Liquid–Liquid Equilibria for the Poly(ethylene glycol) + Water + Copper Sulfate System at Different Temperatures

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The compositions of coexisting phases have been determined for aqueous two-phase systems containing poly(ethylene glycol) of nominal molecular weight 20000 and copper sulfate at (290.15, 299.15, 308.15, and 317.15) K. The effect of temperature on the liquid–liquid equilibrium was discussed. The experimental compositions of coexisting phases of the systems were used to obtain interaction parameters in universal quasichemical theory (UNIQUAC) activity coefficient models. The experimental tie line data were compared with those obtained using the UNIQUAC model. The results of comparison were indicated by calculation of the root-mean-square deviations (rmsd). The calculated results show good agreement with the experimental data.

Introduction

Aqueous polymer−salt systems (APSS) consist of two immiscible aqueous solutions and have several advantages over the aqueous polymer−polymer systems (APPS) due to the larger differences in density, greater selectivity, lower viscosity, and economical superiority.[1,2]

Aqueous two-phase extraction processes have become an important technique for separation, concentration, and purification of a wide range of different biological materials such as proteins, viruses, etc.[3,4]

In the recent years, many research groups focused on the measurements of the phase equilibrium data for ternary aqueous solutions of poly(ethylene glycol) (PEG) and salt systems.[5–7]

Copper is considered as a transition element because it has a partially filled d subshell. In aqueous solutions of copper(II) salts such as $CuSO_4$, the copper is not present as simple Cu^{2+} ions. Instead, each Cu^{2+} ion becomes bonded to four water molecules, which gives a polar blue complex ion with the formula $Cu(H_2O)_4{}^{+2}$. Copper(II) also forms stable complexes with o-doner ligands. A number of copper proteins including enzymes have been isolated from plants and microorganisms. Therefore, aqueous two-phase extraction processes containing copper(II) salts such as $CuSO_4$ may be considered as a suitable technique for extraction of biological materials.

A comprehensive review of the early experimental liquid–liquid equilibrium (LLE) of the aqueous two-phase systems (ATPS) containing two different kinds of polymers or a polymer and a salt has been reported by Albertsson[3] and Walter et al.[7] The phase equilibrium data for such systems have also been compiled by Zaslavsky.[8] The phase equilibrium data for aqueous polymer−salt systems have been reported by many research groups.[4–8] However, phase equilibrium data for aqueous PEG−sulfate salt systems at different temperatures are limited.

Some successful models based on the osmotic virial expansion and the lattice theories in the representation of phase behavior of ATPS have been proposed in the literature.[9–11] The Flory−Huggins theory,[4] the UNIQUAC[12] model, and the NRTL[13] model and their various modified versions are the popular models for the correlation of the tie line data of aqueous APSS.[4,7,14–16] Recently, authors successfully used the Flory–Huggins model to determine the phase separation conditions of the (water + PEG + salt) ternary systems.[4] A simple linear temperature composition dependent interaction parameter was applied for correlation of the measured cloud point temperatures. Gao et al.[14] and Peng et al.[17] used the UNIQUAC model for correlation of the LLE data of APSS. Wu et al.[18] investigated the LLE of APSS using the NRTL model. Although, the NRTL model is one of the most successful and practical models for electrolyte solutions with limited salt concentrations in solution,[19] the UNIQUAC model may be used for the correlation of APSS tie line data with reasonable accuracy.

Table 1. Comparison of the Measured Refractive Index with Those Calculated by Equation 1 for Ternary Aqueous ($CuSO_4$ + PEG) Solutions at 293.15 K

$100\ w_{CuSO_4}$	$100\ w_{PEG}$	n_{obsd}	n_{calcd}
1.14	17.99	1.3579	1.3574
1.33	21.10	1.3620	1.3616
1.48	12.68	1.3519	1.3516
5.71	10.20	1.3571	1.3569
6.50	9.15	1.3575	1.3572
7.08	8.10	1.3572	1.3571
7.94	7.33	1.3581	1.3578
8.45	6.04	1.3573	1.3573
9.31	5.06	1.3576	1.3578
11.76	1.78	1.3582	1.3586

In the present work, we report the compositions of coexisting phase data for aqueous PEG(20000)−$CuSO_4$ systems at (290.15, 299.15, 308.15, and 317.15) K. The original UNIQUAC activity coefficient model was used for the correlation of the phase behavior of the systems. The obtained calculated results are compared with the experimental data. The comparisons indicate the good ability of the UNIQUAC model for correlation and prediction of equilibrium phase compositions of the APSS.

Experimental

Chemicals. PEG of nominal molecular weight 20000 and copper sulfate were supplied by Merck Co. Inc., Germany.

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10.1021/je700643u CCC: $40.75

Table 2. Binodal Curve Data for the {PEG (1) + Water (2) + $CuSO_4$ (3)} System at (290.15 and 299.15) K

100 w_{CuSO_4}	100 w_{PEG}	100 w_{CuSO_4}	100 w_{PEG}
290.15 K		299.15 K	
2.70	34.12	2.22	35.31
2.74	33.50	2.75	30.74
3.04	31.05	2.81	29.74
3.20	29.81	2.99	28.63
3.70	25.96	3.22	27.25
3.87	24.48	3.43	25.50
3.93	24.18	3.53	24.76
4.22	21.68	3.58	24.46
4.54	19.57	3.89	21.57
4.59	19.34	4.25	19.45
5.14	16.43	4.83	16.52
5.97	13.70	5.48	13.94
6.64	11.67	6.04	12.14
7.12	10.38	6.48	10.78
7.67	8.95	6.86	9.71
8.22	7.68	7.22	8.75
8.49	7.12	7.42	7.95
8.70	6.63	7.84	7.18
8.97	6.25	8.38	6.38
9.36	5.82	10.02	4.92
10.77	4.97	12.00	3.98
12.35	4.60	12.60	3.75
14.01	4.10	12.80	3.66
14.98	3.83	13.12	3.50
15.93	3.60	14.96	3.00
17.01	3.20	16.10	2.60
17.98	2.86		

Table 3. Binodal Curve Data for the {PEG (1) + Water (2) + $CuSO_4$ (3)} System at (308.15 and 317.15) K

100 w_{CuSO_4}	100 w_{PEG}	100 w_{CuSO_4}	100 w_{PEG}
308.15 K		317.15 K	
1.95	36.27	1.50	38.25
2.43	31.78	1.90	34.36
2.49	31.38	2.14	31.97
2.51	31.27	2.21	31.07
2.80	27.94	2.61	26.72
2.88	27.69	2.72	25.37
3.12	25.05	2.80	25.37
3.17	24.77	2.80	25.10
3.62	21.28	2.88	24.21
3.88	19.25	3.20	21.67
4.35	17.11	3.36	20.42
4.82	15.00	3.61	19.19
5.40	12.82	3.74	18.28
5.80	11.39	4.03	16.90
6.40	9.77	4.18	16.12
6.71	8.64	4.39	15.12
6.95	7.98	4.52	14.48
7.18	7.32	4.77	13.50
7.54	6.70	4.95	12.73
9.52	4.01	7.24	6.55
11.74	2.58	10.25	2.58
12.01	2.50	12.37	1.39
13.08	2.01	13.20	0.99
13.18	1.95	13.98	0.59
13.37	1.90	14.14	0.47
15.53	1.00	14.48	0.47

Copper sulfate was dried in an oven at 373.15 K for 48 h before use. All compounds were used without further purification.

Procedure. The equilibrium apparatus is a laboratory scale glass vessel with a water jacket. Samples of the top phase and bottom phase were taken from two different valves. The solutions were made by mass using a Sartorius analytical balance (model A200S, precise to 0.0001 g). The mixtures were prepared inside the cell and were vigorously agitated with a magnetic stirrer for 1 h at constant temperature. The temperature of the circulating water in the external jacket was controlled to within ± 0.01 K using a thermostatic water bath (model RE 207, Lauda, Germany). The agitated turbid mixture was left to settle for at least 10 h. The mixture split into two clear and transparent liquid phases, with a well-defined interface. The samples of phases at equilibrium were collected and analyzed.

The salt concentrations in the two phases were found using a complexometric titration method using ethylene diamine tetraacetic acid (EDTA) in the presence of Eriochrome black T (EBT). The concentration of PEG was determined by refractive index measurements at 293.15 K using a Kruss Abbe refractometer AR3D. Since the refractive index of the phase samples depends on PEG and salt concentration, calibration plots of refractive index versus polymer concentration were prepared for different concentrations of salt.[16]

The following equation describes the relation between the refractive index (n), the salt (W_S), and the PEG (W_P) mass fractions, respectively.

$$n = 1.3332 + 0.19787W_S + 0.12189W_P \tag{1}$$

The values of constants of eq 1 obtained were based on the measurements of refractive index for binary aqueous salt solutions. Table 1 shows the comparison of the measured refractive index with those calculated by eq 1 for the ternary aqueous ($CuSO_4$ + PEG) solutions. According to this table, eq 1 can be used for determination of the PEG concentrations in the ternary aqueous ($CuSO_4$ + PEG) solutions with good accuracy.

The binodal curve data were also obtained by titration of the aqueous polymer solutions with a copper sulfate solution of known concentration at constant temperature. The titration end point was indicated by the turbidity of the solution. The analysis was repeated at least three and two times for the tie line and the binodal curve measurements, respectively. The average of these readings was taken for the component compositions. The uncertainty for each mass fraction, w, in the tie line analysis, binodal curve measurements, and constant temperature T was less than (0.004, 0.001, and 0.01) K, respectively.

Results and Discussion

The measured mass fractions w of the binodal curve for systems of {PEG (1) + water (2) + $CuSO_4$ (3)} at (290.15, 299.15, 308.15, and 317.15) K are presented in Tables 2 and 3. The obtained mass fractions of the equilibrium phases (tie line data) are reported in Table 4. The UNIQUAC model was used to correlate the experimental data by minimizing the following objective function[1,7]

$$\text{O.F.} = \sum_{i=1}^{3} \sum_{j}^{N} \left(w_{i,j,\text{exptl}}^{\text{I}} - w_{i,j,\text{calcd}}^{\text{I}}\right)^2 + \left(w_{i,j,\text{exptl}}^{\text{II}} - w_{i,j,\text{calcd}}^{\text{II}}\right)^2 \tag{2}$$

where w_{exptl} and w_{calcd} are the experimental and calculated mass fractions of the two phases at equilibrium (I and II) and the subscripts i and j, respectively, designate the component and the number of tie lines. For the UNIQUAC model, the pure component structural parameters (r and q) were calculated by the method previously outlined[12] and are listed in Table 5. The calculated interaction parameters[20] of the UNIQUAC model are presented in Table 6. The root-mean-square deviation (rmsd)

Table 4. Experimental Tie Line Data for the {PEG (1) + Water (2) + $CuSO_4$ (3)} System at (290.15, 299.15, 308.15, and 317.15) K

feed		top phase		bottom phase	
100 w_{CuSO_4}	100 w_{PEG}	100 w_{CuSO_4}	100 w_{PEG}	100 w_{CuSO_4}	100 w_{PEG}
290.15 K					
5.3	15.2	4.6	19.3	10.8	5.0
8.1	9.1	4.2	21.7	12.3	4.6
6.6	15.4	3.7	26.0	14.0	4.1
6.4	18.0	3.2	29.8	15.0	3.8
5.1	21.4	3.0	31.0	15.9	3.6
4.7	20.2	2.7	33.5	17.0	3.2
9.2	14.6	2.7	34.1	18.0	2.9
299.15 K					
6.1	15.4	3.6	22.1	10.4	4.0
5.5	20.3	3.4	25.1	12.1	4.0
7.0	14.1	3.2	29.2	12.6	3.7
5.9	17.5	2.8	32.1	13.8	3.6
5.4	19.5	2.7	34.1	15.8	3.0
9.2	13.6	2.2	36.9	17.2	2.6
308.15 K					
6.8	14.45	2.88	25.0	10.5	2.6
5.8	15.4	2.80	27.9	11.2	2.5
5.5	19.2	2.51	29.3	11.5	2.0
5.7	18.2	2.49	32.1	13.2	1.9
5.6	19.4	2.44	33.9	15.1	1.9
9.5	13.2	1.95	37.5	17.3	1.0
317.15 K					
4.1	18.7	2.8	25.1	10.2	2.6
8.2	10.7	2.6	26.7	12.4	1.4
5.6	19.4	2.2	30.1	13.2	1.0
6.7	14.5	2.1	32.0	14.7	0.6
7.6	14.8	1.9	34.4	16.3	0.5
9.5	13.2	1.5	38.2	18.5	0.5

Table 5. Calculated UNIQUAC Structural Parameters

component	*r*	*q*
$CuSO_4$	8.6237	7.1581
H_2O	0.9200	1.4000
PEG	2.4088	2.2480

Table 6. Binary Interaction Parameters of the UNIQUAC Model for the {PEG (1) + Water (2) + $CuSO_4$ (3)} System at Different Temperatures

T/K	*i*–*j*	τ_{ij}	τ_{ji}
290.15	1–2	4.763	0.022
	1–3	0.569	0.594
	2–3	2.524	3.672
299.15	1–2	4.544	0.024
	1–3	0.578	0.603
	2–3	2.454	3.531
308.15	1–2	4.348	0.027
	1–3	0.588	0.612
	2–3	2.391	3.403
317.15	1–2	4.173	0.030
	1–3	0.597	0.621
	2–3	2.333	3.287

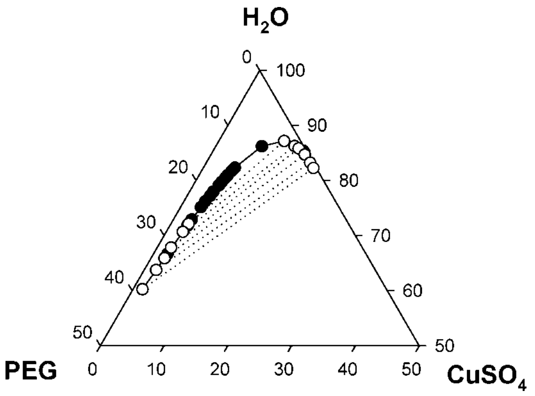

Figure 1. ○, Tie line and ●, binodal curve data for the {PEG (1) + water (2) + $CuSO_4$ (3)} system at 290.15 K.

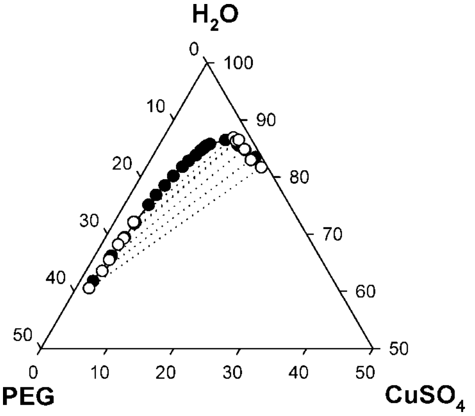

Figure 2. ○, Tie line and ●;, binodal curve data for the {PEG (1) + water (2) + $CuSO_4$ (3)} system at 299.15 K.

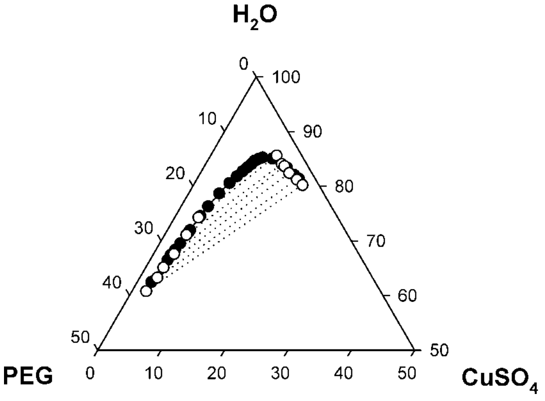

Figure 3. ○, Tie line and ●, binodal curve data for the {PEG (1) + water (2) + $CuSO_4$ (3)} system at 308.15 K.

which is a measure of the agreement between the experimental data and the calculated values is defined as[3]

$$\mathrm{rmsd} = \left[\sum_{i=1}^{3}\sum_{j}^{N}\left[\left(w^{\mathrm{I}}_{i,j,\mathrm{exptl}} - w^{\mathrm{I}}_{i,j,\mathrm{calcd}}\right)^2 + \left(w^{\mathrm{II}}_{i,j,\mathrm{exptl}} - w^{\mathrm{II}}_{i,j,\mathrm{calcd}}\right)^2\right]/2nM\right]^{1/2} \quad (3)$$

where *n* and *M* are, respectively, the number of components and the total number of tie lines. The measured binodal curve and tie line data for the system of {PEG (1) + water (2) + $CuSO_4$ (3)} at (290.15, 299.15, 308.15, and 317.15) K are presented in Figures 1 to 4. The rmsd calculated values are 0.051, 0.035, 0.038, and 0.029 for (290.15, 299.15, 308.15, and 317.15) K, respectively. Therefore, the results of rmsd calculations by UNIQUAC indicate a good agreement with the experimental data. The effect of temperature on the binodal curve is shown in Figure 5. According to this figure, an increase in temperature causes an expansion of two-phase region.

Conclusion

The binodal curve and LLE data for the systems {PEG (1) + water (2) + $CuSO_4$ (3)} at (290.15, 299.15, 308.15, and 317.15) K were obtained. The obtained tie line data have been correlated by the UNIQUAC activity coefficient model, and the interaction parameters are presented. The calculated rmsd for mass fractions of the equilibrium phases indicate that the

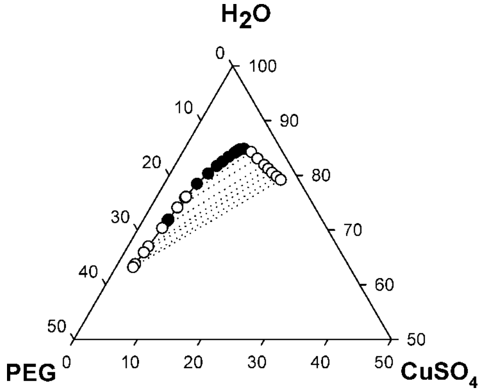

Figure 4. ○, Tie line and ●, binodal curve data for the {PEG (1) + water (2) + $CuSO_4$ (3)} system at 317.15 K.

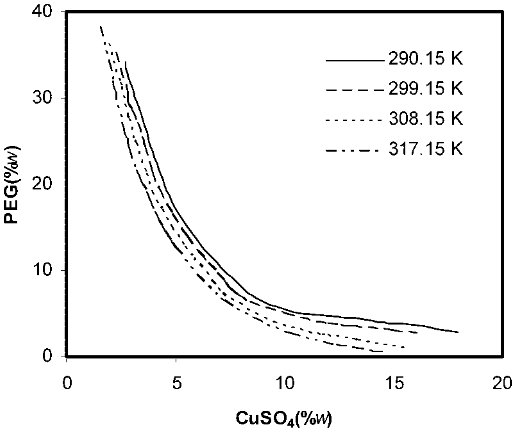

Figure 5. Effect of temperature on the binodal curve for the {PEG (1) + water (2) + $CuSO_4$ (3)} system.

UNIQUAC activity coefficient model correlates the LLE data with reasonable accuracy. The effect of temperature on the binodal curve data was also investigated. According to the results obtained, an increase in temperature caused the expansion of the two-phase region. However, the optimum temperature operation especially in industrial scale design may be affected by economical considerations and some practical factors such as aqueous polymer solution viscosity.

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Received for review November 5, 2007. Accepted February 8, 2008.

JE700643U