Effects of Polydispersivity on the Phase Behavior of Aqueous Two-Phase Polymer Systems

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ABSTRACT: In this paper the effects of polydispersivity on the liquid–liquid phase behavior of dextran/poly(ethylene glycol)/water systems are investigated. The UNIQUAC model is used for the thermodynamic description of these systems together with the assumption of a continuous distribution for the molecular weights of the polydisperse polymers. The polydispersivity of the polymers is taken into account with pseudocomponents chosen by a generalized Gaussian quadrature method. From our calculations, it is found that the liquid–liquid immiscible region becomes larger with a broader molecular distribution of either polymer at fixed number-average molecular weight. It is also observed that a polymer fractionation occurs on phase splitting with the larger dextran molecules tending to remain in the bottom dextran-rich phase while the larger poly(ethylene glycol) molecules remain in the upper PEG-rich phase. We also find that the representation of each polymer by as few as four pseudocomponents chosen by the Gauss–Hermite quadrature method accurately represents the phase behavior of these polydisperse polymer systems.

Introduction

The fact that polymers are not of a single molecular weight (monodispersed) is frequently ignored in the study of phase equilibrium in polymer solutions. The Flory–Huggins theory for a monodisperse polymer system in a solvent was first extended to polydisperse polymer systems in a mixture of solvents by Scott and Magat.[1] Koningsveld and Staverman[2] have extensively investigated phase separations in solutions containing polydisperse macromolecules using the Flory–Huggins theory and concluded that polymolecularity of the macromolecules affects their phase diagrams to such an extent that it should not be ignored in treatments intended to be quantitative. It has also been experimentally observed that in the liquid–liquid equilibrium of two-polymer systems in an organic solvent the molecular weight distribution of the polymers can cause differences in the phase behavior from that in monodispersed systems[3] and that the molecular weight distributions of the same polymer in the different phases can differ significantly from each other, and from that of the initial feed.[4] The phase behavior of polydisperse polymer solutions has been used for the fractionation of homologous polymers to produce fractions with different average chain lengths.[5,6]

Polydisperse species have been described by a continuous distribution characterized by using one or more intensive properties such as true boiling point (TBP) for heavy oils and the molar mass distribution function in polymer chemistry. Average distributed properties, such as an average molecular weight in polymer systems, have been used to treat polydisperse systems as monodisperse. However, there are important differences between monodisperse and polydisperse systems. For example, the sharp phase transition boundaries that exist in monodisperse mixtures are not found in systems containing polydispersed species. Usually, especially when dealing with oils, the polydispersivity of a mixture is approximately accounted for by some number of pseudocomponents chosen in a relatively arbitrary manner. A tuning procedure is then followed to fit the parameters to limited experimental data.[7] For polydisperse dextran/polyethylene glycol/water systems, Shishov et al.[8] calculated turbidity curves using arbitrarily chosen pseudocomponents for polydisperse polymers. The inherent shortcomings in such a procedure are that it is nonunique and that trial-and-error calculations are needed to obtain a good fit of limited experimental data.

Recent work[9] has centered on the use of continuous distributions to characterize the intensive properties of polydisperse species. The influence of polymer polydispersivity on the liquid–liquid equilibrium (LLE) of polymer solutions was recently treated by using the continuous thermodynamics by Rätzsch and Kehlen.[10] Cotterman et al.[11] introduced the method of moments to investigate the vapor–liquid equilibrium (VLE) of fluid mixtures containing several homologous series. To use this method, a single form of the distribution function for some property, such as the molecular weight, of the feed and all coexisting phases is assumed prior to the calculation, and then the parameters of the distribution in each phase are determined. However, it is easily shown that this approximation cannot be exact for the distributions commonly used, since they cannot be separated into two nonidentical distributions of the same form.

Based on the Gauss quadrature method, a systematic procedure, called the quadrature method, has been developed by Cotterman and co-workers[12,13] for simple exponential distribution functions and by Behrens and Sandler[14] and Shibata et al.[15] for more diverse distributions. In these methods pseudocomponents are chosen to represent a continuous distribution in a mathematically correct and optimal way.

In the work here the phase boundaries of aqueous two-phase, two-polymer systems containing dextran (Dx) and poly(ethylene glycol) (PEG) were found by an LLE calculation algorithm with pseudocomponents chosen by using the quadrature method, and the effects of polymer polydispersivity on the phase boundary were investigated.

Thermodynamic Description

Scott and Magat[1] have extended the Flory–Huggins theory for a monodisperse polymer system in a solvent to the case of polydisperse polymer mixtures in a mixture of solvents. For polydisperse polymer systems Shishov and co-workers[8,16] retained up to the third term in the osmotic virial equation and calculated the turbidity curve of a polydisperse Dx/PEG/water system. We have shown[17,18] that for various Dx/PEG/water systems the UNIQUAC model, with fewer adjustable parameters (since a number of the parameters can be fixed a priori as shown in ref 18), leads to more accurate phase boundary predictions than the Flory–Huggins equation. Also, as has been shown previously,[15] a polydisperse system can be treated as a collection of carefully chosen individual components so that thermodynamic models for multicomponent systems can be used without modification.

Assuming that the interactions between two segments on different polymer chains are independent of the poly-

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mer chain length, the UNIQUAC model in terms of weight fraction for a polydisperse system is given by[17]

$$\ln a_j = \ln \phi'_j + \frac{z}{2}M_j q'_j \frac{\theta'_j}{\phi'_j} + M_j l'_j - \frac{M_j \phi'_j}{x_j}\sum_k l'_k x_k + M_j q'_j\left(1 - \ln \sum_k \theta'_k \tau_{kj} - \sum_k \frac{\theta'_k \tau_{jk}}{\sum_m \theta'_m \tau_{mk}}\right) \quad (1)$$

where

$$\phi'_j = r'_j x_j / \textstyle\sum_j r'_j x_j \quad (2)$$

and

$$\theta'_j = q'_j x_j / \textstyle\sum_j q'_j x_j \quad (3)$$

Here a_j denotes the activity of the jth fraction; r'_j and q'_j are the volume and surface area parameters of the jth fraction per unit mass. The activity a_j is related to the chemical potential μ_j by $\mu_j(T,P,x) = \mu^\circ_j(T,P) + \mathrm{RT} \ln a_j$ where μ°_j is the chemical potential of pure component j in its standard state, and ϕ'_j, θ'_j, and x_j are volume, surface area, and weight fractions, respectively, of jth fraction. Also l'_j and τ_{jk} are given by

$$l'_j = \frac{z}{2}(r'_j - q'_j) - \left(r'_j - \frac{1}{M_j}\right) \quad (4)$$

$$\tau_{jk} = \exp\left(-\frac{A_{jk}}{T}\right) \quad (5)$$

and

$$A_{jk} = \frac{u_{jk} - u_{kk}}{R} \quad (6)$$

where R and T refer to the gas constant and temperature, respectively. The interaction energy between j and k species is denoted by u_{jk}, and u_{kk} is related to the isothermal energy of vaporization of species k from saturated liquid to an ideal gas. The interaction parameter u_{jk}, or equivalently A_{jk}, is usually adjusted by fitting experimental equilibrium data, and z is the coordination number which is usually set equal to 10. In the UNIQUAC model, the effects of small volume changes on the entropy and enthalpy of mixing were assumed to cancel. This assumption is appropriate for nonelectrolyte mixtures remote from their vapor–liquid critical point.[19]

Since the UNIQUAC model accounts for difference in molecular size and shape through the structural parameters r' and q', the model can be used for the prediction of the phase equilibrium of polymer solutions which involve molecules of very different structure provided the values of the structural parameters and interaction parameters A_{ij} are given.[19] Furthermore, since the parameters determined from binary data are, in principle, applicable to multicomponent systems, the model contains only two adjustable parameters per binary and no ternary parameters.

Distribution Functions

Published liquid–liquid equilibrium data for Dx/PEG/water of Albertsson[20] and others do not include information on the molecular weight distributions of the polymers used. For branched dextran, the Lansing–Kraemer (or logarithmic–normal and designated by L-K) distribution has been used for the molecular weight distribution[21]

$$F(M) = \frac{1}{\beta \pi^{1/2}} \exp\left(-\frac{1}{\beta^2} \ln^2 \frac{M}{M_0}\right) \quad (7)$$

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

$$M_{\max} = M_0 \exp\left(-\frac{1}{\beta^2}\right) \quad (8)$$

and the average molecular weights are

$$\frac{1}{\bar{M}_n} = \frac{\int_0^\infty \frac{1}{M} F_i(M)\, dM}{\int_0^\infty F_i(M)\, dM} = M_0 \exp\left(-\frac{1}{\beta^4}\right) \quad (9)$$

$$\bar{M}_w = \frac{\int_0^\infty M F_i(M)\, dM}{\int_0^\infty F_i(M)\, dM} = M_0 \exp\left(\frac{1}{\beta^4}\right) \quad (10)$$

where $\bar{M}_n$ and $\bar{M}_w$ denote number- and weight-average molecular weights, respectively. The polydispersivity parameter b for this distribution is

$$b \equiv \bar{M}_w / \bar{M}_n = \exp(2/\beta^4) \quad (11)$$

Thus, the parameters in the distribution can be determined given $\bar{M}_n$ and $\bar{M}_w$ or one of average molecular weights and b.

The molecular weight distributions of T500 ($\bar{M}_n = 1.812 \times 10^5$ and $b = 2.726$) and T10 ($\bar{M}_n = 6.0 \times 10^3$ and $b = 1.683$) determined by gel permeation chromatography (supplied by the manufacturer) were correlated by using both the L-K and exponential distribution functions, which are commonly used to describe the polymer molecular weight distribution.[22] The results are compared in Figure 1. In this figure values of b and $\bar{M}_n$ from experiment were used to calculate the parameters in exponential distribution. The parameters in the L-K distribution were adjusted by fitting the experimental peak height. The L-K distribution shows reasonably good agreement with the experimental distribution for both dextrans. The L-K and exponential distributions were also used to describe the molecular weight distribution of PEG. In Figure 2, the exponential and L-K distribution representations of PEG are compared with experimental data. The height of the peak of the L-K distribution was also fitted to experimental data for PEG ($\bar{M}_n = 7.2 \times 10^3$, $b = 1.16$), which were generously supplied by Waters.[22] The fitted L-K distribution again shows good agreement with the experimental data. Consequently, the L-K distribution function was used to represent the molecular weight distribution of the polymers in this study.

Quadrature Method

By using the systematic pseudocomponent or lumping procedure based on a continuous distribution introduced by Cotterman and his co-workers[12,13] and Shibata et al.,[15] equilibrium calculations can be done by using a small number of properly chosen pseudocomponents rather than the much less convenient thermodynamics of continuous mixtures. In particular, for the phase equilibrium calculations here, the molecular weight distributions of the polymers in the feed are described by a continuous distribution function and the pseudocomponents to be used in the phase equilibrium calculations are then obtained using the generalized Gaussian quadrature method appropriate to the distribution function chosen. Thus the overall system is represented by a number of pseudocomponents, and a liquid–liquid equilibrium calculation is performed to obtain the compositions of these pseudocomponents in the coexisting phases.

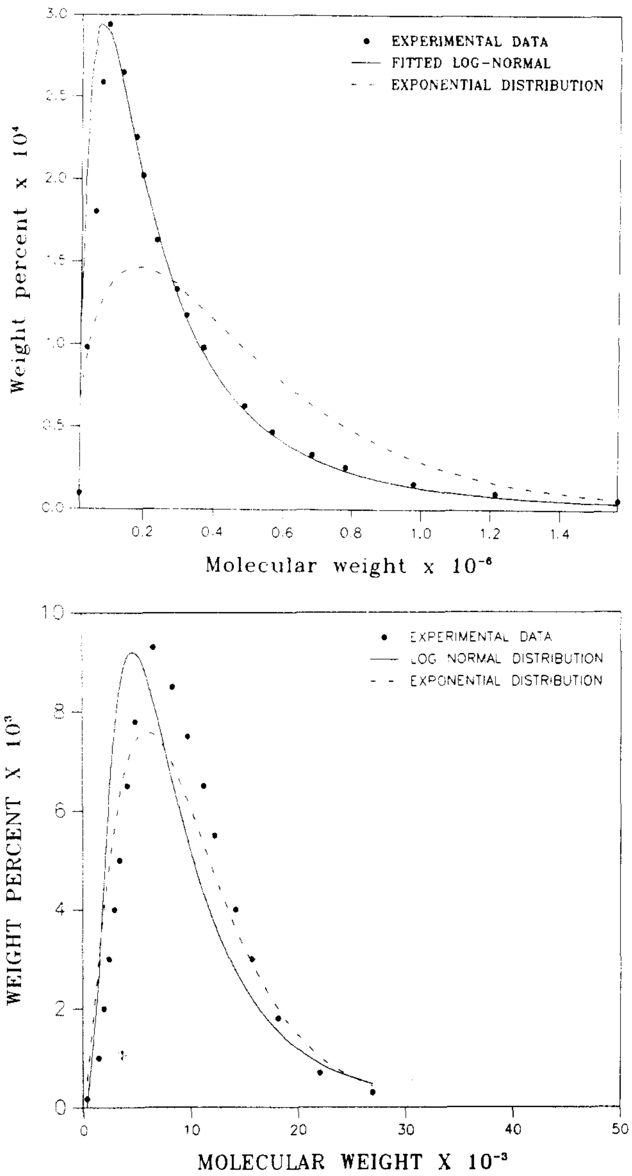

Figure 1. Molecular weight distribution of (top) T500 ($\bar{M}_n = 1.81 \times 10^5$ and $b = 2.73$) in and (bottom) T10 ($\bar{M}_n = 6.0 \times 10^4$ and $b = 1.68$).

For the L-K function, the average value of the function $\theta(M)$ is calculated from

$$\int_0^\infty F(M)\theta(M)\,\mathrm{d}M = \frac{1}{\beta\pi^{1/2}}\int_0^\infty \exp\left(-\frac{1}{\beta^2}\ln^2\frac{M}{M_0}\right)\theta(M)\,\mathrm{d}M \qquad (12)$$

Using Gauss-Hermite quadrature, we have that

$$\int_{-\infty}^{\infty}\exp(-x^2)G(x)\,\mathrm{d}x = \sum_{k=1}^{n} W_k G(z_k) \qquad (13)$$

where $G(x) = \theta(M)$, $x = (1/\beta)\ln(M/M_0)$, and n is the number of quadrature points (pseudocomponents) used. The optimal quadrature points z_k are calculated from the zeros of the Hermite polynomials[23]

$$H_n(x) = n!\sum_{m=0}^{[n/2]}(-1)^m\frac{(2x)^{n-2m}}{m!(n-2m)!} \qquad (14)$$

and the weight factors are

$$W_k = \frac{n!\pi^{1/2}(z_k)^{n+1}}{[H_{n+1}(z_k)]^2} \qquad (15)$$

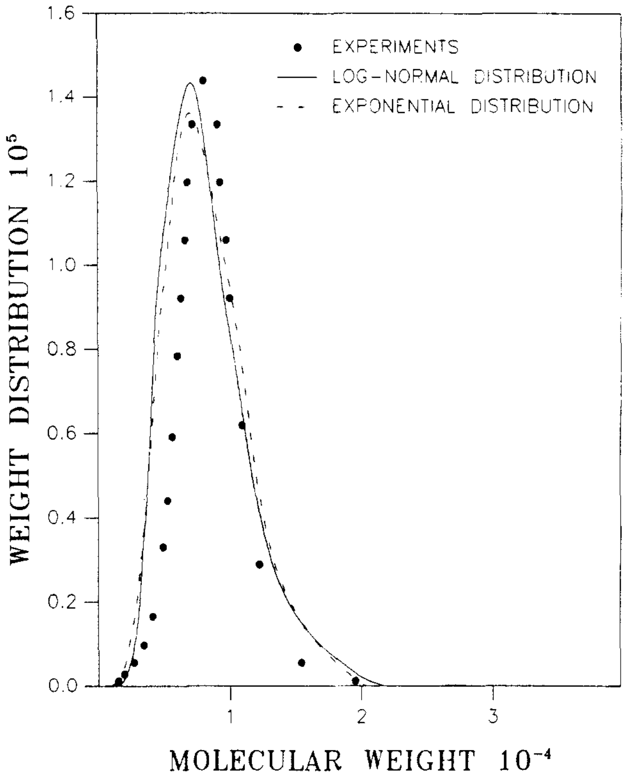

Figure 2. Molecular weight distribution of PEG 8000 ($\bar{M}_n = 7.2 \times 10^3$ and $b = 1.16$).

The numeric values of the locations of the zeros and weight factors may be found in the work of Abramowitz and Stegun.[24] Thus, the molecular weight of the kth pseudocomponent is calculated from $M_k = M_0 \exp(\beta z_k)$, where z_k is the zero of the Hermite polynomial and its weight fraction is gotten from $w_k = W_k/\sum_j W_j$ and is therefore normalized to unity.

With the quadrature points and weight factors determined as described above, the average molecular weights are calculated from

$$\frac{1}{\bar{M}_n} = \frac{\sum_{k=1}^{N} w_k/M_k}{\sum_{k=1}^{N} w_k} \qquad (16)$$

$$\bar{M}_w = \frac{\sum_{k=1}^{N} w_k M_k}{\sum_{k=1}^{N} w_k} \qquad (17)$$

In Figure 3, the convergence of the quadrature method is examined by computing the polydispersivity parameter b calculated from eq 16 and 17 using the L-K and exponential distributions for fixed values of this parameter. The L-K distribution leads to rapid and accurate recovery of the polydispersity of the distribution with fewer quadrature points regardless of the breadth of the distribution. In contrast, slow convergence of the calculation is found with the exponential distribution, and convergence becomes poorer with an increase in the value of b. This is another reason why we use the L-K distribution here.

Once the pseudocomponents for a specific feed composition have been determined by the procedure above, the LLE calculation is performed by using the equilibrium conditions

$$\Delta\mu'_0 = \Delta\mu''_0 \qquad (18)$$

$$\Delta\mu'_{ij} = \Delta\mu''_{ij} \qquad (19)$$

and the material balances

$$\sum_i\sum_j x'_{ij} = \sum_i\sum_j x''_{ij} = \sum_i\sum_j x_{ij}^{\mathrm{F}} = 1 \qquad (20)$$

Here the subscript 0 refers to the solvent, x_{ij} indicates the weight fraction of pseudocomponent j belonging to species i, and the superscript F refers to the feed.

The physical properties of the polymers considered here are given in Table I. For the calculations here the UNIQUAC parameters for the D17/PEG 6000/water system at 293 K reported in our previous work[17,18] were used, assuming that these parameters are independent of polymer chain length. In that work the polymer–water interaction parameters were found from osmotic pressure data for binary mixtures and the polymer–polymer parameters were estimated by fitting the model to ternary equilibrium data. With these parameters the UNIQUAC model led to good phase behavior predictions for Dx/PEG/water systems of various molecular weights.[16] Thus the UNIQUAC model with parameters listed in Table II was used in the LLE calculations here.

Results and Discussion

In practice, dextran becomes very polydisperse in molecular weight with the increase in $\bar{M}_n$ while PEG remains more or less narrowly dispersed up to several thousand in molecular weight. Thus we have assumed first that only dextran is polydisperse and have performed LLE calculations to investigate the shift of the phase boundary for various degrees of polydispersivity of dextran.

Cotterman and co-workers[12,13] and Shibata et al.[15] showed that relatively a few pseudocomponents chosen by the quadrature method could predict accurate phase equilibria of oil mixtures. To investigate the effect of the number of pseudocomponents on the liquid–liquid equilibrium predictions, we have used up to seven pseudocomponents for polydisperse dextran with the quadrature method. The phase boundaries thus obtained are compared in Figure 4 for different numbers of pseudocomponents when the polydispersivity parameter b for dextran is 1.5. It is clear that representing the polydisperse polymer by as few as four quadrature-chosen pseudocomponents is sufficient to obtain converged phase boundaries. In the region dilute in dextran, the polydispersivity of dextran reduces the immiscibility region, while the phase boundary in the region rich in dextran does not change appreciably.

The average molecular weight and polydispersivity parameter b of the polymer in each phase can be evaluated by using eq 16 and 17, and these are plotted in Figure 5. To plot such figures in a consistent manner, we use tie line length (TLL) as the independent variable. TLL is based on the equilibrium composition calculated for a polydisperse system of the same overall composition in which only dextran is polydisperse with $b = 1.5$ and two quadrature points were used in the equilibrium calculations. Here TLL is calculated from

$$\mathrm{TLL} = 100\left[\sum_{i=1}^{2}(x'_i - x''_i)^2\right]^{1/2} \qquad (21)$$

From this figure we see that more than four pseudocomponents lead to accurate values for the molecular weight. Further, the $\bar{M}_n$ of Dx in the bottom phase remains almost constant with increasing TLL while the $\bar{M}_n$ in the top phase decreases linearly. It is seen in Figure 5b that while the calculated molecular weight appears to converge rapidly with the number of pseudocomponents, the polydispersivity parameter b does not converge until more than six pseudocomponents are used to represent the polydisperse polymer. Thus the polydispersivity parameter more sensitively reflects the convergence of the LLE calculations than does the equilibrium composition.

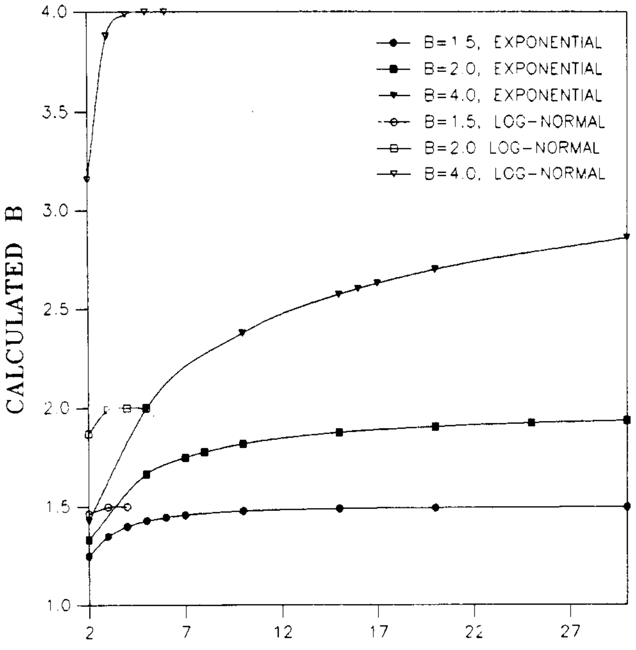

Figure 3. Comparison of calculated b values from the quadrature method with different distributions and various number of quadrature points.

Table I
Physical Properties of Components[17]

component	$r' \times 10^2$	$q' \times 10^2$	v^{*a}
dextran	2.717	1.96	0.626
PEG	3.87	2.57	0.832
water	5.11	7.78	1.00177

[a] Specific volume in mL/g.

Table II
The Parameters[a] of the UNIQUAC Models Used in the Calculations in This Study[18]

A_{12}	A_{13}	A_{21}	A_{23}	A_{31}	A_{32}
2890.0	−273.9	70.0	−243.0	219.1	−130.4

[a] In K, subscripts 1, 2, and 3 denote Dx, PEG, and water, respectively.

We have calculated the phase boundaries for different values of b for dextran of the same number-average molecular weight $\bar{M}_n$ and these are compared in Figure 6. The immiscibility region for the system containing polydisperse dextran is slightly smaller than for the monodisperse dextran system in the dextran-dilute region, while the phase boundary in the dextran-rich region does not show any significant shift. For values of b larger than 1.5, the phase boundary far from the plait point, an increase in the value of b enlarges the two-phase region. Note, however, that the UNIQUAC model, like other semiempirical excess Gibbs free energy models, is not reliable in the critical region. Therefore here and throughout this paper the accuracy of predictions near the plait point may not be high.

Next both polymers were considered to be polydisperse. Figure 7 presents the results of LLE calculations using the L-K distribution for both polymers with their b values equal to 1.5. From this figure it is observed that more than

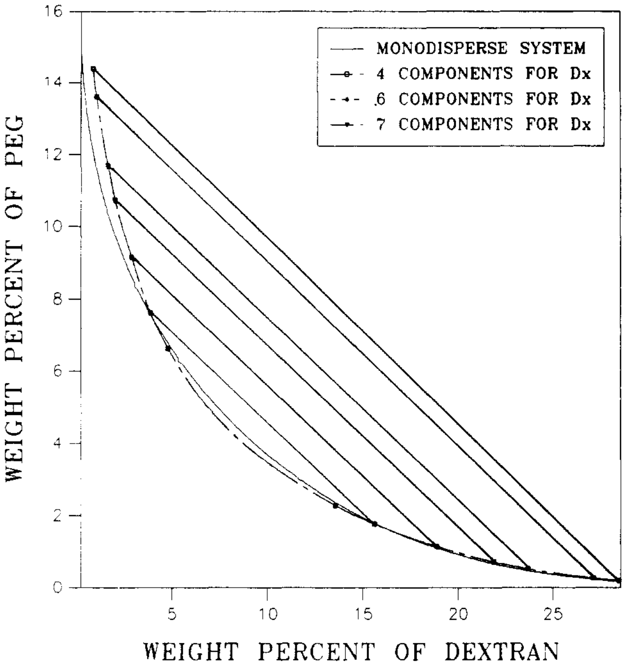

Figure 4. Prediction of phase diagram of the D17/PEG6000/water system at 293 K using the UNIQUAC model when only dextran is polydisperse: the L-K distribution and $b = 1.5$ were used.

four pseudocomponents for each polymer lead to LLE results which no longer change with the number of pseudocomponents. We see that the polydispersivity of the polymers enlarges the two-phase region considerably near the plait point and results in smaller immiscibility regions far from the plait point. This is in contrast with the experimental observations[3] for two-polymer systems in organic rather than aqueous solvents in which a broad molecular weight distribution reduced the incompatible region.

The average molecular weights of dextran and PEG in both phases were calculated by using eq 16 and 17; we found that four or more pseudocomponents for each polymer led to converged results, and that the $\bar{M}_n$ of a polymer in the phase dilute in that polymer decreased almost linearly with an increase of TLL, while the $\bar{M}_n$ of a polymer in the phase dilute in that polymer remains more or less constant. In this case the equilibrium compositions and the average molecular weights approach their asymptotic values rapidly with increase in the number of quadrature points. This is expected since we saw, in Figure 3, that the b value calculated with more than four quadrature points leads to almost exact values for this parameter when the L-K distribution is used. Clearly, the average molecular weight of each polymer in each phase is significantly different. In particular, the average molecular weight of Dx in the bottom phase is slightly larger than that of the feed and the average molecular weight of Dx in the PEG-rich top phase is much smaller. Similarly the average molecular weight of PEG in the top phase is larger than that in the bottom phase. Since the average molecular weight of each polymer decreases with increasing the TLL, it is evident that the larger polymer molecules distribute more unequally between the two phases the farther the system is from the plait point.

We also calculated the b parameters for this system for the case in which the polydispersivity parameters of Dx and PEG in the feed were set to 1.5. The b values of a polymer in a phase dilute in that polymer was found to decrease with increasing TLL, while the b values in the other phase remain almost constant. Koningsveld and Staverman[2] investigated the change in the polydispersivity, that is, in the value of the b parameter, in the coexisting

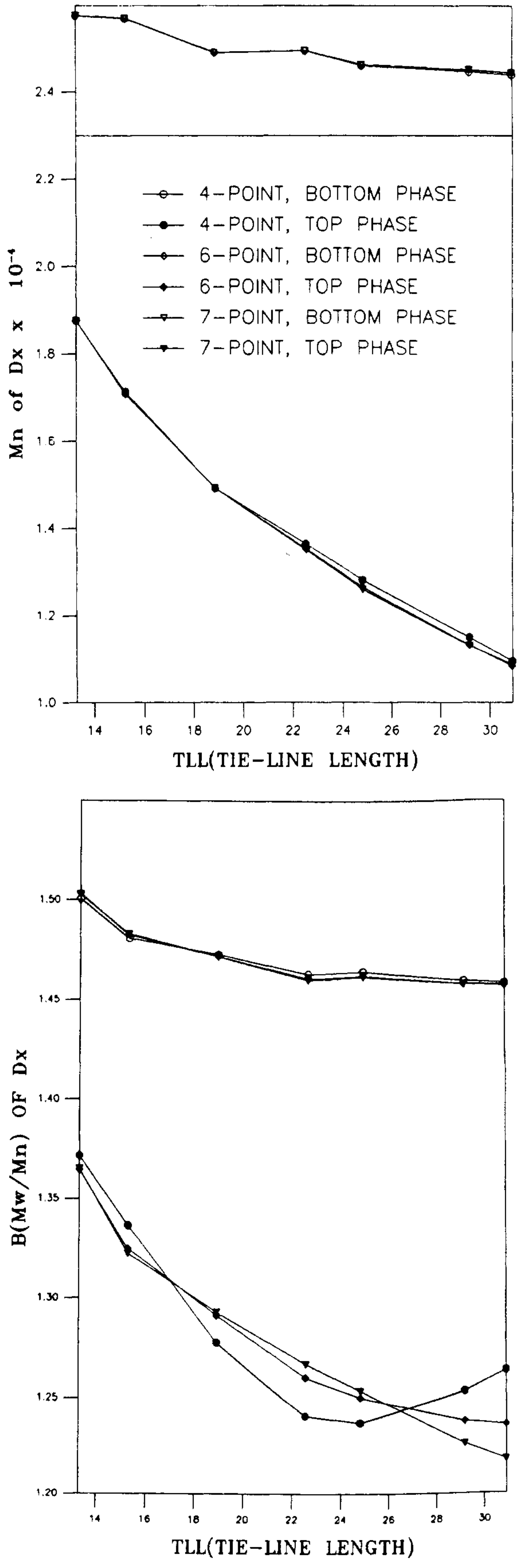

Figure 5. Number-average molecular weights (a, top) and polydispersivity parameters (b, bottom) of dextran in the phases for Figure 4.

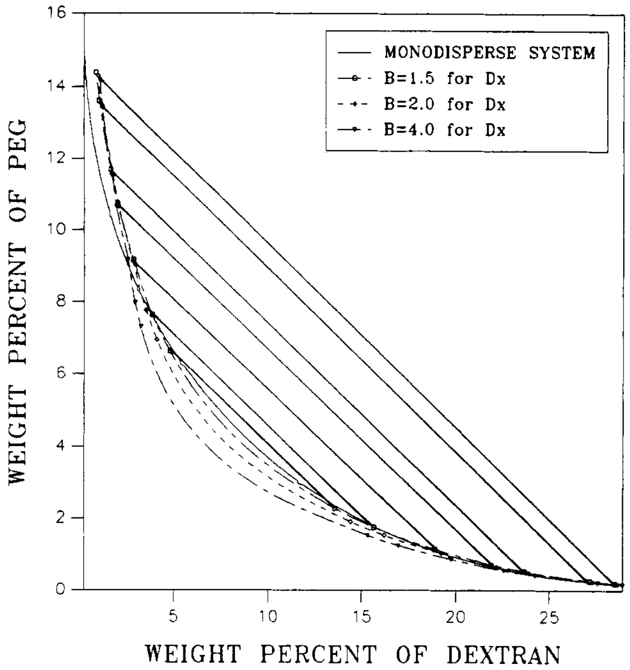

Figure 6. Effects of the polydispersivity of dextran on the phase behavior when the dextran alone is polydisperse.

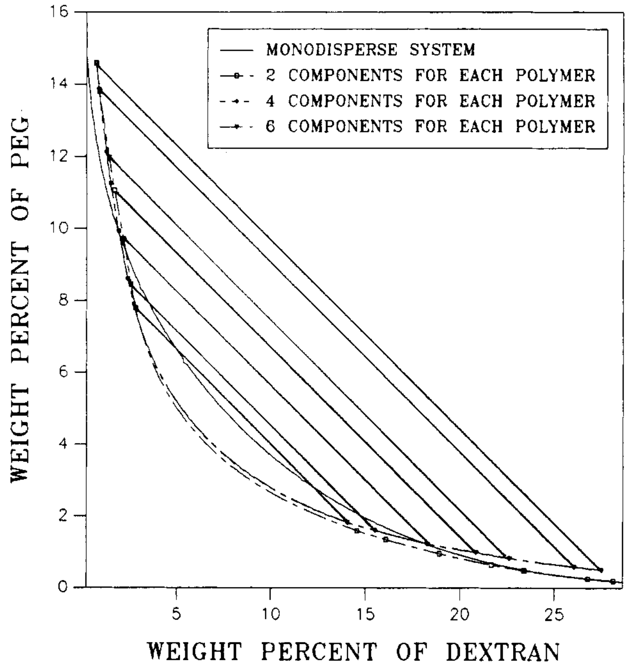

Figure 7. Prediction of the phase diagram of D17/PEG 6000/water system at 293 K when *b* values of both polymers are equal to 1.5; the UNIQUAC model and the L-K distribution were used.

phases in a liquid–liquid equilibrium process using various molecular weight distributions. They observed that the *b* parameters in both phases were less than that of the feed when the exponential distribution was used. We found that the values of polydispersivity parameter *b* for both polymers in each phase is less than 1.5, establishing that the molecular weight distributions in both phases are narrower than that of the feed.

To accurately calculate the average molecular weights in the coexisting phases it is necessary to obtain the complete distributions of the polymers in both phases so that the average molecular weights can be calculated (see eq 9 and 10). Tompa[5] derived expressions for the distribution of polydisperse species in both phases for binary polymer solutions using the Flory–Huggins model. Here, we derive the analogous fractionation equation using the UNIQUAC model.

From the material balance, we have

$$x_{ij}^{\mathrm{F}} = (1-q)x'_{ij} + qx''_{ij} \tag{22}$$

where q is the ratio of the mass of the top phase to that of the feed. By setting equal the chemical potentials of each fraction in both phases and again assuming the interaction parameters are independent of the chain length, we obtain from eq 1 and 19

$$\ln\frac{x''_{ij}}{x'_{ij}} = \ln Y_i(M) = \ln\frac{R''}{R'} - \frac{z}{2}\frac{M_i q_i'^2}{r'_i}\left(\frac{R''}{Q''} - \frac{R'}{Q'}\right) + M_i r'_i\left(\frac{L''}{R''} - \frac{L'}{R'}\right) - M_i q'_j\left(\ln\sum_k \bar{\theta}'_k\tau_{ik} + \sum_k\frac{\bar{\theta}'_k\tau_{ik}}{\sum_m\bar{\theta}'_m\tau_{mk}} - \ln\sum_k\bar{\theta}''_k\tau_{ik} - \sum_k\frac{\bar{\theta}''_k\tau_{ik}}{\sum_m\bar{\theta}''_m\tau_{mk}}\right) \tag{23}$$

Here $\bar{\theta}_i$ refers to the total area fraction of i species, $R = \sum_i r'_i X_i$, $Q = \sum_i q'_i X_i$, and $L = \sum_i l'_i X_i$. Also X_i is the total weight fraction of species i. Note that eq 23 is only a function of the molecular weight of fraction i and the total weight fractions of polymer species and is independent of the compositions of the individual fractions. Combining eq 22 and 23, the distribution of species i in phase $''$ is given by

$$F''_i(M) = \frac{Y_i(M)F_i^{\mathrm{F}}(M)}{(1-q) + qY_i(M)} \tag{24a}$$

$$F'_i(M) = \frac{F_i^{\mathrm{F}}(M)}{(1-q) + qY_i(M)} \tag{24b}$$

where $F_i^{\mathrm{F}}(M)$ is the distribution of species i in the feed. From this equation and the material balances it is obvious the molecular weight distribution of the polymers in the coexisting phases differ from those in the feed and can be calculated provided the total weight fractions of each polymer species in both phases and the molecular weight distribution of the polydisperse species in the feed are given.

In Figure 8, the molecular weight distributions of the polymers (dextran in part a and PEG in part b) calculated by using the fractionation equation are compared to the feed distributions for both polymers. In these figures, $X_i^{\mathrm{F}}F_i^{\mathrm{F}}(M)$, $(1-q)X'_iF'_i(M)$, and $qX'_iF''_i(M)$ are plotted so that the two phase fractions sum to the feed. From these figures we see once again that the larger Dx molecules tend to remain in the Dx-rich bottom phase and the larger PEG molecules tend to remain in the PEG-rich top phase. Consequently, as suggested by Narasimhan et al.,[3] the interactions of the more mobile, smaller polymer chains may be determining factor in the phase equilibrium of polydisperse polymer systems.

To further investigate the effects of the polydispersivity on the phase behavior, we next used the L-K distribution with $b = 2.0$ for both polymers. The resulting phase diagrams for various numbers of pseudocomponents are shown in Figure 9. Comparing this with Figure 7, we see that an increase in the value of the polydispersivity parameter b altered the phase boundary more in the PEG-dilute region than in the dextran-dilute region. Though not shown, the calculated number-average molecular weights of the polymers in both phases converged when four or more pseudocomponents were used to represent each polymer, and $\bar{M}_n$ of a polymer in the phase dilute in

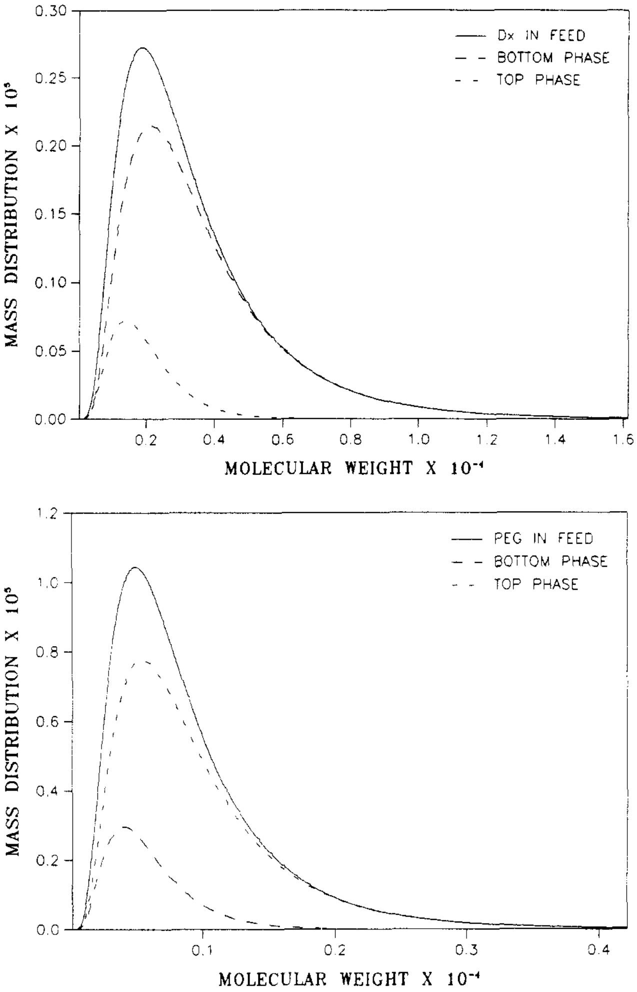

Figure 8. Molecular weight distributions of the polymers in the coexisting phases for a tie line in Figure 7 from the fractionation equation: dextran (a, top); PEG (b, bottom).

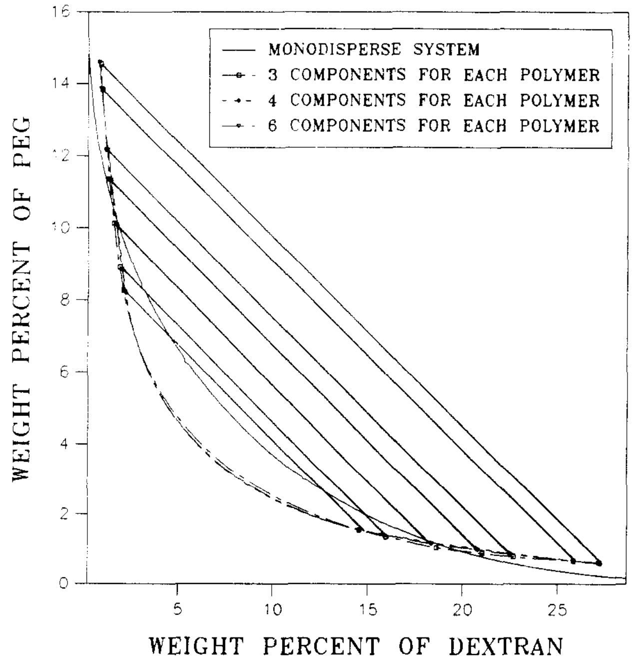

Figure 9. Prediction of the phase diagram of D17/PEG 6000/water system at 293 K when b values of both polymers are equal to 2.0: the UNIQUAC model was used.

that polymer is far smaller than that in the feed. In particular, for dextran $\bar{M}_n$ of the feed was 2.3 × 10^4, while that of the bottom phase was about 2.6 × 10^4, and that of the top phase ranged between 0.8 × 10^4 and 1.25 × 10^4, depending on the tie-line length. Similarly for PEG, $\bar{M}_n$ was 6.0 × 10^3, while that for the top and bottom phases ranged from 6.3 × 10^3 to 6.8 × 10^3 and 2.3 × 10^3 to 3.7 × 10^3, respectively, depending on the length of the tie line.

Table III
LLE Calculation Results Using the UNIQUAC Model[a]

		dextran		PEG	
		bottom	top	bottom	top
X_i[b]	L-L[c]	87.37	12.63	9.53	90.47
	exptl[d]	88.0	12.0	11.2	88.8
M_n	L-L	116180	46715	6150	7342
	exptl	94275	66540	6880	7066
b	L-L	1.8347	1.3901	1.1329	1.1589
	exptl	1.82	1.72	1.136	1.126

[a] Feed composition is 4 wt % T500 (M_n = 9.88 × 10^4, b = 1.98) and 5 wt % PEG 8000 (M_n = 7.2 × 10^3, b = 1.16). [b] Total weight percent of chemically same species on water-free basis. [c] The L-K distribution for both polymers. [d] Experimental results from Waters.

Comparing Figures 6, 7, and 9, we see that systems containing polymers with a broader molecular weight distribution phase separate over a larger composition range and that the equilibrium compositions of the coexisting phases for different values of the polydispersivity parameter b are located on tie lines of the same slope but different lengths. Also the average molecular weights calculated by using eq 16 and 17 required a larger number of pseudocomponents to reach their asymptotic values as the value b increases.

For liquid–liquid equilibrium in aqueous polydisperse two-polymer systems, broader two-phase regions which lie outside the binodal curve for monodisperse systems have been qualitatively reported by Albertsson.[20] The results of this study also show that broader molecular weight distributions of the polymers result in a larger immiscibility region. Unfortunately, there are no published quantitative data for the systems studied with which to compare our predictions.

We have also performed similar calculations using the Flory–Huggins model and the exponential distribution. From those calculations, which are not reported here, essentially the same effects of the polydispersivity on the phase behavior were observed.

Example

In this section, the results of calculations, using the UNIQUAC model with parameters given in Table II and the pseudocomponent method developed here, are compared with experimental data provided by Waters.[22]

An aqueous two-phase two-polymer system was prepared from aqueous solutions of 4 wt % T500 ($\bar{M}_n$ = 9.88 × 10^4 and b = 1.98) and 5 wt % PEG 8000 ($\bar{M}_n$ = 7.2 × 10^3 and b = 1.16). To calculate the equilibrium composition of the given overall system, the L-K distribution was used for both T500 and PEG, and we have used eq 16 and 17 for the calculation of average molecular weights in the equilibrium phases. For this system six quadrature points for each polymer led to convergence in the equilibrium calculations, and this was used for what follows.

The calculated equilibrium compositions of the system are compared with experimental data in Table III. Clearly the predictions overestimate the fractionation. In particular, the difference in average molecular weights between predictions and experiments is larger in the phase dilute in that polymer, such as dextran in the top phase and PEG in the bottom phase. One reason for this may be that the molecular weight distribution of a polymer in a phase dilute in that polymer can be considerably different from that for the feed, so that the average molecular weights calculated by using the quadrature points based on the feed distribution may not be completely accurate. This same problem does not arise for the phase rich in that polymer, since in this case the molecular weight distribution must be similar to that of the feed so that the calculation would be reasonably accurate. Nonetheless, we see from the experimental data that the polymer fraction effect is a real one and that the number-average molecular weights of the same polymer in the two phases are quite different. Further, the polydispersivity parameter of each polymer in each phase is experimentally found to be less than in the feed.

Conclusions

To predict LLE of the polydisperse D17/PEG6000/water system at 293 K, the UNIQUAC model and the pseudocomponent method based on the generalized Gaussian quadrature procedure have been used with the logarithmic normal distribution function to represent the polydispersivity of each polymer. The main conclusion of this work is that only four properly chosen pseudocomponents for each polydisperse polymer are needed to predict phase boundaries of reasonable accuracy for the polydisperse systems, and it is found that the immiscibility region becomes broader if the polymers are polydisperse. As the broadness of the molecular weight distributions of the polymers increases, the binodal curve shifts, so that while the incompatible region is enlarged, the slopes of the tie lines are essentially unchanged.

Explicit expressions for the molecular weight distributions of the polydisperse polymers in both phases were obtained by using a thermodynamic model in which the interactions between constituents are independent of polymer chain length. As shown here, the molecular weight distributions of both phases cannot be of the same form as that of the feed. Also it is found that larger Dx molecules concentrate in the Dx-rich bottom phase and larger PEG chains concentrate in the PEG-rich top phase. Thus the average molecular weights of polymers in the each phases are different, and this difference becomes larger as the polydispersivity of the polymers increases. Further, as a result of the polymer fractionation which occurs in the liquid–liquid equilibrium process, the polydispersivity of each polymer in each phase is less than that in the feed.

Finally, we note that since the extent of polydispersivity has been shown to effect the binodal curve in liquid–liquid equilibrium, different results would be obtained for the parameters in a thermodynamic model when correlating LLE or other data, depending on whether the polymers were considered to be mono- or polydisperse. This problem has largely been ignored in the analysis of phase equilibrium data involving polymers.

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Registry No. PEG, 25322-68-3; Dx, 9004-54-0; H_2O, 7732-18-5.

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