

Solubility and Miscibility in Ternary Systems: Polymer Liquid Crystal + Flexible Polymer + Solvent

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ABSTRACT: We use the Matheson-Flory theory,¹¹ with the orientational contribution represented by the Flory-Irvine term¹² in the partition function. Polymer liquid crystal (PLC) molecules have a fraction θ of thermotropic sequences, with the remainder $1 - \theta$ fully flexible. The excess Gibbs function of mixing for the ternary system is formulated, and chemical potentials of the components in the anisotropic phase are derived; a set of five equations defines the anisotropic-isotropic phase equilibrium. Calculated miscibility gaps have the usual base on the PLC + flexible polymer side, but unusual shapes (cusps) are predicted for values of the characteristic temperature of the mixture T^* in certain intervals; such shapes appear for fully rigid rods as well as for $\theta < 1$. Moving from the Gibbs triangle base toward the top (solvent), we find the LC order parameter s quite high, except in the immediate vicinity of pure solvent. As an example, $s \approx 0.97$ for the volume fraction of PLC in the anisotropic phase as low as 0.170. Thus, solvent molecules must be channeled by the thermotropic sequences, with perhaps unwilling flexible PLC sequences participating in the channeling. Available experimental data for one ternary system¹⁹ are compared with predictions from the theory.

1. Introduction and Scope

Thermodynamic properties and phase diagrams of systems containing rigid-rod molecules can be predicted for a number of cases and correlated using a lattice model Flory: the first version was proposed in 1956^{1,2} and expanded considerably later by Flory and collaborators.³⁻¹⁴ Numerous properties of polymer liquid crystals (PLCs) and their blends are advantageous in comparison to flexible polymers.¹⁵⁻¹⁷ For this reason, in the preceding paper¹⁸ we adapted the Flory formalism to investigate the effects of varying the concentration θ of liquid-crystalline sequences in PLC copolymers on their properties. We shall now consider ternary systems of the type PLC + flexible polymer (FP) + solvent. Each PLC chain consists of both rigid (mesogenic, liquid-crystalline) and flexible sequences. A solvent molecule is assumed to be isodiametric with a polymer segment, be it rigid or flexible—a standard assumption in lattice models.

One of the motivations of the present work was the existence of experimental data for systems of the type just defined, namely, LC copolymers of poly(ethylene terephthalate) with *p*-hydroxybenzoic acid, PET/*x*PHB (*x* is the mole fraction of PHB, the LC constituent) + poly-(bisphenol-A carbonate) (PC) + CHCl₃. An attempt to use a version of the Flory theory assuming that the PLC chains are fully rigid did not produce satisfactory results;¹⁹ hence careful inclusion of the feature of partial flexibility of PLC chains was indicated.

2. Derivation of Principal Equations

The ternary system contains n_s solvent molecules and n_p polymer chains. We have $n_p = n_2 + n_3$, where the index 2 pertains to PLC and 3 to flexible chains. Each PLC chain is characterized by the fraction of LC sequences $\theta = r_h/(r_h + r_c)$, where r_h denotes the total number of LC (hard) segments in the chain and r_c the respective number of flexible sequences.

We shall take advantage of the work of Matheson and Flory,¹¹ who considered a mixture of n_r copolymers of

various length r (r represents the degree of polymerization) in a solvent of n_s quasi-spherical molecules. Our system may be recovered from theirs, by restricting the copolymers to only two classes: one with $\theta \neq 0$ and the other with $\theta = 0$. Beyond this simplification of the Matheson-Flory approach, however, we introduce additional terms dealing in a more rigorous way with anisotropic interactions between segments belonging to rigid sequences.

So, specializing an expression of Matheson and Flory (eq 12 in ref 11) to our system, we have for the excess Gibbs function of mixing

$$\frac{G^M}{RT} = n_s \ln n_s + n_2 \ln n_2 + n_3 \ln n_3 - (n_s + n_2 + n_3) \ln n_0 + \bar{r} n_p \left(1 - \frac{1}{\bar{r}} \right) - n_0 [(1 - Q) \ln (1 - Q) + Q] - [r_2 n_2 (1 - \theta) + r_3 n_3] \ln Z_c + \chi \bar{r} \frac{n_p n_s}{n_0} - n_2 \sum_y \frac{n_{\eta y}}{n_2} \ln \left(\omega_{\eta y} \frac{n_\eta}{n_{\eta y}} \right) + \frac{n_2}{2kT} \sum_y \frac{n_{\eta y}}{n_2} \eta \epsilon_{\eta y} \quad (1)$$

where Z_c is the internal partition function of a flexible segment; $n_0 = n_s + r_2 n_2 + r_3 n_3 = n_s + \bar{r} n_p$, where r_2 and r_3 are lengths of copolymers and flexible chains, respectively; n_η is the total number of rigid sequences, each of average length η ; $n_{\eta y}$ is the number of such rigid sequences characterized by an average disorientation parameter y ; and $\epsilon_{\eta y}$ is the mean orientation-dependent interaction energy for a rodlike segment (belonging to such LC sequences) in the field of its neighbors; the quantity Q is given by

$$Q = \phi_h \left(1 - \frac{y}{\eta} \right) \quad \phi_h = \frac{\theta r_2 n_2}{n_0} = \theta \phi_2 \quad (2)$$

ϕ_h and ϕ_2 denote respectively volume fractions of rigid sequences and PLC copolymer chains. In the preceding paper¹⁸ we have used symbols $\bar{\eta}$ and \bar{y} ; since now only the

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average values are of interest, in the present paper the bars have been dropped.

The last two terms in (1) replace the last term in the Matheson-Flory eq 12, because we have made use of the Flory-Irvine version¹² for the orientational contribution to the mixture partition function.

We take partial derivatives of G^M/RT with respect to n_s , n_2 , and n_3 , using the fact that the distribution n_{ny}/n_η is assumed to have its equilibrium value, so that

$$\partial(G^M/RT)/\partial(n_{ny}/n_\eta) = 0 \quad (3)$$

Thus, we obtain expressions for the various chemical potentials in the anisotropic phase, with properties of that phase indicated by superscript prime

$$\frac{\mu'_s - \mu'_s(0)}{RT} = \ln \phi'_s + \phi'_p \left(1 - \frac{1}{\bar{r}}\right) - \ln(1-Q) - Q + \chi \phi'_p{}^2 \quad (4)$$

$$\begin{aligned} \frac{\mu'_2 - \mu'_2(0)}{RT} = & \ln \left(\frac{\phi'_2}{r_2}\right) + r_2 \phi'_p \left(1 - \frac{1}{\bar{r}}\right) - r_2 Q + r_2 \chi \phi'_s{}^2 + \\ & r_2 \left[\theta \left(1 - \frac{y}{\eta}\right) - 1 \right] \ln(1-Q) + r_2(1-\theta) \ln Z_c - \\ & \gamma_\eta \sum \frac{n_{ny}}{n_\eta} \ln \left(\omega_{ny} \frac{n_\eta}{n_{ny}}\right) + \frac{\gamma_\eta \eta}{2kT} \sum_y \frac{n_{ny}}{n_\eta} \epsilon_{ny} \quad (5) \end{aligned}$$

$$\begin{aligned} \frac{\mu'_3 - \mu'_3(0)}{RT} = & \ln \left(\frac{\phi'_3}{r_3}\right) + r_3 \phi'_p \left(1 - \frac{1}{\bar{r}}\right) - r_3 Q + r_3 \chi \phi'_s{}^2 + \\ & r_3 \left[\theta \left(1 - \frac{y}{\eta}\right) - 1 \right] \ln(1-Q) + r_3 \ln Z_c \quad (6) \end{aligned}$$

The volume fractions are related by $\phi'_s = 1 - \phi'_p$; ϕ'_2 and ϕ'_3 are the respective volume fractions of polymer constituents in the anisotropic phase, so that $\phi'_p = \phi'_2 + \phi'_3$. γ_η is the number of rigid sequences in a copolymer, hence $\gamma_\eta = \Theta r_2/\eta$.

The corresponding chemical potentials in the isotropic phase (which we denote by unprimed symbols) can be readily written down by observing that $Q = 0$ and $s = 0$ for this phase. By using the equilibrium conditions

$$\mu'_i - \mu'_i(0) = \mu_i - \mu_i(0) \quad (7)$$

for each component in the mixture, we arrive at the equations for equilibrium between an isotropic and anisotropic phase. After applying the Flory-Ronca^{3,4} explicit forms for the distribution n_{ny}/n_η , and the interaction energy ϵ_{ny} , to rewrite the last two terms in (5), these assume the following forms:

$$\ln \left(\frac{\phi'_s}{\phi_s}\right) + (\phi'_p - \phi_p) \left(1 - \frac{1}{\bar{r}}\right) + \chi(\phi'_p{}^2 - \phi_p{}^2) = \ln(1-Q) + Q \quad (8)$$

$$\begin{aligned} \frac{1}{r_2} \ln \left(\frac{\phi'_2}{\phi_2}\right) + (\phi'_p - \phi_p) \left(1 - \frac{1}{\bar{r}}\right) + \chi(\phi'_s{}^2 - \phi_s{}^2) = \\ \left[1 - \theta \left(1 - \frac{4f_2}{\pi f_1}\right)\right] \ln(1-Q) + \\ Q + \frac{\Theta}{\eta} \left[\ln f_1 + \gamma \frac{f_2}{f_1} + \Theta \phi'_{2s} \bar{T}^{-1} \left(1 - \frac{s}{2}\right) \right] \quad (9) \end{aligned}$$

$$\begin{aligned} \frac{1}{r_3} \ln \left(\frac{\phi'_3}{\phi_3}\right) + (\phi'_p - \phi_p) \left(1 - \frac{1}{\bar{r}}\right) + \chi(\phi'_s{}^2 - \phi_s{}^2) = \\ \ln(1-Q) + Q \quad (10) \end{aligned}$$

where

$$\gamma = -\frac{4}{\pi} \eta \ln(1-Q) \quad (11)$$

$$\frac{f_3}{f_1} = \frac{2}{3}(1-s) \quad (12)$$

f_j ($j = 1, 2, 3$) and Q are given by

$$f_j = \int_0^{\pi/2} \sin^j \Psi \exp\left(-\gamma \sin \Psi - \frac{3}{2} \Theta \phi'_{2s} \bar{T}^{-1} \sin^2 \Psi\right) d\Psi \quad (13)$$

$$Q = \Theta \phi'_2 \left(1 - \frac{4f_2}{\pi f_1}\right) \quad (14)$$

$$\bar{T}^{-1} = \eta(T^*/T) \quad (15)$$

s is the usual order parameter for LC systems; T^* is a characteristic temperature which here serves as a measure of the interactions between rigid segments. In general, T^* , as introduced by Flory and collaborators,^{20,21} is related to interaction energies, numbers of interacting sites per segment, and numbers of external degrees of freedom; a detailed discussion is provided in ref 22.

The set of five equations (8-12) defines the biphasic equilibrium (anisotropic-isotropic) for our ternary mixture of semirigid and flexible chains in a solvent of quasi-spherical molecules. In the next section, we shall examine numerical solutions of this system of equations. As discussed in ref 18 and implied also by Matheson,¹⁴ "anisotropic" is not limited to nematic phases.

3. Results for $\chi \neq 0$

A question of effects of inclusion of the usual (spherical force field) attractions represented by the Flory-Huggins-Staverman parameter²³⁻²⁶ χ arises. Calculations for $\chi \neq 0$ are presented in this and for $\chi = 0$ in the following section. We recall that χ represents a superposition of polymer + polymer, polymer + solvent, and solvent + solvent interactions. The higher a positive value of χ , the poorer the solvent; $\chi \leq 0$ corresponds to good solvents.

In view of this, we have performed calculations for values of $-10 \leq \chi \leq 10$. Each time the set of eqs 8-12 was solved in the following way. Assuming values of Θ , r_2 , r_3 , T , T^* , and χ , we calculated $\eta = \Theta r_2$ and $\bar{r} = (r_2 + r_3)/2$. For a given value of ϕ'_2 , the set of five equations consists of two independent subsets: one of three equations (8-10) and the other of two equations (11 and 12). First, the set of two equations was solved using the Newton-Raphson method. Thus, values of γ and s were found. To solve the equations, the procedure MNEWT from ref 27 was used. Integration in eq 13 was done by the routine QROMB based on the Romberg adaptive method.²⁷ Both codes have been slightly modified to assure correct results. In the second step, the same procedures were used to solve the set of three equations. Values of volume fractions ϕ'_3 , ϕ_2 , and ϕ_3 were found in this way. Initial values of these variables needed for using the Newton-Raphson method were found from contour plots of eqs 8-10 vs ϕ_2 and ϕ_3 , assuming a value of ϕ'_3 .

The shape of the top part of the miscibility gap is interesting, but it will be discussed in the following section in which similar results are assembled. In general, the results obtained show that the presence—or otherwise—of the energy χ term hardly makes a difference. For instance, phase diagrams calculated by the method described above are presented in Figure 1 for ternary systems with $\Theta = 0.35$, $r_2 = 600$, $r_3 = 1200$, and $T^* = 300$ K, at the temperature $T = 295$ K, and for $\chi = -10, -1, 0, 1$, and 10 . We see that

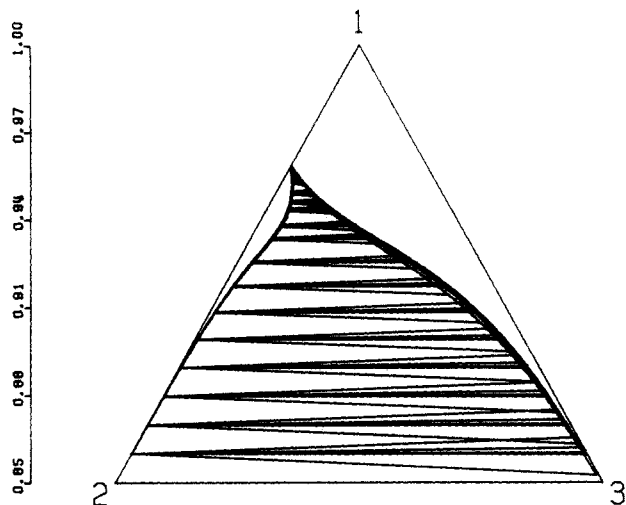


Figure 1. Phase diagrams for the ternary systems consisting of a solvent (1), a PLC (2), and a flexible polymer (3). Parameters of the systems: $\theta = 0.35$, $r_2 = 600$, $r_3 = 1200$, $T^* = 300$ K, and $T = 295$ K. The diagrams were calculated for $\chi = -10, -1, 0, 1$, and 10.

there is little difference between binodals obtained for various values of χ . The most distinctive curve is that for $\chi = 1$. Only slopes of the tie lines are slightly different. In other words, variations of the solvent quality affect the equilibrium compositions very little: with χ values positive as well as negative, phase behavior of this ternary system is almost unchanged. As Flory argued in 1956,¹ *intramolecular* forces in chains have profound effects on properties if inflexibility is present.

Our systems should be contrasted with flexible chains systems, including solutions, in which much larger numbers of conformational states are allowed. We know that in solutions which do *not* contain rigid rods or PLCs, the polymer + solvent interactions are quite important. The hydrodynamic volume per chain determines the chain overlap²⁸ and equilibrium properties, as well as transport properties and flow behavior, including drag reduction and mechanical degradation in solution flow.²⁹⁻³¹ In our case, in view of the above results, in subsequent computations we have confined ourselves to $\chi = 0$, with virtually negligible effects upon the generality of the conclusions.

4. Results for $\chi = 0$

We have studied first the effects of varying the characteristic temperature T^* . In Figure 2A we show the miscibility gap and the connodes (tie lines) for $\theta = 1$, $T = 300$ K, $T^* = 50$ K and $r_2 = r_3 = \bar{r} = 20$. Since $\theta = 1$ corresponds to fully rigid rods in a ternary system containing a solvent + flexible polymer and treated before by Flory,⁹ we can compare diagram A with his results. His Figure 2 has been computed for the axial ratios $x_2 = x_3 = 20$, which is exactly $r_2 = r_3 = 20$ in our notation. Our results are quite similar to those of Flory.

In Figure 2B we show results for $T^* = 100$ K, while the remaining parameters are the same as before. This time we see that the present somewhat more complex version of the theory shows a distinct kind of behavior. When we start from the PLC + flexible polymer pair, their usual immiscibility manifests itself. Consider a composition with a large excess of PLC, containing small amounts of FP. We replace gradually FP by the solvent; that is, we move upward along the 1-2 side, slightly inside the triangle. Several things happen. First, numerical values show that the order parameter s decreases with increasing solvent

concentration, slowly at first and then at a gradually increasing rate; the same is also true for all χ values for the results shown in Figure 1. Second, the PLC + solvent miscibility is lower than that of the FP + solvent pair. This has been already predicted by Flory and collaborators, found experimentally,¹⁹ and is also visible in our Figures 1 and 2A. The tie lines, which close to the 2-3 side of the triangle were not far from horizontal, have an increasingly upward slope when moving from the anisotropic phase to the isotropic one. Moreover, the tie lines become shorter and the difference $\phi'_2 - \phi_2$ becomes smaller. We have a region where the miscibility gap departed from the 1-2 side while a slow increase in solvent concentration is accompanied by a *much faster* decrease of ϕ_2 . In turn, since so much less PLC is needed for the solvent-rich isotropic phase, *more PLC becomes available* for the anisotropic one. The line representing compositions of the anisotropic phase moves to the left, back toward the pure 1-2 side. The liquid-liquid critical point at which $\phi'_2 - \phi_2$ becomes zero is located in this area. These phenomena and the resulting shape of the miscibility gap are only weakly related to the values of χ ; see again Figure 1, where positive and negative χ values affect the slopes of the connodes, but hardly affect the shape of the two-phase region.

In Figure 2C we see the results of computations for a related set of parameters; now $T^* = 200$ K, while the other parameters are the same. The unusual shape of the miscibility gap disappeared; the gap looks "normal". In reality, there is a continuity going from A to C and increasing T^* : the miscibility in the PLC + solvent pair increases, and the liquid-liquid critical point moves accordingly. In Figure 2C that point is much closer to the 1-3 side than before. An equation for T^* in ternary systems (without, however, taking explicitly into account orientational effects caused by rigidity) has been derived;²² T^* for the system is a function of T_i^* values of all the individual components. Given that T^* thus represents an interplay of the characteristics of components, qualitative and quantitative changes in the miscibility gap caused by varying T^* are understandable.

Given the interesting behavior shown in Figure 2B, the question arises as to whether this is another consequence of full rigidity, $\theta = 1$, assumed for our PLC. We have made also calculations for $\theta < 1$, as shown in Figure 2D. Here $\theta = 0.7$, while we have taken $r_2 = r_3 = 20$, $T = 300$ K, and $T^* = 100$ K, that is, the same parameters as for Figure 2B; consequently, $\eta = 14$. As expected, a decrease in PLC rigidity has increased the area of the homogeneous region—not only from the solvent side but also creating a partial miscibility with FP. This constitutes one more proof of the validity of the model, since parameter variations result in system behavior predictable from the physical significance assigned to the parameters. At the same time, we recover the qualitative behavior seen in Figure 2B. With other parameters the same, it is the characteristic temperature T^* representing the strength of the interactions that determines the type of behavior of the system. The extent of PLC rigidity θ influences the area of the miscibility gap but not its shape.

So far, our calculations were of the model type, to study effects of various parameters on the phase behavior. However, we mentioned in the beginning the existence of pertinent experimental data.¹⁹ We have now focused on comparing the phase diagrams determined in ref 19 with predictions of the theory. These diagrams were obtained as cloud point curves from the absorbance E at 800 nm determined on a UV-visible light spectrometer. A solution

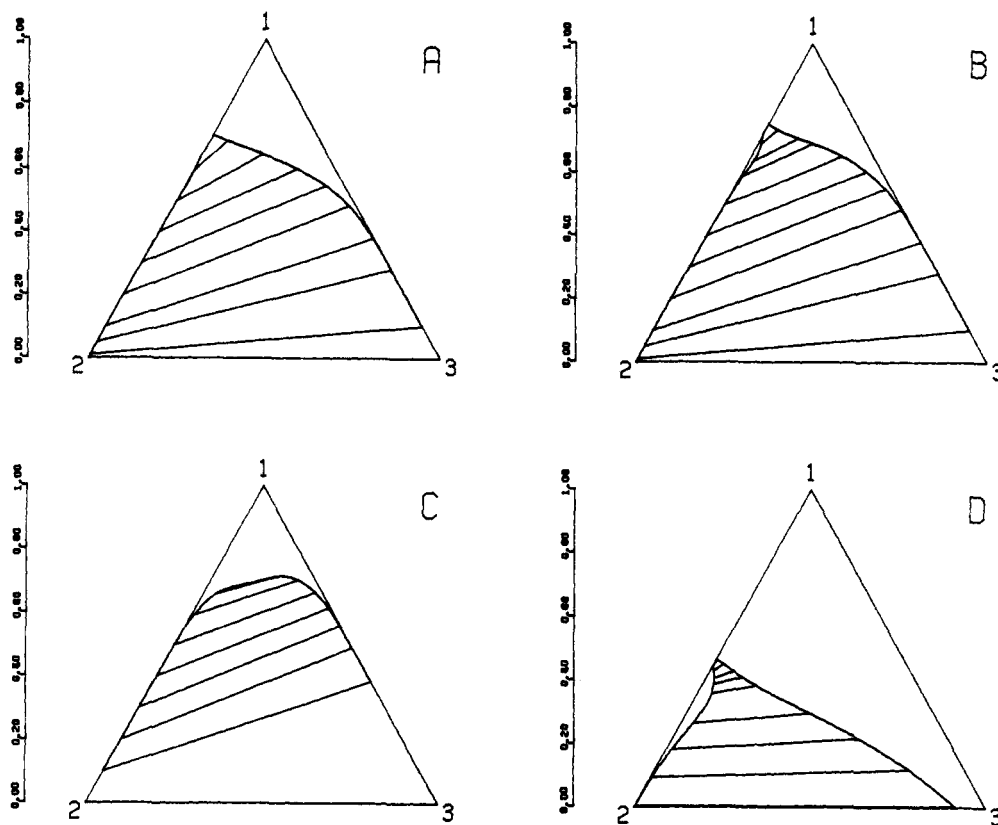


Figure 2. Phase diagrams for the ternary systems with $r_2 = r_3 = 20$, at the temperature $T = 300$ K: (A) $\theta = 1$, $T^* = 50$ K; (B) $\theta = 1$, $T^* = 100$ K; (C) $\theta = 1$, $T^* = 200$ K; (D) $\theta = 0.7$, $T^* = 100$ K.

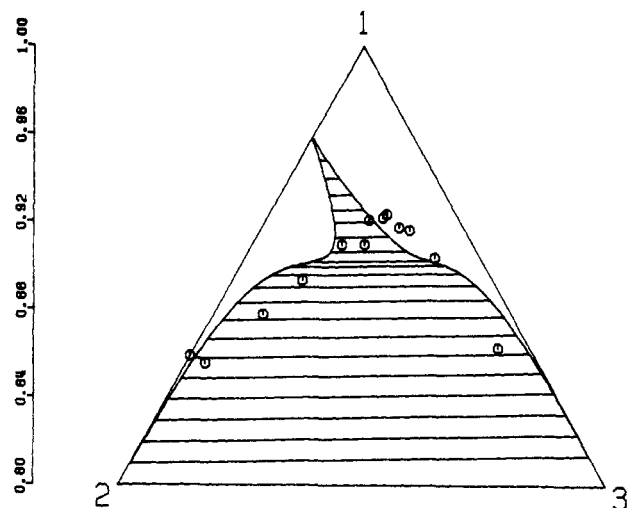


Figure 3. Comparison of experimental and calculated phase diagrams. Points (circles) are from the cloud point measurements described in the text. Lines were calculated for the system with $\theta = 0.27$, $r_2 = 600$, $r_3 = 1200$, and $T^* = 600$ K, at the temperature $T = 295$ K.

was defined turbid when E reached a predetermined (low, rather arbitrarily defined) value.

In Figure 3 we display experimental (circles) and calculated (a continuous contour plus tie lines) results for $\theta = 0.27$ (the PHB concentration) and $T = 295$ K. Other parameters used in the computations are $T^* = 600$ K, $r_2 = 600$, and $r_3 = 1200$; hence $\bar{r} = 900$ and $\eta = 162$. Only the pertinent top part of the triangle is shown. A listing of numerical data shows on inspection features similar to those in the data sets corresponding to Figure 2B and D. In particular, the decrease of the order parameter with decreasing PLC concentration is also here slow at first, and much more rapid afterward. Values of $\phi'_2 = 0.190$, 0.180 , and 0.170 correspond to $s = 0.972$, 0.969 , and 0.966 , respectively, that is, a nearly constant decrement $\Delta s / \Delta \phi'_2$

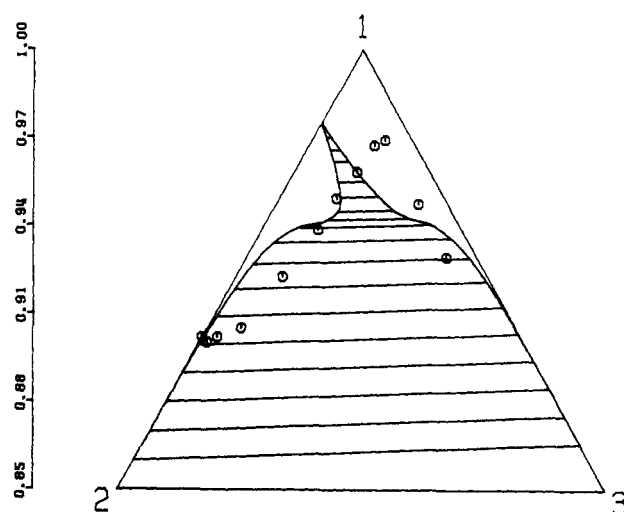


Figure 4. Symbols and parameter values the same as in Figure 3, except that $\theta = 0.35$.

$= 0.3$. However, for $\phi'_2 = 0.052$ and 0.042 , that is, $\Delta \phi'_2$ the same, we have, respectively, $s = 0.761$ and 0.541 , resulting in $\Delta s / \Delta \phi'_2 = 24.7$. We see that the computed miscibility gap shows most of the essential features of the experimental cloud point curve. With increasing solvent concentration, the anisotropic branch is first close to the pure 1-2 side and then ventures "inland". The isotropic branch does a similar thing, but at higher solvent concentration, which is consistent with the presence of the cusp (Zipfel in German). While the cloud points do not exhibit the cusp, they do not contradict its presence either; the experimental technique is not sensitive enough to give an unequivocal answer.

Figure 4 shows a similar comparison of experimental and computed miscibility gaps for $\theta = 0.35$ and $T = 295$ K. Consequently, $\eta = 210$ while r_2 , r_3 , and T^* are the same as for Figure 3. The conclusions are basically the same.

In Figure 3 as well as in Figure 4 we see a much better agreement of computation and experiment than when fully rigid rods (Figure 1 in ref 19) were assumed. The presence of a cusp at the top of the miscibility gap, appearing repetitively in our modeling, deserves a careful experimental study if such is possible.

5. Some Concluding Remarks

Essentially, we have explored further the Matheson-Flory theory¹¹ with the Flory-Irvine orientational contribution¹² included. We have recovered phase diagrams of the kind predicted before and found some new features. The χ interaction parameter has only a limited effect on the ternary diagrams we consider. The extent of rigidity Θ and the strength of the intermolecular and intersegmental interactions as represented collectively by T^* appear to dominate the situation. The order parameter s remains a useful measure of the structure of the anisotropic phase. Apparently, when solvent is added, the LC sequences cause *channeling* of the solvent molecules for a long time ($s \approx 0.97$ for ϕ'_2 as low as 0.170). Given that each PLC chain contains liquid-crystalline as well as flexible sequences, orientation of the former is to some extent imparted to the latter. Thus, flexible sequences appear to participate in channeling solvent molecules. Only when the concentration of solvent molecules becomes really high does "capitulation" of PLC orientation accompanied by a fast decrease of s ensue. We recall that the problem of formation of an orientationally ordered phase was already dealt with by Flory in 1956,¹ while much later Matheson¹⁴ has generalized the Flory results dealing with the chain geometry in such a way that the average width of the rigid sequences is also taken into account.

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