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# Liquid−Liquid Equilibria of Aqueous Two-Phase Systems Containing Ethylene Oxide−Propylene Oxide Random Copolymer and Ammonium Sulfate

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Liquid−liquid equilibria of aqueous two-phase systems, water + ammonium sulfate + ethylene oxide−propylene oxide (EOPO) random copolymer, were studied experimentally. Experimental techniques and analytical methods are described. Equilibrium data at 298.15 K along with the phase diagrams are given. The number average molecular weights of EOPO used in the three series of experiments were 3640, 2340, and 780, respectively. The modified NRTL model was extended for the calculation of the phase equilibria of $H_2O$ + EOPO + $(NH_4)_2SO_4$ systems with various molecular weights. The predicted results are in good agreement with the experimental data.

## Introduction

Aqueous two-phase systems (ATPS) are widely used for separation and purification of biomolecules. A large number of articles have been published dealing with a wide range of applications of this method, including the separation of macromolecules, cell organelles, and viruses (Walter et al., 1985; Albertsson, 1986; Tjerneld, 1992). The most frequently used two-phase systems are aqueous solution of polyethylene glycol (PEG) and dextran or PEG and potassium phosphate. Applications in biotechnology have been prevented by the high costs of the polymers used and the difficulties in polymer recycling. These systems would also be more cost-efficient if the polymer could be readily recycled without costly ultrafiltration or chromatography steps. Recently, an aqueous two-phase system combined with temperature-induced phase separation, which offers an effective solution to the problems of polymer removal and recycling, has been introduced for separation and purification of biomolecules (Alred et al., 1993; Li et al., 1997; Li, 1998). A nonionic random copolymer of ethylene oxide−propylene oxide (EOPO) can be used to form temperature-induced phase separation. The ability of PEG (100% ethylene oxide) to phase separate in water + PEG systems at increased temperatures is well-known (Saeki et al., 1976; Florin et al., 1984). In this case, a two-phase system composed of a PEG-rich bottom phase and an aqueous top phase is thus formed. The temperature at which this phenomenon occurs is called the cloud point of the polymer. The problem with water + PEG systems is the high cloud point of PEG. PEG20 000 in water has a cloud point of 117.7 °C (Harris et al., 1991). EOPO has properties very similar to PEG while a water + EOPO system has a lower cloud point than the water + PEG system. For example UCON 50 HB-5100 (commercial name, a copolymer of 50% ethylene oxide and 50% propylene oxide with an average molecular weight of 4000) in water has a cloud point of 50 °C (Farkas et al., 1996). The cloud-point temperature can be modified by the ratio of EO to PO groups, the molecular weight of polymer, and the addition of appropriate salts (Harris et al., 1991). Thus temperature-induced phase separation can be easily used for polymer recycling and for obtaining the target biomolecules in a polymer-free solution after extraction with aqueous two-phase systems.

Many phase diagrams of ATPS containing PEG have been reported (Albertsson, 1986; Snyder et al., 1992; Zaslavsky, 1995). Recently there has been much interest in the separation and purification of biomolecules by use of ATPS containing EOPO. Experimental liquid−liquid equilibria (LLE) of EOPO + dextran + water and EOPO + hydroxypropyl starch (HPS) + water systems have been reported (Harris et al., 1991; Modlin et al., 1994). However, LLE of aqueous EOPO + salt two-phase systems are scarce. In a previous paper (Li et al., 1998), our research group has already reported phase behavior data for ATPS composed of EOPO ($M_n = 4200$) and various kinds of salts (such as $Na_2SO_4$, $K_2HPO_4$, $KH_2PO_4$, and the mixture of $K_2HPO_4$ + $KH_2PO_4$). As part of a continuing study to describe the phase equilibrium, we report experimental results for the effect of the molecular weight of EOPO on the LLE of water + EOPO + ammonium sulfate systems. Further, The modified NRTL (nonrandom two-liquid) model proposed by our research group (Wu et al., 1996) will be extended to calculate the phase equilibria of $H_2O$ + EOPO + $(NH_4)_2SO_4$ systems.

## Experimental Section

***Materials.*** EOPO4000, EOPO2000, and EOPO800 were obtained from Zhejiang University Chemical Factory (People's Republic of China). The average molecular weight and the molecular weight distribution of EOPO were determined by gel permeation chromatography (GPC, Waters 150C). Three-column systems (Ultrastyragel linear, 500A, and 100A) were used, and the column temperature was set to 30 °C. The solvent was tetrahydrofuran. The flow rate was 1.0 mL/min. The number average molecular weights ($M_n$) of EOPO4000, EOPO2000, and EOPO800 were 3640, 2340, and 780, respectively. The polydispersities of EOPO4000, EOPO2000, and EOPO800 were 1.1095, 1.0611, and 1.1080, respectively. EOPO samples used in this work have an equal molar number of ethylene oxide (EO) and propylene oxide (PO). $(NH_4)_2SO_4$ was analytical regent

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grade (Shanghai Chemical Regent Corp., People's Republic of China). Double distilled water was used in all aqueous solutions. All other chemicals were of analytical grade.

***Liquid−Liquid Equilibria.*** The systems were prepared from stock solutions, 50 mass % EOPO, and 40 mass % $(NH_4)_2SO_4$. All these solutions and water were weighted into a test tube to have the desired initial overall compositions. The total amount was 20 g. After the solution was mixed sufficiently in a closed test tube, phase separation was speeded up by centrifugation at 2500 rpm for 5 min. Then the tube was placed in an equilibrium cell at (25 ± 0.05) °C for 48 h, waiting for proper phase equilibration and separation, as indicated by the absence of turbidity in both top and bottom phases. Portions of solutions in both phases were taken out carefully for analysis.

***Analytical Methods.*** After separation of the two-phases, the concentrations of ammonium sulfate in the top and bottom phases were determined by the formaldehyde method. The chemical reaction is as follows:

$$2(NH_4)_2SO_4 + 6HCHO = 2H_2SO_4 + (CH_2)_6N_4 + 6H_2O$$

The sulfuric acid formed was titrated against sodium hydroxide solution. The analysis of samples with given a composition of EOPO, and $(NH_4)_2SO_4$ aqueous solution showed that the presence of EOPO did not interfere with the determination. A statistical analysis of the data showed that the relative deviation of the titration was about 0.35%.

The concentration of water was determined by drying the sample solution in a drying oven at 70 °C and then weighing. A preparatory experiment showed that ammonium sulfate did not decompose and EOPO was not degraded at that temperature.

The concentration of EOPO can be obtained by the difference of $(NH_4)_2SO_4$ and water concentrations. The drying−weighing method is simpler and gives even better accuracy than an interferometer. The average relative error is within 0.3%.

## Theoretical Section

***Extension of the Modified NRTL Model.*** In order to generalize the modified NRTL model for binary solutions, proposed in our previous paper (Wu et al., 1996), to multicomponent salt-containing polymer solutions, the excess Gibbs free energy, $G^E$, is expressed as a sum of three contributions:

$$G^E = G^{E,LR} + G^{E,comb} + G^{E,SR} \qquad (1)$$

Where the first term, $G^{E,LR}$, is the long-range electrostatic contribution taken from the expression of Fowler and Guggenheim (1949). The second term, $G^{E,comb}$, is the combinatorial entropy contribution obtained directly from the extension of the modified NRTL model. The third term, $G^{E,SR}$, is the short-range contribution derived from the incorporation of the modified NRTL model and the electrolyte NRTL model (Chen et al., 1982; Chen and Evans, 1986). In this model, the segment−segment interactions substitute for the molecule−molecule interactions, because the molecule−molecule short-range interactions cannot reflect the similarity in thermodynamic properties of polymer solutions of the same series (only differing in the molecular weights of the polymers).

The activity coefficients of the components in the system can be written as

$$\ln \gamma_j = \ln \gamma_j^{LR} + \ln \gamma_j^{comb} + \ln \gamma_j^{SR} \qquad (2)$$

Furthermore, the right-hand side of eq 2 can be expressed as

$$\ln \gamma_i^{LR} = -Z_i^{\,2} A I^{1/2}/(1 + bI^{1/2}) \qquad (3)$$

$$\ln \gamma_m^{LR} = \frac{2AV_m d}{b^3}[1 + bI^{1/2} - (1 + bI^{1/2})^{-1} - 2\ln(1 + bI^{1/2})] \qquad (4)$$

$$\ln \gamma_j^{comb} = \ln \phi_j/x_j + 1 - \phi_j/x_j + (r_j/2)[2\sum_k \beta_{kj}\phi_k(1 - \phi_j) - \sum_{k\neq j}\sum_{l\neq j}\beta_{kl}\phi_k\phi_l] \qquad (5)$$

$$\frac{1}{q_m}\ln \gamma_m^{SR} = \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_k X_k G_{km}} + \frac{X_m G_{mm}}{\sum_k X_k G_{km}}\left(\tau_{mm} - \frac{\sum_k X_k G_{km}\tau_{km}}{\sum_k X_k G_{km}}\right) + \frac{X_c G_{mc,ac}}{\sum_k X_k G_{kc,ac}}\left(\tau_{mc,ac} - \frac{\sum_k X_k G_{kc,ac}\tau_{kc,ac}}{\sum_k X_k G_{kc,ac}}\right) + \frac{X_a G_{ma,ca}}{\sum_k X_k G_{ka,ca}}\left(\tau_{ma,ca} - \frac{\sum_k X_k G_{ka,ca}\tau_{ka,ca}}{\sum_k X_k G_{ka,ca}}\right) \qquad (6)$$

$$\frac{1}{Z_c}\ln \gamma_c^{SR} = \frac{\sum_k X_k G_{kc,ac}\tau_{kc,ac}}{\sum_k X_k G_{kc,ac}} + \sum_m \frac{X_m G_{cm}}{\sum_k X_k G_{km}}\left(\tau_{cm} - \frac{\sum_k X_k G_{km}\tau_{km}}{\sum_k X_k G_{km}}\right) + \frac{X_a}{\sum_k X_k G_{ka,ca}}\left(- \frac{\sum_k X_k G_{ka,ca}\tau_{ka,ca}}{\sum_k X_k G_{ka,ca}}\right) \qquad (7)$$

$\gamma_a$ can be obtained from eq 7 by replacing the subscript of $c$ with $a$, and $a$ with $c$, where the subscripts $i$, $j$, and $m$ are used to denote ion, any species, and neutral species, respectively. The subscripts of $c$ and $a$ stand for cations and anions, respectively. $r_j$ is the number of segments of species $j$, and $r = 1$ for a simple ion or the smallest molecular solvent which is denoted by the subscript of "1" (such as water for ATPS). $A$ and $b$ are the Debye−Huckel constants calculated as

$$A = 1.327757 \times 10^5 d^{0.5}/(DT)^{1.5}$$

$$b = 6.359696 d^{0.5}/(DT)^{0.5}$$

$Z$ and $I$ are the number of charge and the strength of the

**Table 1. Liquid−Liquid Equilibrium Data for $H_2O$ + EOPO + $(NH_4)_2SO_4$ Systems at 298.15 K**

| | total system (100w) | | | bottom phase (100w) | | | top phase (100w) | | |
|---|---|---|---|---|---|---|---|---|---|
| no. | EOPO | $(NH_4)_2SO_4$ | $H_2O$ | EOPO | $(NH_4)_2SO_4$ | $H_2O$ | EOPO | $(NH_4)_2SO_4$ | $H_2O$ |
| | | | | $H_2O$ + EOPO4000 + $(NH_4)_2SO_4$ | | | | | |
| 1 | 12.05 | 7.05 | 80.90 | 2.47 | 10.03 | 87.50 | 31.47 | 2.22 | 66.31 |
| 2 | 11.96 | 8.01 | 80.03 | 1.15 | 12.18 | 86.67 | 36.42 | 1.79 | 61.79 |
| 3 | 12.06 | 10.51 | 77.43 | 0.77 | 14.70 | 84.53 | 45.13 | 1.01 | 53.86 |
| 4 | 11.97 | 13.01 | 75.02 | 0.39 | 17.10 | 82.51 | 51.90 | 0.59 | 47.51 |
| 5 | 12.0 | 14.81 | 73.19 | 0.41 | 18.92 | 80.67 | 57.52 | 0.36 | 42.13 |
| | | | | $H_2O$ + EOPO2000 + $(NH_4)_2SO_4$ | | | | | |
| 1 | 15.12 | 8.18 | 76.70 | 2.21 | 11.55 | 86.24 | 32.24 | 2.66 | 65.10 |
| 2 | 15.05 | 9.01 | 75.94 | 1.51 | 12.83 | 85.66 | 36.30 | 2.10 | 61.60 |
| 3 | 14.98 | 10.00 | 75.02 | 1.19 | 14.41 | 84.40 | 40.08 | 1.60 | 58.32 |
| 4 | 14.95 | 11.97 | 73.08 | 0.86 | 16.50 | 82.64 | 47.49 | 0.99 | 51.52 |
| 5 | 15.03 | 14.02 | 70.95 | 0.49 | 19.06 | 80.45 | 53.62 | 0.48 | 45.90 |
| | | | | $H_2O$ + EOPO800 + $(NH_4)_2SO_4$ | | | | | |
| 1 | 20.05 | 9.99 | 69.96 | 2.90 | 17.03 | 80.07 | 38.39 | 2.92 | 58.69 |
| 2 | 20.01 | 11.05 | 68.94 | 1.93 | 18.68 | 79.39 | 42.21 | 2.26 | 55.53 |
| 3 | 20.17 | 12.08 | 67.75 | 1.76 | 19.77 | 78.47 | 45.76 | 1.70 | 52.54 |
| 4 | 20.06 | 14.07 | 65.87 | 1.03 | 22.28 | 76.69 | 50.86 | 1.40 | 47.74 |
| 5 | 20.03 | 15.91 | 64.06 | 1.43 | 23.78 | 74.79 | 55.70 | 0.75 | 43.55 |

ion. *V*, *d*, and *D* are molar volume, density, and dielectric constant, respectively. Other symbols are defined as follows:

$$\phi_j = n_j r_j / \sum n_k r_k, \quad \theta_j = n_j q_j / \sum n_k q_k$$

$$q_i = r_i[1 - 2\alpha_{1i}(1 - 1/r_i)], \quad \beta_{jk} = \alpha_{jk}(1/r_j - 1/r_k)^2$$

$$X_j = \theta_j C_j \qquad (\text{if } j = \text{ion}, C_j = Z_j; \text{ else}, C_j = 1)$$

$n_k$ is the molar number of species *k*; the meaning of α, *G*, and τ are similar to the electrolyte NRTL model. Because the activity coefficients of ions are usually normalized to the infinite dilution reference state, we normalize the activity coefficients of all solutes, including ions and polymers, to the infinite dilution reference state for aqueous two-phase systems; thus

$$\ln \gamma_j^* = \ln \gamma_j - \ln \gamma_j^{\text{ref}} \qquad (j \neq 1) \tag{8}$$

where $\gamma^{\text{ref}}$ is the activity coefficient at the infinite dilution reference state and is calculated from eq 2 by assuming that $x_1 = 1$, $x_j = 0$ ($j = 2, 3, 4, ...$).

For more details, one can review the relevant literature (Wu et al., 1998).

***Estimation of Parameters.*** For the $H_2O$ (1) + EOPO (2) + $(NH_4)_2SO_4$ (3) ATPS at 298.15 K, described in this paper, the pure substance parameters, molecular weight ($M_j$), number segments ($r_j$), molar volume ($V_j$), and density ($d_j$), are needed for the calculation. $M_j$ is set equal to the number average molecular weight ($M_n$) for polymer *j*. Since the van der Waals volume of a repeat unit in the EOPO molecule is very close to quintuple that of a water molecule, $V_2$ is approximated as $(5n_p + 1)V_1$, where $n_p$ is the polymerization degree of a EOPO molecule and can be calculated from $M_2$. For water, $r_1 = 1$, $V_1 = 18.05 \times 10^{-6}$ $m^3\ mol^{-1}$, and $D_1 = 78.3$. Thus, $r_2 = V_2/V_1$, and $d_j = M_j/V_j$. In addition, $D_2$ of EOPO is calculated according to the method proposed by van Krevelen and Hoftyzer (1976). An average value of the dielectric constant for all EOPOs was taken in this work, $D_2 = 2.12$. The unknown parameters are $\alpha_{jk}$ (or $\alpha_{m,ca}$) and $\tau_k$ (or $\tau_{m,ca}$ and $\tau_{ca,m}$). The values of α are not treated as adjustable model parameters but previously selected to be 0.1, 0.15, 0.2, and so on. The criteria of selection is based on a trial and error method in the procedure of correlating the model parameters of τ. The following objective function and procedure are used to evaluate the model parameters.

**Table 2. Critical Compositions for $H_2O$ + EOPO + $(NH_4)_2SO_4$ Systems at 298.15 K**

| system | 100w (EOPO) | 100w [$(NH_4)_2SO_4$] |
|---|---|---|
| $H_2O$ + EOPO4000 + $(NH_4)_2SO_4$ | 12.4 | 5.1 |
| $H_2O$ + EOPO2000 + $(NH_4)_2SO_4$ | 13.8 | 6.2 |
| $H_2O$ + EOPO800 + $(NH_4)_2SO_4$ | 14.5 | 8.2 |

**Table 3. Model Parameters for $H_2O$ (1) + EOPO (2) + $(NH_4)_2SO_4$ (3) Systems at 298.15 K**

| | | |
|---|---|---|
| $\alpha_{12} = 0.25$ | $\tau_{21} = 2.0134$ | $\tau_{12} = -0.1508$ |
| $\alpha_{13} = 0.2$ | $\tau_{31} = -3.7840$ | $\tau_{13} = 8.0238$ |

| no. | system | $\alpha_{23}$ | $\tau_{32}$ | $\tau_{23}$ |
|---|---|---|---|---|
| 1 | $H_2O$ + EOPO4000 + $(NH_4)_2SO_4$ | 0.03 | −23.0818 | 51.8077 |
| 2 | $H_2O$ + EOPO2000 + $(NH_4)_2SO_4$ | 0.03 | −23.1493 | 51.0066 |
| 3 | $H_2O$ + EOPO800 + $(NH_4)_2SO_4$ | 0.03 | −23.1848 | 48.8815 |

$$F = \sum_i^{CN_1} \sum_j^{N_2} \sum_k^{N_3} [1 - Q_{ijk}(\text{calc})/Q_{ijk}(\text{expt})]^2 \tag{9}$$

where $N_1$, $N_2$, and $N_3$ are the numbers of experimental points, phases, and components in the system, respectively. *C* is a constant: $C = 1$ for the correlation of VLE, and $C = 0.5$ for the correlation of LLE. *Q* denotes any thermodynamic property, and “expt” and “calc” refer to experimental data and data calculated by means of the model. Equation 9 is solved by the simplex method of Nelder and Mead (1965).

The model parameters, $\tau_{12}$ and $\tau_{21}$, between the segments of the EOPO and water are refitted to the experimental water activities at 298.15 K determined by our laboratory (Li, 1998). The model parameters, $\tau_{13}$ and $\tau_{31}$, between salt and water are calculated from VLE data of the corresponding aqueous electrolyte solution by simultaneously fitting the experimental electrolyte activity coefficients and the osmotic coefficients of water. The experimental data of the $H_2O$ + $(NH_4)_2SO_4$ system are taken from Robinson and Stokes (1965).

The model parameters, $\tau_{23}$ and $\tau_{32}$, between the segments of EOPO and $(NH_4)_2SO_4$ have to be correlated using the LLE data of EOPO + $(NH_4)_2SO_4$ ATPS. In the correlation, the data on one tie line from one system are, in principle, enough to estimate the two model parameters. We use here

**Table 4. Calculated Results and Their Comparison with the Experimental Data for EOPO + $(NH_4)_2SO_4$ Aqueous Two-Phase Systems at 298.15 K**

| no. | system | $N_1$ | $\delta W_2^T$ | $\delta W_3^T$ | $\delta W_2^B$ | $\delta W_3^B$ | $\delta W$ | $\delta W_{max}$ | note |
|---|---|---|---|---|---|---|---|---|---|
| 1 | EOPO4000 + $(NH_4)_2SO_4$ | 10 | 2.17 | 0.16 | 0.22 | 0.52 | 0.97 | 3.16 | partial pred |
| 2 | EOPO4000 + $(NH_4)_2SO_4$ | 10 | 2.89 | 0.32 | 0.55 | 0.20 | 1.26 | 3.98 | pred |
|  | EOPO2000 + $(NH_4)_2SO_4$ | 10 | 1.20 | 0.28 | 0.34 | 0.35 | 0.56 | 2.37 | partial pred |
|  | EOPO800 + $(NH_4)_2SO_4$ | 10 | 1.43 | 0.26 | 4.96 | 2.38 | 2.14 | 6.08 | pred |
| 3 | EOPO800 + $(NH_4)_2SO_4$ | 10 | 0.50 | 0.63 | 0.40 | 0.62 | 0.58 | 1.21 | partial pred |

two tie-line data and set $N_1 = 4$ in eq 9; thus other tie lines in this system or from the systems with different molecular weights of EOPO can be predicted according to the equality of component activities in both phases when the feed compositions are given.

## Results and Discussion

Experimental liquid−liquid equilibrium results for the aqueous two-phase systems with different EOPO molecular weights are listed in Table 1. The tie lines for each system were constructed by plotting the best line that could fit the three points of total compositions of the top and the bottom phases. The linear correlation factor ($r^2$) in most cases is greater than 0.9990, which indicates that the analytical determination of the constituents of the two equilibrium liquid phases was accurate and consistent.

An estimation of the critical compositions was obtained by drawing a straight line connecting the midpoints of all experimental tie lines and extrapolating it to the point of intersection with the binodal curve. The experimental critical compositions are given in Table 2.

The evaluated model parameters of EOPO + $(NH_4)_2SO_4$ ATPS for different molecular weights of EOPO are listed in Table 3. The liquid−liquid equilibrium compositions for polymer + salt ATPS, EOPO4000 + $(NH_4)_2SO_4$, EOPO2000 + $(NH_4)_2SO_4$, and EOPO800 + $(NH_4)_2SO_4$, were predicted. Table 4 shows the predicted results and the comparison with the experimental data. The ordinal numbers on the first row of Table 4 correspond to those in Table 3. The expressions for $\delta W_j^{\alpha}$, $\delta W$, and $\delta W_{max}$ in Table 4 are as follows

$$\delta W_j^{\alpha} = \sum_k^{CN_1} |W_{k,j}^{\alpha}(\text{calc}) - W_{k,j}^{\alpha}(\text{expt})|/CN_1$$

$$\delta W = \sum_{\alpha}\sum_{j} \delta W_j^{\alpha}/2N_3$$

$$\delta W_{max} = \max\{|W_{k,j}^{\alpha}(\text{expt}) - W_{k,j}^{\alpha}(\text{calc})|\}$$

where $\delta W_j^{\alpha}$, $\delta W$, and $\delta W_{max}$ mean the average absolute deviation in mass percentage of component $j$ in phase α, the overall average absolute deviation, and the maximum absolute deviation, respectively.

Figure 1 demonstrates the comparison of the predicted tie lines for EOPO4000 + $(NH_4)_2SO_4$ ATPS with the experimental ones as an example. Figure 2 illustrates the dependence of the phase diagrams of EOPO + $(NH_4)_2SO_4$ ATPS on the EOPO molecular weights by the model. It is shown that all the above results are in good agreement with the experimental data, with most values of $\delta W_j^{\alpha}$ and $\delta W$ being less than 2.5% and all values of $\delta W_{max}$ not larger than 6.1%.

Furthermore, it is found in Table 4 that the accuracy of partial prediction for a EOPO + $(NH_4)_2SO_4$ ATPS is somewhat enhanced because the model parameters correlated from the LLE data of its own system are used. For example, the partial prediction for the EOPO4000 + $(NH_4)_2SO_4$ system, numbered 1 in Table 4, is more accurate than the complete prediction for the same system numbered 2. Similar phenomena are found in the case of the EOPO800 + $(NH_4)_2SO_4$ system.

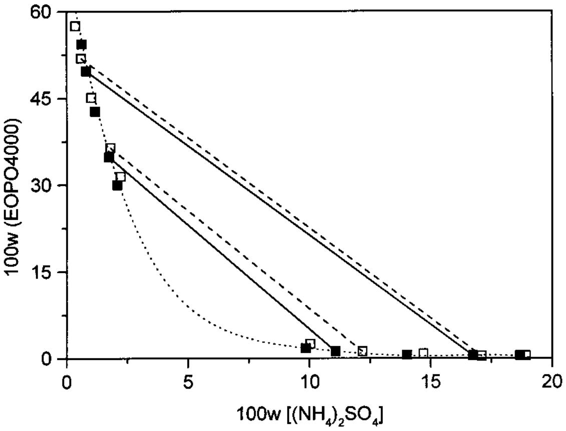

**Figure 1.** Phase diagram for EOPO4000 + $(NH_4)_2SO_4$ ATPS at 298.15 K: (□- -□) experimental data and tie lines; (■—■) predicted data and tie lines; (···) predicted binodals with the model parameters of no. 1 in Table 3.

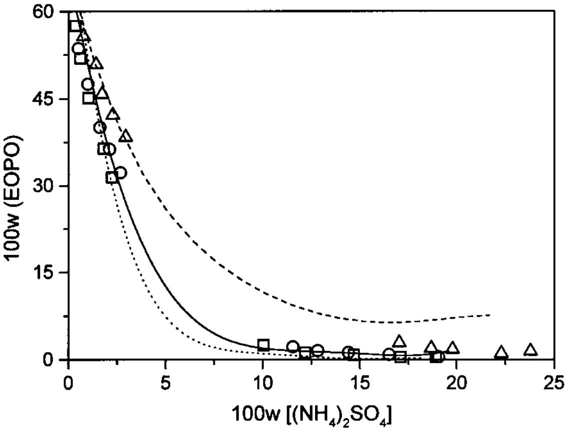

**Figure 2.** Effect of the molecular weights of EOPOs on the phase diagram of EOPO + $(NH_4)_2SO_4$ ATPS at 298.15 K: experimental data for (□) EOPO4000, (○) EOPO2000, and (△) EOPO800; predicted binodals for (···) EOPO4000, (—) EOPO2000, and (- -) EOPO800 with the model parameters of no. 2 in Table 3.

## Conclusion

The drying−weighing and titration methods were established to determine the concentrations of the copolymer of ethylene oxide−propylene oxide and ammonium sulfate in aqueous solution. The liquid−liquid equilibrium data at 298.15 K along with the critical compositions for $H_2O$ + EOPO 4000 + $(NH_4)_2SO_4$, $H_2O$ + EOPO 2000 + $(NH_4)_2SO_4$, and $H_2O$ + EOPO 800 + $(NH_4)_2SO_4$ ternary systems were measured.

The modified NRTL model was extended for the calculation of the phase equilibria of $H_2O$ + EOPO + $(NH_4)_2SO_4$ systems with various polymer molecular weights. The predicted results are in good agreement with the experimental data.

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