2CO_3, and K_2CO_3.

Snyder et al.[8] provided partial information for the phase diagrams for aqueous solutions of PEG with $MgSO_4$, Na_2SO_4, $CaCO_3$, $(NH_4)_2SO_4$, and K_2HPO_4. Ho-Gutierrez et al.[9] presented data on liquid−liquid equilibria (LLE) for aqueous mixtures of PEG with Na_2SO_4 and NaCl at (301 and 308) K and with PEG molecular weights of 1000, 3350, and 8000. Hammer et al.[10] measured the concentrations at LLE in aqueous solutions of PEG and sodium sulfate, with PEG molecular weights between 1550 and 6000, pH between 5.2 and 8.1, and temperatures between (293.15 and 313.15) K. González-Tello et al.[11] studied the LLE of the PEG + $MgSO_4$ + H_2O system at 298 K with PEG molecular weights of 1000, 3350, and 8000.

Taboada et al.[12] measured LLE and liquid−solid equilibrium of the polyethylene glycol + sodium sulfate + water systems at 298.15 K. Graber et al.[13] presented data on the LLE of the PEG + $NaNO_3$ + H_2O system at 298.15 K using PEG with a molecular weight of 4000. Graber et al.[14] complemented this study using PEG with molecular weights of 2000, 6000, and 10000. This ATPS was of potential interest for the extraction of iodine and other anions originating in sodium nitrate and iodine in mineral deposits in northern Chile.

Reliable data on the composition of properties of ATPS are necessary for the design of extraction processes and for the development of both thermodynamic and mass-transfer models. Thermodynamic models have been used to predict LLE in polymer−polymer−water and to a lesser degree in polymer−inorganic saltwater systems.[15] The models used have included coefficients of virial osmotic expansion, integral equation theory, group contribution method, local composition methods, and others.

Gao et al.[16] reproduced the binodal curve for the magnesium sulfate + PEG + water system from data on the activity of the water by applying the UNIQUAC method. Hammer et al.[10] used the virial osmotic equation to model the sodium sulfate + PEG-3000 +water system. King et al.,[17] applied a thermodynamic model with the virial equation to predict the experimentally obtained binodal curve for PEG + potassium chloride + water systems and PEG + potassium sulfate + water systems, also using data on the activity of the water.

Wu et al.[18] predicted LLE lines for ATPSs formed by PEG, water, and bivalent salts (ammonium sulfate, sodium sulfate, and sodium carbonate) from a modification of the Pitzer virial equation. The parameters of the virial equation were obtained from liquid/vapor equilibrium data in which they were assumed to be independent of the molecular weight of the PEG.

Chen et al.[19] extended the original nonrandom two-liquid (NRTL) model to electrolyte systems containing small molecules, while Wu et al.[20] proposed an NRTL model modified for a multicomponent saline system which was satisfactorily applied to ATPS polymer−polymer and polymer−salt systems. Sé and Aznar[15] applied the original

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NRTL model for describing the LLE of the ATPS PEG-4000 + water + potassium phosphate at four temperatures.

We report in this paper LLE dates for the aqueous biphasic system formed by lithium sulfate + polyethylene glycol 4000 + water at 5, 25,, and 45 °C. The experimental data were correlated with NRTL model.

Experimental Section

Materials. Solutions were prepared using lithium sulfate (Merck > 99.9%) and were predried in an oven at 120 °C for 24 h. The PEG was of synthesis grade (Merck) and had a nominal molecular weight of 4000. This reagent was subjected to drying in an oven for 7 days at 50 °C. Gel permeation chromatography (GPC) evaluation of the PEG showed a mean molecular weight of 3819, average number of molecular weights of 3737, and a polydispersity of 1.02. Both reagents were used without further purification. Ultrapure water (conductivity = 0.05 μS/cm) obtained by passing distilled water through a Millipore ultrapure cartridge kit, was used in all measurements.

Experimental Procedure. Details of the experimental procedure were previously described by Graber et al.[14] The binodal curve of each ATPS was determined using a turbidimetric method, adding small quantities of Li_2SO_4 or PEG (typically 0.01 g) to shaken 10 g solutions of each phase until the characteristic change in turbidity appeared, indicative of the formation of a second liquid phase. All points of the binodal curve were determined isothermically at work temperature.

The tie lines were determined in triplicate from a mixture of known overall composition above the binodal curve (typically 40 g in capped, graduated flasks), which were agitated for 48 h in a rotatory bath with the temperature controlled to within ±0.1 K. Biphasic solutions obtained were separated by isothermic sedimentation over 48 h. Longer stirring and settling periods did not result in any observable changes in the phase compositions.

Once the solutions in equilibrium were separated, samples were taken in triplicate to determine the composition of each phase. The density and refractive index were also measured for each solution in equilibrium.

The refractive index was measured using a Mettler Toledo model RE50 refractometer having an uncertainty of ±0.0001 nD, and density was measured in a Mettler Toledo model DE50 densimeter with an uncertainty of ±0.00005 g/mL. Both physical properties were measured under isothermic operating conditions ±0.1 K.

The concentration of PEG in the samples was determined by measurement of the refractive index and density.[14] Calibration curves were obtained by preparation of standard solutions of Li_2SO_4 and PEG.

Lithium was determined by atomic absorption spectrometry at 670.8 nm using a Varian SpectrAA model 220. The initial PEG concentration did not show a significant effect on the spectrophotometric reading within the used dilution range. Three measures of concentration of each sample were made, and reproducibility was estimated as ±0.5%. The procedure to determine the concentration of the solutions was checked with a gravimetric standard analysis of sulfate.

Thermodynamic Model

The NRTL thermodynamic model is based on the concept of local composition and is applicable to partially soluble systems. Chen et al.[19] extended the original NRTL model to electrolyte systems that contained small molecules. A modified NTRL was proposed by Wu et al.[20] for aqueous biphasic systems containing polymers and a salt. Sé and Aznar[15] successfully applied the original NRTL model to describe the liquid−liquid equilibrium of the ATPS PEG 4000 + water + and potassium phosphate at four temperatures.

Table 1. Mass Fractions for the Binodal Curve Data of the Li_2SO_4 (1) + PEG 4000 (2) + H_2O (3) System

$t = 5$ °C		$t = 25$ °C		$t = 45$ °C	
w_2	w_1	w_2	w_1	w_2	w_1
0.0030	0.2612	0.0007	0.2464	0.0027	0.2485
0.0046	0.2489	0.0008	0.2319	0.0045	0.1406
0.0066	0.1852	0.0014	0.1996	0.0120	0.1302
0.0242	0.1659	0.0020	0.1959	0.0315	0.1162
0.0696	0.1396	0.0023	0.1834	0.0476	0.1048
0.0892	0.1319	0.0033	0.1765	0.0908	0.0906
0.1120	0.1219	0.0052	0.1678	0.1430	0.0751
0.1482	0.1075	0.0084	0.1611	0.1704	0.0682
0.1849	0.096	0.0232	0.1416	0.2107	0.0576
0.2376	0.0811	0.0302	0.1364	0.2755	0.0444
0.2678	0.0732	0.0436	0.1287	0.3389	0.0318
0.4066	0.0426	0.0657	0.1158	0.3904	0.0239
0.4865	0.0271	0.0791	0.1101	0.4420	0.0177
0.5397	0.0188	0.1031	0.1028	0.4933	0.0133
		0.1360	0.0936	0.5458	0.0096
		0.1744	0.0831	0.5963	0.0062
		0.2254	0.0692		
		0.2835	0.0551		
		0.3337	0.0466		
		0.3848	0.0380		
		0.4369	0.0291		
		0.4887	0.0226		
		0.5408	0.0167		
		0.5932	0.0114		

The NRTL is a conceptual model in which each coefficient has a physical meaning. Nevertheless, by use of this original version with dissociated molecules, a semiempirical model is being used, as the interactions coefficients do not account to actual physical interactions among dissolved species. Despite this new conceptualization, the performance of the model in achieving a correlation of equilibrium points was significantly better than alternative formulations such as the Othmer−Tobias equation. The NRTL model typically uses mole fractions, but when using polymer systems, conversion to mass fractions is more convenient since polymers have high molecular weights giving extremely small mole fractions. The NRTL model using mass fractions, as employed by various authors (Sé and Aznar,[15] Batista et al.,[21] Litomen et al.[22]), was used in the present study. For a multicomponent mixture, the NRTL equation, expressed in terms of mass fraction, is[15]

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

where

$$\tau_{ij} = \frac{A_{ij}}{T} \quad (2)$$

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

Table 2. LLE of the ATPS Formed by Li_2SO_4 (1) + PEG 4000 (2) + H_2O (3)

	initial composition		top phase			bottom phase		
t/(°C)	w_1	w_2	w_1	w_2	ρ/(kg/m^3)	w_1	w_2	ρ/(kg/m^3)
5	0.1350	0.3000	0.0197	0.5338	1134	0.2829	0.00	1244
	0.1330	0.2630	0.0280	0.4836	1126	0.2582	0.00	1226
	0.1267	0.2130	0.0411	0.4119	1120	0.2180	0.00	1195
	0.1230	0.1690	0.0601	0.3213	1115	0.1928	0.00	1168
25	0.1270	0.3690	0.0112	0.5973	1110	0.3139	0.00	1231
	0.1280	0.3190	0.0139	0.5653	1107	0.2757	0.00	1212
	0.1180	0.2750	0.0215	0.4955	1102	0.2384	0.00	1181
	0.1100	0.2190	0.0366	0.3900	1095	0.2039	0.00	1149
45	0.1240	0.3898	0.0053	0.6299	1099	0.3164	0.00	1221
	0.1230	0.3250	0.0080	0.5676	1095	0.2770	0.00	1191
	0.1030	0.2999	0.0103	0.5303	1089	0.2238	0.00	1158
	0.0880	0.2350	0.0196	0.4263	1080	0.1720	0.00	1118

where M = molecular weight of the components, w = mass fraction of the components, T = absolute temperature of the system, A_{ij} and A_{ji} are the characteristic patterns of the interaction energies $i - j$, and α_{ij} are the parameters related to the nonrandom behavior of the mixture. That is, the components are distributed according to local determinate patterns of the mixture

Estimation of Parameters

The experimental data obtained on the LLE were used to estimate the molecular interaction and the nonrandom parameters of the mixture. These parameters were determined minimizing the objective function f_{obj} defined by

$$f_{\mathrm{obj}} = \sum_{i=1}^{3} \sum_{k=1}^{n} ({w_{ik}}^{T,\mathrm{exp}} - {w_{ik}}^{T,\mathrm{mod}})^2 + \sum_{i=1}^{3} \sum_{k=1}^{n} ({w_{ik}}^{B,\mathrm{exp}} - {w_{ik}}^{B,\mathrm{mod}})^2 \quad (4)$$

Here ${w_{ik}}^{T,\mathrm{exp}}$ and ${w_{ik}}^{T,\mathrm{mod}}$ represent the experimental and NRTL calculated mass fractions of component i in the top phase, ${w_{ik}}^{B,\mathrm{exp}}$ and ${w_{ik}}^{B,\mathrm{mod}}$ represent the experimental and NRTL calculated mass fractions of component i in the bottom phase, and n represents the total number of data or interconnecting lines modeled. Optimization was achieved using the generalized reduced gradient algorithm in which the original problem is reduced to another problem not having restrictions and which is solved using a system of equations which are basic for some variables and nonbasic for the remaining variables. A quasi-Newton method was used as a criterion for determining the direction of the search, which instead of using a Hessian matrix, uses an approximation of this matrix. This methodology requires a large capacity for storage which, however, is compensated for by the production of good results.

The comparison between the experimental data and those obtained from the model were made using the relative root-mean-square deviation, given by

$$\Delta w = 100 \left(\frac{\sum_{i=1}^{3} \sum_{k=1}^{n} [({w_{ik}}^{T,\mathrm{exp}} - {w_{ik}}^{T,\mathrm{mod}})^2 + ({w_{ik}}^{B,\mathrm{exp}} - {w_{ik}}^{B,\mathrm{mod}})^2]}{n} \right)^{1/2} \quad (5)$$

Results and Discussion

Binodal Curve and Tie Lines. Table 1 shows the experimental data obtained for the binodal curves at (5, 25, and 45) °C. Table 2 shows the equilibrium compositions for each phase.

Table 3. Parameters of the Model for the ATPS Li_2SO_4 + PEG 4000 + H_2O[a]

$i-j$	A_{ij}/K	A_{ji}/K	α_{ij}
PEG 4000 + water	*−3001.2*	*5527.8*	*0.2000*
PEG 4000 + Li_2SO_4	2589.1	−435.0	0.3187
Li_2SO_4 + water	−3496.9	−2474.1	0.3640

[a] Italic font denotes Sé and Aznar[15] parameters (nonfitted in this work).

Table 4. Mean Deviations of the LLE after Correlation with Model Parameters in Table 3

system	no. tie lines	mean deviation (%)
water + PEG 4000 + Li_2SO_4 at 5 °C	4	0.245
water + PEG 4000 + Li_2SO_4 at 25 °C	4	0.857
water + PEG 4000 + Li_2SO_4 at 45 °C	4	2.10

Results after fitting are shown in Table 3. One of the main advantages of the NRTL conceptualization lies in the possibility of using independent estimates of model parameters. In this work, we used the values of PEG 4000/water parameters given by Sé and Aznar[15] and then only six parameters were fitted (Table 3).

Table 4 lists the mean deviations for each data set. No significant improvement was found when the PEG 4000 + water parameters were also included in the fitting. This result is interesting as we mentioned above that ionic interactions are not considered, and thus, the used model cannot be considered as fully conceptual. However, based on the results obtained here, one can conclude that the PEG−water interaction keeps, to a certain extent, the physical meaning of the original NRTL model and parameters could be valid for other similar systems. Another point of interest can be the small differences between nominal and actual molecular weight of PEG, which was in our case 3819.

Figures 1 and 3 show the equilibrium phase diagrams for the ATPS formed by Li_2SO_4 + H_2O + PEG 4000 at (5, 25, and 45) °C. In the figures, symbols represent the experimental points of equilibrium, and the solid lines represent those derived by calculation from the model. Also included are the experimental points of the binodal curve. These figures show that there is a displacement of the binodal curve toward the origin with increase in temperature and an increase in the biphasic region, where a lower concentration of Li_2SO_4 and PEG are required to form the aqueous biphasic system. This is because an increase in temperature produces an increase in folding of the PEG molecule and in the hydration layer of this molecule.

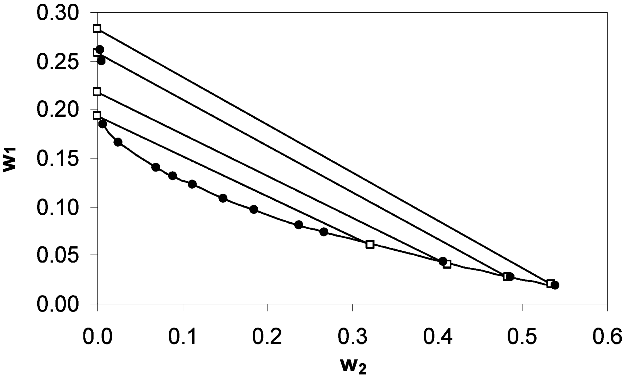

Figure 1. Experimental and calculated LLE for the system Li_2SO_4 (1) + PEG 4000 (2) + H_2O (3) at 5 °C. ●, Experimental binodal curve; □, experimental tie lines; solid line, NRTL tie lines.

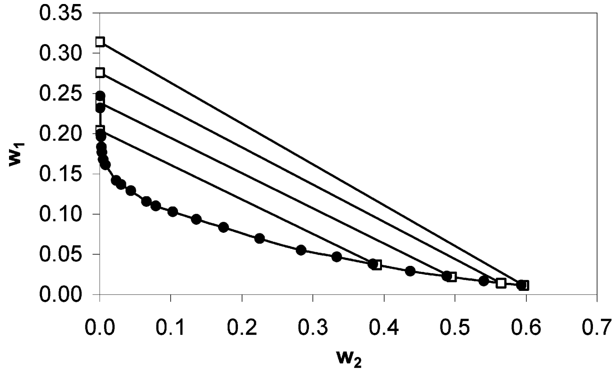

Figure 2. Experimental and calculated LLE for the system Li_2SO_4 (1) + PEG 4000 (2) + H_2O (3) at 25 °C. ●, Experimental binodal curve; □, experimental tie lines; solid line, NRTL tie lines.

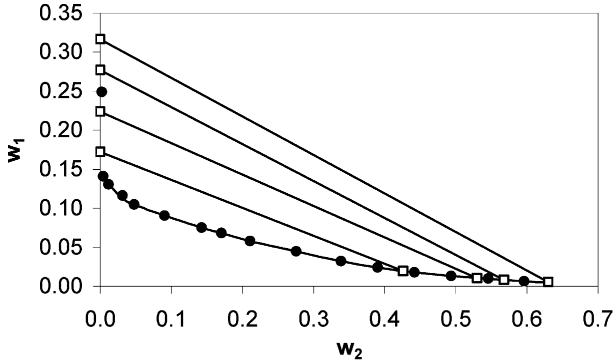

Figure 3. Experimental and calculated LLE for the system Li_2SO_4 (1) + PEG 4000 (2) + H_2O (3) at 45 °C. ●, Experimental binodal curve; □, experimental tie lines; solid line, NRTL tie lines.

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