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Liquid−Liquid Equilibria in Aqueous Two-Phase Systems of Poly(ethylene glycol) and Poly(ethyleneimine): Experimental Measurements and Correlation

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In this paper, which forms part of a study on aqueous two-phase systems (ATPS) for separation of low molar mass organic acids in the biotechnology industry, we present experimental and modeling results on the phase equilibria of an ATPS containing poly(ethylene glycol) (PEG) and poly(ethyleneimine) (PEI). The measurements were made at a temperature of 25 °C and a pressure of 1 bar, at pH = 5.3, 7.5, and 9.2. The PEG had a mass-average molar mass of 4000 $g \cdot mol^{-1}$ and a polydispersity index of 1.05, while the PEI had a mass-average molar mass of 25 000 $g \cdot mol^{-1}$ and a polydispersity index of about 2.5. A UNIQUAC model, incorporating the polydispersity of the PEI, was found to give a satisfactory correlation of the experimental data. The experiment results demonstrated that the polymers are distributed unevenly in the two phases, and this suggests that organic acids (e.g., lactic acid) will partition preferentially to the PEI-rich phase through acid−base association.

Introduction

Aqueous two-phase systems (ATPS), consisting of two structurally different polymers (e.g., poly(ethylene glycol) and dextran) or a polymer and an inorganic salt have been employed extensively in biotechnology for the separation and purification of biologically active proteins and for the production of valuable biomolecules. Reviews have been published[1−3] of previous experimental studies on liquid−liquid equilibria (LLE) in ATPS containing two different kinds of polymers or a polymer and a salt.

It is possible to design an ATPS in which the cells *always* concentrate either in one of the phases or at the phase boundary, allowing the removal of the product from the cell-free phase. Thus, in a biotechnological production of valuable low molar mass products, the cell-containing phase remains in the reactor, while the other phase is repeatedly renewed in a semi-batch or continuous process. However, the low molar mass components (e.g., organic acids) are invariably distributed *equally* between the two phases leading to sub-optimal recovery and less effective pH control.

The broad aim of our studies is to identify and test ATPS suitable for the separation of low molar mass organic acids of importance to the biotechnological industry (e.g., lactic acid). The purpose of the present paper is to outline the experimental and modeling results on the phase equilibria of an ATPS containing poly(ethylene glycol) (PEG) and poly(ethyleneimine) (PEI). PEG has been chosen because of its well-documented application in such systems, while PEI has been selected with a view to obtaining high equilibrium concentration of the valuable acid product in the PEI-rich phase through acid−base association. To the best of our knowledge, there are only two papers devoted to the experimental determination of the binodal curve of the ATPS formed from PEI and PEG;[4,5] no data on tie-lines have previously been published.

Materials and Methods

Materials. PEG 4000 was obtained from Fluka. It is a narrowly distributed technical product, with a polydispersity index of about 1.05 as determined in the present study by gel permeation chromatography (GPC). PEI was obtained from Aldrich. According to the manufacturer, the number-average molar mass M_n of the PEI was approximately 10 000 $g \cdot mol^{-1}$ by GPC, and the mass-average molar mass M_w was approximately 25 000 $g \cdot mol^{-1}$ by light scattering; so the PEI sample was characterized by a polydispersity index of about 2.5.

Stock solutions of the polymers in distilled water were prepared gravimetrically on an analytical balance with 0.0001 g resolution. The expanded uncertainty of the gravimetric measurements was $\pm\ 5.3 \cdot 10^{-4}$ g with coverage factor 2. For the PEG, the mass fraction of the stock solution was 0.4, while for PEI a mass fraction of 0.2 was chosen. To be able to form an ATPS with PEG solutions, the PEI solution must be titrated with either a bi- or trivalent counterion.[4] Accordingly, the PEI solutions were titrated with H_2SO_4 to pH = 5.3, 7.5, or 9.2, with uncertainty in the range (0.048 to 0.056) pH units.

Methods. (a) Determination of the Equilibrium Compositions (Tie-Lines). Equilibrium measurements were carried out on 25 mL samples prepared gravimetrically by mixing appropriate quantities of the two stock solutions with distilled water in 50 mL beakers. Each sample was stirred vigorously for 15 min and then transferred into a graduated (0.1 mL) test tube fitted with a stopper. The tubes were placed in a water bath thermostated at (25.0 ± 0.1) °C, and the system was left to settle for 15 h, during which time it separated into two clear and transparent liquid phases separated by a well-defined interface. The volumes V_{top} and V_{bottom} of the top and bottom phases were estimated from the graduation of the test tubes with uncertainties of ± 0.1 mL, and volume ratios were calculated.

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The ATPS were then transferred into separating funnels and thermostated for additional (6 to 8) h to ensure equilibrium. After that period, the top and bottom phases were carefully separated and diluted with known amounts of distilled water. Samples of the clear solution formed from each equilibrium phase were collected by syringe and analyzed by HPLC. The equilibrium concentrations of the two polymers were obtained from experimentally determined calibration data, which showed that the response of the HPLC detector was linear up to $w_i = 0.05$, where w_i is mass fraction of polymer component i. All analyses were based on three replicate chromatographic measurements made on each sample, and the results were reproduced with accuracy within $\pm\ 0.01 \cdot w_i$, while the corresponding uncertainty was ± 1.5 % of the values measured.

The HPLC system comprised an eluent pump (K-120, Knauer), an injection valve fitted with a 20 μL loop, two gel exclusion columns connected in series (Ultrahydrogel 120 and Ultrahydrogel 250, 300 mm × 7.8 mm i.d., Waters), and a refractive index detector (LC 25, Perkin-Elmer). The mobile phase (0.5 $\text{mol} \cdot \text{L}^{-1}$ sodium acetate + 0.5 $\text{mol} \cdot \text{L}^{-1}$ acetic acid in distilled water) was delivered at a flow rate of 0.6 $\text{mL} \cdot \text{min}^{-1}$. The columns were maintained at the ambient temperature of (23 ± 2) °C. In a few cases, the pH values of the separated top and bottom phases were also measured and found to differ by not more than 0.2.

(b) Determination of the Binodal Curve. The binodal curve was determined by dropwise addition of water to the well-stirred ATPS prepared as described above. Water was added until turbidity disappeared and the solution became transparent, which indicated the transition from heterogeneous to homogeneous phase behavior. All solutions were maintained at (25 ± 0.1) °C in a temperature-controlled bath. The composition of the last point in the two-phase region and the composition of the first point in the homogeneous region were determined gravimetrically, and the mean value of the two was taken as a point on the binodal. This typically introduced an ambiguity not worse than $\pm\ 0.005 \cdot w_i$ in the binodal composition.

Thermodynamic Framework

Polydispersity. An important feature of ATPS that must be accounted for in thermodynamic studies is the polydispersity of large polymer molecules such as PEI. Although polydispersity is often neglected when calculating phase equilibrium in ATPS, its influence on phase equilibrium calculations could and should be evaluated.

The size distribution of a polymer may be provided by the manufacturer in some cases, but typically only the number-average M_n and the mass-average M_w molar masses are reported. These quantities are defined as follows:

$$M_n = \sum_i x_i M_i \tag{1}$$

$$M_w = \sum_i w_i M_i \tag{2}$$

There are two different possibilities to account for the molar mass distribution of polydisperse polymers.[6] The first one[7−9] is to treat the distribution with continuous distribution functions, such as the Schulz−Flory distribution or the Wesslau distribution, and to apply functional theory to derive an expression for the chemical potential. Phoenix and Heidemann[10] applied this approach to develop an algorithm for determining the cloud- and shadow-point curves of polydisperse polymer solutions. However, there is loss of rigor when phase-equilibrium problems are solved using a continuous distribution function, as the same distribution function may not necessarily describe the equilibrium compositions.[11]

Another approach is to treat the distribution with a set of discrete pseudocomponents.[12−15] For unimodal molecular weight distribution curves, pseudocomponents are generated either by matching the statistical moments of the experimental distribution to those of the pseudocomponents to be determined[16] or by using a systematic pseudocomponent or lumping procedure based on a continuous distribution function and a Gaussian quadrature method (see, for example, Cotterman et al.[11]). With the latter technique, LLE calculations can be made using a small number of properly chosen pseudocomponents to represent the various molecule sizes rather than the much less convenient thermodynamics of continuous mixtures.

In the present study, the polydispersity of the PEI has been accounted for by the method of Sandler and co-workers.[17−19] In this method, a continuous statistical distribution is first determined from the available experimental data and then used in a mathematically consistent quadrature procedure to obtain a limited number of pseudocomponents to represent the polydisperse polymer. In what follows a brief summary of this procedure is presented.

Distribution Functions. For a polydisperse polymer, it is assumed that the molar masses follow the Lansing−Kraemer logarithmic normal distribution[20] (denoted hereafter as the L−K distribution) which is given by

$$F(M) = \frac{1}{\beta\pi^{1/2}} \exp\left(-\frac{1}{\beta^2} \ln^2 \frac{M}{M_0}\right) \tag{3}$$

where β and M_0 are adjustable parameters. The L−K distribution has a maximum at

$$M_{\max} = M_0 \exp\left(-\frac{1}{\beta^2}\right) \tag{4}$$

and the average molar masses are given by

$$\frac{1}{M_n} = \frac{\int_0^\infty \frac{1}{M} F_i(M)\, dM}{\int_0^\infty F_i(M)\, dM} = \frac{1}{M_0} \exp\left(\frac{1}{\beta^4}\right) \tag{5}$$

and

$$M_w = \frac{\int_0^\infty M F_i(M)\, dM}{\int_0^\infty F_i(M)\, dM} = M_0 \exp\left(\frac{1}{\beta^4}\right) \tag{6}$$

The polydispersity parameter b for this distribution is therefore

$$b = \frac{M_w}{M_n} = \exp\left(\frac{2}{\beta^4}\right) \tag{7}$$

Thus, the parameters in the distribution can be determined given M_n and M_w or one of these averages and b.

Quadrature Method. After choosing the distribution function, the optimal pseudocomponents to represent the continuous distribution are chosen on the basis of a Gaussian quadrature method. Thus, the polydisperse polymer feed is considered to be a multicomponent mixture in which each psudocomponent has a specified molar mass and mass fraction. LLE calculations are then performed to obtain the mass fractions of these same pseudocomponents in the coexisting phases.

The average value of a function $\theta(M)$ weighted by the L−K distribution is given by

$$\int_0^\infty F(M)\theta(M)\,\mathrm{d}M = \frac{1}{\beta\pi^{1/2}}\int_0^\infty \left(\exp\left(-\frac{1}{\beta^2}\right)\ln^2\frac{M}{M_0}\right)\theta(M)\,\mathrm{d}M \tag{8}$$

If the following substitutions are made

$$x = \frac{1}{\beta}\ln\frac{M}{M_0} \tag{9}$$

and

$$\mathrm{G}(x) = \theta(M) \tag{10}$$

the Gauss−Hermite quadrature can be applied to replace the integral with a sum over n terms, where n is the number of pseudocomponents or polymer fractions to be used. The appropriate expression is

$$\int_{-\infty}^{\infty}\exp(-x^2)G(x)\,\mathrm{d}x = \sum_{k=1}^{n} W_k G(z_k) \tag{11}$$

where z_k are the zeros of the Hermite polynomials and W_k are the weight factors in the expansion. Thus, the optimal quadrature points are determined from the zeroes of the Hermite polynomials:

$$H_n(x) = n!\sum_{m=0}^{n/2}(-1)^m\frac{(2x)^{n-2m}}{m!(n-2m)!} \tag{12}$$

and the weight factors are

$$W_k = \frac{n!\pi^{1/2}(z_{ki})^{n+1}}{[H_{n+1}(z_{ki})]^2} \tag{13}$$

The molar mass of pseudocomponent k is therefore given by

$$M_k = M_0\exp(\beta z_k) \tag{14}$$

and the corresponding mass fraction is given by

$$w_k = \frac{W_k}{\sum_j W_j} \tag{15}$$

and is thus normalized to unity. With the quadrature points and weight factors determined as described above, the average molar masses are given by

$$\frac{1}{M_\mathrm{n}} = \frac{\sum_{k=1}^{n} w_k/M_k}{\sum_{k=1}^{n} w_k} \tag{16}$$

and

$$M_\mathrm{w} = \frac{\sum_{k=1}^{n} w_k M_k}{\sum_{k=1}^{n} w_k} \tag{17}$$

Numerical values of z_k and W_k can be found in handbooks, for example, ref 21.

Liquid−Liquid Flash Calculations. Once the pseudocomponents for a specific feed composition have been determined by the procedure above, isothermal LLE calculations may be performed. These of course require both an appropriate thermodynamic model and a robust and efficient numerical procedure to solve the system of strongly nonlinear equations derived from the phase equilibrium conditions and mass balances.

Equilibrium Conditions and Mass Balance. The equilibrium conditions for the monodisperse components are given by

$$\mu_i^\mathrm{I} = \mu_i^\mathrm{II} \tag{18}$$

and for the polydisperse polymer by

$$\mu_{ji}^\mathrm{I} = \mu_{ji}^\mathrm{II} \tag{18a}$$

where μ_i is the chemical potential of a monodisperse polymer of type i; μ_{ji} is the chemical potential of pseudocomponent j belonging to a polydisperse polymer of type i; and I and II denote phases 1 and 2, respectively. The material balance for the monodisperse components is

$$w_i^\mathrm{F} = (1-\alpha)w_i^\mathrm{I} + \alpha w_i^\mathrm{II} \tag{19}$$

and for the polydisperse component is

$$w_{ji}^\mathrm{F} = (1-\alpha)w_{ji}^\mathrm{I} + \alpha w_{ji}^\mathrm{II} \tag{19a}$$

where superscript F denotes properties of the feed and α is the ratio of the mass of the top phase to that of the feed. Finally, the summation of mass fractions of all components in each phase must be unity.

Thermodynamic Model. In the present study, the UNIQUAC model of Abrams and Prausnitz[22] is applied to the water + PEG + PEI system. The logarithm of the activity for each component in a mixture of n components is given by

$$\ln a_i = \ln\Phi_i^* + \frac{z}{2}M_i q_i^*\ln\left(\frac{\theta_i^*}{\Phi_i^*}\right) + M_i l_i^* - \frac{M_i\theta_i^*}{w_i}\sum_{j=1}^{n} w_j l_j^* + M_i\Phi_i^*\left[1 - \ln\left(\sum_{k=1}^{n}\Phi_k^*\tau_{ki}\right) - \sum_{j=1}^{n}\frac{\theta_j^*\tau_{ij}}{\sum_{k=1}^{n}\theta_k^*\tau_{kj}}\right] \tag{20}$$

where

$$\Phi_i^* = \frac{w_i r_i^*}{\sum_{j=1}^{n} w_j r_j^*} \tag{20a}$$

$$\theta_i^* = \frac{w_i q_i^*}{\sum_{j=1}^{n} w_j q_j^*} \tag{20b}$$

$$l_i^* = \frac{z}{2}(r_i^* - q_i^*) - (r_i^* - 1/M_i) \tag{20c}$$

and $z = 10$. Here, r_i^* and q_i^* are volume and surface area

Table 1. Experimental LLE Data for PEI (1) + PEG (2) + Water (3) at $T = 298.15$ K and pH = 5.3

feed		top phase		bottom phase		
$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$	V_{top}/V_{bottom}
2.63	3.00	1.12	3.55	10.71	0.36	4.9
3.41	3.45	0.66	4.49	13.03	0.31	3.5
4.12	2.04	1.27	3.11	8.51	0.38	1.5
4.22	4.16	0.52	5.35	16.64	0.17	3.3
4.87	4.98	0.33	6.42	19.93	0.19	3.2

Table 2. Binodal Curve for PEI (1) + PEG (2) + Water (3) at $T =$ 298.15 K and pH = 5.3

$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$
0.20	7.89	2.12	2.23	6.59	0.68
0.27	6.77	2.85	1.80	8.93	0.37
0.65	4.00	3.50	1.52	9.83	0.36
1.35	2.95	5.16	1.06		

Table 3. Experimental LLE Data for PEI (1) + PEG (2) + Water (3) at $T = 298.15$ K and pH = 7.5

feed		top phase		bottom phase		
$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$	V_{top}/V_{bottom}
3.97	4.00	2.90	4.49	10.58	0.93	5.9
4.44	4.58	1.70	6.00	12.23	0.63	3.0
4.45	5.46	0.89	7.55	12.96	0.58	2.1
5.45	6.19	0.85	9.34	13.25	0.60	1.8
5.90	6.79	0.73	10.48	14.38	0.61	1.6

Table 4. Binodal Curve for PEI (1) + PEG (2) + Water (3) at $T =$ 298.15 K and pH = 7.5

$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$
9.14	1.18	5.25	2.97	1.38	6.53
8.68	1.21	4.50	3.34	0.99	7.38
8.28	1.37	3. 43	4.06	0.86	7.71
7.21	1.97	2.11	5.41		

Table 5. Experimental LLE Data for PEI (1) + PEG (2) + Water (3) at $T = 298.15$ K and pH = 9.2

feed		top phase		bottom phase		
$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$	V_{top}/V_{bottom}
5.71	5.76	2.86	8.87	8.49	2.80	1.4
5.98	6.21	1.69	10.81	9.69	2.20	1.2
6.80	6.99	1.13	13.17	11.80	1.25	1.2
6.87	7.49	0.98	14.08	12.68	1.13	1.0
7.74	7.99	0.95	15.69	14.08	0.85	1.1

Table 6. Binodal Curve for PEI (1) + PEG (2) + Water (3) at $T =$ 298.15 K and pH = 9.2

$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$	$10^2 \cdot w_1$	$10^2 \cdot w_2$
1.31	12.04	2.74	8.51	5.79	5.18
1.40	11.41	4.32	6.58	6.83	4.45
1.96	9.94	4.69	6.20	9.00	2.53
2.49	9.17	4.70	6.19		

parameters of component (pseudocomponent) i per unit mass, w_i is the mass fraction, and M_i is the molar mass of component (pseudocomponent) i. The binary interaction parameters between species i and j are given by

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T}\right) \tag{21}$$

where

$$a_{ij} = \left(\frac{u_{ij} - u_{jj}}{R}\right) \tag{21a}$$

Initialization Strategy. Conventional flash algorithms applied to polymer solutions are usually unreliable and the convergence is strongly dependent on whether the starting values are in the vicinity of the solution (fixed point). In the present study, the robust flash algorithm and initialization strategy advocated in ref 23 were applied, as these are targeted particularly at the solution of the LLE and LLLE problems. In all cases, this leads to good convergence characteristics of the LL flash and avoids well-known problems such as convergence to a trivial solution or a failure to converge to a physically feasible solution at all.

Table 7. UNIQUAC Parameters a_{ij}/K for PEI (1) + PEG (2) + Water (3) System

component	1	2	3
(a) $T = 298.15$ K and pH = 5.3			
1		103.08	−640.08
2	69.78		−571.26
3	836.63	142.08	
(b) $T = 298.15$ K and pH = 7.5			
1		398.72	−447.51
2	80.32		−123.58
3	334.63	224.65	
(c) $T = 298.15$ K and pH = 9.2			
1		715.06	−1060.23
2	206.11		−665.7
3	2034.1	592.97	

Results and Discussion

Experimental Equilibrium Compositions and Binodal Curve. The equilibrium compositions of the ATPS PEG + PEI were measured at $T = 298.15$ K and $p = 1$ bar. The results for pH = 5.3, 7.5, and 9.2 are given in Tables 1, 3, and 5, while the corresponding binodal data are given in Tables 2, 4, and 6. Tables 1, 3, and 5 show also the ratios of the phase volumes.

LLE Calculations. For the ATPS under consideration in the present study, the PEG remains narrowly dispersed, and we have assumed that it can be treated as a monodisperse polymer. The PEI, however, is polydisperse with $b = 2.5$. Thus, the L−K distribution was applied to account for the polydispersity of PEI.

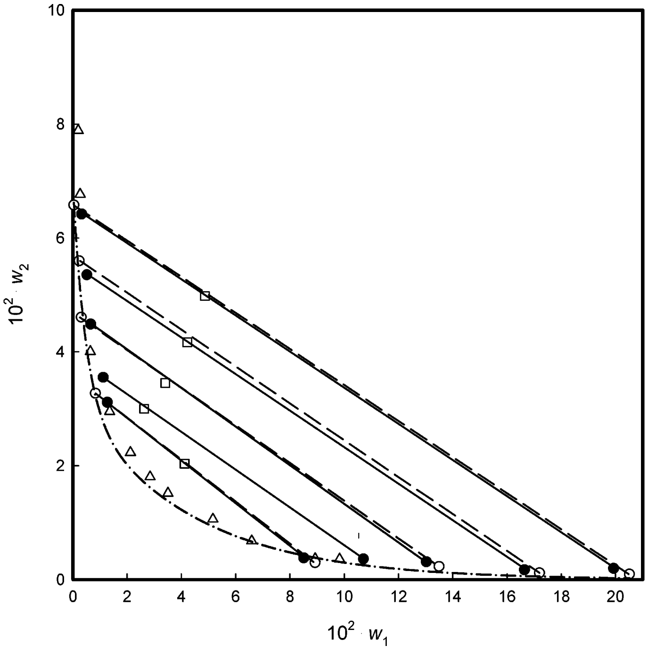

Figure 1. Comparison between the experimental data and the UNIQUAC LL calculations at $T = 298.15$ K and pH = 5.3. □, feed; ●, experimental equilibrium points; △, experimental binodal; ○, equilibrium points UNIQUAC calculations; solid line, experimental tie-line; dashed line, tie-line UNIQUAC calculations; dash−dot line, binodal line UNIQUAC calculations.

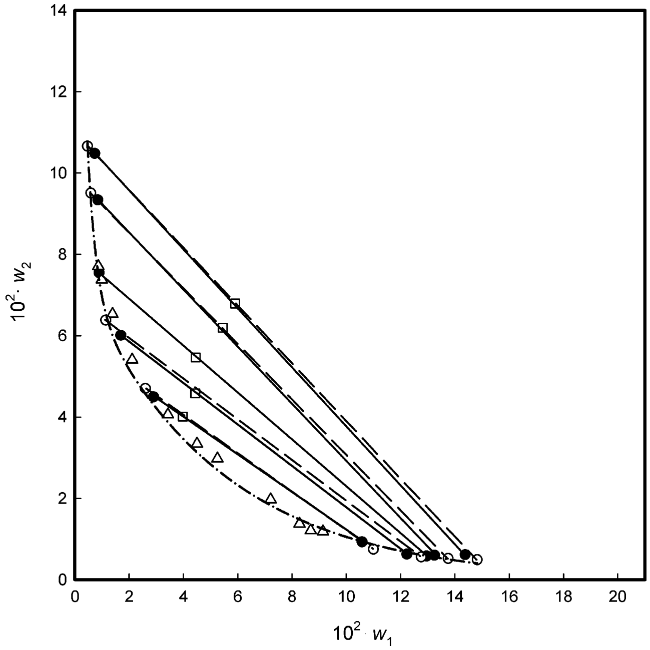

Figure 2. Comparison between the experimental data and the UNIQUAC LL calculations at T = 298.15 K and pH = 7.5. □, feed; ●, experimental equilibrium points; △, experimental binodal; ○, equilibrium points UNIQUAC calculations; solid line, experimental tie-line; dashed line, tie-line UNIQUAC calculations; dash−dot line, binodal line UNIQUAC calculations.

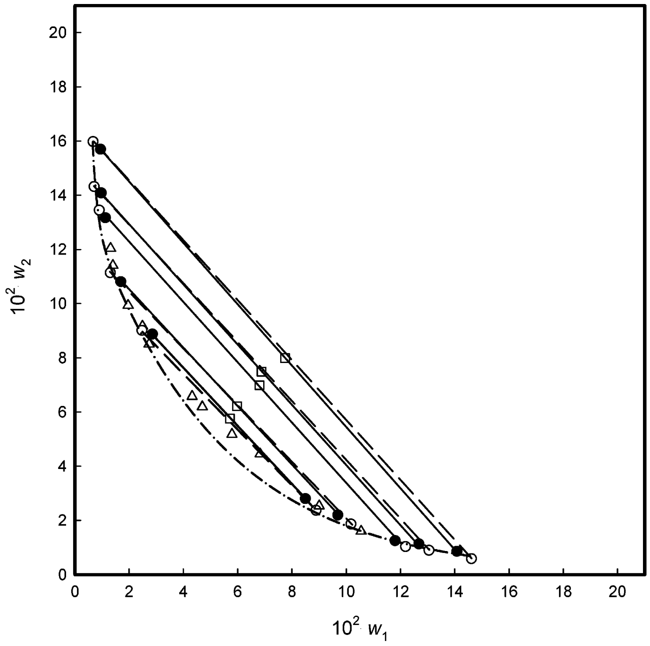

Figure 3. Comparison between the experimental data and the UNIQUAC LL calculations at T = 298.15 K and pH = 9.2. □, feed; ●, experimental equilibrium points; △, experimental binodal; ○, equilibrium points UNIQUAC calculations; solid line, experimental tie-line; dashed line, tie-line UNIQUAC calculations; dash−dot line, binodal line UNIQUAC calculations.

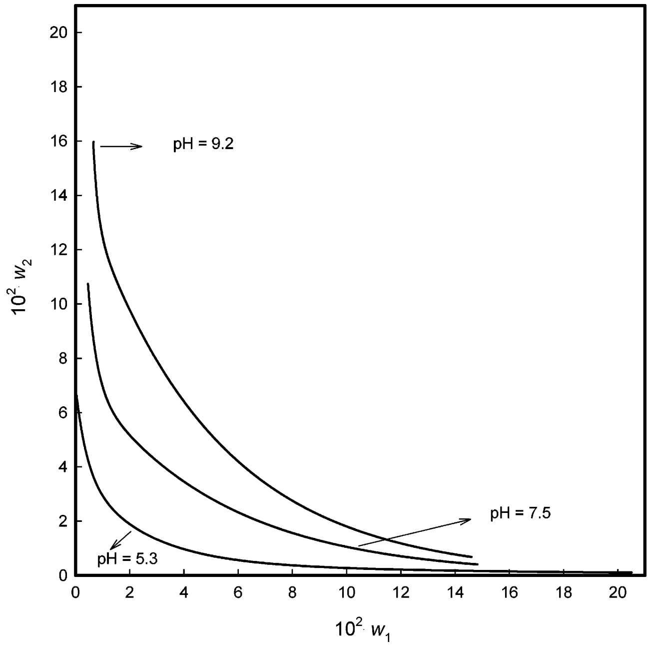

Figure 4. Influence of pH at T = 298.15 K on the phase diagram of the ATPS. Solid line, UNIQUAC calculations.

Table 8. Comparison of Experimental and Calculated Equilibrium Compositions and Polydispersity Index of PEI for PEI (1) + PEG (2) + Water (3)

	top phase, $10^2 \cdot w_i$		bottom phase, $10^2 \cdot w_i$	
component	experimental	calculated	experimental	calculated
(a) T = 298.15 K and pH = 5.3 (feed no. 3)				
1	1.27	0.84	8.51	8.93
2	3.11	3.27	0.38	0.30
M_n	7830	5615	12 600	13 216
b	1.70	1.45	2.44	2.46
(b) T = 298.15 K and pH = 7.5 (feed no. 5)				
1	0.73	0.46	14.38	14.82
2	10.48	10.66	0.61	0.49
(c) T = 298.15 K and pH = 9.2 (feed no. 1)				
1	2.86	2.40	8.49	8.89
2	8.87	9.08	2.80	2.37

Four pseudocomponents were found sufficient to represent the extent of polydispersity for the PEI and to obtain converged phase boundaries. Once the number of pseudocomponents representing the polydisperse polymer is determined, application of the thermodynamic model is straightforward, provided that the model required parameters are available.

For the ATPS under consideration, the pure substance parameters r_i^* and q_i^* per unit mass for PEG and water are taken from the literature,[24] while those for PEI were calculated by us from the molecular structure of the polymer. The corresponding values are $r_i^* = 0.0387$ and $q_i^* = 0.0257$.

The binary interaction parameters were considered as adjustable parameters and the goal was to determine values of a_{ij} and a_{ji} that provided the best fit to the experimental LLE data at each pH value in turn. This determination is usually based on some type of least squares or maximum likelihood criterion and requires the solution of a nonlinear optimization problem. In the present paper, the absolute average deviation between the experimental and calculated equilibrium compositions of the two liquid phases was minimized. It should be pointed out, however, that it is not uncommon for the objective function in such nonlinear parameter estimation problems to be nonconvex and thus to have several local minima. Furthermore, the methods typically used to solve such problems, like the one used in the present study, are local methods that provide no guarantee that the global optimum has been found. Thus, the sets of the binary interaction parameters obtained probably represent just one of the possible sets of parameters. The values for the binary parameters obtained for the three different pH values studied are given in Table 7. We note that there is no noticeable trend in the parameter values as functions of the pH.

Comparisons between the experimental and calculated LLE data are presented in Figures 1 to 3, and the effect of pH on the binodal curve is summarized in Figure 4. As a result of the incorporating the polydispersity of the PEI in the model, good agreement between the measured and calculated compositions of the equilibrium phases has been achieved (see Table 8). Table 8a (at pH = 5.3) shows also a comparison of the PEI polydispersity index measured experimentally by us in the top and bottom phases with the values obtained from the calculations. Analogous results were obtained for the other two pH values studied. The observation made here, that the PEI molar mass distribution in each phase differs from that of the feed, is similar to that made for polydisperse dextran in the ATPS formed between dextran and PEG.[17,18]

Conclusions

In the ATPS formed from PEG + PEI, the two polymers were found to be distributed unevenly between the two phases, with PEI concentrated in the bottom phase and PEG in the top phase. This makes the ATPS PEG + PEI favorable for the separation of organic acids; our future work will be devoted to the study of lactic acid distribution in this particular ATPS with the view to obtaining high equilibrium concentration of the valuable acid product in the PEI-rich phase through acid−base association.

The UNIQUAC model, with the polydispersity of the PEI taken into account, is a good framework for correlating the experimental data, despite the fact that different parameter sets are required for each pH with no obvious systematic trends.

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