

Ternary Phase Equilibria of Tetrahydrofuran-Polystyrene-Polytetrahydrofuran

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SYNOPSIS

Phase diagrams including tie lines for three ternary solvent-polymer-polymer systems consisting of tetrahydrofuran-polystyrene-polytetrahydrofuran at 30°C have been obtained using size exclusion chromatography. The effect of molecular weight on polymer-polymer compatibility has been investigated. A liquid-liquid equilibria (LLE) database has been used to compare UNIQUAC and a modified Flory-Huggins model with respect to their ability to correlate LLE data. Both models contain six adjustable parameters. As previously observed in the literature, the estimation of the UNIQUAC parameters is troublesome due to the model's complexity and the intercorrelation of the parameters. On the basis of better performance and ease of use, the Flory-Huggins model is recommended. The Flory-Huggins model is capable of accurately describing LLE of systems which exhibit quite complex tie line behavior. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In order to develop models for predicting liquid-liquid equilibria of polymer solutions, phase data for numerous combinations of solvents and polymers must first be acquired. This investigation obtained phase equilibria data using size exclusion chromatography (SEC) for the ternary systems consisting of tetrahydrofuran (THF) with various molecular weights of polytetrahydrofuran (PT) and polystyrene (PS). PT, commonly called poly(oxytetramethylene)glycol, is a polyether used in the preparation of thermoplastic elastomers such as polyamide, polyester, and polyurethane.¹ Whereas thermodynamic studies of PT are essentially nonexistent, PS is among the most widely researched and understood polymers.

The advent of SEC in the 1960s provided an improved method for analyzing solvent-polymer-polymer systems. SEC separates solvents from polymers and to a varying extent, polymers from polymers, based on the size of the molecules in so-

lution. Ultraviolet and refractive index detectors have been used to determine the concentrations of each of the polymers in each of the phases.²⁻⁸

The usual LLE problem consists of determining if phase separation occurs, and if so, what are the compositions of the phases. For this purpose, a thermodynamic model for the Gibbs free energy (or an equation of state) is needed. Currently, there are no methods available that can predict LLE of polymer solutions. Kang and Sandler⁹ have correlated LLE of water-dextran-poly(ethylene glycol) (PEG), however, using the UNIQUAC¹⁰ and Flory-Huggins^{11,12} models. UNIQUAC has been successfully used to correlate LLE of low molecular weight components.¹³ It is, in principle, also applicable to polymer solutions. Kang and Sandler found UNIQUAC to be superior to the Flory-Huggins model for representing the water-dextran-PEG systems. This is not surprising as UNIQUAC contains two adjustable parameters per binary, whereas the Flory-Huggins model contains only one. In an earlier paper, we modified the Flory-Huggins model for ternary systems to account for one of its greatest weaknesses, the concentration dependence of the interaction parameters.¹⁴ The modified Flory-Huggins model consists of two interaction parameters per binary. It was shown to be capable of accurately

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representing a number of solvent-polymer-polymer systems.

The purpose of this research was to obtain phase equilibria data using SEC for a number of systems containing THF-PS-PT and to investigate the effect of molecular weight on polymer-polymer compatibility. In addition, the ability of the UNIQUAC and modified Flory-Huggins models to correlate solvent-polymer-polymer systems was compared.

THEORY

The interaction between a polymer and a solvent has been extensively investigated in terms of the Flory-Huggins theory. This treatment is based on statistical mechanics and uses a quasicrystalline lattice model to describe the polymer solution. This same statistical approach has been generalized for any n -component solution.^{11,12} For isothermal ternary systems, the reduced total Gibbs free energy of mixing is given by^{8,14}

$$\begin{aligned} \frac{\Delta G_M}{RT} = & n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 \\ & + g_{12}(u_{12})m_1n_1\phi_2 + g_{13}(u_{13})m_1n_1\phi_3 \\ & + g_{23}(u_{23})m_2n_2\phi_3 \end{aligned} \quad (1)$$

where n_i and ϕ_i are the number of moles and the volume fractions of the ternary components, respectively, R is the gas constant, T is the temperature in kelvins, and the interaction parameters, g_{ij} , are defined on a per segment basis. m_i is the ratio of the molar volume of i to a reference component's volume and u_{ij} is defined as the ratio of the volume of the j th component to the combined volume of the i th and j th components, or

$$u_{ij} = \frac{\phi_j}{(\phi_i + \phi_j)} \quad (2)$$

In the modified Flory-Huggins model,⁸ the concentration dependence of the interaction parameters is approximated as a linear function of u_{ij} .

$$g_{ij} = g_{ija} + g_{ijb}u_{ij} \quad (3)$$

Therefore, for isothermal ternary systems, the Gibbs energy is a function of composition and the following parameters: g_{12a} , g_{12b} , g_{13a} , g_{13b} , g_{23a} , and g_{23b} .

Abrams and Prausnitz¹⁰ derived UNIQUAC by extending the quasichemical theory of Guggenheim¹⁵ for nonrandom mixtures to solutions containing

molecules of different size. The UNIQUAC equation for the excess Gibbs energy is

$$\begin{aligned} \frac{G^E}{RT} = & \sum_i x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} \\ & - \sum_j q_j x_j \ln \left(\sum_i \theta_i \tau_{ij} \right) \end{aligned} \quad (4)$$

where segment fraction, Φ_i , and area fraction, θ_i , are given by

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}, \theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (5)$$

Here, x_i denotes the mole fraction of the i th component. The volume and surface area parameters of the i th component on a per mole basis, r_i and q_i , are pure-component molecular-structure constants. The interaction parameter, τ_{ij} , is defined by

$$\tau_{ij} = \exp \left(- \frac{a_{ij}}{T} \right) \quad (6)$$

Because $a_{ij} \neq a_{ji}$, the UNIQUAC model for ternary systems also contains six adjustable parameters.

EXPERIMENTAL

Characteristics of the polymer samples are given in Table I. Included are data on the number-average molecular weight, M_n , and the polydispersity, M_w/M_n , both provided by the suppliers and experimentally determined in our laboratory using SEC. The polymers were placed in a vacuum to remove any solvents present. Narrow molecular weight distribution polymer samples were used to minimize polydispersity effects on phase behavior. Baker Analyzed HPLC reagent grade THF was used as re-

Table I Characteristics of Polymer Samples

Sample	Manufacturer's Data ^a		Experimental Data by SEC	
	M_n	M_w/M_n	M_n	M_w/M_n
PS(13,000)	12,987	1.05	13,000	1.05
PS(275,000)	274,600	1.05	239,000	1.08
PT(38,000)	37,600	1.07	—	—
PT(300,000)	300,000	1.13	—	—

^a Supplied by Pressure Chemical Co. (Pittsburgh, PA).

ceived for ternary sample preparation. It was also used as the mobile phase and was kept under nitrogen to prevent organic peroxides from forming that affect ultraviolet transparency at 254 nm.

A detailed discussion of the use of SEC using sequential ultraviolet and refractive index detectors to determine the phase compositions, tie lines, and binodal curve for incompatible solvent-polymer-polymer systems has been given in an earlier publication.⁸

RESULTS AND DISCUSSION

THF-PS-PT Experimental Results

The effect of molecular weight on the compatibility of PS-PT in THF was investigated. The systems studied were THF-PS(13,000)-PT(300,000), THF-PS(275,000)-PT(38,000), and THF-PS(275,000)-PMMA(300,000) at 30°C. Data were collected at only one temperature because the effect of temperature on the location of the binodal curve is minimal compared to that of molecular weight.^{2,7,16} The results are presented in Table II. Figure 1 shows the binodal curves and, for one pair of molecular weights, the composition of the initial mixtures and the tie lines are given. For each tie line, the end points and the mixture point are nearly linear; in fact, the material balances are within 2%.

Table II Equilibrium Compositions for THF(1)-PS(2)-PT(3) Systems at 30°C (wt %)

w'_1	w'_2	w'_3	w''_1	w''_2	w''_3
System A: THF-PS(13,000)-PT(300,000)					
71.07	17.14	11.79	68.45	30.84	0.70
72.66	18.81	8.54	69.86	28.56	1.58
72.93	20.41	6.65	70.58	27.23	2.19
System B: THF-PS(275,000)-PT(38,000)					
84.13	0.02	15.85	75.80	22.76	1.44
86.25	0.21	13.53	79.94	17.91	2.15
87.88	0.40	11.72	81.92	15.48	2.60
89.14	3.48	7.38	87.48	7.22	5.30
System C: THF-PS(275,000)-PT(300,000)					
91.67	0.21	8.13	87.08	12.62	0.31
92.59	0.35	7.06	88.53	11.23	0.23
94.07	0.77	5.15	90.89	8.49	0.62
94.49	1.97	3.54	92.73	6.30	0.97

The positions of the binodals are as expected based on the relative molecular weights of the polymers. For the higher molecular weight polymers, the system is less compatible, hence, the binodal is moved upward. Also, the binodal is shifted toward the axis of the polymer with the lower molecular weight. These observations are in agreement with the experimental work of Narasimhan et al.,⁴ Robledo-Muniz et al.,⁶ Tseng et al.,⁷ and Geveke and Danner,⁸ and the theoretical work of Hsu and Prausnitz.¹⁷

Computation of Liquid-Liquid Equilibrium Compositions

Assuming that the model parameters are known, the computed tie lines and binodal curve may be obtained. This is accomplished using the necessary, but not sufficient, condition of equilibrium that the chemical potential of each component, μ_i , must be equal in both phases.

$$\mu_i^I = \mu_i^{II} \quad i = 1, 2, \dots, N \quad (\text{components}). \quad (7)$$

The chemical potential of the i th component may be obtained from eqs. (1) or (4). In addition, the following material balances must be satisfied.

$$\sum_i \phi_i^I = \sum_i \phi_i^{II} = 1. \quad (8)$$

For ternary systems, there are five equations and six unknowns. Therefore, one composition must be specified, for example, ϕ_3^{II} , enabling the remaining five to be computed. The IMSL routine DBCPOL was used.¹⁸

Parameter Estimation From Liquid-Liquid Equilibrium Data

Given experimental phase composition data, the model parameters may be estimated. The parameters may then be used to correlate the original data or to predict unmeasured data. The parameter estimation is carried out by minimizing an objective function.

There are two main strategies for obtaining parameters, p (p_1, p_2, \dots), from LLE data at constant temperature and pressure.^{13,19} The first of these is the minimization of chemical potential differences according to eq. (7). Expressed in terms of the least-squares principle, the objective function used is

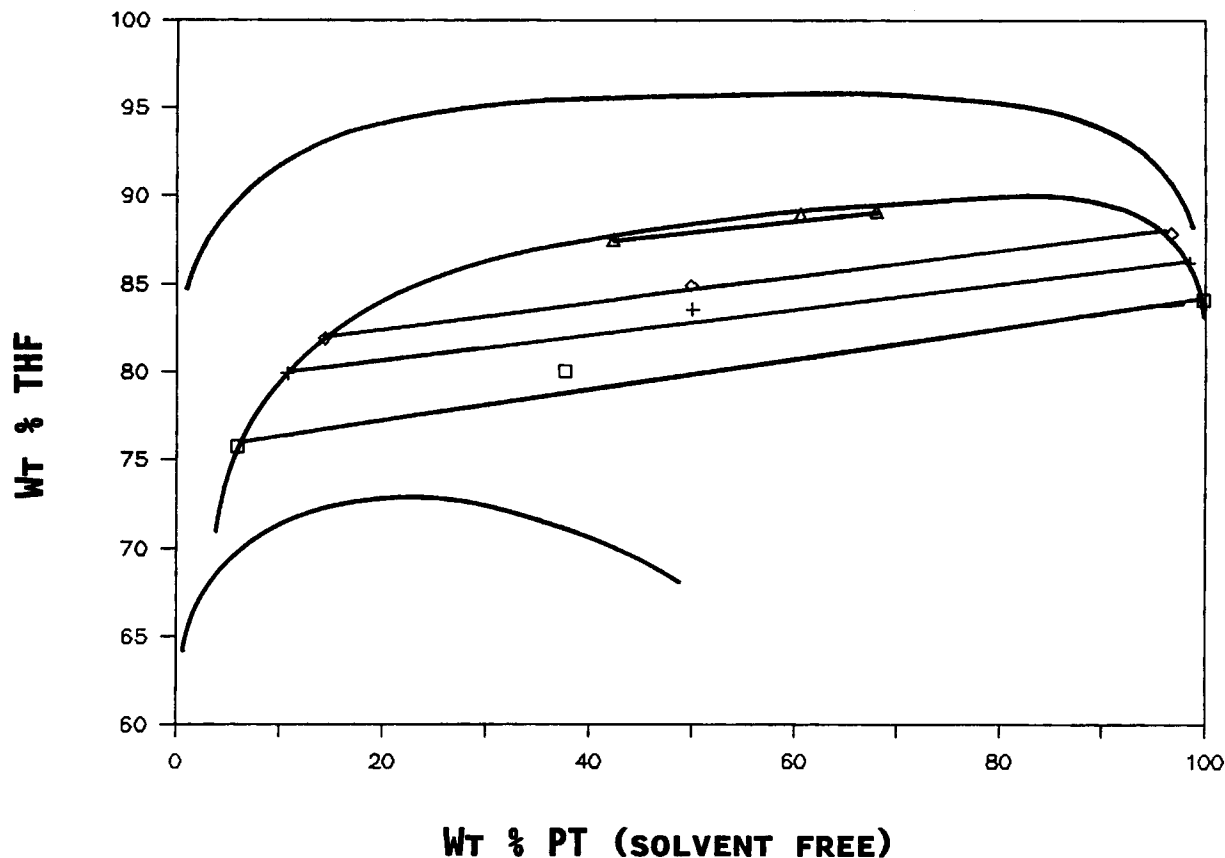


Figure 1 Effects of molecular weight on the location of the phase diagram for THF-PS-PT at 30°C. PS/PT molecular weights are 275,000/300,000; 275,000/38,000; and 13,000/300,000 from the top to the bottom curves.

$$F(p) = \sum_k \sum_i W_i^2 [\Delta\mu_{ik}^I(\phi_{ik}^I, p) - \Delta\mu_{ik}^{II}(\phi_{ik}^{II}, p)]^2$$

$$i = 1, 2, \dots, N \quad (\text{components})$$

$$k = 1, 2, \dots, M \quad (\text{tie lines}) \quad (9)$$

where W_i is the weighing factor associated with component i . Altena and Smolders²⁰ propose W_i be set equal to the reciprocal of m_i to account for the large differences in molar volumes between solvents and polymers. ϕ_{ik}^I is the experimental volume fraction of component i in phase I at tie line k . The calculated chemical potentials depend on the experimental volume fractions and the parameters.

The second strategy for obtaining parameters is the minimization of the experimental volume fractions, ϕ_{ijk} , and the calculated volume fractions, ϕ_{ijk}^c , differences.

$$F(p) = \sum_k \sum_j \sum_i [\phi_{ijk} - \phi_{ijk}^c(p)]^2$$

$$j = I, II \quad (\text{phases}) \quad (10)$$

where ϕ_{ijk} is the volume fraction of component i in phase j at tie line k . The calculated volume fractions depend on the parameters.

To compare the results obtained using the modified Flory-Huggins and UNIQUAC models, a residual was calculated as follows

$$R = \left[\frac{\sum_k \sum_j \sum_i (\phi_{ijk} - \phi_{ijk}^c)^2}{5M} \right]^{1/2} \quad (11)$$

Here, M is the number of tie lines.

The objective function based on the isochemical potential criterion does not guarantee that the differences between the experimental and calculated volume fractions will be minimized. This is what is most often wanted. The objective function stated in terms of compositions directly expresses the goal of accurately representing the experimental data. It is computationally more complicated, however, be-

cause it contains the computed volume fractions, ϕ_{ijk}^c , that for a given set of parameter estimates, must be predicted for each tie line using the method outlined in the previous section.

For ternary systems, in using the composition form of the objective function, one must, for each current parameter estimate, choose a predicted tie line to compare with an experimental one. Renon et al.²¹ accomplished this by setting one composition in one phase of the predicted tie line equal to the corresponding experimental value: $\phi_{32k} = \phi_{32k}^c$.

The objective function stated in terms of compositions requires qualified initial guesses of the parameters in order to compute the predicted tie lines. Therefore, the parameter estimation first uses the objective function based on the isochemical potential criterion because this does not require qualified initial guesses. The IMSL minimization procedure DBCPOL, which employs a direct search complex algorithm, was used.¹⁸

The regression program to obtain the parameters in the modified Flory-Huggins model always converged quickly regardless of the values used for the initial guesses. Due to the complexity of the UNIQUAC model, however, the parameters and residuals obtained from the regression program were dependent on the initial guesses. This was also observed

by Kang and Sandler.⁹ Several other regression algorithms were tried, but the same behavior was observed. To find an optimum set of parameters, an initial guess of either -10 or 10 K was used for each a_{ij} . This resulted in 2^6 or 64 sets of initial guesses. The resulting parameter set with the lowest residual was then selected.

An additional problem occurred with the UNIQUAC regression program. Occasionally the numerical values of the parameters were unrealistically large. As previously pointed out,^{9,19} the surface of the Gibbs energy becomes more complicated as the parameter values increase. Thus, the risk of multiple solutions is increased. We have minimized this problem by bounding the interaction parameters, a_{ij} , to between -1040 and 1040 K. This is typical of the range of values obtained from binary systems. The residuals were not appreciably increased because the parameters are highly intercorrelated. This problem did not occur in the estimation of the Flory-Huggins parameters.

Finally, using the parameters estimated from the isochemical potential criterion as the initial guesses, the objective function stated in terms of compositions was used. The IMSL minimization procedure DUNLSF, which employs a modified Levenberg-Marquardt algorithm, was used.¹⁸

Table III Ternary Systems Used in the Investigation

System	Components (1-2-3)	Temperature (°C)	References
1	Water-dextran(23,000)-Poly(ethylene glycol) (PEG) (7,000)	0	26
2	Water-dextran(23,000)-PEG(7,000)	20	26
3	Water-dextran(83,000)-PEG(7,000)	20	26
4	Cyclohexane-polystyrene (PS)(13,000)-Butadiene Rubber (BR)(23,000)	75	8
5	Tetrahydrofuran (THF)-PS(13,000)-poly(methyl methacrylate) (PMMA) (33,000)	30	8
6	THF-PS(13,000)-PMMA(296,000)	30	8
7	THF-PS(275,000)-PMMA(33,000)	30	8
8	THF-PS(275,000)-PMMA(296,000)	30	8
9	Toluene-PS(53,000)-isoprene rubber (IR) (11,000)	30	8
10	Toluene-PS(13,000)-BR(23,000)	30	8
11	THF-PS(275,000)-poly(butyl methacrylate) (PBMA) (54,000)	30	8
12	THF-PS(13,000)-Polytetrahydrofuran(PT) (300,000)	30	This study
13	THF-PS(275,000)-PT(38,000)	30	This study
14	THF-PS(275,000)-PT(300,000)	30	This study
15	THF-BR(16,000)-PS(9,000)	23	3
16	THF-BR(16,000)-PS(33,000)	23	3

Table IV Regressed Interaction Parameters and Residuals for Systems Using the Flory–Huggins Model

System	g_{12a}	g_{12b}	g_{13a}	g_{13b}	g_{23a}	g_{23b}	Residual
1	0.622	0.137	0.0924	-0.440	-0.240	0.0406	1.59×10^{-3}
2	0.680	0.119	0.444	-0.235	-0.0575	-0.0330	1.04×10^{-2}
3	0.699	0.135	0.401	-0.333	-0.113	0.0180	1.25×10^{-3}
4	0.768	0.157	0.464	-0.429	-0.143	0.102	1.67×10^{-3}
5	0.870	-0.0118	0.880	0.151	0.150	-0.0691	4.28×10^{-3}
6	0.691	-0.0225	0.694	0.0265	0.0362	-0.00182	8.74×10^{-3}
7	0.572	-0.0714	0.653	0.0408	0.0130	-0.0262	1.39×10^{-3}
8	0.556	-0.00594	0.560	0.000656	0.00586	0.0000166	7.28×10^{-4}
9	0.609	0.0658	0.532	-0.106	0.0252	0.0368	9.05×10^{-3}
10	0.719	0.0351	0.672	-0.0609	0.0414	0.0228	3.78×10^{-3}
11	0.639	-0.0107	0.652	0.00788	0.0128	-0.00733	1.44×10^{-3}
12	0.669	0.00158	0.690	0.0654	0.0693	-0.00844	7.91×10^{-4}
13	0.689	0.141	0.436	-0.238	-0.0797	0.0498	3.70×10^{-4}
14	0.643	0.107	0.310	-0.292	-0.164	0.0238	4.46×10^{-4}
15	0.702	-0.102	0.753	0.0000054	0.00866	-0.0281	1.07×10^{-4}
16	0.591	-0.0326	0.599	-0.0204	0.0069	-0.0031	3.40×10^{-3}
Average							3.09×10^{-3}

Correlation Results

Table III lists the systems investigated. The data were regressed using both the modified Flory–Huggins and UNIQUAC models to obtain interaction parameters. The parameters obtained are presented in Tables IV and V, along with the residuals calculated using eq. (11).

The average residual for the Flory–Huggins model is approximately half of that for the UNIQUAC model. The Flory–Huggins model outperformed the UNIQUAC model in 12 of the 16 systems.

In general, the values of the parameters obtained for the Flory–Huggins model in Table IV are realistic: their values are between zero and one. Although the negative values of g_{23a} suggest that dextran and PEG, PS and butadiene rubber, and PS and PT are compatible,²² the binodal can be computed due to the “ $\Delta\chi$ effect”; that is, the difference in strengths of the solvent–polymer interactions.^{17,23,24}

Because both of the models are semiempirical, the values of the individual parameters in Tables IV and V should not be interpreted quantitatively. For instance, the parameters for the THF–PS in-

Table V Regressed Interaction Parameters and Residuals for Systems Using the UNIQUAC Model

System	a_{12}	a_{13}	a_{21}	a_{23}	a_{31}	a_{32}	Residual
1	196.	-378	-249	-398	-190	223	7.58×10^{-3}
2	7.93	-551	-197	-452	-183	348	1.55×10^{-2}
3	103	-550	-223	-309	-157	155	8.74×10^{-3}
4	150	395	-64.6	116	-233	-103	2.85×10^{-3}
5	56.1	-28.4	-7.87	-88.9	157	87.4	6.48×10^{-3}
6	-177	-63.8	879	522	210	-238	4.06×10^{-3}
7	-81.2	-38.3	150	-79.5	156	68.1	3.21×10^{-3}
8	25.1	8.36	-4.19	-43.6	65.2	19.1	3.68×10^{-3}
9	-53.3	-63.9	155	-34.1	143	17.6	2.42×10^{-3}
10	60.5	76.1	15.1	15.6	-11.6	-19.1	6.24×10^{-3}
11	-18.6	2.48	56.6	-57.9	82.3	-41.4	1.78×10^{-2}
12	46.8	33.4	-12.7	17.1	40.0	-29.7	5.43×10^{-4}
13	23.9	202	2.98	46.9	-128	-53.2	3.41×10^{-3}
14	-170	25.0	585	43.9	44.6	20.5	7.88×10^{-4}
15	-114	-179	368	-30.0	1040	33.9	2.72×10^{-3}
16	-30.0	-63.0	119	-20.7	112	9.40	3.11×10^{-3}
Average							5.57×10^{-3}

teraction at 30°C, which is involved in half of the systems studied, are seen to vary widely from system to system. This is especially true for the UNIQUAC model and is caused by the parameters being highly intercorrelated.^{9,25}

Nonetheless, the utility of the models, and the parameters obtained using them, are that an analytical expression can be found that is capable of accurately describing the system. For example, the correlated phase diagrams for three systems are shown in Figures 2-4. Note that these systems exhibit rather complex tie line behavior. Figure 2 shows the system water-dextran (23,000)-PEG (7,000) at 0°C. The Flory-Huggins model is clearly superior. Comparing the residuals in Tables IV and V for all of the water-dextran-PEG systems supports this result. Kang and Sandler⁹ also compared the Flory-Huggins and UNIQUAC models with respect to their ability to correlate water-dextran-PEG systems. They compared the UNIQUAC model with six pa-

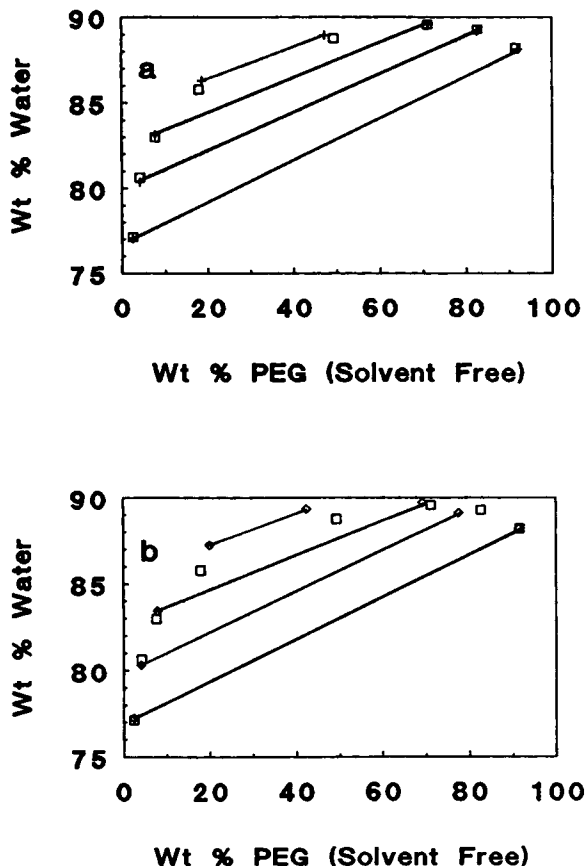


Figure 2 (a) Correlation using Flory-Huggins model (crosses) for the Water-Dextran(23,000)-PEG(7,000) system at 0°C. Experimental data²⁶ (squares). (b) Correlation using UNIQUAC (diamonds).

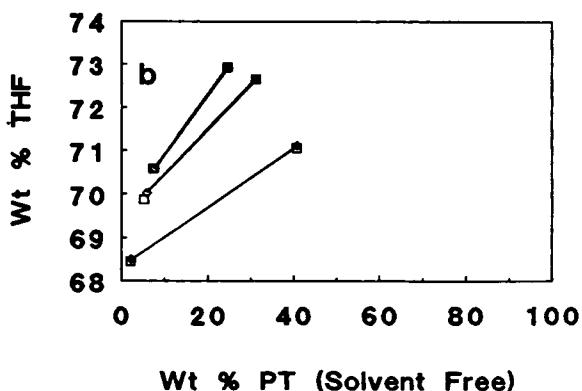
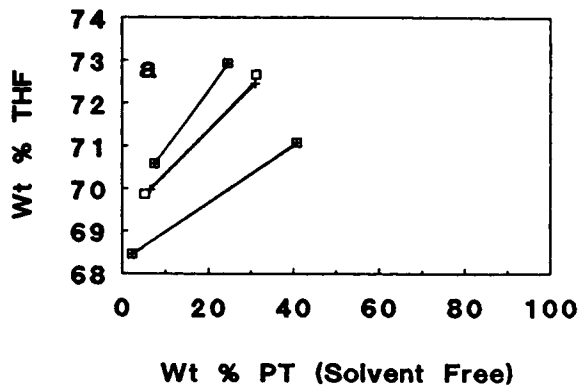


Figure 3 (a) Correlation using Flory-Huggins model (crosses) for the THF-PS(13,000)-PT(300,000) system at 30°C. Experimental data from this study (squares). (b) Correlation using UNIQUAC (diamonds).

rameters to the original Flory-Huggins model that contains only three parameters. They concluded that the original Flory-Huggins model is inadequate. In the present study, however, a modified Flory-Huggins model with six parameters has been used. The experimental results for two of the THF-PS-PT systems obtained by SEC in this investigation are shown in Figures 3 and 4. Systems 12 and 13 are best represented by the UNIQUAC and Flory-Huggins model, respectively.

CONCLUSIONS

Phase diagrams including tie lines for three solvent-polymer-polymer ternary systems have been successfully obtained using SEC. These systems represent a significant increase in the available well-documented ternary LLE database. Errors of less than 2% were observed.

A database consisting of these 3 systems and an additional 13 systems from the literature was used

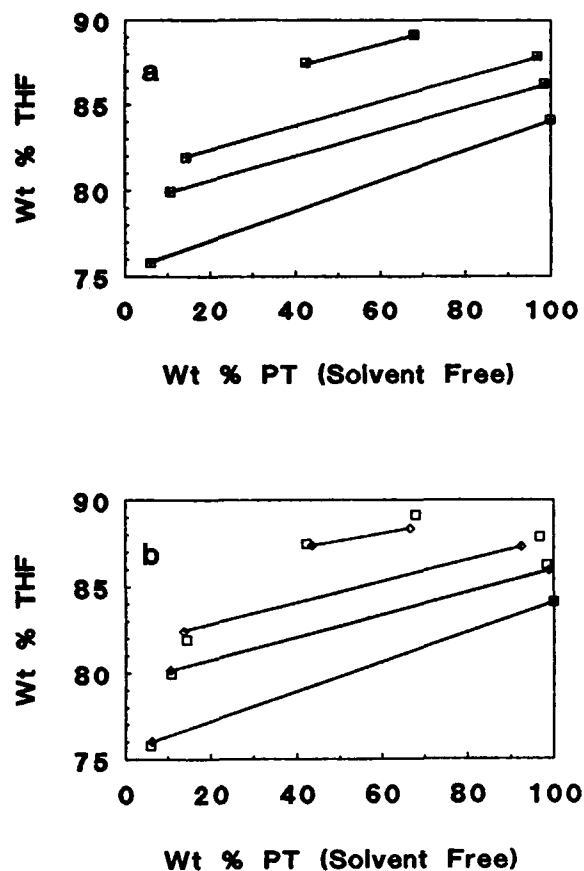


Figure 4 (a) Correlation using Flory-Huggins model (crosses) for the THF-PS(275,000)-PT(38,000) system at 30°C. Experimental data from this study (squares). (b) Correlation using UNIQUAC (diamonds).

to compare the modified Flory-Huggins and UNIQUAC models with respect to their ability to correlate LLE data. Because of its better performance and ease of use, the modified Flory-Huggins model is recommended for the correlation of ternary LLE. This model and the accompanying regression procedure may be universally used to correlate both polar and nonpolar systems including those exhibiting complex tie line behavior.

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