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Phase Separation in Ternary Systems Solvent–Polymer 1–Polymer 2. 2. General Conditions for Multiple Critical Points

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ABSTRACT: Homogeneous and heterogeneous double critical points play an important role in the phase behavior of ternary systems. Criteria for these points have been derived in three ways: by two conceptually clear well-established methods (Korteweg's based on partial derivatives of free energy of mixing and Tompa's based on the shape of the critical line) and by a novel approach resting on double roots of the modified cloud-point function. Consistency of all three results proves the validity of the new approach, thus opening the way to generalizing it to critical points of higher multiplicity (a triple critical point condition is given as an example) and to systems with more than three components where the established methods fail. The present approach also improves our understanding of the phenomenon: it reveals the fundamental difference in the origin of multiplicity between the two kinds of double critical points.

1. Introduction

Most often the notion of a liquid–liquid phase equilibrium is associated with its simplest form, namely, a two-phase equilibrium that exists in a single region of the composition space of the given system. The crucial role played here by (single) critical points (CP's) is well-known. Particularly in multicomponent systems, however, the situation may be more complex: For instance, at some temperatures the two-phase equilibrium may exist in two or more distinct composition regions, separated from each other by a one-phase stable region. One can also encounter regions with multiphase equilibria (involving more than two conjugated phases). In such cases the source of this "anomalous" phase behavior can be traced to multiple CP's existing under some conditions somewhere in the system.

Mathematically speaking, multiple CP's arise as multiple roots of the set of equations defining the critical conditions. Physically, this is reflected in isothermal diagrams (e.g., in binodals) by two or more separate CP's approaching each other upon perturbation of the system variables and eventually merging into one multiple CP. Since each of the single CP's composing a given multiple CP can be either *stable or unstable* relative to the decomposition into infinitesimally close phases, one can distinguish multiple CP's of various kinds, each associated with a different type of phase behavior. For instance, the double CP's naturally fall into two categories, namely *homogeneous and heterogeneous*, depending on whether the two merging CP's are of the same type or not. This classification was proposed almost 100 years ago by Korteweg,[1] who had been studying plait points on deforming surfaces and formulated criteria for both categories in terms of partial derivatives of the surface.

Korteweg's reflections found their physical interpretation in the thermodynamics of ternary systems. Stable homogeneous double CP's (HODCP's) were located in some regular systems[2] as points of coalescence of two two-phase regions into a single one or points of disappearance of a loop-shaped two-phase region from the system. Thus, their existence is associated with the *change in the number* of distinct two-phase regions due to a change in temperature. On the other hand, the heterogeneous double CP's (HEDCP's) were found to play a crucial role in the mechanism of three-phase separation in quasi-binary ternary systems consisting of a solvent and of two fractions of the same polymer with widely differing molecular weights.[3] Consequently, they seem to be associated with the formation (or vanishing) of new regions with a *higher number of phases* than originally present. In contrast to HODCP's, the HEDCP's are not thermodynamically stable, being located on the boundary between metastable and unstable regions.

The triple CP existing in some ternary systems can be viewed as an overlap of two HEDCP's or of three single critical points (one unstable sandwiched between two stable ones). Although experimentally this case is somewhat illusive since for a quasi-binary ternary system it demands a unique chain-length ratio and a unique polymer composition, it is not unimportant: it marks the onset of systems with HEDCP's, hence, with three-phase separations. For instance, in the limiting case of $r_1 \rightarrow \infty$, the triple CP appears for the chain-length ratio $r_2/r_1 \cong 10$, and any system with the ratio higher than that will have an experimentally observable three-phase region.[3-5]

The question of multiple CP's in ternary systems has been examined in detail in both extreme simple cases: in *regular* solutions (yielding exclusively HODCP's[2]) where the nonideal behavior is strictly due to the difference in interactions between the three components and in *quasi-binary* solutions (producing exclusively HEDCP's[3,4]) where the only "ternary" factor is the difference in chain lengths between the two polymeric components. Our objective here will be to extend these considerations to the general case where both of the above features are present, i.e., to a "true" ternary system consisting of a solvent and of two chemically different polymers with different chain lengths. Obviously such a system could have either one (or both) of the double-CP types. Another objective is to develop a new way of identifying multiple CP's since the established methods rely heavily on geometrical interpretation, simple and appropriate for ternary systems but failing if the number of components becomes large. A

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preliminary report on this subject has been given in ref 6 and 7.[8]

2. Criteria for Multiple Critical Points

Criteria for multiple critical points can be obtained in several different ways:

(i) They are derived from Korteweg's conditions for partial composition derivatives of the free energy of mixing;[1] this route is available only for HODCP's and HEDCP's in ternary systems.

(ii) They are derived by Tompa's method based on a simple geometric interpretation of HEDCP's and of the triple CP in ternary systems: they appear as extrema and as a point of inflection, respectively, of the critical line passing through the temperature–composition space.[3,4] This method should be equally applicable for HODCP's (as shown below).

(iii) The disadvantage of both of the above approaches is that they were designed specifically for ternary systems, and their generalization to systems with more than three components is far from being obvious.[9] Yet, one would like to have a way of recognizing the multiple CP's in systems with any number of components. Such a general method has been devised for solutions of polydisperse polymers[5,10] with the criteria given in terms of partial derivatives of the cloud-point function with respect to the separation factor σ of Flory.[11] Below, this method is extended to systems with chemically different polymeric components. Since it partly relies on intuition, we consider it essential that its equivalence to the first two methods (which are conceptually very clear) be proven for the case of ternary solutions beyond any doubt; only then can one generalize its application to multicomponent systems with confidence. Another advantage of this approach is that the results are packaged in reasonably compact form which does not discourage from their further analysis.

2.1. Critical State in Ternary Systems. The ternary system under consideration consists of a solvent, (0), and of two polymeric components, (1) and (2), with chain lengths $r_0 < r_1 < r_2$. It is described by the Flory–Huggins free energy of mixing[11] per unit volume, with three temperature-dependent parameters, $g_1(T)$, $g_2(T)$, and $g_x(T)$, characterizing the interactions of the two polymers with the solvent and interactions between the polymer segments of 1 and 2, respectively,

$$\Delta G^u/RT = \sum_{i=0}^{2} \frac{\varphi_i}{r_i} \ln \varphi_i + \varphi_0(\varphi_1 g_1 + \varphi_2 g_2) + \varphi_1\varphi_2 g_x \quad (1)$$

where φ_i is the volume fraction of component i.

As shown recently, the cloud-point analysis is greatly simplified by introducing two new variables, η and ξ, defined by

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

$$\sigma_1 = \eta/\xi \qquad \sigma_2 = \eta\xi \quad (2b)$$

where the separation factors of Flory[11] are defined by the expression

$$\sigma_j = r_j^{-1} \ln (\varphi_j^*/\varphi_j) \qquad j = 1, 2 \quad (2c)$$

with the asterisk (*) denoting the incipient phase and plain symbol standing for the principal phase at the cloud point. The nature of these variables has been discussed in detail in our previous report.[12] Briefly, η is an equivalent of σ of quasi-binary systems, being a measure of the "distance" of a cloud point from the critical point; note that $\eta = 0$ at the CP. The variable ξ reflects the nature of interactions, being positive real in systems with "coexisting" polymers and imaginary in systems with "segregating" polymers.

With this formalism, the critical point conditions (derived as the limit of general cloud-point equilibrium for $\eta \rightarrow 0$) can be expressed in the form of the following three equations.[12]

(a) The relation for the critical concentration is

$$\Phi^2 \equiv \left(\frac{\varphi}{1-\varphi}\right)^2 = r_0 \frac{w_1 r_1{}^2 \xi^{-3} + w_2 r_2{}^2 \xi^3}{(w_1 r_1 \xi^{-1} + w_2 r_2 \xi)^3} = r_0 \frac{\langle r^2\xi^3\rangle}{\langle r\xi\rangle^3} \quad (3)$$

where φ is the total polymer volume fraction, $\varphi = \varphi_1 + \varphi_2$; the moments are defined as

$$\langle r^i\xi^j\rangle = w_1 r_1{}^i \xi^{-j} + w_2 r_2{}^i \xi^j \quad (4)$$

and $w_i = \varphi_i/\varphi$, $i = 1, 2$, is the volume fraction of component i in the mixture of the two polymers.

(b) The deviations from quasi-binary character are subject to the condition

$$G_c \equiv \xi^2(1 - \varphi w_2 r_2 P) - (1 - \varphi w_1 r_1 M) = 0 \quad (5)$$

where P stands for the sum $P \equiv g_x + \Delta g$, M stands for the difference $M \equiv g_x - \Delta g$, and Δg is the difference in solvent interaction parameters, $\Delta g \equiv g_2 - g_1$.

(c) The third equation is

$$H_c \equiv \xi^2 + 1 + \varphi\left[\xi\langle r\xi\rangle\left(\frac{2}{\varphi_0 r_0} - 4\bar{g}\right) + w_1 r_1 P + \xi^2 w_2 r_2 M\right] = 0 \quad (6)$$

where the mean value of the solvent interaction parameters is $\bar{g} \equiv (g_1 + g_2)/2$. Other handy compact forms of the third critical function arise by combinations of eq 5 and 6; e.g.,

$$K_c \equiv \xi^2 w_2 r_2 \boldsymbol{g}^+ - w_1 r_1 \boldsymbol{g}_1 = 0 \quad (6a)$$

where

$$\boldsymbol{g}^+ \equiv 2\bar{g} - g_x - (1/\varphi_0 r_0)$$

$$\boldsymbol{g}_i \equiv (1/\varphi_0 r_0) + (1/\varphi_i r_i) - 2g_i \qquad i = 1, 2$$

are the terms turning up in the spinodal condition

$$\mathrm{Sp} \equiv \boldsymbol{g}_1\boldsymbol{g}_2 - (\boldsymbol{g}^+)^2 = 0 \quad (6b)$$

or

$$L_c \equiv \boldsymbol{g}^+\varphi\langle r\xi\rangle - \xi(1 - \varphi_2 r_2 P) = 0 \quad (6c)$$

The corresponding quasi-binary system with $\sigma_1 \equiv \sigma_2$, $\xi = 1$, and $g_x = \Delta g = P = M = 0$ can be viewed as a reference system for which (a) eq 3 reduces to the well-known formula $\Phi^2 = r_0 r_z/r_w{}^2$ where r_z and r_w are the z and weight averages of the chain length;[13] (b) eq 6, 6a, and 6c reduce to the spinodal condition; and (c) eq 5 looses its relevance and yields a trivial identity $0 = 0$.[14]

It is apparent that multiple CP's have to satisfy eq 3, 5, and 6 too, in addition to any special criteria derived below.

2.2. Korteweg's Partial-Derivative Method. Korteweg's criterion for the instability of a critical point in a ternary system is (see ref 1, eq 40)

$$\begin{aligned} G_{11}(m^4 G_{1111} + 4m^3 G_{1112} + 6m^2 G_{1122} + 4m G_{1222} + \\ G_{2222}) - 3(m^2 G_{111} + 2m G_{112} + G_{122})^2 < 0 \quad (7) \end{aligned}$$

where subscripted G's are partial composition derivatives of ΔG^u, e.g., $G_{112} \equiv (\partial^3\Delta G^u/\partial\varphi_1{}^2\partial\varphi_2)_{T,P}$, and m specifies the direction of the binodal at the critical point, $m \equiv (\mathrm{d}\varphi_1/\mathrm{d}\varphi_2)_c$. Hence, a *heterogeneous double critical point* marking the boundary between (meta)stable and unstable CP's should be defined by the left-hand side of eq 7 being equal to zero.

With partial derivatives evaluated from eq 1, Φ substituted from eq 3, and the critical binodal direction given by[12]

$$m = w_1 r_1/(w_2 r_2 \xi^2) = [\langle r\xi\rangle/(\xi w_2 r_2)] - 1 \tag{8}$$

the HEDCP's criterion becomes

$$2\left[\frac{r_0^{1/2}\langle r^2\xi^3\rangle^{3/2}}{\langle r\xi\rangle^{1/2}} + \langle r^3\xi^4\rangle\right] - \frac{3}{\varphi \boldsymbol{g}_1}\left[\frac{\langle r^2\xi^3\rangle}{\langle r\xi\rangle} - \frac{r_1}{\xi^2}\right]^2 = 0 \tag{9}$$

The form of (9) is not particularly attractive: it is asymmetric, it contains $\boldsymbol{g}_1$, and it is not immediately obvious how it reduces for $\xi \rightarrow 1$ to the simple relation valid for quasi-binary systems.

On the other hand, the criterion for a homogeneous double critical point comes out very simply. Applying an analogous procedure as described above to the Korteweg's condition,[1]

$$m^2 G_{111} + 2mG_{112} + G_{122} = 0 \tag{10}$$

one obtains the criterion

$$\xi^4 = r_1/r_2 \tag{11}$$

The HODCP's are thus limited to only two values of ξ^2, i.e., $\xi^2 = \pm(r_1/r_2)^{1/2}$.

2.3. Tompa's Critical Line Method. For every composition $\boldsymbol{w}$ of the polymer mixture in a given system, its critical point $(\varphi,T)_c$ is uniquely defined.[15] Varying the composition w_2 between 0 and 1 thus generates a *critical line* in the space $\boldsymbol{w},\varphi,T$. If the critical temperature is then plotted as a vertical above the triangular composition diagram, double and triple critical points have to appear as extrema and the point of inflection of this line. The task of determining these points, relatively simple in quasi-binary systems,[3,4] becomes here quite complex, and at present we limit ourselves just to double CP's. It is apparent that this method cannot distinguish between HEDCP's and HODCP's (both of which appear as extrema), i.e., it should yield simultaneously criteria for both types.

The condition for the critical line is that three functions become zero: e.g., $K_c(w_2,\varphi,\xi,T)$ of eq 6a, $G_c(w_2,\varphi,\xi,T)$ of eq 5, and $F_c(w_2,\varphi,\xi)$ defined from eq 3 as

$$F_c \equiv \Phi^2\langle r\xi\rangle^3 - r_0\langle r^2\xi^3\rangle = 0 \tag{12}$$

Thus, any infinitesimal step along the critical line has to be accompanied by perturbations of variables such that the above three functions do not change. For instance, choosing w_2 as the (only) independent variable for the one-dimensional critical line, the variation in G_c is

$$\delta G_c = \left[G_w + G_\xi \frac{d\xi^2}{dw_2} + G_\varphi \frac{d\varphi}{dw_2} + G_T \frac{dT}{dw_2}\right]\delta w_2 \tag{13}$$

where the subscripted G's stand for the partial derivatives, $G_w \equiv (\partial G_c/\partial w_2)$, $G_\xi \equiv (\partial G_c/\partial \xi^2)$, etc. Obviously along the critical line the bracket of eq 13 has to be zero. Analogous conditions apply to functions K_c and F_c.

At a double CP, the equations are simplified since the last term in the bracket drops out ($dT/dw_2 = 0$). In principle, one could now solve two such linear equations for the total derivatives $d\xi^2/dw_2$ and $d\varphi/dw_2$ and by substituting these into the third relation obtain the sought criterion.

In fact, even a simpler procedure is available by utilizing the fact that φ can be expressed explicitly from eq 3 as a function of w_2 and ξ^2; one of the above needed total derivatives can thus be calculated directly in terms of the other as

$$\frac{d\varphi}{dw_2} = \left(\frac{\partial\varphi}{\partial w_2}\right)_{\xi^2} + \left(\frac{\partial\varphi}{\partial\xi^2}\right)_{w_2}\frac{d\xi^2}{dw_2} \tag{14}$$

with partial derivatives taken from eq 3. This procedure then leads to the double-CP condition

$$\left(G_w + G_\varphi \frac{\partial\varphi}{\partial w_2}\right)\left(K_\xi + K_\varphi \frac{\partial\varphi}{\partial\xi^2}\right) - \left(G_\xi + G_\varphi \frac{\partial\varphi}{\partial\xi^2}\right)\left(K_w + K_\varphi \frac{\partial\varphi}{\partial w_2}\right) = 0 \tag{15}$$

2.4. General Method Utilizing the η, ξ Formalism. It is apparent that it would be difficult to generalize either Korteweg's or Tompa's method to a system with many components. It is preferable to base the approach on strictly mathematical grounds and define the multiple CP simply as a multiple root of the cloud-point function; such a definition shall be independent of the number of components.

Since the origins of root multiplicity for the homogeneous and heterogeneous case are distinctly different, each type shall be treated separately.

2.4.1. Heterogeneous Multiple Critical Points. It has been shown that in quasi-binary systems, the HEDCP's (as well as all higher CP's arising by combination thereof—such as, e.g., the triple CP) can be located as multiple roots of the modified cloud-point function $\bar{F}(\sigma,\varphi)$ from the conditions of the type $(\partial^n\bar{F}/\partial\sigma^n)_\varphi = 0$.[5,10]

In the presently examined ternary system, the cloud-point function has the form $F(\sigma_1,\sigma_2,\phi)$ [eq 4 and 17 of ref 12] which, after transformation, becomes $F(\eta,\xi,\phi)$. With η assuming the role of the parameter σ of quasi-binary systems, it is obvious that the HEDCP criterion has to contain the partial derivative $(\partial\bar{F}/\partial\eta)_{\varphi,\xi}$ where the expanded modified cloud-point function, $\bar{F} \equiv 6F/\eta^3$, can be written in terms of moments as

$$\bar{F} = 6\sum_{k=0}^{\infty}\frac{k+1}{(k+3)!}\left[\langle r^{k+2}\xi^{k+3}\rangle\eta^k - \frac{\Phi^2}{r_0}\left(\frac{\nabla}{\eta}\right)^3 (k+1)!(\Phi\nabla)^k\right] \tag{16}$$

with

$$\nabla \equiv \frac{\varphi^* - \varphi}{\varphi} = \sum_{i=1}^{\infty}\frac{\eta^i\langle r^i\xi^i\rangle}{i!}$$

Just as in quasi-binary systems, the concentration-derivative term $(\partial\bar{F}/\partial\varphi)_{\eta,\xi}$ can be ignored since the HEDCP is positioned on a cusp where $d\varphi/d\eta = 0$. The contribution due to changing ξ, however, is significant, and the criterion for a HEDCP has to be written as

$$\left(\frac{\partial\bar{F}}{\partial\eta}\right)_{\varphi,\xi} + \left(\frac{\partial\bar{F}}{\partial\xi}\right)_{\varphi,\eta}\frac{d\xi}{d\eta} = 0 \tag{17}$$

The partial derivatives needed in eq 17 are taken at the CP, yielding

$$2\left(\frac{\partial\bar{F}}{\partial\eta}\right)_{\varphi,\xi} = \langle r^3\xi^4\rangle - \langle r^2\xi^3\rangle\left(3\frac{\langle r^2\xi^2\rangle}{\langle r\xi\rangle} + 2r_0^{1/2}\frac{\langle r^2\xi^3\rangle^{1/2}}{\langle r\xi\rangle^{1/2}}\right) \tag{18}$$

$$\left(\frac{\partial\bar{F}}{\partial\xi}\right)_{\varphi,\eta} = 6\frac{w_1 w_2 r_1 r_2(r_2\xi^2 - r_1\xi^{-2})}{\xi\langle r\xi\rangle} \tag{19}$$

The "total" critical derivative $\mathrm{d}\xi/\mathrm{d}\eta$ required for eq 17 has to be obtained from some other equilibrium function, say $\bar{G} \equiv G\xi/\eta$, where G has been defined by eq 5 of ref 12,

$$\bar{G} \equiv \xi^2 - 1 + \xi\varphi\sum_{i=1}^{\infty}\frac{\eta^{i-1}}{i!}[w_1M(r_1/\xi)^i - w_2P(r_2\xi)^i] = 0 \quad (20)$$

with the result

$$\frac{\mathrm{d}\xi}{\mathrm{d}\eta} = -\frac{(\partial\bar{G}/\partial\eta)_{\varphi,T,\xi}}{(\partial\bar{G}/\partial\xi)_{\varphi,T,\eta}} = \frac{\varphi_2{r_2}^2\xi^2P - \varphi_1{r_1}^2\xi^{-2}M}{4(1 - \varphi_2r_2P)} \quad (21)$$

The HEDCP criterion 17 with the derivatives substituted from eq 18, 19, and 21 is attractive in explicitly displaying the effect of heterointeractions. For quasi-binary systems ($\Delta g = g_x = P = M = 0$), it lucidly reduces to the known results: $\mathrm{d}\xi/\mathrm{d}\eta = 0$ (as it has to, since $\xi = 1$ by definition), and condition 17 becomes $r_{z+1} = 3r_z + 2(r_0r_z)^{1/2}$.[4,5,10]

As explained in section 2.2, eq 17 also determines the stability of a single CP in a ternary system: if its left-hand side is positive, then the CP is thermodynamically unstable, whereas if it is negative the CP is stable or metastable.

The criterion for the triple critical (tricritical) point is obtained by taking an η derivative of eq 17

$$\left(\frac{\partial^2\bar{F}}{\partial\eta^2}\right) + 2\left(\frac{\partial^2\bar{F}}{\partial\xi\,\partial\eta}\right)\frac{\mathrm{d}\xi}{\mathrm{d}\eta} + \left(\frac{\partial^2\bar{F}}{\partial\xi^2}\right)\left(\frac{\mathrm{d}\xi}{\mathrm{d}\eta}\right)^2 + \left(\frac{\partial\bar{F}}{\partial\xi}\right)\frac{\mathrm{d}^2\xi}{\mathrm{d}\eta^2} = 0 \quad (22)$$

with $\mathrm{d}^2\xi/\mathrm{d}\eta^2$ again calculated from eq 20. It is apparent that this form is much simpler than any result that could be obtained by utilizing Tompa's method of the critical line inflection.

2.4.2. Homogeneous Double Critical Points. While in the previous case the multiplicity arose as a consequence of multiple roots of the cloud-point function $\bar{F}$, eq 16, aligned *along* the cloud-point curve, in case of HODCP's the responsible element is the double root of ξ^2 in the function F_c, eq 12, valid strictly for the *critical point* alone.

The distinction can be perhaps clarified in terms of the critical ξ^2 surface.[12] The critical value of the parameter ξ^2 can be computed from eq 12 and plotted as a surface above the triangle of composition φ, $\mathbf{w}$. This surface in fact consists of three portions, each associated with one apex of the triangle, partly overlapping and fused in the middle. The central three-valued region has exceedingly simple boundaries: they are linear segments connecting the critical points of the three binary mixtures. And it is along these boundaries that double roots of ξ^2 have to appear: when moving out of the three-valued region, two of the three real roots approach each other, merge (forming a *double* root), and eventually become complex, leaving just a single real root for the apex region. It has been shown[12] that depending on their location, the double roots of ξ^2 can assume only the values of $+(r_1/r_2)^{1/2}$ or $-(r_1/r_2)^{1/2}$, which is entirely consistent with the results derived above by Korteweg's method and qualifies these points as HODCP's. Hence, there is also a crucial difference between the HEDCP's and HODCP's regarding their position in the ξ^2 surface: the former ones are located somewhere within one of the three portions, with both CP's (merging into the double point) residing on the *same* portion of the ξ^2 surface. On the other hand, the HODCP's position is severely restricted to the above linear segments where two different portions of the ξ^2 surface are fused together, and each of the two CP's forming the double point originates in a *different* portion of the surface. In other words, a HODCP will mark the point where the critical line crosses from one portion of the ξ^2 surface to another.

Now the question is whether a general criterion for a HODCP could be also expressed in terms of the cloud-point function $\bar{F}$. Since the double character here exists *within* the CP itself rather than *along* the cloud-point curve, the condition should be recovered by varying ξ^2 alone, with η and φ kept constant at $\eta = 0$, $\varphi = \varphi_c$. Thus, the general criterion for a HODCP should read

$$\left(\frac{\partial\bar{F}}{\partial\xi}\right)_{\varphi,\eta} = 0 \quad (23)$$

where the left-hand side of eq 23 is defined by eq 19.

2.5. Comparison of Different Methods. The equivalence of the general criterion 23 for a HODCP with the result of Korteweg's method, eq 11, is obvious. On the other hand, it is not immediately clear that the three relations, (9), (15), and (17), obtained for a HEDCP by different methods are mutually consistent nor is it apparent that the critical line result (15) also covers the HODCP condition (11). Rigorous proof of these statements is displayed in the Appendix sections. Specifically, in Appendix A, Korteweg's form (9) is shown to be consistent with our formula (17), while in Appendix B the critical line result (15) is rearranged into a product of two criteria, one for a HODCP and the other for a HEDCP.

Thus, our method of identifying multiple critical points in ternary systems has been proven to be valid. Since it is based on the behavior of the modified cloud-point function $\bar{F}$, eq 16, around the CP, a concept that is independent of the number of components in the system, this approach should be easily applicable also to quaternary and higher systems that can be characterized by η and more than one ξ_i variable (see ref 12, eq 8).

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Appendix A

It will be shown that the HEDCP criterion 9 derived by Korteweg's method can be rearranged into eq 17 (whose terms are defined by eq 18, 19, and 21). We invoke the moment definition 4 and use eq 6a and 6c valid at any CP to write the negative square term (NST) of eq 9 as

$$\mathrm{NST} = -3w_1w_2r_1r_2(r_2\xi^2 - r_1\xi^{-2})^2/[\xi\langle r\xi\rangle(1 - \varphi_2r_2P)] \quad (\mathrm{A1})$$

Furthermore, it can be shown with the aid of eq 5 that

$$r_2\xi^2 - r_1\xi^{-2} = \varphi_2{r_2}^2\xi^2P - \varphi_1{r_1}^2\xi^{-2}M + \xi(r_2\xi - r_1\xi^{-1})(1 - \varphi_2r_2P) \quad (\mathrm{A2})$$

With this substitution, NST of eq A1 takes the form

$$\mathrm{NST} = -2\left(\frac{\partial\bar{F}}{\partial\xi}\right)_{\varphi,\eta}\frac{\mathrm{d}\xi}{\mathrm{d}\eta} - 3w_1w_2r_1r_2\frac{(r_2\xi^2 - r_1\xi^{-2})(r_2\xi - r_1\xi^{-1})}{\langle r\xi\rangle} \quad (\mathrm{A3})$$

where the derivatives are defined by eq 19 and 21. Finally, the last term of (A3) is rearranged by using the identity

$$\langle r^3\xi^4\rangle\langle r\xi\rangle - \langle r^2\xi^3\rangle\langle r^2\xi^2\rangle = w_1w_2r_1r_2(r_2\xi^2 - r_1\xi^{-2})(r_2\xi - r_1\xi^{-1}) \quad (\mathrm{A4})$$

and NST is substituted into eq 9; this step leads to the negative of doubled eq 17. This concludes the proof.

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Appendix B

Criterion 15 for an extremum of the critical line can be transcribed as

$$\Gamma_{w\xi} + \frac{\partial\varphi}{\partial w_2}\Gamma_{\varphi\xi} + \frac{\partial\varphi}{\partial\xi^2}\Gamma_{w\varphi} = 0 \tag{B1}$$

where $\Gamma_{\alpha\beta} \equiv G_\alpha K_\beta - G_\beta K_\alpha$. With the aid of critical eq 3, 5–6a, and 6c, this complicated expression can be simplified as follows: The partial derivatives of φ from eq 3 are

$$\frac{\partial\varphi}{\partial\xi^2} = 3\varphi(1-\varphi)w_1r_1w_2r_2\frac{r_2\xi^2 - r_1\xi^{-2}}{2\xi^2\langle r\xi\rangle\langle r^2\xi^3\rangle} \tag{B2}$$

$$\frac{\partial\varphi}{\partial w_2} = \varphi(1-\varphi)\frac{(r_2^2\xi^3 - r_1^2\xi^{-3})\langle r\xi\rangle - 3(r_2\xi - r_1\xi^{-1})\langle r^2\xi^3\rangle}{2\langle r\xi\rangle\langle r^2\xi^3\rangle} \tag{B3}$$

whereas the Γ terms obtained by taking derivatives of the critical functions G_c and K_c, eq 5 and 6a, can be rearranged into the forms

$$\Gamma_{w\xi} = -\boldsymbol{g}^+(r_2\xi^2 - r_1\xi^{-2}) \tag{B4}$$

$$\Gamma_{\varphi\xi} = \boldsymbol{g}^+w_1w_2(r_2\xi^2 - r_1\xi^{-2})(r_2\xi - r_1\xi^{-1})/(\varphi\langle r\xi\rangle) \tag{B5}$$

$$\Gamma_{w\varphi} = 4\xi\,(\mathrm{d}\xi/\mathrm{d}\eta)\,\boldsymbol{g}^+(r_2\xi^2 - r_1\xi^{-2})/(\varphi\langle r\xi\rangle) \tag{B6}$$

where $\mathrm{d}\xi/\mathrm{d}\eta$ is specified by eq 21. After the quantities defined above are substituted in eq B1, the common term

$$\boldsymbol{g}^+(r_2\xi^2 - r_1\xi^{-2})(1-\varphi)/(\langle r\xi\rangle\langle r^2\xi^3\rangle) \tag{B7}$$

can be factored out, and the two products of differences of $r_i^m\xi^n$ terms appearing in the second term of eq B1 can be expressed as differences of moments from the formula

$$w_1w_2(r_2^m\xi^n - r_1^m\xi^{-n})(r_2^{i-m}\xi^{j-n} - r_1^{i-m}\xi^{n-j}) = \langle r^i\xi^j\rangle - \langle r^m\xi^n\rangle\langle r^{i-m}\xi^{j-n}\rangle \tag{B8}$$

This operation and some subsequent rearrangement finally make the residue identical with criterion 17.

The extremal condition for the critical line thus leads in fact to the product of two criteria as expected: one for a HODCP contained in the factor (B7) (cf. eq 11); the other for a HEDCP remaining in the residue.

References and Notes

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(8) Equations 7 and 8 of ref 7 are erroneous in lacking the contributions due to changing ξ. Through misunderstanding, their correction requested in time by the author has not been carried out.

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(14) Strictly speaking, variables φ, ξ, and g in eq 3 and 5–6c and elsewhere should bear a subscript c specifying their critical character. However, since the entire report is on the critical state, the distinction seems useless and the subscripts have been dropped for the sake of simplicity.

(15) With the exception of Scott systems[12,16] where the critical concentration depends on g_x.

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Microphase Formation in Solutions of Diacetylene-Containing Segmented Block Copolymers

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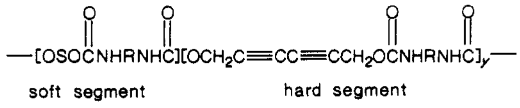
ABSTRACT: In solutions of the diacetylene-containing segmented block copolymers described earlier, micelles are formed which consist of a compact hard segment core surrounded by a less dense shell of soft segment. The diacetylene units are built into the hard segments and can polymerize only in more or less ordered aggregates. Micelle formation can, therefore, be monitored by the appearance of the characteristic purple color of the polydiacetylenes. The effect of polymer concentration and of solvent composition on micellization is investigated, and the criteria for the formation of unimolecular and multimolecular micelles are considered. The kinetics of the micellization process are characterized by an activation energy of 3.7 kcal/mol. An estimate of micelle size is obtained by gel permeation chromatography. The overall size of the micelles in the early stages of microphase formations is estimated at 180 Å.

Earlier we reported on the photoreactivity of diacetylene-containing block copolymers.[1,2] The photoreactivity of these materials depends on the degree of phase separation between a predominantly hard segment microphase and a predominantly soft segment continuum. It also depends on the size and the degree of order in the diacetylene stacks of the hard segment phase. This molecular morphology which determines the photochemical behavior of the solid is preformed in polymeric micelles while the system is still in a fluid state. The present paper is concerned with the formation of micelles in solutions of diacetylene-containing block copolymers.

Our investigation was conducted on copolymers of the general composition



$$-[\mathrm{OSO\overset{O}{\overset{\|}{C}}NHRNH\overset{O}{\overset{\|}{C}}}][\mathrm{OCH_2C{\equiv}CC{\equiv}CCH_2O\overset{O}{\overset{\|}{C}}NHRNH\overset{O}{\overset{\|}{C}}}]_y-$$

Here R stands for $-(\mathrm{CH_2})_6-$, S stands for $-(\mathrm{CH_2})_5\mathrm{CO}-$, the hard segment content is either 35% or in some cases 25%,

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