SOLVENT-INDUCED ASSOCIATION OF POLYMERS: PHASE STABILITY

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Received March 18, 2005
Accepted June 23, 2005

In the preceding paper, basic thermodynamic functions have been derived for a solution of macromolecules associating by means of functional groups (stickers), thus forming junctions, each of which consists of m stickers and bm molecules of solvent. In the present communication, phase stability of the systems under consideration is analyzed. For several values of parameters m and b, spinodal curves are calculated and their minima (i.e. critical solution points) are localized. At higher junction multiplicity values (e.g. at $m = 10$), a local maximum appears on the spinodal, dividing it into two lobes, each displaying a different critical point. The effect of the stoichiometric parameter b on splitting the spinodal and on positions of the critical solution points is described.

Keywords: Polymer association theory; Multiple chain junctions; Solvent-complexed chain junctions; Folded spinodal curves; Two critical solution points; Thermodynamics.

It is well known that self-association stimulates the phase instability in solution. In the case of an associating polymer forming multiple aggregation junctions, curves of unusual shape may appear in the phase diagram[1]. In our previous work, we used a thermodynamic procedure to analyze clustering and network building in systems where solvent participates in the formation of multiple polymer junctions[2]. In this context a question arises, how the incorporation of solvent into junctions affects the phase stability of the associating system. The answer is sought in the present work.

Basic Relations

In ref.[2], an equation for the Helmholtz energy of mixing, ΔF, of our model system was derived. Per one mol of lattice sites $F_N = \Delta F/N$, it takes the form

$$F_N / RT = (\varphi_A / r)\ln\varphi_A + \varphi_B \ln\varphi_B + F_{assoc,N} / RT + \chi\varphi_A\varphi_B . \qquad (1)$$

doi:10.1135/cccc20052014

Here φ_A, φ_B are volume fractions of polymer and solvent, respectively, χ is the Flory–Huggins parameter of contact interaction and $F_{\mathrm{asoc,N}}/RT$ is the association contribution

$$F_{\mathrm{assoc,N}} / RT = (f\varphi_{\mathrm{A}} / r)\ln[y_{\mathrm{A}} / (\varphi_{\mathrm{A}} y^{\mathrm{o}}_{\mathrm{A}})] + \\ + \varphi_{\mathrm{B}} \ln(y_B / \varphi_{\mathrm{B}}) + (b + 1 - 1/m)(X - \varphi_{\mathrm{A}} X^{\mathrm{o}}_{\mathrm{A}}) \tag{2}$$

where r is the number of lattice sites occupied by a macromolecule, f the number of functional groups (stickers) per chain, m is the junction multiplicity, i.e. the number of stickers constituting a junction, bm is the number of solvent molecules incorporated in a junction; X, y_A and y_B are number densities of associated stickers, unassociated stickers and unassociated solvent molecules, respectively. The superscript $^{\mathrm{o}}$ refers to the standard state.

The number densities X, y_A and y_B are interrelated by the equation of association equilibrium

$$X = k^{m-1} y^{m}_{\mathrm{A}} y^{bm}_{\mathrm{B}} \tag{3}$$

and by mass-balance equations

$$f\varphi_{\mathrm{A}} / r = y_{\mathrm{A}} + X \tag{4a}$$

$$\varphi_{\mathrm{B}} = y_{\mathrm{B}} + bX\ . \tag{4b}$$

In the phase diagram T vs φ_A, the region of phase instability is delimited by the spinodal curve, defined by the relation

$$(\partial^2 F_{\mathrm{N}} / \partial\varphi^2_{\mathrm{A}})_{T,N} = 0\ . \tag{5}$$

Using Eqs (1)–(5), the second derivative of F_N can be expressed in the form

$$\frac{\partial^2 (F_{\mathrm{N}} / RT)}{\partial\varphi^2_{\mathrm{A}}} = \frac{1}{r\varphi_{\mathrm{A}}} + \frac{1}{\varphi_{\mathrm{B}}} - 2\zeta - 2\chi \tag{6}$$

where

$$2\zeta = -\left(\frac{\partial^2 F_{\mathrm{assoc,N}} / RT}{\partial\varphi^2_{\mathrm{A}}}\right)_{T,N} \tag{7}$$

or

$$2\zeta = z\frac{(f/r)[(m-1)y_B - b^2 m y_A z]/\varphi_A + b(bm-1-mz)y_A/\varphi_B - 2(f/r)bm}{y_B + mz(y_B + b^2 y_A)} \qquad (8)$$

with

$$z = X/y_A\ . \qquad (9)$$

Combining Eqs (*5*) and (*6*), we have

$$2\chi = \frac{1}{r\varphi_A} + \frac{1}{\varphi_B} - 2\zeta\ . \qquad (10)$$

Using the latter equation, the value of parameter χ can be calculated that is necessary for the system of a given composition φ_A to be situated on the spinodal. Now, following ref.[1], we assume that

1) χ is determined by temperature, e.g.

$$\chi = a_0 + a_1/T\ . \qquad (11)$$

2) The association parameters *k*, *m* and *b* are temperature-independent. Then the function $\chi(\varphi_A)$ is a simple transformation of $T(\varphi_A)$ and can be used as an alternative to the spinodal curve.

If the polymer does not associate, the last term of Eq. (*10*) is zero and we have the classical Flory–Huggins spinodal relation. Therefore, the inert system ($k = 0$ or $f = 0$) can, at a given φ_A, serve as a reference system in the discussion of phase instability of associating solutions. The spinodal of an inert system (at a given value of *r*) will be called "reference curve".

In the following paragraphs, calculation results for systems with $m = 3$ and $m = 10$ will be compared. For the latter value of junction multiplicity, a more complicated form of spinodal curves is expected[1].

Junction Multiplicity m = 3

In Figs 1 and 2, spinodal curves of systems with triple association junctions are shown at various values of the stoichiometric coefficient *b*. If the association equilibrium parameter is relatively small ($k = 20$; Fig. 1), the left-hand branches of the spinodal curves are nearly identical for various *b*; the position of the critical point and the shape of the right-hand branches differ only moderately from the reference curve. At higher parameter *k* ($k = 60$; Fig. 2), the critical solution point is considerably shifted toward lower χ values and higher volume fractions φ_A. Its position, as well as that of the right-hand branch, is strongly differentiated with respect to the stoichiometric coefficient *b*: increasing *b* results in diminishing the instability region.

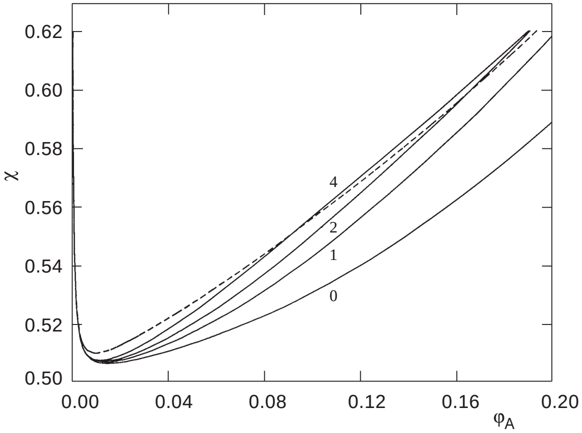

FIG. 1
Spinodal curve (contact interaction parameter vs volume fraction of polymer) for junction multiplicity $m = 3$ and association equilibrium parameter $k = 20$ at various values of solvent proportion *b*. $r = 10\,000$, $f = 900$. Full curves are labeled by *b* values. Dashed line – reference curve ($k = 0$)

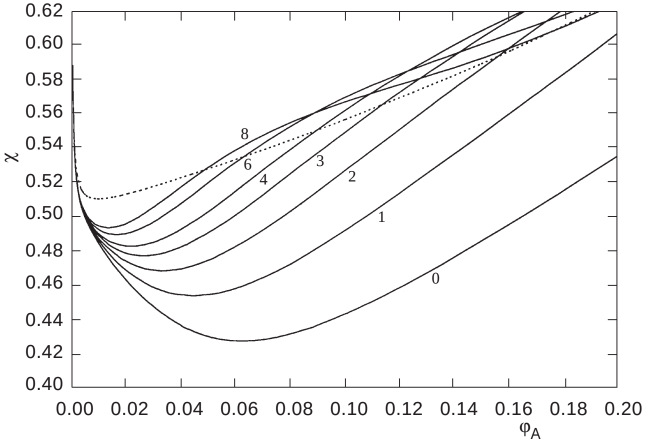

FIG. 2
Spinodal curve for junction multiplicity $m = 3$ and equilibrium parameter $k = 60$ at various values of solvent proportion *b*. $r = 10\,000$, $f = 900$. Full curves are labeled by *b* values. Dashed line – reference curve ($k = 0$)

We see from Eq. (*10*) that at a given φ_A, the difference of χ values for the spinodal and the reference curve is equal to -2ζ, representing the association contribution to the second derivative of Helmholtz energy. A positive value of ζ indicates the trend towards phase instability, due to polymer association.

If the solvent does not participate in junction formation ($b = 0$), Eq. (*8*) simplifies to

$$2\zeta = \frac{f}{r}\frac{m-1}{1+mz}\frac{z}{\varphi_A} . \qquad (12)$$

In this case, ζ is always positive depending primarily on the association ratio z. At low polymer concentrations, z is small and ζ is negligible in comparison with the contact-interaction parameter χ. At a concentration proportional to $r/(fk)$, the growth of z accelerates and ζ becomes a significant term in Eq. (*10*).

Returning to Eq. (*8*) for $b > 0$, we find again z to be a multiplicative factor. At first sight, ζ should decrease with increasing b, as z does. However, the b-terms in the numerator of Eq. (*8*) can invert its sign in a certain bilaterally limited range of φ_A; thus the spinodal intersects the reference curve twice, cf. Fig. 2. The φ_A-values of the intersection points shift to the left if b increases. We may infer that the indispensability of solvent in junction formation brings about a trend towards polymer–solvent mixing, which is similar to that found on immediate solvation of polymer sites. A negative contribution to Helmholtz energy of mixing then results, corresponding to a negative contribution to ζ.

Now we turn our attention to the influence of association parameters k and b on the position of the critical solution point in the $(\chi;\varphi_A)$ diagram. In Figs 3–5 we have a set of two-dimensional representations of the three-dimensional curve

$$F(k,\chi_c,\varphi_{A,c}) = 0 \qquad (13)$$

for $b = 0, 1, 2$, the subscript c denoting the critical solution point. For instance, Fig. 4 displays a projection to a plane perpendicular to the χ_c-axis. Then the coordinates are k and $\varphi_{A,c}$ and, if we proceed along the curve towards higher k, the parameter χ_c decreases (cf. Fig. 3). The curve Eq. (*13*) will be called critical curve.

It can be seen from the shape of the latter curves that at constant m and b, the set of association systems separates into three zones with respect to k:

1) For small values of *k*, the critical point coordinate χ_c is nearly constant, while $\varphi_{A,c}$ increases slightly. This indicates that in this zone, the critical point is determined nearly exclusively by binary Flory–Huggins interactions.

2) If *k* ranges from 20 to about 70, χ_c decreases due to association of functional groups into triple junctions. As their frequency increases slower than

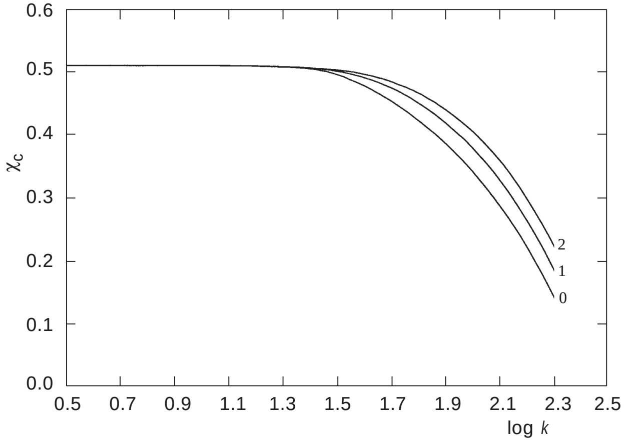

FIG. 3
Critical curves for *m* = 3: critical interaction parameter χ_c vs equilibrium parameter *k*. *r* = 10 000, *f* = 900. Curves are labeled by *b* values

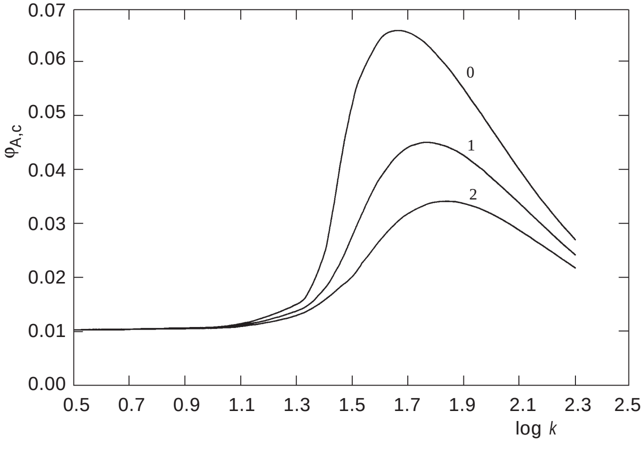

FIG. 4
Critical curves for *m* = 3: critical volume fraction $\varphi_{A,c}$ vs equilibrium parameter *k*. *r* = 10 000, *f* = 900. Curves are labeled by *b* values

that of binary segment contact interactions, $\varphi_{A,c}$ shifts towards higher values. The decrease in χ_c can be only partly compensated by inclusion of solvent into junctions ($b > 0$), but the increase in $\varphi_{A,c}$ is affected strongly.

3) If we have $k > 70$, the decrease in χ_c with k accelerates. The frequency of junctions is now significant even at lower concentrations, so that $\varphi_{A,c}$ decreases after having passed through a maximum.

Junction Multiplicity m = 10

We have seen that at low concentrations, the shape of the spinodal is determined by Flory–Huggins interactions only; the influence of association becoming perceivable at higher φ_A. This is due to a very low rate of the increase in the association degree with concentration in dilute solutions. The φ_A range of negligible association broadens with increasing junction multiplicity, m; cf. Fig. 1 in ref.[2]. For $m > 3$, this segregation of influence domains may result in splitting the spinodal into lobes in the part adjacent to the complete miscibility region. Thus we have two pairs of conjugate phases and two critical points, displaying minima of χ. Between the latter, we find a local maximum point joining the two lobes.

Kudlay and Erukhimovich[1] offered an analysis of this phenomenon for the case of association through solvent-free junctions. The ultimate goal of the present work is to elucidate the influence of the solvent proportion coefficient b on the spinodal shape.

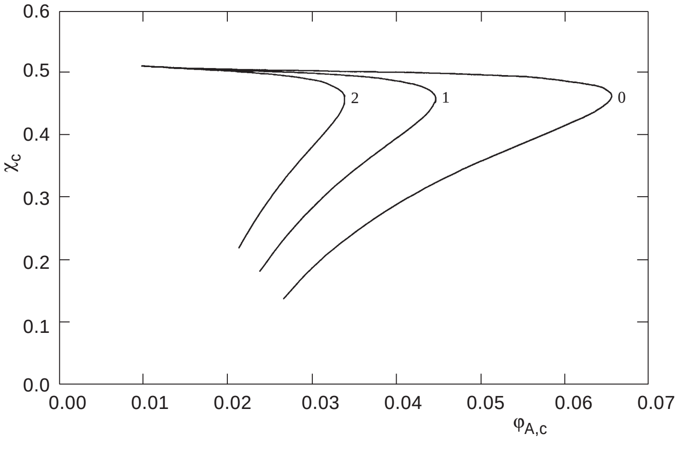

FIG. 5
Critical curves for $m = 3$: critical interaction parameter χ_c vs critical volume fraction $\varphi_{A,c}$. $r = 10\,000$, $f = 900$. Curves are labeled by b values

In Figs 6–8, spinodals are shown for three values of equilibrium parameter (k = 56, 82, 108) and for three stoichiometric coefficients (b = 0, 1, 2). Comparing, e.g., curves for b = 2, one sees that if k increases starting from low values, we have at first a simple spinodal curve and later an S-shaped spinodal with positive slope in the inflexion point. Then, at a certain value

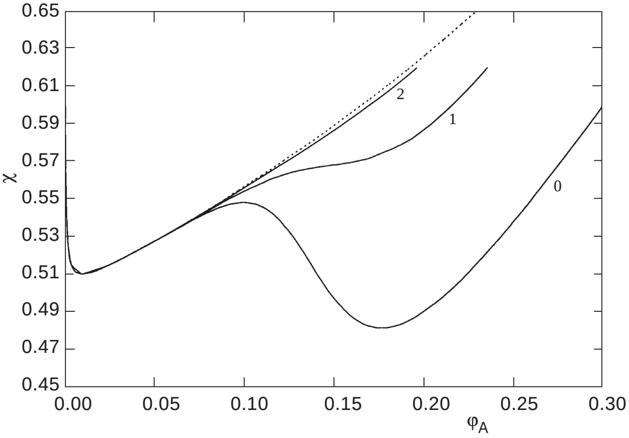

FIG. 6
Spinodal curve for junction multiplicity m = 10 and equilibrium parameter k = 56 at various values of solvent proportion b. r = 10 000, f = 900. Full curves are labeled by b values. Dashed line – reference curve (k = 0)

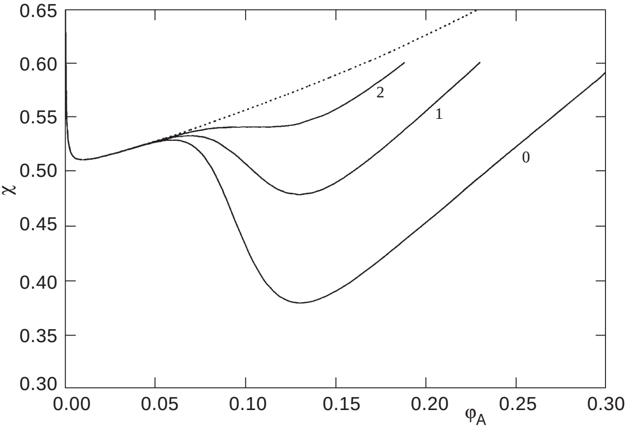

FIG. 7
Spinodal curve for junction multiplicity m = 10 and equilibrium parameter k = 82 at various values of solvent proportion b. r = 10 000, f = 900. Full curves are labeled by b values. Dashed line – reference curve (k = 0)

of k, the slope is zero (for $b = 2$ this occurs at $k = 81.3$ in the point $\chi = 0.5416$, $\varphi_A = 0.104$). This is the start of splitting the inflection into a minimum and a maximum, a folded spinodal curve being developed. Its right-hand minimum becomes deeper and the local maximum shifts towards the left-hand minimum. At a sufficiently large value of k, the latter two points would merge into an inflection point and, finally, a spinodal curve would appear with a single critical point.

If the solvent participates in the junction formation, the trend to spinodal splitting is reduced with b increasing at constant k.

In folded-spinodal systems shown in Figs 6–8, the association degree α [$\alpha = z/(1 + z)$] assumes values not larger than 10^{-9} in the first critical point. In the local maximum it is of the order 10^{-4}–10^{-3}, and only in the second critical point it amounts to 10^{-1}. Indeed, the immediate measure of the influence of association on the spinodal shape is the association contribution ζ, Eqs (*7*) and (*8*). It can be determined from the phase diagram as difference between the reference curve and the spinodal under consideration, taken at a given φ_A. It can be seen from Figs 6–8 that ζ is negligible up to the first critical point and significant but small in the interval between the first minimum and local maximum. However, at the maximum of χ a rapid growth of ζ sets in continuing until the second critical point is reached. The evoluation of α and ζ documents the delimitation of the influence of contact interaction and multiple association between two concentration zones.

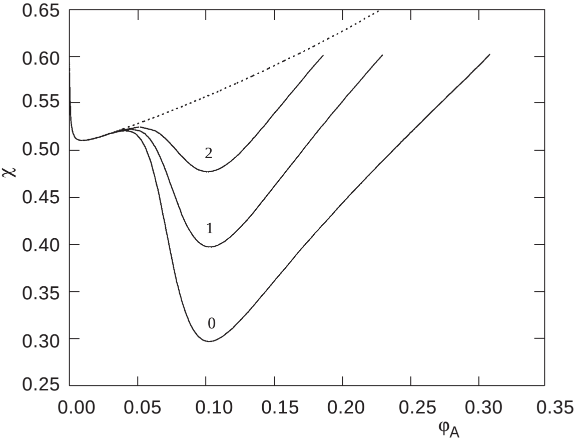

FIG. 8

Spinodal curve for junction multiplicity $m = 10$ and equilibrium parameter $k = 108$ at various values of solvent proportion b. $r = 10\,000$, $f = 900$. Full curves are labeled by b values. Dashed line – reference curve ($k = 0$)

Indeed, if $b > 0$, the effect of association is diminished or (e.g. in Fig. 6, curve 2) disappears.

In Figs 9–11, the function $F(k,\chi_c,\varphi_{A,c}) = 0$ is shown for systems with m = 10. In distinction to analogous graphs for triple junctions (Figs 3–5), the

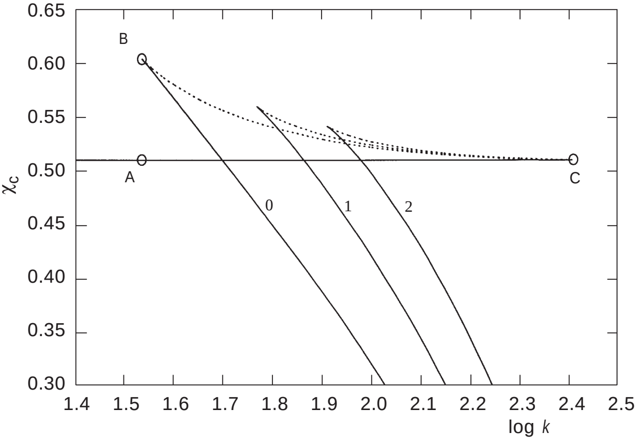

FIG. 9

Critical curves for m = 10: critical interaction parameter χ_c vs equilibrium parameter k. r = 10 000, f = 900. Curves are labeled by b values. Points A, B: lower limit of k for folded spinodal curves at b = 0; point C: upper limit. Full lines – loci of critical points, dotted lines – loci of local maxima

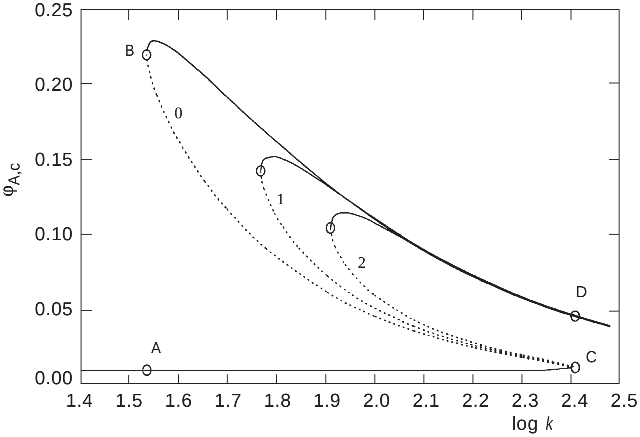

FIG. 10

Critical curves for m = 10: critical volume fraction $\varphi_{A,c}$ vs equilibrium parameter k. r = 10 000, f = 900. Curves are labeled by b values. Points A, B: lower limit of k for folded spinodal curves at b = 0; points C, D: upper limit. Full lines – loci of critical points, dotted lines – loci of local maxima critical curve for a given *b* value includes three branches, corresponding to the loci of the two critical solution points and the local maximum.

Let us survey the branches of the critical curve for $b = 0$.

1) Locus of the first critical points: From $k = 0$ to $k = 34.4$, i.e. up to point A, there exists a single critical point as a part of a simple spinodal typical of contact interactions. Its position in the phase diagram ($\chi_c = 0.510$; $\varphi_{A,c} = 0.0099$) is essentially the same as that found for $k \to 0$ at multiplicity $m = 3$ (cf. Figs 3, 4). At $k = 34.4$, a zero-slope inflection appears on the spinodal at $\varphi_{A,c} = 0.219$ (point B), constituting a primordial form of the other critical point, so that we enter the zone of a double spinodal curve. However, the coordinates of the first critical point are unaffected by further increase in *k* unless we are closely approaching the point C (e.g., points C and A nearly merge in Fig. 11). At the latter point ($k = 251.8$), the first critical point vanishes, merging with the local maximum.

2) Locus of maxima: Moving from B to C, i.e. increasing the association constant again, the local maximum shifts to lower χ_c as well as to lower φ_A values, which means that it is moved from the neighbourhood of the first minimum towards that of second one.

3) Locus of the second critical points: Starting at B and increasing *k*, the parameter χ_c diminishes rapidly. In the intersection with the line AC, we have a system with identical χ_c values for both critical points. The critical

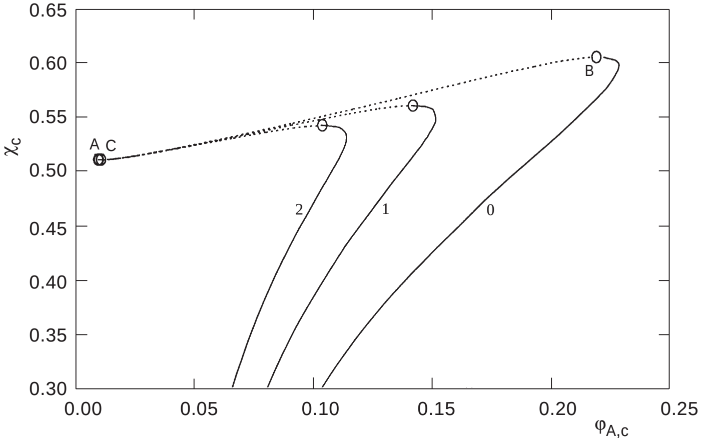

FIG. 11
Critical curves for $m = 10$: critical interaction parameter χ_c vs critical volume fraction $\varphi_{A,c}$. $r = 10\,000$, $f = 900$. Curves are labeled by *b* values. Points A, B: lower limit of *k* for folded spinodal curves at $b = 0$; point C: upper limit. Full lines – loci of critical points, dotted lines – loci of local maxima

value of volume fraction decreases with growing *k* (except a small region in the neighborhood of point B). The transition to a simple spinodal curve would occur at the point D (k = 251.8) through disappearance of the first critical point in C. Indeed, point D corresponds to unusually low values of the contact interaction parameter ($\chi_c << 0.3$ would be required).

Now, we turn our attention to the influence of solvent incorporated in the junctions. From Figs 9 to 11, we see that the higher *b*, the higher is the minimum value of association constant *k* compatible with the occurrence of a split spinodal. The (χ_c;$\varphi_{A,c}$) coordinates of the first critical point are essentially the same for any value of *b*. As regards the second critical point, one observes a rapid growth of χ_c with increasing *b* (considerably larger than at $m = 3$, cf. Fig. 3). On the other hand, the differences in $\varphi_{A,c}$, as found for various *b*, are significant only in the region of relatively small *k* values, when the second critical point is close to the local maximum. On increasing *k*, the φ_A coordinates of the latter two points shift in opposite direction, until they reach a constant difference and become unaffected by *b*.

CONCLUSION

In the limit case $k = 0$, the coordinates of the critical point assume a value which is independent of f/r, *m* and *b*. If *k* increases, the critical points behave in two possible ways depending on the value of junction multiplicity.

1) In systems with triple association junction ($m = 3$), there is a single critical point. At small values of the equilibrium parameter *k*, the distinction between the critical point coordinates for different values of parameter *b* occurs very slowly, but continuously. On further increase in *k*, the growth of the span $\Delta\chi_c/\Delta b$ accelerates. This indicates that the influence of association on the critical point increases gradually along the critical curve.

2) At a higher junction multiplicity (e.g. at $m = 10$), there may be two critical points due to the spinodal splitting. The coordinate of the first of them is invariant with respect to *k* and *b* essentially in the whole *k*-range compatible with the existence of minimum. One sees that the first critical point is fully determined by contact Flory–Huggins interactions. In contrast, the loci of the second critical points are strongly affected by the *b*-value, as it is seen from differences in the lower boundary value of *k* and in the χ_c-values at a given *k*. Here, the decisive role of association is evident.

Thus, by observing the influence of the solvent stoichiometry in a two-component junction, we have arrived at conclusions consistent with those following from a comparison of spinodal curves shape by means of the variable ζ.

Support by the grant AVOZ 405 0913 is acknowledged.

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