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Phase Separation in Ternary Systems Solvent–Polymer 1–Polymer 2. 1. Cloud Point and Critical Concentration

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ABSTRACT: A novel approach is proposed for analysis of phase equilibria in Flory–Huggins (FH) ternary systems solvent–polymer 1–polymer 2. It is based on the separation factors σ_1 and σ_2, familiar from the theory of quasi-binary systems, and on two related variables $\eta^2 = \sigma_1\sigma_2$ and $\xi^2 = \sigma_2/\sigma_1$. While η is a measure of the distance of a cloud point from the critical point (CP), ξ characterizes the compatibility of the two polymers and their relative tendency to accumulate in one phase over the other due to molecular interactions. A single formally temperature-independent cloud-point equation, $F(\sigma_1,\sigma_2,\phi) = 0$, can be formulated; unlike in quasi-binary systems, however, here it is not self-contained and has to be solved in conjunction with two other equilibrium equations. Expansion of F around the CP leads to a simple closed expression for the critical concentration ϕ_c in terms of polymer mixture composition, chain lengths r_1 and r_2, and ξ_c^2. The formal separation of ϕ_c from the triplet of interaction parameters thus achieved simplifies greatly the analysis of ϕ_c. It is shown that for a given set of r_i's, the critical binodal direction depends only on the location of the CP in the composition triangle; this fact invites a simple test of the FH theory. Scott's segregating systems appear in our general theory as a special singular case.

1. Introduction

Most of the detailed liquid–liquid phase separation studies have been done in quasi-binary systems consisting of a solvent and a polydisperse polymer whose molecules differ only by their chain length. The chemical homogeneity of polymer segments in such solutions translates into a single parameter characterizing interactions with the solvent and a relatively simple form of phase equilibrium equations to be solved. Consequently, the effects of the molecular weight distribution on phase diagrams of quasi-binary solutions are fairly well understood.

The situation is markedly different for systems with a polymeric solute that is chemically inhomogeneous. Our understanding of even the simplest version of such systems, namely, of ternary systems solvent–polymer 1–polymer 2, is scant, and it has not seen much progress over the past 35 years. The only analytical results of which we are aware concern the approximate relations for the critical point published by Scott in 1949, valid for a certain class of ternary systems with segregating polymers.[1] Numerical calculation of binodals, the only type of data that can be legitimately used for discussion of solubility diagrams, is "notoriously difficult",[2] requiring "long and tedious approximation methods",[1] and for this reason usually avoided by authors at the expense of accuracy of their conclusions. The solubilities are routinely estimated just from the position of more easily accessible critical points or spinodals[3–7] and only exceptionally evaluated rigorously from phase equilibrium equations.[8] Even in this case, the numerical methods employed leave something to be desired: for instance, the "brute force" optimization technique for the sum of squared chemical potential differences modified by a penalty function[8] seems to fail around the critical point, presumably because of the computer round-off errors that become serious in this region.

The most fruitful approach to analyzing phase equilibria in Flory–Huggins quasi-binary systems seems to have been the one based on the separation factor σ. For instance, it led to the formulation of a single self-contained equation for the cloud point,[9] whose analysis revealed the existence of and criteria for multiple critical points,[10] and clarified their role in the mechanism of multiphase separations.[11,12] It also simplified numerical solution of cloud points by avoiding multiple iterations commonly employed by other authors. We wish to demonstrate that similar benefits are provided by applying an analogous σ-based analysis to the more complex problem of "true" ternary systems whose polymeric components differ also by the chemical nature of their monomer units.

In this paper the fundamentals of the new approach are presented and the conditions for the critical state are derived. Particular attention is paid to the interpretation of the expression for the critical concentration (that is formally separable from the triplet of interaction parameters g_1, g_2, and g_x) and to the so-called Scott systems and their place in the spectrum of all other cases. Other aspects of ternary equilibria such as the discussion of critical temperatures, criteria for double and triple critical points,

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as well as methods for numerical solution of particular cases, will be the subject of future papers. A brief account of the new approach has been reported in ref 13.

2. Cloud-Point Equation

Assume that the free energy of mixing follows the classical Flory–Huggins expression[1,14]

$$\Delta G^{m}/RT = n_0 \ln \phi_0 + n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_0 r_0(\phi_1 g_1 + \phi_2 g_2) + n_1 r_1 \phi_2 g_x \quad (1)$$

with the chemical potentials of the three components given by relations

$$(\mu_0 - \mu_0^{\circ})/r_0 = r_0^{-1}(\phi + \ln \phi_0) - r_1^{-1}\phi_1 - r_2^{-1}\phi_2 + \phi(g_1\phi_1 + g_2\phi_2) - g_x\phi_1\phi_2 \quad (2a)$$

$$(\mu_i - \mu_i^{\circ})/r_i = r_i^{-1}(1 - \phi_i + \ln \phi_i) - r_0^{-1}\phi_0 - r_j^{-1}\phi_j + (1 - \phi_i)(g_i\phi_0 + g_x\phi_j) - g_j\phi_0\phi_j, \qquad i, j = 1, 2,\ i \neq j \quad (2b)$$

where r_k, n_k, and ϕ_k are the chain length, number of moles, and volume fraction of component k, with $k = 0$, 1, and 2 denoting the solvent, polymer 1, and polymer 2, respectively, and the concentration-independent interaction parameters are g_1 and g_2 for polymer–solvent interactions and g_x for polymer 1–polymer 2 interactions. The overall polymer volume fraction is $\phi = \phi_1 + \phi_2$; conversely, the individual polymer concentrations can be expressed in terms of ϕ as $\phi_i = \phi w_i$, where w_i is the volume fraction of polymer i in the polymer mixture. The component designation is such that $r_2 \geq r_1 \geq r_0$.

At phase equilibrium, the chemical potential of each component has to be identical in both phases (prime and double prime where $\phi'' > \phi'$). Applying this condition to eq 2b, one can define the separation factors σ_1 and σ_2 for the two polymeric species as

$$\sigma_i \equiv r_i^{-1} \ln (\phi''_i/\phi'_i) = \Delta A + (g_j - g_i - g_x)\Delta(\phi_0\phi_j) - g_i\Delta(\phi_0^2) - g_x\Delta(\phi_j^2) \qquad i, j = 1, 2,\ i \neq j \quad (3)$$

where

$$A \equiv \phi_0/r_0 + \phi_1/r_1 + \phi_2/r_2$$

and the symbol Δ denotes the difference between the two phases, $\Delta\phi \equiv \phi'' - \phi'$. Specifically at the cloud point, a simplified notation is preferable: we may replace ϕ'' and ϕ' with ϕ^* and ϕ, the incipient-phase and the overall concentrations, respectively, since the amount of the separated phase is infinitesimal. At the same time we recognize that σ is no longer restricted to nonnegative values. Note that this is the only notation universally applicable to "true" ternary systems; the traditional one based on more (double prime) and less (prime) concentrated phases fails, e.g., in symmetrical systems with segregating polymers,[1,14,15] where both phases are of the same total polymer concentration but differ in the relative amounts of polymers 1 and 2.

It may be recalled that in the analysis of polydisperse homopolymer solutions, the parameter σ played a unique role:[9,10] it changed monotonically along the cloud-point curve and made possible setting up a single cloud-point equation with no explicitly temperature-dependent terms, $F(\sigma,\phi) = 0$, that in fact defined the single-valued function $\phi(\sigma)$ at the cloud point. No multiple iterations were thus needed to compute the equilibrium: for a chosen σ, the value of ϕ was obtained directly from $F(\sigma,\phi)$, and the corresponding temperature was computed from the matching σ, ϕ values with the aid of another equation. Also for ternary systems the temperature-dependent g parameters can be eliminated by multiplying the difference equations for chemical potentials of the type (2a) and (2b) by respective terms $(\phi_i + \phi_i^*)$, $i = 0, 1, 2$ and adding up all three relations, with the result

$$F(\sigma_1,\sigma_2,\phi) \equiv \sigma_1(\phi_1 + \phi_1^*) + \sigma_2(\phi_2 + \phi_2^*) - 2\Delta A + (\phi_0 + \phi_0^*)r_0^{-1} \ln (\phi_0^*/\phi_0) = 0 \quad (4)$$

The former function $F(\sigma,\phi)$ for quasi-binary systems is recovered from eq 4 as a special case. There is, however, an important difference between the two: the ternary cloud-point equation (4) is no longer self-contained, as its analogue for quasi-binary solutions was. For instance, in well-behaved systems, a choice of the concentration ϕ has to fix both σ_1 *and* σ_2 that characterize the separation at the corresponding cloud point, but it is of course impossible to compute both of these unknowns from the single eq 4, and one has to seek recourse to other equilibrium conditions as well. This makes some kind of multiple iteration scheme inevitable. Convenient for this purpose seem to be the functions

$$G \equiv \sigma_2 - \sigma_1 - (g_2 - g_1)\Delta\phi + g_x(\Delta\phi_1 - \Delta\phi_2) = 0 \quad (5)$$

obtained by subtracting eq 3 for $i = 1$ and 2 from one another, and

$$H \equiv 2r_0^{-1}\Delta \ln \phi_0 - (\sigma_1 + \sigma_2) + g_1\Delta(\phi + 2\phi_1) + g_2\Delta(\phi + 2\phi_2) - g_x\Delta\phi = 0 \quad (6)$$

resulting from adding up eq 3 for $i = 1$ and 2 with the double of the difference equation of the type (2a). Note that for a quasi-binary system eq 6 reduces to the relation used to assign the temperature, whereas eq 5 is a truly new relation, relevant only if polymers 1 and 2 are chemically different.

3. New Variables η and ξ and Their Characteristics

The separation factors σ_1 and σ_2 are quantities of the same type: both of them assume zero value at the critical point; hence, both of them could be used as a measure of the "distance" of a cloud point from the critical point. This duplication, however, is neither needed nor desired, and it would be preferable to have some other quantities characterizing two different aspects of phase equilibrium instead. To this end we choose a new set of variables η and ξ, defined by equations

$$\eta^2 = \sigma_1\sigma_2 \qquad \xi^2 = \sigma_2/\sigma_1 \quad (7a)$$

i.e.

$$\sigma_1 = \eta/\xi \qquad \sigma_2 = \eta\xi \quad (7b)$$

It is apparent that, of these two, only η has to become zero at the critical point. The variable ξ, on the other hand, is here formally indeterminate (=0/0), but it is well-defined in the sense of the limit for $\eta \to 0$, and it may assume any value. Another useful transformation might be a symmetrical definition

$$\xi_i = \sigma_i/\eta \qquad \prod_{i = 1,2} \xi_i = 1 \quad (8)$$

While this option is certainly attractive for generalization to multicomponent systems, in this paper we shall use mostly the simpler notation (7), keeping in mind that $\xi \equiv \xi_2 = \xi_1^{-1}$.

Depending on the physical situation, each real parameter σ_i can be either positive or negative, thus implying the existence of four distinct cases (I–IV). The quantities η and ξ, on the other hand, can be either both real or both imaginary and have to be approached as complex variables

$$\eta = |\eta| \exp(i\psi_\eta) \qquad \xi = |\xi| \exp(i\psi_\xi) \quad (9)$$

Their character under the given conditions can be iden-

Table I
Character of Variables η and ξ for Various Physical Situations

										$\|\xi\|^a$	
case	σ_1	$\psi_\eta - \psi_\xi$	σ_2	$\psi_\eta + \psi_\xi$	ψ_η	$\eta/\|\eta\|$	ψ_ξ	$\xi/\|\xi\|$	W	$\sigma_1 + \sigma_2 > 0$	$\sigma_1 + \sigma_2 < 0$
I	>0	0	>0	0	0	+1	0	+1	any	$W/\eta + D_+^{1/2}$	$W/\eta + D_+^{1/2}$
II	<0	π	<0	π	π	−1	0	+1	any	$W/\eta + D_+^{1/2}$	$W/\eta + D_+^{1/2}$
III	>0	0	<0	π	$\pi/2$	+i	$\pi/2$	+i	$<-\|\eta\|$	$-W/\|\eta\| - D_-^{1/2}$	$-W/\|\eta\| - D_-^{1/2}$
IV	<0	π	>0	0	$\pi/2$	+i	$-\pi/2$	−i	$>\|\eta\|$	$W/\|\eta\| + D_-^{1/2}$	$W/\|\eta\| - D_-^{1/2}$

[a] The discriminants are defined as $D_+ \equiv (W/\eta)^2 + 1$, $D_- \equiv (W/\eta)^2 - 1$.

tified by considering the phase angles $\psi_\eta - \psi_\xi$ and $\psi_\eta + \psi_\xi$ of the original separation factors σ_1 and σ_2, respectively. For instance, for $\sigma_1 < 0$ and $\sigma_2 > 0$, these angles are π and 0, respectively, which yields $\psi_\eta = \pi/2$ and $\psi_\xi = -\pi/2$. The results are summarized in the first nine columns of Table I.

Physically, the two variables η and ξ reflect two distinct aspects of the phase equilibrium. The geometrical average η can be considered as an independent variable specifying the position of a cloud point on the cloud-point curve, albeit not uniquely as σ did in quasi-binary systems. (Note, e.g., that η will assume zero value even at a noncritical state if only one of the two σ_i parameters becomes zero.) By definition, η is real in systems with *coexisting* polymers, where both polymers tend to concentrate in the same phase ($\sigma_1\sigma_2 > 0$), and it is imaginary in systems with *segregating* polymers, where each polymer prefers to concentrate in a different phase ($\sigma_1\sigma_2 < 0$).

While η reflects the character of intermolecular forces only qualitatively, ξ is a quantitative measure of their intensity. It is given by the quadratic relation obtained from eq 5

$$\xi^2 - 2W\xi/\eta - 1 = 0 \tag{10}$$

where the single compact interaction term affecting ξ is

$$W \equiv [(g_2 - g_1)\Delta\phi + g_x(\Delta\phi_2 - \Delta\phi_1)]/2 = (\sigma_2 - \sigma_1)/2 \tag{11}$$

The quantity ξ thus expresses the tendency of polymer 2 relative to that of polymer 1 to concentrate in one phase over the other due to the differences in molecular interactions between the components. The character of ξ is identical with that of η: it is real for systems with coexisting polymers (cases I and II), and it is imaginary for systems with segregating polymers (cases III and IV).

The attractiveness of eq 10 lies in its generality: it represents a universal function for ξ containing a single reduced interaction term $\tilde{W} = W/\eta$, and it is valid irrespective of the temperature, concentration, and the specific nature of the system components. The graphical mapping of this relation is done best in logarithmic coordinates that lend to the resulting diagram a high degree of symmetry. The set of all possible values of ln ξ creates a closed infinite one-dimensional space that can be used to order all existing ternary cloud-point systems according to the tendency of their polymeric components (i) to either coexist or segregate, and (ii) to accumulate in one phase over the other. In the complex plane of ln ξ in Figure 1, the global projection of all cloud points generates three horizontal lines with $\tilde{W}$ values given by (cf. eq 10)

$$2\tilde{W} = \xi - \xi^{-1} \tag{12}$$

(1) The central line coinciding with the real axis represents states of the types I (full line) and II (dashed line), where both polymers prefer to accumulate in the same phase. With $\tilde{W}$ being real, the solution of eq 10 is simply

$$\xi = \tilde{W} + (\tilde{W}^2 + 1)^{1/2} \tag{13}$$

The second root with a negative square root sign can be rejected as physically insignificant since ξ cannot be negative (cf. Table I).

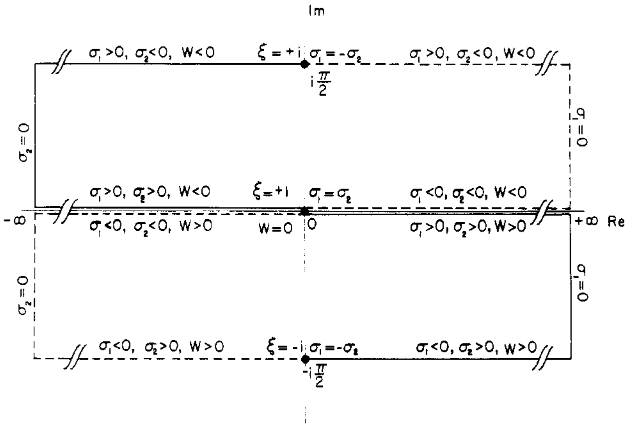

Figure 1. Complex-plane diagram of ln ξ displaying all cloud points that can ever occur in ternary systems. Full and dashed bold lines mark portions where ($\sigma_1 + \sigma_2$) is positive and negative, respectively. The two lines along the real axis are drawn separated only for demonstration purposes; in fact, they overlap with the real axis.

At the origin in Figure 1 there are interaction-neutral cases characterized by $W = 0$ and $\xi = 1$, i.e., $\sigma_1 = \sigma_2$. The equality of σ_i parameters here guarantees that the enrichment in one phase over the other of the two polymers is only due to the chain-length effect. A prominent place among such cases is assumed by quasi-binary systems that occupy this location at all temperatures and concentrations (since $g_2 - g_1$ and g_x of eq 11 are zero by definition). A "true" ternary system may also reside briefly at the origin under some conditions (if W of eq 11 happens to be zero due to the cancellation of the two nonzero terms), but typically a perturbation of temperature or concentration would force its representative point to an off-zero position.

Systems located on the positive real axis of Figure 1 are characterized by a positive $\tilde{W}$, while the negative real axis is the locus of systems with a negative $\tilde{W}$. As the absolute value of $\tilde{W}$ increases, the representative point of the system moves away from the origin toward its infinite limit. This particular state is typically achieved not through the divergence of the interaction term W but rather through η approaching noncritically zero. For instance at $\tilde{W} \rightarrow -\infty$ the variable ξ approaches +0 (i.e., ln $\xi \rightarrow -\infty$), hence also $\sigma_2 \rightarrow 0$ and $\eta \rightarrow 0$, while at the other end of the scale $\tilde{W} \rightarrow +\infty$, $\xi \rightarrow +\infty$ and $\sigma_1 \rightarrow 0$, $\eta \rightarrow 0$. Thus one of the polymers behaves as if it was at its critical point, with its concentration in both phases identical, while the other one remains obviously noncritical.

Note that in this projection the cases I and II overlap; i.e., one cannot tell whether the respective cloud point is situated on the subcritical ($\sigma_1 > 0$, $\sigma_2 > 0$, $\phi^* > \phi$) or supercritical ($\sigma_1 < 0$, $\sigma_2 < 0$, $\phi^* < \phi$) branch of the cloud-point curve from the value of ln ξ alone. Mathematically speaking, this is a consequence of $\tilde{W}$ (hence also ξ) being invariant to the switching of bulk and incipient phases (since both W and η here change their signs simultaneously). On the other hand, the sign of W and the direction from which σ_i and η approach zero at $\tilde{W} \rightarrow \pm\infty$ do depend on the type of the system as indicated in Figure 1.

(2) The other two horizontal lines of Figure 1 map equilibria with segregating polymers characterized by imaginary ξ and η. Since $\ln \xi = \ln |\xi| + i\psi_\xi$, situations of type III generate a horizontal line at $i\pi/2$, while those of type IV project onto its mirror image in the lower half-plane. The quadratic equation 10 can be here written in terms of the absolute values as

$$|\xi|^2 \pm 2W|\xi|/|\eta| + 1 = 0 \qquad (14)$$

where the positive sign holds for case III and the negative sign describes case IV. Since the overall sign of the linear term should be negative to keep $|\xi|$ real, the interaction term W has to be negative in the former and positive in the latter case. The dichotomy of eq 14 combined with plus/minus options in the solution of a quadratic equation result in four different formulas for $|\xi|$ in four portions of the displayed lines that are given in Table I. Specific assignments of $\tilde{W}$ can be better made from the inverse relation

$$\tilde{W} = -iW/|\eta| = \pm i(|\xi| + |\xi|^{-1})/2 \qquad (15)$$

indicating that in the coordinates of Figure 1 $\tilde{W}$ is symmetrical with respect to the imaginary axis, with its absolute value reaching a minimum $|\tilde{W}|_{\min} = 1$ for $\ln |\xi| = 0$ (i.e., $\xi = \pm i$). The existence of this minimum is not surprising; intuitively one would expect segregation behavior only when the intensity of effective interactions between chains 1 and 2, here expressed by the absolute value of the reduced interaction term $\tilde{W}$, exceeds certain value. This then leads to a stricter condition for $|W|$, namely $|W| \geq |\eta|$ (cf. Table I). A system located at $\xi = \pm i$ represents another special case. With $|\sigma_i|$ being the same for both polymers, the enrichment of ϕ_i in one phase over the other is again affected only by chain lengths r_i (just as it was for $\xi = 1$), but this time each polymer prefers its own phase. It is also the dividing point between segregating systems with a positive and negative "average" σ-parameter. For instance, for cases of type III, $\sigma_1 + \sigma_2 > 0$ if $|\xi| < 1$, and $\sigma_1 + \sigma_2 < 0$ if $|\xi| > 1$. One might be tempted to go on calling the concentrations of such cloud-point systems subcritical and supercritical, respectively, as a continuation of the terminology valid for systems residing on the real axis; however, in equilibria with segregating polymers the correlation between the signs of $\sigma_1 + \sigma_2$ and $\phi^* - \phi$ breaks down, and such terms lose their justification. This is also apparent from the following comparison: In quasi-binary systems (residing at $\xi = 1$) at noncritical concentrations, one phase at the cloud point is always more concentrated than the other, and if it happens to be, e.g., the bulk phase, the system's concentration might be referred to as supercritical. On the other hand, in symmetrical systems with segregating polymers,[1,14,15] the total polymer concentration in both phases is identical and the above distinction cannot be made.

There are several aspects of Figure 1 that should be addressed:

(a) While the global diagram comprises all cloud-point situations that can ever occur in ternary systems and emphasizes their continuity, a specific ternary system typically does not get a chance to probe the entire one-dimensional infinite space of ξ. At a given temperature and mixed polymer composition (and at the solvent concentration fixed by the above two), the cloud-point system is of course represented by a single point located somewhere on the displayed lines, and variation of state variables results in moving the representative point around. Surprising, however, are preliminary numerical results indicating that at constant polymer composition w_2 the position of the representative point is not too sensitive to the temperature (and the associated total polymer concentration); across the entire cloud-point curve, with ϕ, T, and η varying widely, the parameter ξ changed typically by only 10–15%. Thus the reduced interaction term $\tilde{W}$ (and ξ tied to it) appears to characterize fairly well the effective interactions in solutions of a given polymer mixture, without much regard to the solvent content and temperature.

(b) Although the two lines for sub- and supercritical concentrations on the real axis seemingly overlap, they keep their identity (as they have to because of the deterministic nature of change in the cloud point for a given system upon perturbation of state variables). They differ by the signs of σ_1, σ_2, and W. Thus, the diagram should be viewed like a figure 8 (as indicated in Figure 1) rather than a singly crossed O. Note that in this rendition, all cloud points with $W > 0$ (i.e., $\sigma_2 > \sigma_1$) are in the lower half-plane, while those with $W < 0$ reside in the upper one.

(c) At first sight the diagram seems to be unable to cope with the critical state. It is not as much the matter of definition of critical $\tilde{W}$ and ξ (both of them become of the 0/0 type yet are well-defined in the sense of the limit) as it is the question of where to plot the representative point; critical values $\sigma_1 = \sigma_2 = 0$ do not seem to fit onto any of the displayed lines characterized by definite signs of the separation factors. Crossing the critical state (i.e., mutual switching of bulk and incipient phases) corresponds to a change in signs of W, σ_1, and σ_2 (and, consequently, also η for types I and II and ξ for types III and IV). In the diagram of Figure 1, this process results in the transfer of the representative point either (i) from one real axis line to its overlapping counterpart, or (ii) from one imaginary line to its counterpart in the other half-plane. In either case, the transition process possesses axial symmetry around the real axis, with the critical state apparently somewhere in the middle. Such ambiguity, however, is rather typical of critical states—recall, e.g., the discontinuous jump in phase volume ratio from infinity to zero under similar circumstances. Formally one could avoid this problem by following both phases simultaneously, i.e., by representing a given equilibrium by a pair of points (rather than by a single one) symmetrically positioned around the real axis; such configuration would be stable even when passing through the critical point. Important is to realize that the above mentioned discontinuous behavior does not invalidate the applicability of eq 10 and 12–15 to the critical state.

(d) Another kind of symmetry appears when using perhaps the more consistent notation of eq 8 with ξ_1 and ξ_2. Then a particular cloud point is represented by a pair of points symmetrically positioned in Figure 1 around the origin (recall that $\xi_2 = \xi_1^{-1}$, i.e., $\ln \xi_2 = -\ln \xi_1$), with $W_2 = -W_1$. The quadruplet of points in the "total" representation described in the preceding paragraph would thus possess an axial symmetry about the real axis and a planar symmetry about the vertical plane passing through the imaginary axis.

4. Critical State

Critical conditions can be derived from ΔG^{m} of eq 1 by the classical Gibbs method of determinants.[16,17] The resulting relations for the spinodal and critical point respectively are

$$U \equiv |G_{kl}| \equiv G_{11}G_{22} - G_{12}^2 = 0 \qquad (16a)$$

$$U_iG_{jj} - U_jG_{ij} = 0 \qquad i, j = 1, 2, i \neq j \qquad (16b)$$

where the second derivatives $G_{ij} \equiv (\partial^2 \Delta G^{\mathrm{m}} / \partial\phi_i \partial\phi_j)$ are

$$-G_{ii} \equiv 2g_i - (\phi_0 r_0)^{-1} - (\phi_i r_i)^{-1}$$

$$-G_{12} \equiv g_1 + g_2 - g_{\mathrm{x}} - (\phi_0 r_0)^{-1}$$

and

$$U_i = 2\phi_j^2 r_j (g_{\mathrm{x}} \phi_i^2 r_i - g_j \phi_0^2 r_0) + \phi_j [\phi_j r_j (\phi_0 - \phi_i) + \phi_0^2 r_0 - \phi_i^2 r_i]$$

After some rearrangement the spinodal equation 16a becomes quadratic in concentration ϕ and can be easily solved for any particular temperature. The critical point can then be located by testing the critical equation 16b for each of the computed spinodal points. As shown recently,[18] it may not be enough to test (16b) just for one value of i as originally implied by Gibbs, since there are equilibria where this equation is satisfied for $i = 1$ but not for $i = 2$ (or vice versa). Obviously such states are not critical.

Critical conditions can also be obtained by expanding the phase equilibrium functions around $\sigma_1 = \sigma_2 = 0$, analogously to the procedure applied by Stockmayer[19] for quasi-binary systems. The general formula for the function $F(\sigma_1,\sigma_2,\phi)$ of eq 4 expanded in terms of σ_1 and σ_2 at constant ϕ is given in the Appendix (eq A1). Not surprisingly, the first few coefficients identically vanish (just as they did for quasi-binary systems), and F converges to zero as a cube of σ_i

$$6F(\sigma_1,\sigma_2,\phi) \equiv w_1 \sigma_1^3 r_1^2 X(\sigma_1 r_1) + w_2 \sigma_2^3 r_2^2 X(\sigma_2 r_2) - \Phi^2 \nabla^3 Y(\Phi\nabla) r_0^{-1} + \ldots = 0 \quad (17)$$

where

$$\Phi \equiv \phi/(1 - \phi)$$

$$\nabla \equiv \frac{\phi^* - \phi}{\phi} = \sum_{i=1}^{\infty} \frac{w_1(\sigma_1 r_1)^i + w_2(\sigma_2 r_2)^i}{i!}$$

and the functions $X(z)$ and $Y(z)$ are defined as

$$X(z) = 6\sum_{i=0}^{\infty} \frac{i+1}{(i+3)!} z^i = 1 + \tfrac{1}{2}z + \tfrac{3}{20}z^2 + \tfrac{1}{30}z^3 + \ldots$$

$$Y(z) = 6\sum_{i=0}^{\infty} \frac{i+1}{(i+2)(i+3)} z^i = 1 + z + \tfrac{9}{10}z^2 + \tfrac{4}{5}z^3 + \ldots$$

In order to remove the trivial zeros assumed at $\sigma_1 = \sigma_2 = 0$ by the function F itself and its first and second derivatives with respect to σ_1 and σ_2, we generalize our previous procedure[10] and divide F by $(\sigma_1\sigma_2)^{3/2} \equiv \eta^3$. The critical-state condition is then extracted by requesting that the modified function $\bar{F} \equiv 6F/\eta^3$ be zero at the critical point, i.e.

$$\lim_{\substack{\sigma_1 \to 0 \\ \sigma_2 \to 0}} \bar{F} \equiv w_1 r_1^2 \xi_c^{-3} + w_2 r_2^2 \xi_c^3 - \Phi_c^2 (w_1 r_1 \xi_c^{-1} + w_2 r_2 \xi_c)^3 / r_0 = 0 \quad (18a)$$

which can be written more succintly as

$$\Phi_c^2 \equiv [\phi_c/(1 - \phi_c)]^2 = \langle r^2 \xi_c^3 \rangle r_0 / \langle r\xi_c \rangle^3 \qquad (18b)$$

where the moment $\langle\ \rangle$ is defined by

$$\langle r^i \xi^j \rangle \equiv w_1 r_1^i \xi^{-j} + w_2 r_2^i \xi^j = w_1 r_1^i \xi_1^j + w_2 r_2^i \xi_2^j$$

and Φ_c, ϕ_c, and ξ_c represent critical values of these variables. Comparison of (18b) to the critical criterion (16b) makes the advantages of the form (18b) obvious: (i) it is simple; (ii) its reduction to the well-known formula for quasi-binary systems[19] is transparent (put $\xi = 1$); (iii) it elegantly isolates the only new interaction-dependent term ξ_c affecting the critical concentration in ternary systems, in addition to the polydispersity effect known from previous studies.

It is fair to say that this new relation in no way invalidates the statement by Scott[1] of "no exact analytical solution" being possible for the critical point of a general ternary system. The simplicity of eq 18b has been achieved only after paying a price: introducing a new unknown variable, ξ_c, and thus necessarily increasing the number of equations to be satisfied from the usual two [e.g., (16a) and (16b)] to three [eq 18b together with the limiting forms of eq 5 and 6]

$$\lim_{\substack{\sigma_1 \to 0 \\ \sigma_2 \to 0}} \bar{G} \equiv (w_1 r_1 - \xi_c^2 w_2 r_2)\phi_c g_{\mathrm{x}} - (w_1 r_1 + \xi_c^2 w_2 r_2)\phi_c \Delta g + \xi_c^2 - 1 = 0 \quad (19)$$

$$\lim_{\substack{\sigma_1 \to 0 \\ \sigma_2 \to 0}} \bar{H} \equiv (w_1 r_1 - \xi_c^2 w_2 r_2)\phi_c \Delta g + (w_1 r_1 + \xi_c^2 w_2 r_2) \times [g_{\mathrm{x}} - 2(g_1 + g_2 - 1/r_0\phi_0)]\phi_c + \xi_c^2 + 1 = 0 \quad (20)$$

where $\Delta g \equiv g_2 - g_1$, $\bar{G} \equiv G/\eta$, and $\bar{H} \equiv H/\eta$. Multiple iterations are thus unavoidable for numerical solution of eq 18–20 to find the critical point of any particular mixture, and better suited for this purpose seems to be the Gibbs method. On the other hand, these relations are unquestionably superior for analysis where they yield a new physical insight. In particular eq 18b allows the critical concentration to be divorced from the triplet of interaction parameters and discussed in terms of a single variable ξ_c^2 (which, in turn, of course depends on g_1, g_2, and g_{x} through eq 19 and 20).

Another advantage of the moment formulation (18b) is that it stays unchanged regardless of the number of polymeric components N_{p} in the system, if each of them is characterized by ξ_i of eq 8. Note that in this approach the number of independent ξ_i's affecting ϕ_c grows only like $(N_{\mathrm{p}} - 1)$, whereas in the traditional form undivorced from the interaction parameters g_i and g_{ij} their number skyrockets like $N_p(N_p + 1)/2$.

4.1. Critical Concentration and ξ_c^2 Surface. From dealing with quasi-binary systems ($\xi = 1$) one has become accustomed to critical concentrations that are fairly low. There is a good reason for this observation: it is well-known that at the critical point the square term Φ_c^2 equals $r_0 r_z / r_w^2$. For instance, for a ternary quasi-binary system this implies that $\Phi_c^2 < r_0/r_1$ if the chain-length ratio of the two polymer fractions, $\alpha \equiv r_2/r_1$, is lower than 2. For higher ratios the critical line shows a maximum in concentration with coordinates

$$w_{2,\max} = \frac{\alpha - 2}{2(\alpha^2 - 1)}$$

$$\Phi^2_{c,\max} = \frac{4(\alpha + 1)^3}{27 r_1 \alpha^2} r_0 \qquad (21)$$

and the critical concentration at this extremum may become fairly high, but, as eq 21 indicates, this happens at such a low content of component 2 that it does not have much practical importance.

The situation is quite different in "true" ternary systems with polymers 1 and 2 differing in composition. This fact has been pointed out already by Scott:[1] on the basis of approximate formula for a special class of systems with segregating polymers, he concluded that critical concentration may vary widely over the entire interval $0 < \phi_c < 1$, depending mainly on the magnitude of the interaction parameter g_{x}. Our formula (18b) corroborates his claim,

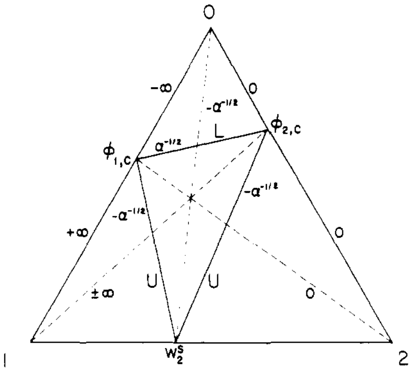

Figure 2. Some important lines of the ξ_c^2 surface. L and U represent the lower and upper boundaries of the three-valued region. ξ_c^2 assumes a constant value as indicated along each of the boundaries, as well as along the displayed dashed lines and some of the binary axes.

only this time in an entirely general fashion. Indeed, the presence of the new parameter ξ_c in it transforms the one-dimensional critical line of quasi-binary systems into a global ξ_c^2 surface spreading over the entire triangle, physically corresponding to the locus of critical points of all imaginable ternary systems (having all possible combinations of interaction parameters) with a given set of chain lengths r_i. Thus it can be expected that a careful analysis of the ξ_c^2 surface will confirm (or disprove) formulas for Scott's systems and clarify how this special class fits into the continuum of all the rest of the cases.

It is obvious that the ξ_c^2 surface is quite complex; the cubic character of eq 18b for ξ_c^2 indicates that in some composition regions the surface may be three valued. Since the number of real solutions ξ_c^2 can be only one or three, the boundaries of the multivalued region can be identified as the loci of double roots. They are surprisingly simple, and in the composition triangle coordinates they appear as straight lines (see Figure 2). The lower boundary (i.e., lower in terms of ϕ_c) is projected as a line connecting the two binary critical points directly

$$\phi_L = [1 + (w_1 r_1^{1/2} + w_2 r_2^{1/2})/r_0^{1/2}]^{-1} \qquad (22a)$$

while the upper boundary ϕ_U consists of two linear segments given as

$$\phi_U = [1 + |w_1 r_1^{1/2} - w_2 r_2^{1/2}|/r_0^{1/2}]^{-1} \qquad (22b)$$

each one connecting the respective binary critical point with a bulk point of composition

$$w_2^S = r_1^{1/2}/(r_1^{1/2} + r_2^{1/2}) \qquad (23)$$

Only single real solutions exist outside the interval $\langle\phi_L,\phi_U\rangle$, whereas three different real solutions exist within it. At the boundaries, the single solutions can be identified as

$$(\xi_1^2)_{L,U} = -\alpha^{-1/2}\frac{w_2\alpha^{1/2} \pm 2w_1}{w_1 \pm 2w_2\alpha^{1/2}} \qquad (24a)$$

while the double roots (representing the other two solutions merged into one) are simply

$$(\xi_{2,3}^2)_{L,U} = \pm\alpha^{-1/2} \qquad (24b)$$

with dual signs (plus/minus) in both formulas corresponding to the lower and upper boundary, respectively.

In order to facilitate visualization of the relatively complex ξ_c^2 surface, we shall display its properties in three different ways.

4.1.1. ξ_c^2 Contour Map. The simplest way of depicting the ξ_c^2 surface is in terms of its contour lines. Examples of such diagrams are shown in Figure 3, with contour lines for positive and negative ξ_c^2 plotted mostly separately to avoid excessive overlap in multivalued region. The following observations can be made:

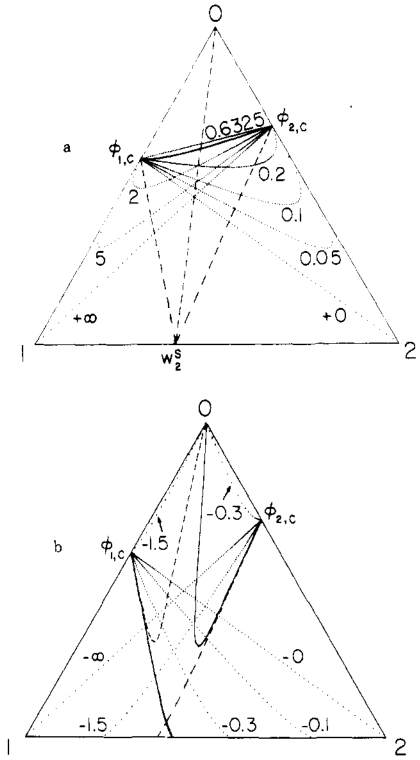

Figure 3. Contour maps of the ξ_c^2 surface for $r_2/r_1/r_0 = 5/2/1$. Values of ξ_c^2 indicated by numbers except where specified otherwise: (a) contour lines for some positive ξ_c^2, including the quasi-binary case with $\xi_c^2 = 1$ (—), and for the special case with $\xi_c^2 = -\alpha^{-1/2} \approx -0.6325$ (- - -); (b) discontinuous contour lines for some other negative ξ_c^2, (—) $\xi_c^2 = -0.58$, (- - -) $\xi_c^2 = -0.70$.

(1) The parameter ξ_c is strictly a ternary quantity; thus it is perhaps not surprising that it becomes ill-behaved at the two binary critical points where all the contour lines converge. Note also its asymptotic behavior as the binary lines are approached (see also Figure 2). At $\phi_c < \phi_{1,c}$ $\lim_{w_2\to 0} \xi_c^2 = -\infty$, at $\phi_c > \phi_{1,c}$ $\lim_{w_2\to 0} \xi_c^2 = +\infty$, and $\lim_{w_2\to 1} \xi_c^2 = 0$.

(2) The contour line for $\xi_c^2 = 1$ (full line in Figure 3a) represents the actual critical line of the corresponding quasi-binary system ($g_1 = g_2$, $g_x = 0$), a sort of reference line in our classification scheme. Critical lines of other specific ternary systems typically do not coincide with any of the plotted contour lines but rather cross them.

(3) For ξ_c^2 growing above unity, a maximum in ϕ_c develops soon on the contour lines (if it has not been present already on the line for $\xi_c^2 = 1$, i.e., if $\alpha < 2$). With further increase in ξ_c^2 the maximum becomes sharper and approaches the binary 0–1 axis, until for $\xi_c^2 \to \infty$ the contour line degenerates into a strictly linear segment running from the apex 1 into the right binary critical point, with the equation

$$\lim_{\xi_c^2\to\infty} \phi_c = [1 + w_2(r_2/r_0)^{1/2}]^{-1} \qquad (25)$$

(Its other branch coincides with the axis 0–1.) For ξ_c^2 decreasing from unity to zero, the contour lines first straighten up at $\xi_c^2 = \alpha^{-1/2}$ (cf. eq. 22a and 24b) and then again start developing a maximum in ϕ_c that moves toward apex 2, eventually approaching for $\xi_c^2 \to 0$ another straight line extending between the left fixed point and the apex 2, with the equation symmetrical to eq 25 (see Figures 2 and 3a).

(4) Equation 18b indicates that no physically meaningful solutions exist for a negative ξ_c^2 between the weight fractions w_2^0 and w_2^1, where

$$w_2^0 = \frac{r_1^2}{r_1^2 - r_2^2\xi_c^6}$$

$$w_2^1 = \frac{r_1}{r_1 - r_2\xi_c^2} \qquad (26)$$

At the former polymer composition, a given contour line exits through the solvent apex ($\phi_c = 0$), at the latter composition it exits through the 1–2 axis ($\phi_c = 1$), and it is not defined at all in the interval (w_2^0, w_2^1) (see Figure 3b).

A very special case occurs at the ξ_c^2 value specified by the condition $w_2^0 = w_2^1 = w_2^S$, i.e., at $\xi_c^2 = -\alpha^{-1/2}$. The discontinuity gap is here reduced to an infinitesimal size, yet in a way it survives as a singularity. The contour line becomes identical with the upper boundary of multiple solutions given by eq 22b, i.e., it consists of two linear segments interesecting each other (and the bulk line) at the singular composition w_2^S of eq 23. Note that at this composition, the expression (18b) for Φ_c becomes of the 0/0 type, i.e., indeterminate, and the critical concentration has to be sought from other relations. The direct consequence of this indeterminacy is the appearance of a third middle linear segment of the $\xi_c^2 = -\alpha^{-1/2}$ contour line, extending between the solvent apex and the bulk singular point of the composition w_2^S (Figures 2 and 3a). While this behavior may seem puzzling at first sight, it logically fits the sequence of negative ξ_c^2 contour lines described above. Note that for $\xi_c^2 < -\alpha^{-1/2}$ we have $w_2^0 < w_2^1$, with the left branch of the respective contour line exiting at the 0 apex and its right branch passing through the bulk line; on the other hand, for $0 > \xi_c^2 > -\alpha^{-1/2}$ the pattern is reversed. The only way to tie these two different patterns together at $\xi_c^2 = -\alpha^{-1/2}$ is to have the minimum of the 0-apex branch descend and merge with the bulk exit point, resulting in the qualitatively symmetrical three-prong structure of this contour line.

4.1.2 Critical Binodal Direction. For a fixed set of r_i's and w_i's, the value of ξ_c^2 determines not only the location of the critical point through eq 18b but also the limiting direction of tie lines as the critical point is approached

$$\lim_{\eta\to 0} \frac{\Delta\phi_2}{\Delta\phi_1} = \frac{w_2 r_2}{w_1 r_1}\xi_c^2 \qquad (27)$$

Consequently there is a strict correlation, independent of interaction parameters g_1, g_2, and g_x, between the position of a critical point within the composition triangle and the slope of the binodal at it. This fact was also noticed by Meijering in his study of ternary regular solutions.[20]

While the resulting plots of critical binodal directions (Figure 4) characterize the ξ_c^2 surface only indirectly, they give some indication of the binodal shapes to expect and offer some insight into the topology of this surface. The separate plots of each of the three solutions in the middle multivalued region in Figure 4a–c clearly show that each fold of the surface is directly continuously connected to one single-valued apex region and thus can be labeled as such. On the other hand, the parallelism of two critical binodal directions at each of the boundaries of the multivalued region (perhaps better apparent from the combined plot in Figure 4d) identifies the two roots that merge into a double root at the boundary or, speaking in terms of surfaces, identifies the two surfaces in the middle multivalued region that are connected at the boundary. For instance, the single-valued surfaces in apex regions 1 and 2 are connected via the boundary in the solvent region (so-called lower boundary of eq 22a); generally, surfaces i and j are fused at the boundary located in the region of apex k, where $i \neq j \neq k$.

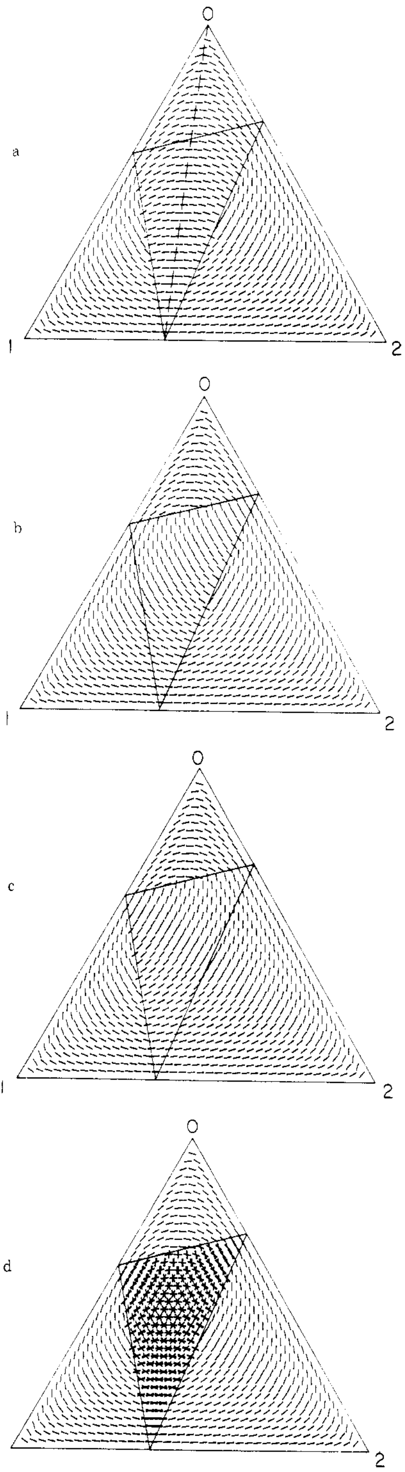

Figure 4. Plots of critical binodal directions as a function of the critical point location for the case $r_2/r_1/r_0 = 5/2/1$. Also indicated are the lower and upper boundaries of the three-valued region. (a)–(c) Separate plots of each of the three solutions in the middle three-valued region. (d) Composite plot of all three solutions.

Checking the consistency of eq 18b and 27 should constitute one possible simple test of adequacy of the Flory–Huggins theory for a given experimental system.

4.1.3. Three-Dimensional Plot of the ξ_c^2 Surface. Probably the best way to view the ξ_c^2 surface is in a semiperspective plot, such as those employed in Figures 5 and 6. The projection is not fully perspective in the sense that

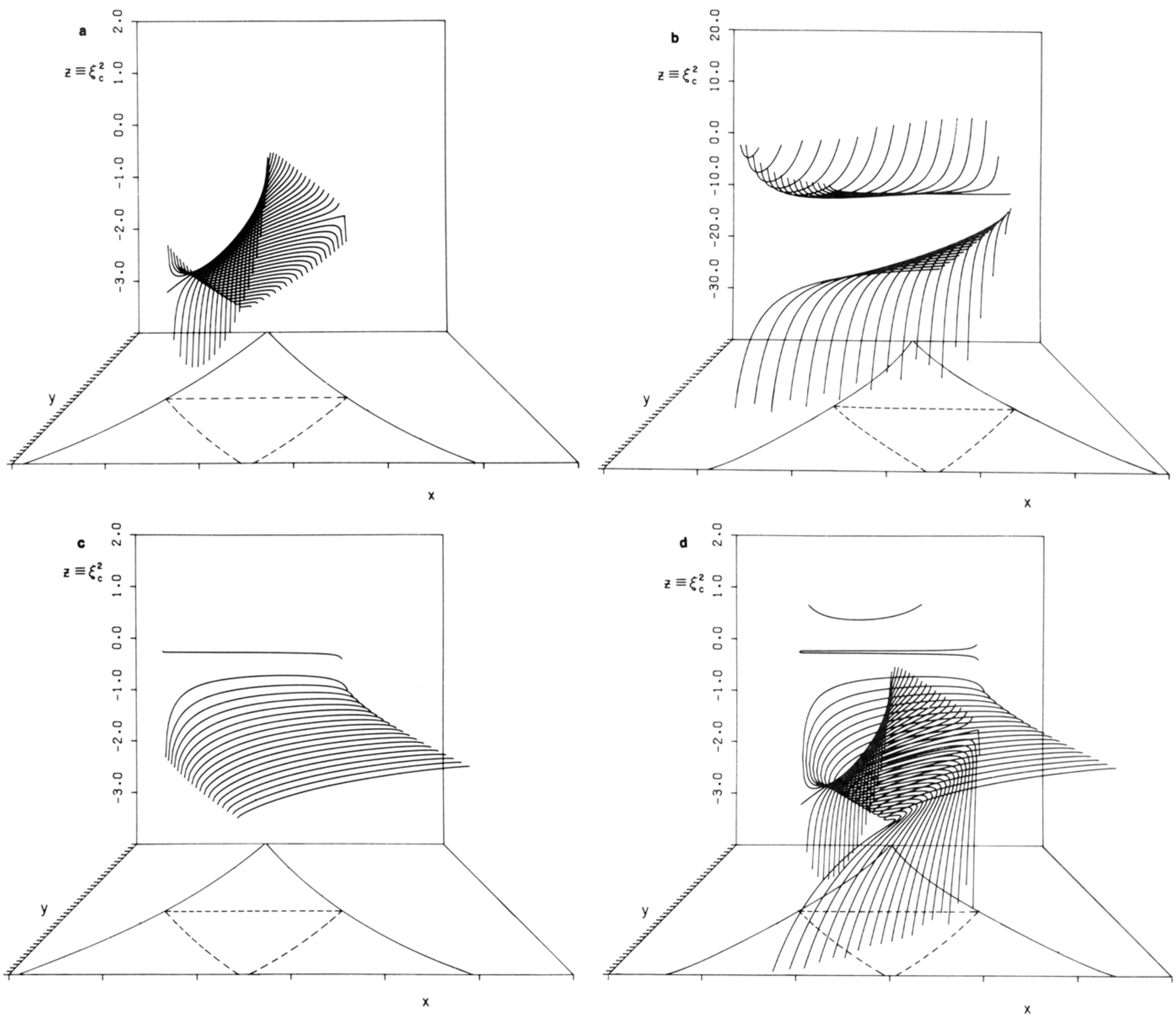

Figure 5. Three-dimensional plots of the ξ_c^2 surface for a "mixture of monomers", $r_2/r_1/r_0 = 1.001/1/1$. Tic marks on the x axis specify intervals of 0.2 in ϕ_2, on y axis intervals of 0.025 in ϕ_0. (a)–(c) Separate plots of surfaces 0, 1, and 2. (d) Composite plot illustrating the threefold surface in the middle.

only y parallels within an x,y plane converge to a common point, whereas y parallels within a y,z plane do not. Also, the y scale is uniform. Since ξ_c^2 is ill-behaving at some of the binary axes, these marginal regions of the composition triangle are excluded from the plots, and the incomplete triangle traced in the base x,y plane, oriented the same as in other figures, is defined by the lines $\phi_0 = 0.025$, $\phi_1 = 0.005$, and $\phi_2 = 0.01$. Dashed lines in it indicate the boundaries of the three-valued region (cf. Figure 2). Plotted curves represent ξ_c^2 values at constant y (i.e., at constant ϕ_0) with an increment of $\Delta\phi_0 = 0.025$. The sudden changes in direction appearing on some curves are not real; they are the result of curves being approximated by a series of linear segments of length $\Delta\phi_2 = 0.004$.

The surfaces are best displayed in Figure 5 drawn for the mixture of "monomers", with $r_2/r_1/r_0$ ratio 1.001/1/1. The front part of the surface 0 (Figure 5a) is of a relatively flat S-shaped form, rising toward the left upper boundary line and dropping toward the right upper boundary line, where in both cases it reaches a constant value of $\xi_c^2 = -\alpha^{-1/2}$ (≈ -1). Its rear part ascends on the right toward $\xi_c^2 = 0$ at the 0–2 binary axis and droops to $-\infty$ on the left. The solvent surface 0 is thus restricted to nonpositive values, $\xi_c^2 \leq 0$. The surface 1 (Figure 5b) is discontinuous, split in two along the $\xi_c^2 = \pm\infty$ contour line. Since it is "hung" to the right upper boundary line, its right lower part is thus limited to $\xi_c^2 \leq -\alpha^{-1/2}$. Its left part, on the other hand, is convex downward, extending to $+\infty$ on two sides (along the 0–1 axis and $\xi_c^2 = \infty$ contour line) and anchored to the lower boundary at its lowest value of $\xi_c^2 = \alpha^{-1/2}$ (≈ 1). It ascends from here very steeply so that on the scale of Figure 5d only two of its lines can be shown; note that the more illustrative Figure 5b spans an interval 10 times larger. It should be emphasized that the discontinuity is strictly a mathematical construct; physically, systems here behave continuously, as apparent from the plot of binodal critical directions in Figure 4. The surface 2 (Figure 5c) is the simplest of all, slightly convex upward and restricted to finite values $-\alpha^{-1/2} \leq \xi_c^2 \leq \alpha^{-1/2}$. It reaches its maximal value along the lower boundary line and its minimal value along the left upper boundary line and is attached to the 0–2 binary axis at $\xi_c^2 = 0$. The above general statements stay valid for any combination of chain lengths r_1 and r_2 where $r_2 > r_1$.

The combined plot of all three surfaces is displayed in Figure 5d. Clearly visible is the two-segment upper boundary, with the left portion formed by surfaces 0 and 2 and the right portion formed by surfaces 0 and 1. The

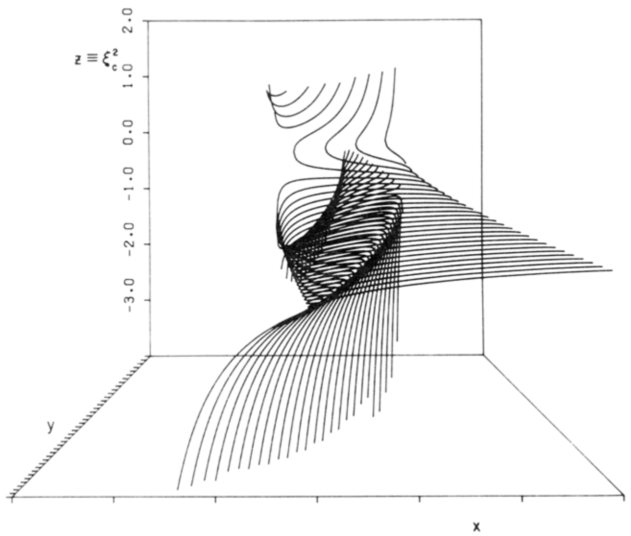

Figure 6. Composite three-dimensional plot of the ξ_c^2 surface for the system $r_2/r_1/r_0 = 5/2/1$.

lower boundary, in this almost symmetrical case almost parallel to the 1–2 axis, is not traced well; its only reminder is the pair of joined lines projected above the main portion of the surface at $\xi_c^2 \approx 1$, with the upper line belonging to the surface 1 and the lower one to the surface 2. The lower 1 × 2 boundary and features associated with it (e.g., the rising left portion of the discontinuous surface 1) are better visible in Figure 6 for the unsymmetrical case 5/2/1.

4.2 Scott's Solution. In 1949 Scott derived his approximate relations for the critical point of ternary systems satisfying the conditions $|g_1 - g_2| \ll 1$ and $(r_1/r_0)^{1/2} < r_2/r_0 < (r_1/r_0)^2$ as[1,21]

$$\phi_c g_x \simeq (r_1^{1/2} + r_2^{1/2})^2/2r_1r_2 \qquad (28a)$$

$$w_2 \simeq r_1^{1/2}/(r_1^{1/2} + r_2^{1/2}) \qquad (28b)$$

This led him to conclude that "the main contribution of the solvent is purely that of lowering the critical solution temperature by dilution; the exact nature of the solvent is of only secondary importance". We wish to make two comments concerning Scott's results.

(1) Surprisingly, relations 28 can be recovered as *exact* solutions for the above-mentioned special singular case of systems residing on the middle line of the three-prong contour line for $\xi_c^2 = -\alpha^{-1/2}$ (Figures 2 and 3a). The identity of w_2 of eq 28b with w_2^S of eq 23 is obvious. Also confirmed is Scott's claim of the critical binodal direction being parallel to the 1–2 axis, $(\Delta\phi_2/\Delta\phi_1)_c = -1$ (cf. eq 27 and Figure 4a). It was mentioned already that for this particular pair of w_2 and ξ_c^2, the critical concentration ϕ_c cannot be determined from eq 18b that becomes of the 0/0 type; rather it has to be calculated from eq 19, with the result identical with the Scott relation (28a). Finally, the critical condition 20 yields for this case a relation between g_x and $g_2 - g_1$

$$(g_2 - g_1)(r_1^{1/2} + r_2^{1/2}) = g_x(r_1^{1/2} - r_2^{1/2}) \qquad (29)$$

Thus Scott in fact underestimated his results:

(i) They are not restricted to any particular ranges of Δg *and* chain lengths but are more general: Δg, g_x, and the chain lengths may assume any values provided that they satisfy the single "new" relation (29). With no more conditions imposed, the sum $g_1 + g_2$ is arbitrary, and in that sense the exact nature of the solvent is indeed unimportant.

(ii) On the composition line $w_2 = w_2^S$ the results become exact rather than just approximate. However, since the probability of an actual system having exactly the composition w_2^S is of the order zero, perhaps it is fitting to relax this condition and to include also systems somewhat perturbed from the ideal composition w_2^S. It is apparent that with this broader definition of Scott systems, relations are indeed approximate as stated in the original work.[1]

Critical points of such perturbed Scott systems slide off the middle line onto some other close 0-apex branch of a contour line with $\xi_c^2 < 0$ (e.g., $\xi_c^2 = -0.58$ or $\xi_c^2 = -0.70$ in Figure 3b), but they remain attached to the 0-apex surface. Note that for truly high polymers with critical concentrations $\phi_{1,c}$ and $\phi_{2,c}$ low, the multivalued triangle becomes very narrow and the critical points of Scott ternary systems are not allowed to stray much from their ideal position at $w_2 = w_2^S$.

(2) On the other hand, there is another restrictive condition for the applicability of eq 28 not explicitly mentioned by Scott. For simplicity imagine a degenerate ternary system whose two polymeric components are identical, i.e., $r_1 = r_2 = r$, $\Delta g = g_x = 0$. Since both of Scott's conditions are here fulfilled there should be no doubt about validity of eq 28a and 28b. Yet it is obvious that with $g_x = 0$ and ϕ_c finite, eq 28a can never be satisfied. In other words, Scott's systems require a certain minimal value of g_x

$$g_{x,\min} \simeq (r_1^{1/2} + r_2^{1/2})^2/2r_1r_2 \qquad (30)$$

guaranteeing sufficient heterosegment repulsive interactions to cause the segregation of the two polymers at least in bulk.

In our present approach this problem does not arise, since we do not claim eq 28 to be the (only) solution under the given conditions; in fact, it is recognized that these equations represent a very special situation out of infinitely many other cases. Specifically for the above degenerate system eq 19 yields $\xi_c^2 = 1$, which, substituted into eq 18b, gives the correct answer $\phi_c = (1 + r^{1/2})^{-1}$. Note that the critical line of this particular quasi-binary system is not located on the ξ_c^2 surface 0 as Scott's systems were, rather it forms the lower boundary of the multivalued region; i.e., it appears as the line joining the surfaces 1 and 2. For quasi-binary systems in general, the critical line is embedded in the left positive part of surface 1.

In spite of the few discrepancies outlined above, however, one has to but marvel at Scott's ability to propose essentially correct formulas without having a clear-cut way of deriving them.

5. Summary

Phase equilibrium conditions for a ternary system solvent–polymer 1–polymer 2 have been written in the form of three functions, with one of them [$F(\sigma_1,\sigma_2,\phi)$ of eq 4] explicitly independent of the triplet of interaction parameters (and thus of temperature) and another (G of eq 5) concisely expressing the effect of inhomogeneous molecular interactions in the solution. Their analysis is facilitated by introducing two new variables defined as $\eta^2 = \sigma_1\sigma_2$ and $\xi^2 = \sigma_2/\sigma_1$, characterizing two different aspects of phase equilibrium. The parameter η is the equivalent of σ of quasi-binary solutions, expressing the distance of the cloud point of a given polymer mixture from its critical point. The quantity ξ, on the other hand, quantitatively characterizes molecular interactions in the solution: its value depends solely on a single compact reduced interaction term $\tilde{W}$ (eq 12). A global diagram of $\ln \xi$ in the complex plane can be constructed, providing one-dimensional space for ordering of all ternary cloud-point equilibria according to the tendency of the two polymers (i) to segregate or to coexist, and (ii) to preferentially concentrate in one phase over the other. Interestingly, in spite of the great variation in ϕ, η, and T along an entire cloud-point curve, the computed values of ξ change very little.

The critical concentration ϕ_c is given by a simple closed expression eq 18b containing the critical parameter ξ_c^2 as the only new interaction-sensitive variable, in addition to quantities well-known from quasi-binary systems. Thus for any given set of chain lengths r_i, a global ξ_c^2 surface can be constructed above the composition triangle, physically corresponding to the locus of critical points for systems with all possible combinations of interaction parameters. The surface has a complex topology, being single valued in the apex regions and three valued in the middle portion of the triangle.

The derived expression for the critical concentration leads to some interesting conclusions:

(i) It is shown that the location of the critical point alone, regardless of the critical temperature, determines for a given set of r_i's the critical direction of the binodal (just as has been demonstrated previously for regular solutions[20]). This correlation should be easy to test, with the result providing the first indication of potential adequacy (or unsuitability) of the Flory–Huggins theory for a given experimental system.

(ii) Approximate relations proposed many years ago for some ternary systems by Scott are obtained from our general analysis as a special singular case. It turns out that, except for some conditions, Scott's approximate relations are essentially correct, and for a subclass of systems of order zero they are even exact.

The complex topology of the ξ_c^2 surface is characterized in this report in three different ways: by contour maps, by plots of critical binodal directions, and by three-dimensional semiperspective plots. There are several reasons (partly only anticipated at this time) for paying close attention to this aspect of the critical state:

(i) A particular surface seems to be correlated with a certain type of behavior. For instance, all Scott's systems (with segregating polymers) have their critical points located on the 0 surface associated with the solvent apex, whereas quasi-binary systems (the archetype of systems with coexisting polymers) occupy surface 1. Related to this point is the fact that numerically computed critical lines for some particular systems show two loops of critical points, presumably each coming from different surface(s).[22]

(ii) Numerical solution of eq 18–20 by multiple iterations is not trivial, and for some particular systems the method does not converge. It seems reasonable to assume that the knowledge of the ξ_c^2 surface topology could be utilized in such cases to make the numerical solution reliable.

(iii) The previous point has implications even for noncritical states. Note that for any constant η (not only for $\eta = 0$) there exists an analogous ξ_η^2 surface whose properties affect numerical solution of general cloud-point equilibria.

(iv) It is expected that the ξ_c^2 surface may play a role in the mechanism of three-phase separation. In quasi-binary systems ($\xi = 1$),[15,23] as well as in some "true" ternary systems[22] with greatly differing chain lengths r_1 and r_2, such separation proceeds via heterogeneous double critical points. On the other hand, there is no a priori reason why the systems under study should not possess under some conditions also homogeneous double critical points, analogous to those observed by Meijering for regular solutions.[20,24] The actual outcome for a particular ternary system will depend on the profile of its critical line that has to be contained within the ξ_c^2 surface.

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Appendix

In the neighborhood of the critical point, the function F of eq 4 can be expanded around $\sigma_1 = \sigma_2 = 0$ at constant ϕ as

$$F = F_0 + \left(\frac{\partial F}{\partial \sigma_1}\right)_0 \sigma_1 + \left(\frac{\partial F}{\partial \sigma_2}\right)_0 \sigma_2 + \frac{1}{2!}\left[\left(\frac{\partial^2 F}{\partial {\sigma_1}^2}\right)_0 {\sigma_1}^2 + 2\left(\frac{\partial^2 F}{\partial \sigma_1 \partial \sigma_2}\right)_0 \sigma_1\sigma_2 + \left(\frac{\partial^2 F}{\partial {\sigma_2}^2}\right)_0 {\sigma_2}^2\right] + \ldots = \sum_{n=0}^{\infty}\frac{1}{n!}\sum_{j=0}^{n}\binom{n}{j}\left(\frac{\partial^n F}{\partial {\sigma_2}^j \partial {\sigma_1}^{n-j}}\right)_0 {\sigma_2}^j {\sigma_1}^{n-j} \quad \text{(A1)}$$

where the subscripts 0 specify that the partial derivatives be taken at the critical point. All terms up to (and including) the second order in σ identically vanish; the critical state is thus characterized by the sum of third-order terms being zero. If σ_1 and σ_2 were both independent variables, each member of the sum would have to be zero; in fact, however, a single variable (e.g., σ_1) at the cloud point of a given polymer mixture **w** fixes the values of all the remaining variables (σ_2, ϕ, and T), and the zero condition can thus be applied only to the entire sum.

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