properties of the charged macromolecule is not only limited to a screening effect of the electrostatic interactions as generally assumed so far in most theoretical treatments.

Registry No. NaPSS, 9080-79-9; NaCl, 7647-14-5.

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Multiphase Equilibria in Solutions of Polydisperse Homopolymers. 2. Fundamentals of Three-Phase Separation in Quaternary Systems[†]

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ABSTRACT: Conditions for three-phase separation are examined for quaternary systems consisting of a solvent and three polymeric homologues and obeying Flory–Huggins thermodynamics with concentration-independent parameter χ. The analysis is carried out in polymer composition space, with the advantage of being simple and easily applicable to systems with more components. The critical surface is topologically simple, either monotonous or containing fold(s) but no extrema nor saddle points. A family of coexistence curves can be drawn in the triangle of polymer compositions, with each curve being the locus of polymer compositions that, diluted with a solvent, can be at equilibrium. Heterogeneous double critical points arise at points where the critical surface displays a constrained extremum in the direction of the coexistence curve. The mechanism of three-phase separation is discussed in detail for the simplest case (three-phase region attached to one binary axis only). Such systems display at least one triple critical point located inside the composition triangle on the line of heterogeneous double critical points. At a given temperature, compositions of three coexisting phases depend on the solvent content and define a curve called the trinodal, anchored by its ends to the boundary of the three-phase region. The three-phase separation starts at the triple critical point; with decreasing temperature the trinodal grows and moves toward the above binary axis, until it exits out of the triangle and the three-phase region ceases to exist.

1. Introduction

The mechanism of three-phase separation in true ternary systems consisting of a solvent and two polymer homologues of chain lengths r_1 and r_2 is well established. Building on the pioneering work of Korteweg,[1] van der Waals and Kohnstamm,[2] and Schreinemakers,[3] Tompa has shown that the separation proceeds via the heterogeneous double-plait point mechanism[4] where, upon a change in temperature, a heterogeneous double critical point splits into a metastable and unstable critical point. Recently, his claim was reinforced by both analytical and numerical arguments.[5] Tompa's approach of analyzing the critical line, however, can be used only for true ternary systems and cannot be directly applied to quasi-ternary systems containing more than two polymeric components.[5,6] Yet any information in this respect would be appreciated since, in practice, all polymeric systems are polydisperse.

As the first step in this direction, we shall examine in this paper the principles of multiphase separation in quaternary systems consisting of a solvent (0) and three polymeric homologues (1, 2, 3) differing just by their chain lengths $r_3 > r_2 > r_1$. Graphical representation of such systems is still simple and helps greatly in understanding the phase separation process. In view of a recent misunderstanding concerning simple ternary systems,[6] such an exercise does not seem superfluous before proceeding to the general case, requiring a more abstract approach. It is assumed that the systems follow Flory–Huggins thermodynamics with concentration-independent parameter χ.[7]

First, let us review the essentials of three-phase separation in true ternary systems. The diagram best suited for this purpose seems to be a front view of the three-phase region of the binodal surface such as depicted in Figure 1. For various special lines, the interaction parameter χ is here plotted against the composition of the polymer mixture $w_2 = \phi_2/(\phi_1 + \phi_2)$, where ϕ_i is the volume fraction of polymer species i in the system. The binodal surface is literally caved in, with the S-shaped three-phase line DGHC (i.e., the locus of three-phase equilibrium compositions) arising as the line of intersection between the upper and lower stable parts of the surface. Both of these parts extend continuously beyond their line of intersection, plunging under the stable binodal surface, and are then "connected" by the unstable portion of the surface. The singular upper and lower cusp lines, DFAC and DBEC, mark the line of contact between the metastable extensions and the inner unstable portion of the surface. Each polymer mixture w_2 has its critical interaction parameter χ_c, and the locus of such points is called the critical line (–GBAH– in Figure 1). It is contained within the binodal surface and passes from the upper stable portion of the

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[†] Dedicated to Professor Dale J. Meier of the Michigan Molecular Institute on the occasion of his 60th birthday.

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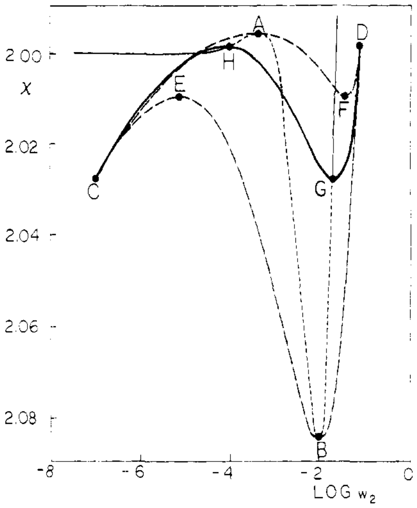

Figure 1. Front view of the three-phase region of the binodal surface for a ternary system solvent (0)–polymer (1)–polymer (2). Chain lengths: $r_1 = 1$ and $r_2 = 25$. (—) Three-phase line; (– – –) upper and lower cusp lines; (——) stable and (- - -) metastable and unstable portions of the critical line. (Reprinted with permission from ref 5. Copyright 1982 John Wiley & Sons.)

surface on the right side, via its metastable, unstable, and metastable parts, to the lower stable portion on the left side.

Both the composition and temperature (i.e., χ) intervals of the binodal surface disturbance (or, physically, of the stable three-phase region) are delimited by the double-cusp points C and D, where the upper and lower cusp lines coalesce with the three-phase line. The roots underlying the three-phase separation, however, extend beyond these limits to the heterogeneous double-plait points A and B. Note that these points lie inside the composition interval but outside the χ interval of the stable three-phase equilibrium region.

Ideally, the delimitation of the three-phase region in a ternary system should thus be given in terms of points C and D. However, it is probably impossible to formulate some general conclusions about these points, since they involve equilibrium between distant phases, e.g., D and H. Although the mathematical criteria for the points C and D are well-known,[5,8] they have to be solved numerically *for each specific case. On the other hand, the conditions* for the double critical points A and B can be well handled analytically and offer some useful, albeit too liberal, conclusions about the χ interval, as well as some information about the general location of the three-phase region. Particularly, the system with a triple critical point can be pinpointed accurately, where the two double critical points merge and *the size of the whole disturbance shrinks to* zero.[4,5] Physically, this case marks the onset of systems with three-phase separations.

The diagram of Figure 1 is discussed in greater detail in our previous report.[5] Its main advantage is that, with the solvent content ϕ_0 ignored, it can present all important features of three-phase separation for ternary systems in just a two-dimensional plot. (The solvent can be ignored since all the points displayed for a particular polymer mixture are unique, and the solvent content required for their appearance is fully determined and known.) The analogue for four-component systems to be discussed below will then require only three dimensions, i.e., a space we are accustomed to and can easily visualize.

2. Extremal Properties of the Critical Surface

Geometrically, double and triple critical points in ternary systems appear as extrema and points of inflection with horizontal slope, respectively, of the critical line. It is reasonable to assume that three-phase separations in quaternary systems could be tied to the equivalents of such points on the critical surface $\chi_c(w_2,w_3)$. Hence, we should first examine the extremal properties of this surface.

The critical value of the concentration-independent interaction parameter χ is[9]

$$\chi_c = \tfrac{1}{2}(1 + r_z^{1/2}r_w^{-1})(1 + r_z^{-1/2}) \qquad (1)$$

where r_w and r_z are the weight and z averages of relative chain length

$$r_w = \sum_{i=1}^{3} w_i r_i$$

$$r_z r_w = \sum_{i=1}^{3} w_i r_i^2 \qquad (2)$$

with the weight fractions w_i of polymer species i being normalized to unity. The requirement that χ_c does not change upon variation $\delta \mathbf{w}$ in composition is satisfied if the resulting changes in weight and z averages comply with the relation

$$\frac{\delta r_z}{\delta r_w} = 2\frac{r_z + r_z^{1/2}}{r_w(1 - r_w r_z^{-1})} \qquad (3)$$

In terms of independent composition variables w_2 and w_3, the changes in average chain lengths are from eq 2

$$\delta r_w = \Delta r_2 \delta w_2 + \Delta r_3 \delta w_3$$

$$r_w \delta r_z = \Delta r_2^2 \delta w_2 + \Delta r_3^2 \delta w_3 - r_z \delta r_w \qquad (4)$$

where $\Delta r_i \equiv r_i - r_1$ and $\Delta r_i^2 \equiv r_i^2 - r_1^2$. Combination of eq 3 and 4 then gives the condition for the direction $\gamma \equiv \delta w_3/\delta w_2$ of the χ_c contour line (i.e., of the locus of polymer compositions having the same value of the critical χ)

$$\psi(\gamma_\chi) \equiv \frac{\Delta r_2^2 + \gamma_\chi \Delta r_3^2}{\Delta r_2 + \gamma_\chi \Delta r_3} = r_z \frac{3r_z + 2r_z^{1/2} - r_w}{r_z - r_w} \qquad (5)$$

Figure 2 shows an example of the χ_c contour line map for a system with a three-phase region attached to the 1–3 axis.

Two aspects of this relation deserve attention:

(i) In the past, attempts have been made to study three-phase equilibrium in a quasi-ternary system consisting of a solvent and two polydisperse polymers by simply analyzing its critical line.[6] Equation 5 confirms our previous contention based on numerical results[5] that this approach is not valid. Unlike in true ternary systems, extrema of the critical line for quasi-ternary systems in general bear no relation to the three-phase separation. In the course of changing the direction γ by 180°, the function $\psi(\gamma)$ (defined as the left-hand side of eq 5) runs through the entire real interval $(-\infty, +\infty)$. Hence, for any point $\mathbf{w} \equiv w_1, w_2, w_3$ of the composition triangle (e.g., the point V of Figure 2) there is always a direction γ_χ along which χ_c does not change (indicated by the line). It is also apparent that the vertical plane passing through the point V tangentially to its χ_c contour line intersects the χ_c surface in the form of a local extremum. Physically, however, such a line of intersection represents the critical line plotted for the quasi-ternary system consisting of a solvent, the binary polymer Q_1, and the ternary polymer Q_2. Thus, the presence of an extremum on the critical line does not convey any special information. In fact, an extremum can be observed at any point $\mathbf{w}$ if the direction γ_χ (hence the corresponding quasi-ternary system) is chosen properly, even in systems undergoing only two-phase separations.

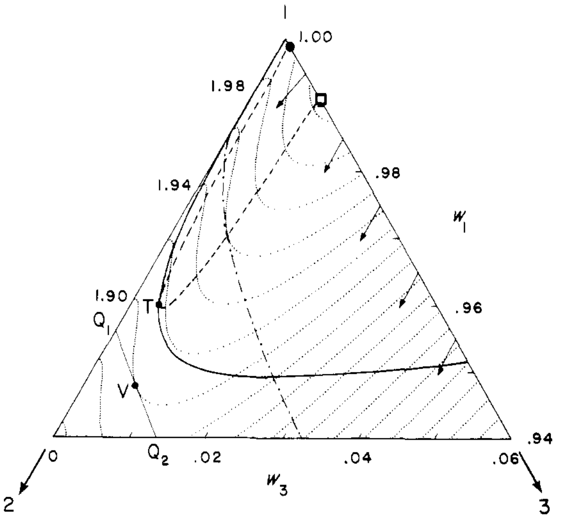

Figure 2. Portion of the critical surface contour map covering the three-phase region in a quaternary system of the first kind. Chain lengths: $r_1 = 1$, $r_2 = 4$, and $r_3 = 20$. χ_c contours are drawn with the increment of 0.02 (some of the values are indicated at the left axis). As a result of a fold in the surface, the 1–3 critical line has a maximum (●) and a minimum (□) while the critical lines for axes 1–2 and 2–3 are monotonous. For a quasi-ternary system solvent–Q_1–Q_2 a minimum is observed on its critical line at point V, although this point is outside the three-phase region. Arrows at the 1–3 axis indicate directions of lines of constant r_z. (---) HDPP line; (-·-) a coexistence curve; T is a triple critical point. Also indicated is the three-phase boundary line (——) although it lies outside the critical surface.

(ii) The direction γ is a single-valued function of ψ, except for $\psi = r_1 + r_3$, where $\gamma \to \pm\infty$ (which is, however, of no concern since both these values still correspond to a single direction parallel to the 1–3 axis). Hence, at any given point **w** there is one and only one direction along which χ_c does not change, and the χ_c contour lines never cross each other. The critical surface contains only partial extrema constrained to a particular direction. There are no free extrema, saddle points, or other complex topological structures; at most, the surface may contain folds (i.e., ridges and valleys) stretching over a portion of it and exiting through the binary side(s) (see Figure 2). Hence, the multiple critical points, if present, will be tied to the thermodynamics of the system more subtly than just through the geometry of the critical surface.

3. Coexistence Curves

A question now arises whether there is, in addition to the χ_c contour lines, another family of curves filling the triangular polymer composition space that would reflect the thermodynamics of the system more directly and perhaps would be helpful in locating multiple critical points. It turns out that such a set of lines indeed exists.

At each critical point one can define the critical separation direction as the limiting direction of tie lines projected into the contour map of Figure 2 as the respective critical temperature is approached. This quantity can be derived as follows: From the known relation for the separation of polymeric species i between the more ($''$) and less ($'$) concentrated phases[7]

$$\phi_i''/\phi_i' = \exp(\sigma r_i) \tag{6}$$

the polymer compositions in the two coexisting phases are

$$w_i' = \phi_i'/\sum_j \phi_j'$$

$$w_i'' = \frac{\phi_i' \exp(\sigma r_i)}{\sum_j \phi_j' \exp(\sigma r_j)} \tag{7}$$

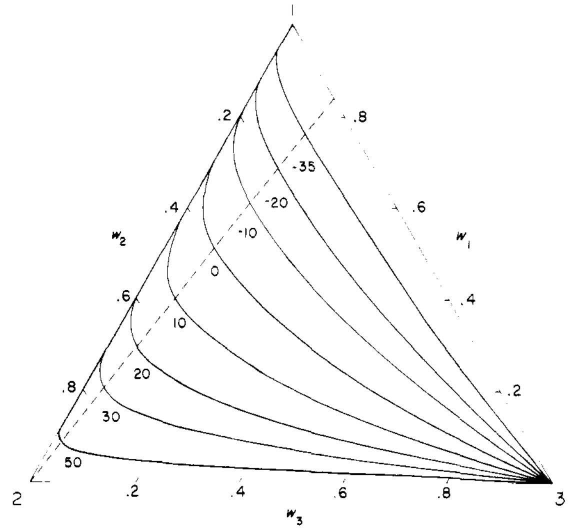

Figure 3. Family of coexistence curves for the quaternary system $r_1 = 1$, $r_2 = 4$, and $r_3 = 20$. Indicated in the diagram are the values of ln C (eq 9). Dashed line is the locus of points where $(\partial C/\partial w_3)_{w_2} = 0$.

In the neighborhood of the critical point, the exponentials can be expanded, and the critical separation direction γ_c becomes independent of the separation factor σ:

$$\gamma_c \equiv \lim_{\sigma \to 0} \frac{w_3'' - w_3'}{w_2'' - w_2'} = \frac{w_3}{w_2} \frac{\Delta r_3(1 - w_3) - \Delta r_2 w_2}{\Delta r_2(1 - w_2) - \Delta r_3 w_3} \tag{8}$$

This differential equation can be viewed as representing the slope of a family of curves, and its integration yields a simple symmetrical relation

$$w_1^{r_2-r_3} w_2^{r_3-r_1} w_3^{r_1-r_2} = C \tag{9}$$

where C is a nonnegative constant. Included in the set of curves obviously have to be also the axes of the triangle; the parameter C is zero for the 1–3 axis, tends to infinity for the 1–2 and 2–3 axes, and stays positive finite within the triangle. Thus the family of curves originates at the apex 1, fans out throughout the composition space, and ends at the apex 3 (see Figure 3). Curves behave very simply: It can be shown that independently of r_i, (i) the parameter C monotonously increases in the direction of the 1–2 axis, $(\partial C/\partial w_2)_{w_3} > 0$, and (ii) in the direction of the 1–3 axis, the parameter C reaches a minimum at the line $w_1/w_3 = (r_3 - r_2)/(r_2 - r_1)$ (indicated by a dashed line in Figure 3) but does not show any point of inflection; i.e., there is no other extremum present.

Inspection of the relation (9), however, reveals that its significance reaches much farther than to the critical point neighborhood. In fact, the left-hand side of eq 9 is identical for any phases at equilibrium, regardless of how remote they are from the critical point. For a principal phase of polymer composition **w**, the incipient phase normalized compositions are $w_i \exp(\sigma r_i)\phi/\phi^*$ (where ϕ and ϕ^* are the overall polymer volume fractions in the principal and incipient phases),[10] and the product of eq 9 appears to be invariant with respect to the values of σ, ϕ, and ϕ^*.

$$(w_1 e^{\sigma r_1}\phi/\phi^*)^{r_2-r_3}(w_2 e^{\sigma r_2}\phi/\phi^*)^{r_3-r_1}(w_3 e^{\sigma r_3}\phi/\phi^*)^{r_1-r_2} = w_1^{r_2-r_3} w_2^{r_3-r_1} w_3^{r_1-r_2} \tag{10}$$

Hence, a curve passing through a particular point in the diagram represents the locus of all phases that can be potentially at equilibrium, at various temperatures and various solvent contents, with the given point. Such curves will be called coexistence curves since they express very succinctly phase equilibria for the given system.

4. Three-Phase Separation

A logical place to start the examination is the binary sides of the triangle, where the χ_c surface is cut by the binary vertical planes to form critical lines for corresponding ternary systems (such as in Figure 1). The three-phase behavior of ternary systems is well understood.

With polymer components ordered so that $r_1 < r_2 < r_3$, the most prone to three-phase separation of all ternary systems is the binary side 1–3, where the ratio r_3/r_1 is the highest. The criterion for the existence of a three-phase region here is $r_3/r_1 \geq \rho(r_1)$, where the implicit formula for $\rho(r)$ can be rewritten from previous results[4,5] as

$$6[(1+\rho)^2 - 12\rho]^2 r + (1+\rho)[(1+\rho)^2 - 108\rho] - [(1+\rho)^2 + 36\rho]^{3/2} = 0 \quad (11)$$

The function ρ ranges from $\rho(1) \simeq 15.645$ to $\rho(r \to \infty) \simeq 9.899$. It is apparent that in the case of equality in the above criterion, $r_3/r_1 = \rho(r_1)$, the binary critical line 1–3 contains a point of inflection with a horizontal slope (a triple critical point) rather than two extrema, and the three-phase region does not penetrate into the triangle.

The binary side 1–3 combining the components with the lowest and highest chain lengths is unique in other respects as well. It is the only binary side containing all possible values of chain-length averages that exist in the entire system (ranging by necessity from r_1 to r_3). Hence, it is the side from which all r contour lines originate. For instance, the r_z contour lines, the loci of compositions having identical r_z values, have the direction

$$\gamma_z \equiv \left.\frac{\delta w_3}{\delta w_2}\right|_{r_z} = -\frac{\Delta r_2}{\Delta r_3}\,\frac{r_1 + r_2 - r_z}{r_1 + r_3 - r_z} \quad (12)$$

and the rate of change in r_w along an r_z contour line is positive

$$\left.\frac{\delta r_w}{\delta w_2}\right|_{r_z} = \frac{(r_2 - r_1)(r_3 - r_2)}{r_1 + r_3 - r_z} > 0 \quad (13)$$

As one moves away from the binary axis 1–3, r_w of eq 13 keeps increasing and χ_c declining. For a given r_z, the points of the binary side 1–3 thus have the lowest r_w and the highest χ_c (cf. eq 1). (This is also obvious from Figure 2, where several directions γ_z are indicated by arrows.) This means that the binary axis 1–3 also contains the mixture with the χ_c value highest of the entire system. If $r_3/r_1 \leq \rho(r_1)$, it is the pure component 1. However, if $r_3/r_1 > \rho(r_1)$, it may be the mixture corresponding to the minimum[11] of the 1–3 binary critical line, as it happens in Figure 2.

4.1. Multiple Critical Points. Let us first address the question of heterogeneous double-plait points (HDPP) in quaternary systems. In true ternary systems these points played a crucial role in the mechanism of three-phase separation and were first defined as extrema of the critical line (points A and B of Figure 1).[4] Only later it was recognized that they can also be interpreted in much broader terms defined for any polydisperse polymer, namely, as critical points located at one of the cusps (singular points) of the cloud-point curve (CPC),[10,12] with a remarkably simple criterion $S = 0$, where

$$S \equiv 3r_z + 2r_z^{1/2} - r_{z+1} \quad (14)$$

and

$$r_{z+1} r_z r_w = \sum_{i=1}^{3} w_i r_i^3 \quad (15)$$

In any event, the HDPP's delineate the boundary between systems with thermodynamically unstable and metastable critical points.[5]

In the present case one has no difficulty with the latter general definition. One can use the condition $S = 0$ to draw in Figure 2 the HDPP line, the locus of heterogeneous double critical points, that encompasses the region of polymer mixtures with thermodynamically unstable critical points. The direction of this line

$$\gamma_S \equiv \left.\frac{\delta w_3}{\delta w_2}\right|_{S=0} = -\frac{\Delta r_2}{\Delta r_3} \times \frac{3(r_1 + r_2 - r_z)(r_{z+1} + r_z) - 2(r_1^2 + r_1 r_2 + r_2^2 - r_z r_{z+1})}{3(r_1 + r_3 - r_z)(r_{z+1} + r_z) - 2(r_1^2 + r_1 r_3 + r_3^2 - r_z r_{z+1})} \quad (16)$$

is again a single-valued function of the composition **w**; i.e., the HDPP line cannot self-intersect. Furthermore, the direction of χ_c contour lines at the HDPP line follows the simple relation

$$\gamma_{\chi,S} \equiv \left.\frac{\delta w_3}{\delta w_2}\right|_{\delta\chi_c=0;S=0} = \frac{w_3[\Delta r_3(1 - w_3) - \Delta r_2 w_2]}{w_2[\Delta r_2(1 - w_2) - \Delta r_3 w_3]} \quad (17)$$

The derivation of eq 16 and 17 is sketched in Appendix I.

It is evident that at least in some cases, the HDPP line originates at the sides of the triangle—namely, if the corresponding ternary systems do have a three-phase region. It is interesting to ask the following question: Is it possible that the HDPP line exists in the form of a closed loop limited entirely to the inside of the triangle? If so, one could have a three-phase quaternary system even if the constituent ternary systems were of strictly two-phase type. Intuitively one feels that the answer should be negative, and this can indeed be proven with the aid of the above relations (see Appendix II). Several kinds of quaternary systems can thus be distinguished, depending on the number of constitutive ternary systems that undergo three-phase separation. Leaving apart the trivial zeroth kind of system [characterized by $r_3/r_1 < \rho(r_1)$] showing only two-phase equilibria, the simplest is the system of the first kind, where only the ternary system solvent (0)–polymer (1)–polymer (3) can separate into three phases [$r_3/r_1 \geq \rho(r_1)$, $r_2/r_1 < \rho(r_1)$, $r_3/r_2 < \rho(r_2)$]. The three-phase region is then expected to be "attached" to the 1–3 axis of the triangular diagram, without touching any of the other axes. If two ternary systems undergo three-phase separation, the multiphase region in this quaternary system of the second kind stretches between the corresponding two axes, anchored to both of them. Finally, the most complex case occurs if all three ternary systems are capable of splitting into three phases.

For the ensuing discussion of important features of three-phase separation in quaternary systems, it is preferable to choose the simplest case possible, i.e., the system of the first kind. More complex systems will be treated in the future.

The two branches of the HDPP line originate on the 1–3 axis at the two extremal points of the binary critical line. The maximum of the critical line is specified by the condition $Z < 0$, where[10]

$$Z \equiv (10r_{z+1} - 15r_z + 6)r_z - r_{z+1}r_{z+2} \quad (18)$$

and it is located at the upper cusp point of the respective CPC. On the other hand, at the minimum of the critical line $Z > 0$, and the critical point is situated at the lower cusp point. The maximum of the critical line occurs at a lower content of the high molecular weight component (in this case 3) than the minimum does.

Equation 17 indicates that at the extrema of the 1–3 critical line, the χ_c contour lines run parallel to the 1–3 axis;

i.e., $\gamma_{\chi,S} \rightarrow \pm\infty$ (cf. Figure 2). This, together with the existence of the r_z contour lines and its implications (eq 12 and 13), makes χ_c decrease as one proceeds from either extremum along the two branches of the HDPP line into the triangle. Since the HDPP line is continuous, and no other side contains a point with $S = 0$, the two branches have to meet at the absolute maximum of the HDPP line (i.e., minimal value of χ), point T of Figure 2. It is to be expected that point T is a triple critical point, since the HDPP line here touches a horizontal plane of constant χ_c, thus possessing a double common point. Indeed, this can be proven: on the one hand, the maximum of the HDPP line can be located as a point where the HDPP line touches one of the χ_c contour lines from the condition $\gamma_S = \gamma_{\chi,S}$ (eq 16 and 17). On the other hand, the two conditions for a triple critical point, derived from the cloud-point curve analysis, are $S = 0$ and $Z = 0$. Physically, this characterizes a polymer mixture where the size of the unstable portion of the CPC has just shrunken to zero, with the critical point superimposed onto the double-cusp point. In Appendix III it is shown that the two above criteria are equivalent; i.e., the maximum of the HDPP line coincides with a triple critical point.

Thus, each quaternary system of the first kind contains at least one mixture exhibiting a triple critical point. It may be recalled that the occurrence of a triple critical point was rare in ternary systems, being restricted only to those systems whose chain-length ratios satisfied the condition $r_2/r_1 = \rho(r_1)$.

After having discussed the more general aspect of heterogeneous double critical points, let us return to their original interpretation as extremal points of the binary critical line in ternary systems and examine whether an analogous meaning exists in quaternary systems. As mentioned above, an HDPP cannot be equaled with just any constrained extremum of χ_c without further qualification since at any point **w**, there exists a direction along which χ_c exhibits an extremum. Examination of the critical surface of Figure 2 reveals that the HDPP line cannot be identified with the crest and/or valley of the fold either; in fact, it is hardly related to the topology of the surface alone at all, except at the fold exit through the 1–3 axis. This is not too surprising since the critical surface is determined entirely by r_w and r_z of each point, whereas the HDPP line also depends on r_{z+1}. The HDPP line is, however, related to the extremal properties of the surface in the critical separation direction. Comparison of eq 8 and 17 shows that at an HDPP point, the χ_c contour line direction becomes identical with the direction of the coexistence curve passing through this point; i.e., the critical surface here possesses a constrained extremum in the direction of critical separation (see Figure 2). With the benefit of hindsight, this is not surprising; for the splitting of an HDPP into two single critical points to be physically real, it has to proceed in the direction where the resulting two critical phases can coexist (although they may not be stable).

In true ternary systems projecting into a plane (such as that of Figure 1), this condition is always met and any extremum of the critical line corresponds to an HDPP. On the other hand, an extremum appearing on the critical line for a quasi-ternary system is in fact an HDPP if, and only if, the phase separation in its immediate neighborhood proceeds along the selected quasi-binary polymer composition axis, i.e., if the phase compositions do not run "out of the plane" of the diagram.

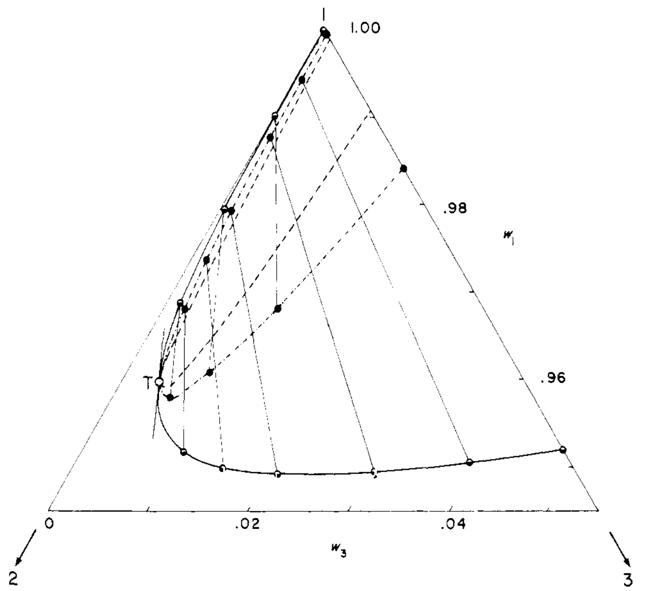

Figure 4. Diagram of three-phase region in the system identical with that of Figure 2. (–◒–) Three-phase boundary line; (– – –) HDPP line; (◒–●) tie lines; (–·–) three-phase critical line. The line drawn through T indicates the critical separation direction at the triple critical point.

4.2. Composition Range of Three-Phase Separations. The composition range of three-phase separations extends in general beyond the region of unstable critical points delimited by the HDPP line. Unfortunately, there is no closed formula that would enable a simple location of this boundary. Unlike in the case of the HDPP line, the equilibrium phases here usually differ greatly in composition, and their determination requires the solution of complete equilibrium equations rather than just their expanded forms. The simplest way is to scan the quasi-binary cloud-point curves, computed by standard methods,[10,13] for the presence of an unstable triangular portion. Its existence unequivocally proves that the examined system splits into three phases within a certain range of polymer concentrations. In this regard, the three-phase boundary line specifies polymer mixtures whose cloud-point curve has just lost its unstable region and "straightened up", with the critical point typically located somewhere else on the CPC, above or below.

Rather than to follow the outcome from the sequence of pairs of computed values χ and ϕ, it is faster to keep checking for the signs of the functions F_c and F_d along the cloud-point curve

$$F_c \equiv 2\chi\phi^* - r_w{}^{*-1} - \phi^*(1 - \phi^*)^{-1}$$

$$F_d \equiv \phi^*(1 - \phi^*)^{-1} - r_z{}^{*1/2} r_w{}^{*-1} \qquad (19)$$

where the asterisk indicates that the values refer to the incipient phase at the cloud point (i.e., to the shadow curve). The condition $F_c = 0$ is satisfied at both cusp points of a cloud-point curve.[8] Hence, for a system splitting into three phases F_c would change its sign twice, having two nontrivial roots where $F_c = 0$. Outside the three-phase range, F_c would keep its sign unchanged all along. The condition $F_d = 0$, satisfied at a double root of F_c, then specifies the case where the size of the unstable portion of the cloud-point curve has just degenerated to zero, and both cusp points coincide in a double-cusp point; i.e., it defines the double-cusp line forming the boundary of the three-phase region in a quaternary system (see Figures 2 and 4).

Physically, the condition $F_c = 0$ means that the incipient phase is located on the spinodal, while the additional condition $F_d = 0$ defines the incipient phase directly as a critical point. Hence, both conditions are automatically

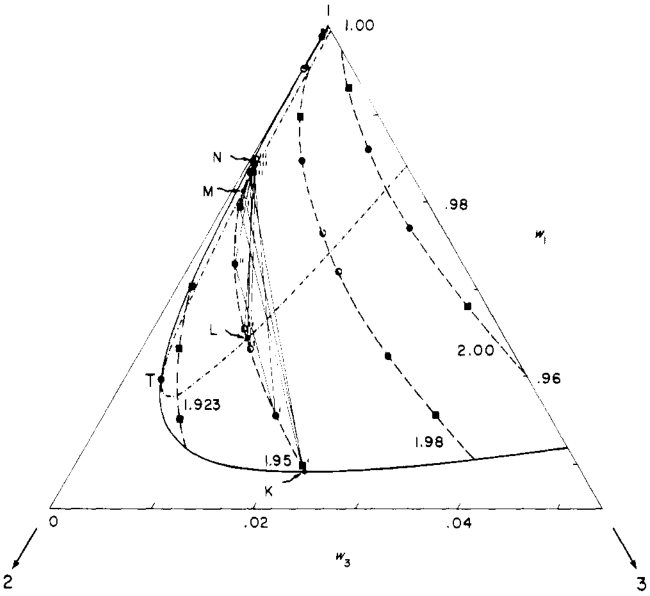

Figure 5. Diagram of three-phase region in the system identical with that of Figure 2. (——) Three-phase boundary line; (–·–) three-phase critical line; (– – –) trinodals for indicated values of the χ parameter. On each trinodal, points of the same type represent phases at equilibrium. Because of insufficient resolution, only two points are displayed for some triplets. Tie lines are drawn only for one of the trinodals.

met also at any critical point where $\sigma \to 0$. (In contrast, at a double-cusp point, σ is typically different from zero.) This fact, however, does not diminish the practical value of these two criteria for tracing the three-phase boundary line. For obvious reasons, it is sufficient to examine only the polymer composition range outside the HDPP line, where the critical point is certainly located outside the unstable portion of the CPC, and thus does not interfere with the sign examination.

Also indicated in Figure 4 are the locus of critical points that are conjugated with the points of the three-phase boundary line (equivalents of critical points H and G and the double-cusp points D and C of Figure 1) and several corresponding tie lines representing equilibria at different temperatures. Since these are the only critical points conjugated in a three-phase fashion with soome distant point (normally, a critical point is conjugated only with itself), the locus of such points will be called the three-phase critical line. Its physical significance can be understood from Figure 1 for a ternary system: At a three-phase equilibrium, independently of χ (i.e., temperature), the composition of the first phase is restricted to the interval $\langle w_C, w_H \rangle$, that of the second phase is restricted to $\langle w_H, w_G \rangle$, and the third phase is located between w_G and w_D. Analogously in quaternary systems, the polymer composition of the "middle" phase will be bound by two branches of the three-phase critical line (each located between the HDPP line and the three-phase boundary line), while the compositions of the remaining two phases will be restricted to the two sectors between the corresponding branches of the three-phase critical line and the double-cusp line. This claim is substantiated by examination of the conjugated phase compositions as outlined below, as well as by numerical results for particular cases treated (see also Figure 5).

Some qualitative conclusions can be drawn simply from the Gibbs phase rule. It is well-known that for a ternary system, the compositions of conjugated three phases at a specified temperature are fixed, appearing as three points of intersection of the corresponding binodals. This is in agreement with the Gibbs phase rule for condensed systems, stating that a three-phase ternary system has just one degree of freedom, e.g., the temperature. However, a quaternary system split into three phases has two degrees of freedom; i.e., one has to choose the temperature *and* one composition variable (e.g., the solvent content) in order to fix the compositions of all three phases. Hence, in the polymer composition coordinates **w**, the locus of such equilibrium compositions for a given temperature has to be a line, usually S-shaped, by analogy called the trinodal, along which the three points representing polymer compositions of three conjugated phases will move, each restricted to one of the three above-discussed sectors.

More specifically, a trinodal is anchored by its end points (K and N of Figure 5) to the two branches of the three-phase boundary line. As indicated above, the double-cusp points K and N are at equilibrium with critical points M and L, respectively, located at the intersections of the trinodal with the three-phase critical line, and the tie lines KM and NL correspond to the two extreme cases where the three-phase triangle has degenerated to a line. If the polymer composition of the three-phase boundary phase, say K, is perturbed to the point ■′, the phase M splits into two phases, ■″ and ■‴, located in front of and beyond the point M, respectively, thus establishing a genuine three-phase equilibrium. Two other triplets of coexisting phases are indicated by points ● and ◐. Note that the degenerated tie line (e.g., NL) is not necessarily a tangent to the trinodal; i.e., it overlaps with other triangular tie lines.

It is apparent that any three points characterizing a three-phase equilibrium have to lie also on the same coexistence curve (i.e., the parameter C of eq 9 is identical for them), and the coexistence curve passing through a double-cusp point becomes a tangent to the corresponding trinodal at the conjugated three-phase critical point. The coexistence curve, however, represents all possible equilibria, two-phase and three-phase, at various temperatures, whereas the trinodal is an isothermal curve depicting exclusively three-phase equilibria.

Although seemingly there are no limits to the number of possibilities the system might choose for its coexisting phases at a particular temperature, the outcome is unambiguously determined by the material balance equations. From the standpoint of the polymer mixture, the obvious requirement is that the point **w** representing its overall composition be within the triangle of three phases; i.e., all triangles of Figure 5 not containing the point **w** can be disregarded. After this procedure one is still left with an infinite number of possible separations, each with different ratios of polymer amounts contained in the three phases, as given by the lever rule. The final determination of the phase compositions for a particular system is made with the aid of material balance for the solvent. At equilibrium (computed, e.g., from the three-phase point of the cloud-point curve), each of the three coexisting points w', w'', and w''' has assigned to it also the corresponding solvent concentrations, which, together with the polymer amount ratios known from the lever rule, fix the overall solvent concentration in the system. Hence, each three-phase triangle encompassing the point **w** corresponds to a different solvent content of the quaternary system, and only one triangle (if any at all) will fit the prescribed solvent level.

The two branches of all of the above-mentioned lines (HDPP line, double-cusp line, and three-phase critical line) approach each other and finally merge with a common tangent into a single point, the triple critical point T. It is apparent that here (i) also the trinodal degenerates into

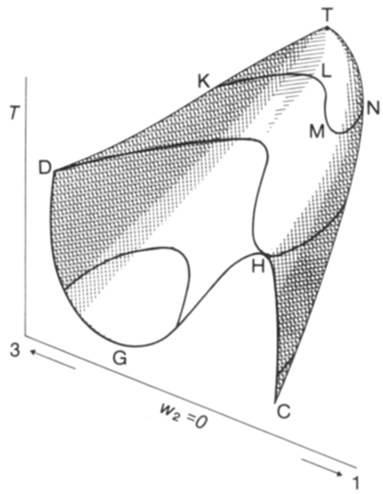

Figure 6. Schematic three-dimensional view of the trinodal surface for a quaternary system of the first kind. Point notation is identical with that used in Figures 1 and 5. Apparent are three sectors of the surface (two shaded, one unshaded), each delineating the composition range for one of three conjugated phases.

a point and (ii) on the cloud-point curve corresponding to T, the critical point "exits" directly from its region of instability "through" the disappearing unstable triangle of the CPC and becomes stable.

A three-dimensional sketch of the three-phase region is outlined in Figure 6. Depicted is the trinodal surface of three-phase equilibria for a quaternary system analogous to that of Figures 2–5, viewed from behind the axis 1–3 (in the direction of arrows in Figure 2). The surface is bound by the double-cusp line CTD and contains two branches of the three-phase critical line HTG, marking the crest and the bottom of its fold. In front, the three-phase surface is intersected by the 1–3–T plane in the form of an S-shaped three-phase line for the ternary system solvent–polymer (1)–polymer (3), analogous to that of Figure 1. Moving into the triangle, we see the surface sloping upward, the extrema becoming less prominent, and the size of the three-phase region diminishing until the region eventually disappears at the triple critical point T. The above-mentioned trinodals arise as the lines of intersection between the three-phase surface and horizontal planes of constant temperature. The set of triangles associated with each trinodal then delineates the polymer composition range in which one can observe three-phase equilibrium at the given temperature.

4.3. Mechanism of Three-Phase Separation. Now we are in a position to examine the evolution of three-phase equilibrium with changing temperature in a quaternary system of the first kind, along the same lines as has been done for ternary systems in the past. Recall that in the latter case the root of the three-phase region was in the heterogeneous double-plait point (characterized by $S = 0$) that split upon change in temperature into a metastable ($S > 0$) and unstable ($S < 0$) critical points, forming the nucleus of a new binodal. This binodal, at first not stable, grew with further change in temperature until it reached and protruded through the old binodal at which point a part of it became thermodynamically stable, providing the basis for a stable three-phase equilibrium.

In section 4.1 the triple critical point T was shown to be at the maximum of the HDPP line (using our convention about the relation between T and χ). Hence, the origin of three-phase separation in the quaternary system under discussion has to be in the triple critical point T located generally *inside* the triangle of polymer compositions. In contrast to a typical ternary case, however, there is no delay here for a given system between the first encounter of a multiple critical root and the three-phase separation. Although the three-phase region at T is infinitesimal as regards the size of its temperature and solvent concentration intervals, it is in principle there. Further development bears certain analogy to the ternary case, although on a higher level: As temperature decreases, the multiple critical point of the highest order (triple critical point T characterized by $Z = 0$, $S = 0$) splits into two critical points of the next lower level (heterogeneous double-plait points). One of them is located on the positive branch of the HDPP line characterized by $Z > 0$, $S = 0$ (i.e., it would appear at the lower cusp of the CPC for the respective polymer mixture), while the other lies on the negative branch, $Z < 0$, $S = 0$ (and at the upper cusp of the CPC). Changing the temperature further then moves the two double critical points closer toward the 1–3 axis and makes the three-phase region around them larger and amenable to experimental verification. The negative branch arrives at the 1–3 axis "sooner", i.e., at a higher T (lower χ), and at a lower value of w_3, than the positive one. The last double heterogeneous critical point registered in the system is the positive one for the ternary mixture solvent–polymer (1)–polymer (3) (equivalent of point B of Figure 1).

At first sight it might be argued that the process described above is not unique since the triple critical point T, being within the critical surface, is surrounded by an infinite number of critical points; hence, it might "split" into any two of those. A genuine splitting, however, has to proceed along the coexistence curve in the critical separation direction, and as such, it is unique and results in two HDPP's. Furthermore, each HDPP of the HDPP line splits similarly in its critical separation direction into metastable and unstable critical points, forming nuclei of new binodals as known from the ternary system theory. Thus we see a heirarchy of critical points of various orders in a quaternary system of the first type, each higher one giving rise to the lower ones: a triple critical point yields an HDPP line of double critical points, while each heterogeneous double critical point in turn generates critical lines of unstable and metastable (later stable) "single" critical points.

In a three-component system, the temperature interval of three-phase equilibria was specified by the double-cusp points D and C, conjugated with the critical points H and G, respectively, of Figures 1 and 6. Analogously, in the quaternary system the confining surfaces are formed by sets of upper and lower tie lines representing equilibria between the points of the double-cusp line (three-phase boundary line) and the critical points forming the crest and the bottom of the fold of the three-phase trinodal surface of Figures 4–6. Note that the upper and lower sets of tie lines are not eclipsed when projected on the polymer composition triangle. Generally, they become parallel only at the 1–3 axis and at the triple critical point T, and the lower set is "shifted" closer to the component 1, compared to the upper set. Starting from the 1–3 axis, the two confining surfaces slope upward toward the triple critical point T, where they shrink and merge into a single point. The HDPP line, although in Figure 4 projected into the three-phase composition region, in fact lies outside the confining surfaces, the positive branch below the lower one, the negative branch above the upper one, and makes contact with them only at the triple critical point T.

The net effect of adding to the ternary system solvent–polymer (1)–polymer (3) a third polymeric component intermediate to the two original ones is then as fol-

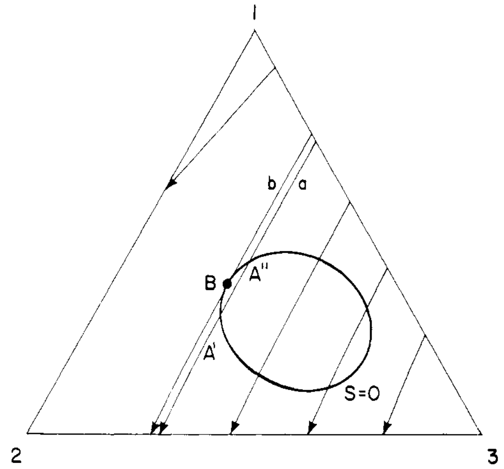

Figure 7. Hypothetical closed-loop type HDPP line for a quaternary system. Arrows indicate lines of constant r_z.

lows: (i) the quaternary system appears to be more prone to three-phase separation than the ternary system was, judged by the solvent power (temperature) at which three-phase equilibrium becomes first possible; (ii) the temperature interval of the three-phase region becomes narrower, until it contracts to zero at the triple critical point; (iii) if the polymer mixture contains a sufficient proportion of the intermediate component 2, three-phase separation is entirely suppressed. The last two points clearly show the compatibilizing effect of an intermediate component on the phase behavior of two polymeric components widely differing in the chain length. While at first sight the first point might be interpreted to the opposite effect, this would not be correct: The temperature of the first three-phase separation in the system has to be sensitive also to the solvent content, which is disregarded in the present diagrams and which certainly varies as one proceeds from the 1–3 axis into the triangle. Hence this temperature alone should not serve as a criterion for judging the compatibility of the system.

The outline above gave a global view of the entire quaternary system, for the sake of simplicity projected into the triangular diagram of polymer compositions. It is equally instructive to examine the development of three-phase equilibrium upon change in temperature for a polymer solution of a particular composition, represented by a single point in the diagram. With decreasing temperature, the corresponding trinodals (and their sets of triangular tie lines) shift from the triple critical point T toward the axis 1–3. The first time the three-phase separation becomes potentially possible for a mixture within the three-phase boundary line is when its representative point is approached and contacted by one of the triangular tie lines associated with the trinodal for the respective temperature. This situation alone, however, does not yet guarantee three-phase separation since, as described above, each triangle of tie lines for the given trinodal corresponds to a different solvent content in the solution. Typically, one will have to decrease the solvent power further in order to enter the three-phase region for the given solvent content. If the solvent concentration has been chosen inconveniently, the solution may never separate into three phases although its representative point is projected into the three-phase region of the triangular diagram; note, that for each such mixture, both the temperature and solvent concentration intervals of three-phase equilibrium are limited.

In the majority of cases the three-phase separation will be preceded by two-phase equilibrium, and the appearing third phase will be of distinctly different composition from the two already present. The direct transition from a one-phase system to a three-phase equilibrium is possible only if the solvent concentration in the system corresponds to the three-phase point of the cloud-point curve for the given polymer mixture. On the other hand, separation of a third phase infinitesimally close to one of the two already present will occur if the tie line representing the first three-phase equilibrium in the system happens to be of the degenerated linear type rather than the common triangular type.

Similar considerations apply for the disappearance of three-phase equilibrium upon further cooling, the only difference being that in this case the system never goes back to the single-phase behavior (excluding systems with some unusual temperature dependence of the interaction parameter χ).

5. Conclusions

The principal conclusions of this work are as follows:

(1) The critical surface in quaternary systems does not have any extrema, saddle points, or other complex topological structures. It is either simply monotonous, or, at most, it possesses fold(s). The geometry of the surface alone is not directly related to the three-phase behavior, except at the surface boundaries, where the fold(s) exit from the triangle of polymer compositions.

(2) A family of coexistence curves can be defined in the triangular diagram of polymer compositions, with each curve being a locus of polymer compositions of phases that can coexist at various temperatures and various solvent contents. Multiple critical points arise as a result of interaction between χ_c contour lines and coexistence curves at points where both sets of curves have a common tangent.

(3) The line of heterogeneous double critical points cannot exist as a closed loop within the triangle of polymer compositions but is always attached to one or more binary sides. As a consequence, a quaternary system separates into three phases if, and only if, its constituent ternary system solvent–polymer (1)–polymer (3) also shows a three-phase behavior (here $r_3 > r_2 > r_1$).

(4) A quaternary system of the first kind (three-phase region attached to the 1–3 axis only) contains at least one triple critical point located on the line of heterogeneous double critical points. The origin of three-phase separation is to be seen in the triple critical point, generally located inside the triangle of polymer compositions, where the three-phase separation begins.

(5) An addition of the intermediate component 2 to the ternary system solvent–polymer (1)–polymer (3) has a compatibilizing effect on its phase behavior: the temperature interval of the three-phase region becomes narrower until this region disappears when a sufficient amount of component 2 has been added.

(6) At a given temperature and polymer mixture composition, the compositions of three conjugated phases depend on the amount of the solvent in the system. This is in contrast to a ternary system, where such compositions are fixed by temperature alone.

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Appendix I

At the HDPP line, the condition $S = 0$ is maintained, where

$$S \equiv 3r_z + 2r_z^{1/2} - r_{z+1} \qquad \text{(A1-1)}$$

and r_z and r_{z+1} are functions of w_2 and w_3 (cf. eq 2 and 15).

The slope of the HDPP line, γ_S, is then calculated as

$$\gamma_S \equiv \left.\frac{\delta w_3}{\delta w_2}\right|_{S=0} = -\frac{(\partial S/\partial w_2)_{w_3}}{(\partial S/\partial w_3)_{w_2}} \qquad \text{(A1-2)}$$

with the result given in eq 16.

At $S = 0$, the function ψ of eq 5 is simply

$$\psi(\gamma_\chi) = r_z\frac{r_{z+1} - r_w}{r_z - r_w} \qquad \text{(A1-3)}$$

Substitution from eq 2 and 15 for r's and the inversion of the function then yield eq 17 for the direction of the χ_c contour lines at the HDPP line.

Appendix II

Assume for a while that the HDPP line can indeed exist as a closed loop inside the triangle of polymer compositions.

The direction of an HDPP line at a particular point for a given system is a function of only r_z; this is apparent from eq 16 if r_{z+1} is expressed in terms of r_z from the condition $S = 0$. Then at all points of intersection of the HDPP line with a given r_z line running through the loop (at least two for each such r_z line—one entry and one exit), the direction of the HDPP line γ_S would have to be identical. This requirement, however, cannot be satisfied. For instance, the two points of intersection A′ and A″ of Figure 7, infinitesimally close to the tangential point B, are by definition on the same side of the tangential r_z line b. Since the HDPP line is continuous, however, it is bound to have different slopes at points A′ and A″, although both points arise as points of intersection with the same r_z line a.

This proves that no r_z line can form a tangent to the HDPP line and, consequently, that the HDPP line cannot exist as a closed loop entirely contained within the physically significant triangle of compositions where $w_i > 0$, $i = 1, 2,$ and 3.

Appendix III

We wish to prove the equivalence of two interpretations of the triple critical point in quaternary systems: (i) as an extremal point of the HDPP line, i.e., a point where the slopes of the HDPP line and of a χ_c contour line are identical (cf. eq 16 and 17)

$$\gamma_S = \gamma_{\chi,S} \qquad \text{(A3-1)}$$

(ii) as a point of the HDPP line where (cf. eq 18)

$$Z = 0 \qquad \text{(A3-2)}$$

Since the two conditions contain variables of different nature, the compositions w_2 and w_3 of $\gamma_{\chi,S}$ and the average r_{z+2} of Z are first expressed in terms of r_1, r_2, and r_3 and the averages r_z and r_{z+1}, with the result

$$\gamma_{\chi,S} = -\frac{\Delta r_2}{\Delta r_3}\,\frac{r_z(r_{z+1} - r_1 - r_2) + r_1r_2}{r_z(r_{z+1} - r_1 - r_3) + r_1r_3}\,\frac{r_z(r_{z+1} - R) + r_1r_3 + r_2r_3}{r_z(r_{z+1} - R) + r_1r_2 + r_2r_3} \qquad \text{(A3-3)}$$

$$Z \propto Rr_zr_{z+1} - Pr_z - r_z^2(10r_{z+1} - 15r_z + 6) + T \qquad \text{(A3-4)}$$

where

$$R = r_1 + r_2 + r_3$$

$$P = r_1r_2 + r_2r_3 + r_1r_3$$

$$T = r_1r_2r_3$$

Using these two forms, one can prove after some tedious rearrangements that the above conditions (i) and (ii) are indeed equivalent.

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(11) The parameter χ is plotted in Figures 1 and 2 in the negative sense (i.e., increasing downward) in order to make the graphs qualitatively similar to temperature diagrams typical for solutions of polymers in poor solvents, where $\mathrm{d}\chi/\mathrm{d}T < 0$. The same sign convention is used for discussion of quaternary systems. Hence, a minimum of the critical line corresponds to a maximum value of the parameter χ.
(12) A critical point of multiplicity n can be defined in terms of derivatives of the CPC function $F(\sigma,\phi)$ (see, e.g., eq 7 of ref 10) at the critical point by the condition $(\partial^kF/\partial\sigma^k)_{\phi,\sigma=0} = 0$; $k = 0, 1, ..., n + 2$.[10]
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Depression of Glass Transition Temperatures of Polymer Networks by Diluents

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ABSTRACT: A classical thermodynamic theory is used to derive expressions for the depression of the glass transition temperature T_g of a polymer network by a diluent. The enhanced sensitivity of T_g in cross-linked systems to small amounts of diluent is explained. Predictions of the theory are in satisfactory agreement with the experimental values of a particular polymer network/diluent system.

Introduction

Some years ago Couchman and Karasz[1] presented a classical thermodynamic analysis of the effect of composition on glass transition temperatures of binary mixtures. This theory has been used to describe successfully the glass transition temperature of compatible polymer blends.[2] Recently,[3-5] this was also applied to polymer/diluent systems, proving the ability of the theory to deal with a

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