PHASE STABILITY OF HYDROGEN-BONDED POLYMER MIXTURES. II. MIXTURES OF INTERCOMPLEXING POLYMERS

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Equations for the second derivative of the Gibbs energy of mixing with respect to composition were derived on the basis of the Barker–Guggenheim theory of quasichemical equilibrium for mixtures of two polymers containing polar groups and a nonpolar rest. Using equations derived, conditions for the phase separation in mixtures of two strongly intercomplexing polymer components were evaluated. The phase instability appears when the components differ in their polar group contents (strictly speaking, in their surface fractions in respective macromolecules), or due to an unfavorable interaction between nonpolar groups of the components. The effect is conditioned by small affinity of polar to nonpolar groups and may be influenced by the difference in this affinity between both components; nevertheless, the latter factors are not sufficient for a phase instability to occur.

Key words: Phase stability; Polymer mixtures; Hydrogen bonds; Intercomplexing polymers; Quasichemical equilibrium theory.

The study of phase separation in polymer mixtures often brings unexpected findings. Most of them could be explained by assuming merely an incomplete establishment of phase equilibrium due to small mobility of macromolecules in systems without solvents, but some of them could be interpreted by means of a theoretical model derived from equilibrium thermodynamics. The latter are represented by the behaviour of a mixture of two polymers in which phase separation may occur regardless of the fact that both components form a polymer–polymer complex bound by strong interactions (hydrogen bond, as a rule). For example, measurements of T_g's of polymer mixtures led to the conclusion that the mixture of poly(oxyethylene) and poly(methacrylic acid) shows limited miscibility[1] in a certain concentration range. Only small attention has been devoted to the problem of phase separation in complex-forming synthetic polymers. Haraguchi *et al.*[2,3] measured phase equilibria in a ternary mixture toluene/ω-aminopolystyrene/ω-sulfopoly(oxyethylene) where the complex formation occurs through functional end groups and manifests itself by an unusual splitted form of the coexistence curve (binodal). The results could be interpreted by the mean-field theory of the Flory–Huggins type. A theory of association in binary mixtures of hydrogen-bonded polymers was formulated by Tanaka *et al.* who were dealing with systems where the association leads to formation either of reversible diblock copolymers[4] or of reversible graft copolymers[5]. Assuming uniformity of both nominal polymer components, phase diagrams were obtained which, in addition to macroscopically heterogeneous regions, show regions of mesophases containing ordered microdomains of molecular dimensions. In an ample series of papers (see *e.g.* refs[6,7]), Painter, Coleman *et al.* dealt both experimentally and theoretically with mixtures of polymers bearing a proton-donor or proton-acceptor group on each of their monomer units.

All theories mentioned above were based on the concept of chemical equilibrium among species formed by association, constituting a mixture of the Flory–Huggins type. Non-specific interactions were treated by conventional interaction parameter χ and phase separation of the complex-forming mixture was brought about by a sufficiently high positive value of this quantity. But this parameter involves only a global description of the whole spectrum of nonspecific interactions. For example, in mixing of two components, the one containing polar group A and nonpolar P and the other polar group B and nonpolar Q, new binary contacts of the types A–B, A–Q, P–B and P–Q are formed at the expense of contacts A–A, P–P, A–P, B–B, Q–Q, B–Q. Of these contacts, only A–B, and possibly A–A or B–B are hydrogen bonds, which are active in complexation equilibria; the other interactions are incorporated into parameter χ. The fact that this parameter is not included in equations describing the association equilibrium originates in a simplifying assumption that the contribution of nonspecific interactions to the Gibbs energy of mixing is given by nominal concentrations of both initial components only and does not depend on the degree of their engagement in the association equilibria.

A more detailed analysis of the problem would evidently need a detailed description of the so-called nonspecific interactions. This is enabled by the use of the Barker–Guggenheim theory which treats all sorts of pair contacts in the same manner without regard to “chemical” or “physical” interactions. The basic concept of this theory is represented by a set of equations (for different pairs *K*, *L*) describing the “quasichemical” equilibrium of the physical process during which two heterocontacts between groups *K* and *L* are formed at the expense of homocontacts *K*–*K* and *L*–*L*. On the basis of this theory, we have derived equations for the second derivative of the Gibbs energy of mixing with respect to composition[8]. As it is known, the derivative acquires negative values under the conditions of the phase instability and is equal to zero along the spinodal line. In this paper, we will use the derived equations for characterization of conditions under which phase instability in a mixture of strongly complexing polymers appears (phase instability in a range of composition indicates phase separation in a wider range). The equations were derived under the assumption that polymer components 1 and 2 differ in nature of their polar groups, but have chemically similar nonpolar groups. Finally, we will treat some consequences which could follow from the different character of nonpolar groups in both components.

THEORETICAL

Basic Equations

Equations of quasichemical equilibria between contacts *K*–*L*, *K*–*K* and *L*–*L* are usually written in the form

$$N_{KL}^2 = 4\eta_{KL}^2 \, N_{KK} \, N_{LL} \quad , \qquad (1)$$

where N_{KL} is the number of contacts of the *K*–*L* type and parameter η_{KL} is a function of temperature and/or pressure only.

In our preceding communication[8], equations of quasichemical equilibria were advantageously expressed by means of quantities related to the unit number of interaction sites. That is why the site or surface fraction is defined again

$$\theta_j = \frac{zq_j \, n_j}{\sum_i zq_i \, n_i} = \frac{s_j \, \phi_j}{\sum_i s_i \, \phi_i} \quad , \qquad (2)$$

where n_j is the amount of the *j*-th component, *z* is the lattice coordination number, zq_j is the number of surface sites interacting with nearest neighbours, ϕ_j is the segment fraction, and s_j characterizes the surface-to-volume ratio

$$s_j = \frac{zq_j}{r_j} \quad , \tag{3}$$

where r_j is the number of segments in a molecule of j-th component.

Further we define

$$\Delta G_s = \frac{\Delta G}{\sum_i zq_i\, n_i} = \frac{\Delta G}{\sum_i s_i\, \phi_i} \quad , \tag{4}$$

where ΔG is Gibbs energy of mixing, and ΔG_N and ΔG_s are related to the unit quantities of segments and sites, respectively. The fractions of interaction sites (A and B are polar groups in molecules of components 1 and 2, respectively, R is nonpolar group in each component) are defined as

$$\psi_\mathrm{A} = \alpha_\mathrm{A}\, \theta_1 \quad , \tag{5a}$$

$$\psi_\mathrm{B} = \alpha_\mathrm{B}\, \theta_2 \quad , \tag{5b}$$

$$\psi_\mathrm{R} = (1 - \alpha_\mathrm{A})\, \theta_1 + (1 - \alpha_\mathrm{B})\, \theta_2 \quad , \tag{5c}$$

where α_A and α_B give the proportion (relative area) of contact sites of type A and B, respectively, in the corresponding molecule. It is obvious that $\psi_\mathrm{A} + \psi_\mathrm{B} + \psi_\mathrm{R} = 1$.

Consistently, we define

$$y_{KL} = \frac{(1 + \delta_{KL})\, n_{KL}}{z\,(q_1 n_1 + q_2 n_2)} \qquad (K; L \equiv \mathrm{A\ \ B\ \ R} \quad , \tag{6}$$

where n_{KL} is the number of contacts between groups of types K and L, δ_{KL} is the Kronecker delta, and further

$$y_K = y_{KK}^{1/2} \quad . \tag{7}$$

Equations of quasichemical equilibria between contacts of different type are then

$$y_{KL} = \eta_{KL}\, y_K\, y_L \quad , \tag{8}$$

where η_{KL} is a parameter independent of composition. There are also balance equations

$$y_{\mathrm{AA}} + y_{\mathrm{AB}} + y_{\mathrm{AR}} = \psi_{\mathrm{A}} \quad , \tag{9a}$$

$$y_{\mathrm{AB}} + y_{\mathrm{BB}} + y_{\mathrm{BR}} = \psi_{\mathrm{B}} \quad , \tag{9b}$$

$$y_{\mathrm{AR}} + y_{\mathrm{BR}} + y_{\mathrm{RR}} = \psi_{\mathrm{R}} \quad . \tag{9c}$$

By substitution from Eq. (*8*), we obtain the following set of three equations

$$y_{\mathrm{A}}^2 + \eta_{\mathrm{AB}}\, y_{\mathrm{A}}\, y_{\mathrm{B}} + \eta_{\mathrm{AR}}\, y_{\mathrm{A}}\, y_{\mathrm{R}} = \psi_{\mathrm{A}} \quad , \tag{10a}$$

$$\eta_{\mathrm{AB}}\, y_{\mathrm{A}}\, y_{\mathrm{B}} + y_{\mathrm{B}}^2 + \eta_{\mathrm{BR}}\, y_{\mathrm{B}}\, y_{\mathrm{R}} = \psi_{\mathrm{B}} \quad , \tag{10b}$$

$$\eta_{\mathrm{AR}}\, y_{\mathrm{A}}\, y_{\mathrm{R}} + \eta_{\mathrm{BR}}\, y_{\mathrm{B}}\, y_{\mathrm{R}} + y_{\mathrm{R}}^2 = \psi_{\mathrm{R}} \quad . \tag{10c}$$

The Barker–Guggenheim form of the Gibbs energy of mixing can be split into a combinatorial part (designed by superscript C) and an interactional part (designed by I)

$$\Delta G_{\mathrm{N}}^{\mathrm{C}} / \boldsymbol{R}T = \sum_i \left(\phi_\iota / r_i\right) \ln \phi_i + \frac{1}{2} \sum_i s_i \phi_i \ln \left(\frac{s_i}{\sum_j s_j \phi_j} \right) , \tag{11}$$

$$\Delta G_{\mathrm{N}}^{\mathrm{I}} / \boldsymbol{RT} = \sum_i s_i \phi_i \left[\sum_K \psi_K \ln \frac{y_K}{\psi_K} - \sum_i \theta_i \left(G_s^{\mathrm{I}} \right)_i^0 / \boldsymbol{RT} \right], \qquad (12)$$

where $(G_s^{\mathrm{I}})_i^0$ relates to neat component *i*. The second derivative of the Gibbs energy with respect to composition is then given by the relation

$$\partial^2 \Delta G_{\mathrm{N}} / \partial \phi_1^2 = \boldsymbol{RT} \left[1/\left(r_1 \phi_1\right) + 1/\left(r_2 \phi_2\right) - \frac{1/2\left(s_1 - s_2\right)^2}{\sum_j s_j \phi_j} - 2\chi_{\mathrm{sc}}^{\mathrm{I}} \right], \qquad (13)$$

where the interaction parameter $\chi_{\mathrm{sc}}^{\mathrm{I}}$ is defined as

$$\chi_{\mathrm{sc}}^{\mathrm{I}} = -\left(1/2\boldsymbol{RT}\right)\left(\partial^2 \Delta G_{\mathrm{N}}^{\mathrm{I}} / \partial \phi_1^2\right) \qquad (14)$$

and is given by the equation

$$\chi_{\mathrm{sc}}^{\mathrm{I}} = -\frac{\langle s \rangle}{2\boldsymbol{RT}} \left(\frac{\partial^2 \Delta G_s^{\mathrm{I}}}{\partial \theta_1^2} \right), \qquad (15)$$

where

$$\langle s \rangle = \frac{\left(s_1 s_2\right)^2}{\left(\sum_j s_j \phi_j\right)^3}. \qquad (16)$$

In our preceding communication, equation for calculation of this parameter was given in the form (see Eq. (*75*) in ref.[8])

$$\chi_{\mathrm{sc}}^{\mathrm{I}} = -\frac{\langle s \rangle}{2} \left[\frac{(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})^2 D_{\mathrm{AB}} + \alpha_{\mathrm{B}}^2 D_{\mathrm{AR}} + \alpha_{\mathrm{A}}^2 D_{\mathrm{BR}}}{D_{\mathrm{AB}} D_{\mathrm{AR}} + D_{\mathrm{AB}} D_{\mathrm{BR}} + D_{\mathrm{AR}} D_{\mathrm{BR}}} - \frac{\alpha_{\mathrm{A}} \theta_2 + \alpha_{\mathrm{B}} \theta_1 - \alpha_{\mathrm{A}} \alpha_{\mathrm{B}}}{\theta_1 \theta_2 \psi_{\mathrm{R}}} \right] \qquad (17)$$

where

$$D_{KL} = 2 \psi_K \psi_L - y_{KL} \qquad (K; L \equiv \mathrm{A\ B\ R} \qquad (18)$$

and y_{KL} is given by Eq. (*8*). The values of y_K and y_L for a given composition need to be calculated by numerical solution of the set of equations (*10a*), (*10b*) and (*10c*).

Approximate Equations for Very Strong Interactions

Now we introduce approximate equations valid in the case when polar groups A and B strongly attract each other (large η_{AB}) while polar (A, B) and nonpolar (R) groups strongly repel each other (small η_{AR} and η_{BR}). An inspection of these equations enables qualitative conclusions about the influence of individual factors on the value of χ^{I}_{sc} and thus of the second derivative of the Gibbs energy.

1. Suppose first that groups A are in excess over groups B ($\psi_A > \psi_B$). The following hypothetical case

$$\eta_{AR} = 0 \qquad \eta_{BR} = 0 \qquad 1/\eta_{AB} = 0 \tag{19}$$

can be described by simple analytical expressions. The frequency of A–B contacts is given by the content of the minor group and hence

$$y^{\infty}_{AB} = \psi_B \quad , \tag{20}$$

where the superscript ∞ denotes the system specified by Eq. (*19*).

It is also valid that

$$y^{\infty}_{AR} = 0 \quad , \tag{21}$$

$$y^{\infty}_{BR} = 0 \quad . \tag{22}$$

After substitution into Eqs (*9a*), (*9b*) and (*9c*) and their solution using Eq. (*7*), we obtain

$$y^{\infty}_{A} = \sqrt{\psi_A - \psi_B} \quad , \tag{23a}$$

$$y_B^\infty = 0 \quad , \tag{23b}$$

$$y_R^\infty = \sqrt{\psi_R} \quad . \tag{23c}$$

Using expressions (*18*) and after substitution into Eq. (*17*) and rearrangement, we obtain

$$(\chi_{sc}^I)^\infty = -\frac{\langle s\rangle}{2} \frac{2\psi_R\,(\alpha_A^2\,\psi_B + \alpha_B^2\,\psi_A) - (\alpha_A - \alpha_B)^2\,\psi_A\,(1 - 2\psi_B)}{2\,(\psi_A - \psi_B)\,\psi_A\,\psi_B} \quad . \tag{24}$$

If ψ_B approaches ψ_A from the bottom, χ_{sc}^I decreases to infinitely negative values. On the other hand, for small ψ_B, when $\psi_A \to \alpha_A$, χ_{sc}^I can, at sufficiently large difference $(\alpha_A - \alpha_B)$, acquire positive values so that the mixture may show phase instability in this region.

If A is the minor polar group ($\psi_A < \psi_B$), the equations given above are valid after exchange of subscripts A and B.

2. If parameters η_{AR}, η_{BR} and $1/\eta_{AB}$ acquire nonzero, but small values, we can calculate correction terms for Eq. (*24*). By an approximate solution of equations for contact balances, we obtain in the case of $\psi_A > \psi_B$

$$y_{AR} = \eta_{AR}\sqrt{(\psi_A - \psi_B)\,\psi_R} - \left(\frac{\eta_{AR}^2}{2}\right)(1 - 2\psi_B) \quad , \tag{25a}$$

$$y_{BR} = (\eta_{BR} / \eta_{AB})\psi_B\sqrt{\psi_R / (\psi_A - \psi_B)} \quad , \tag{25b}$$

$$y_{AB} = \psi_B - y_{BR} - \eta_{AB}^{-2}\psi_B^2 / (\psi_A - \psi_B)\,. \tag{25c}$$

Finally, using Eqs (*16*) and (*17*), we have

$$\chi_{sc}^I = (\chi_{sc}^I)^\infty + \frac{\langle s\rangle}{2}\left[\eta_{AR}Q_{AR} + (\eta_{BR} / \eta_{AB})Q_{BR} + \eta_{AB}^{-2}Q_{AB}\right] , \tag{26}$$

where

$$Q_{AR} = -\frac{(\alpha_A + \alpha_B - 2\alpha_A\alpha_B)^2}{4(\psi_A - \psi_B)^{3/2}\psi_R^{3/2}} \quad , \tag{27a}$$

$$Q_{BR} = \frac{(\alpha_A + \alpha_B - 2\alpha_A\alpha_B)\left[4\alpha_A\alpha_B\psi_R - (\alpha_A + \alpha_B - 2\alpha_A\alpha_B)\psi_B\right]}{4(\psi_A - \psi_B)^{5/2}\psi_R^{3/2}} \, , \tag{27b}$$

$$Q_{AB} = \frac{\alpha_A^2\,\alpha_B^2}{(\psi_A - \psi_B)^3} \quad . \tag{27c}$$

The frequency of contacts A–R and B–R is no longer zero; this fact must lead to a lowering of the value of the interaction parameter, and thus we would expect a negative sign with Q_{AR} and Q_{BR}. This is unequivocally the case with Q_{AR} because, owing to an excess of groups A, the formation of A–R contacts does not disfavour the frequency of A–B contacts. On the other hand, at high values of η_{AB}, almost all groups B are involved in contacts A–B, and thus contacts B–R can form only at the expense of A–B contacts, as is obvious from the second term on the right-hand side of Eq. (*25c*). The Q_{BR} coefficient then consists of two terms; the term corresponding to the formation of B–R contacts is negative (analogously to Q_{AR}), but it prevails only if α_B is sufficiently larger than α_A and the concentration of component 2 is sufficiently large. Otherwise, the term expressing competition of B–R and A–B contacts prevails and Q_{BR} has positive sign. The positive sign of the Q_{AB} coefficient reflects an increase in χ_{sc}^{I} with decreasing η_{AB}. When constants η_{AR}, η_{BR} and $1/\eta_{AB}$ are small quantities of the same order of magnitude x, the term $\eta_{AR}Q_{AR}$ in Eq. (*27b*) is the only term of the order x, the other two terms being of the order x^2. The next possible term of the same order, containing η_{AR}^2, is zero. The value of correction terms in Eq. (*27b*) will obviously grow rather fast when the composition approaches a value at which the concentrations of A and B groups are equal ($\psi_A = \psi_B$). In this case, even terms of higher orders, not discussed here, are operative.

3. A special analysis is required in the case when the concentration of A groups is equal to that of B groups (“point of equivalence”)

$$\psi_A = \psi_B = \psi \quad . \tag{28}$$

This situation becomes operative at θ_1 given by the relation

$$\theta_1 = \alpha_B / (\alpha_A + \alpha_B) , \tag{29}$$

so that

$$\psi = \alpha_A \alpha_B / (\alpha_A + \alpha_B) . \tag{30}$$

For such composition, in the hypothetical case where $\eta_{AR} = 0$ and $\eta_{BR} = 0$, it is possible to obtain an analytical solution for any value of η_{AB}. By solving the equation set (*9a*), (*9b*) and (*9c*) for this case, we obtain

$$y_A = y_B = \sqrt{\frac{\psi}{1 + \eta_{AB}}} , \tag{31a}$$

$$y_{AB} = \eta_{AB} \psi / (1 + \eta_{AB}) , \tag{31b}$$

$$y_R = \sqrt{1 - 2\psi} , \tag{31c}$$

and, after substituting into Eqs (*16*) and (*17*), we have

$$\chi^{I}_{sc} = -\frac{\langle s \rangle}{8\psi} \Big[(\alpha_A + \alpha_B)^2 (\eta_{AB} - 1) - (\alpha_A - \alpha_B)^2 / (1 - 2\psi) \Big] . \tag{32}$$

If η_{AB} attains high values, we can simplify the equations given by neglecting terms which do not contain this constant; we obtain, *e.g.*, $y_{AB} \approx \psi$ (for instance, the concentration of complex is equal to the concentration of groups A or B).

4. Let us consider again a system, in which parameters η_{AR}, η_{BR} and $1/\eta_{AB}$ attain nonzero, but small values. Solving equations (*9a*) and (*9b*), we obtain

$$y_{AB} \approx \psi - \frac{1}{2}(y_{AR} + y_{BR}) - \frac{1}{2}\sqrt{(y_{AR} - y_{BR})^2 + 4\psi^2 / \eta^2_{AB}} ; \tag{33}$$

here y_{AR} and y_{BR} can be approximately expressed using Eqs (*31a*) and (*31b*) as

$$y_{K\mathrm{R}} = \eta_{K\mathrm{R}}\eta_{\mathrm{AB}}^{-1/2}\psi^{1/2}(1-2\psi)^{1/2} \qquad K \equiv \mathrm{A;B}\,. \tag{34}$$

After substitution into Eq. (*75*) from ref.[8] and rearrangement, we obtain

$$\chi_{\mathrm{sc}}^{\mathrm{I}} = -\frac{\langle s\rangle}{2}\left[\frac{(\alpha_{\mathrm{A}}+\alpha_{\mathrm{B}})^2}{y_{\mathrm{AR}}+y_{\mathrm{BR}}+2\sqrt{(y_{\mathrm{AR}}-y_{\mathrm{BR}})^2+4\psi^2/\eta_{\mathrm{AB}}^2}} - \frac{\alpha_{\mathrm{A}}^2(1-\alpha_{\mathrm{B}})+\alpha_{\mathrm{B}}^2(1-\alpha_{\mathrm{A}})}{\psi\psi_{\mathrm{R}}}\right]. \tag{35}$$

The second term in square brackets is the limit of the first term for hypothetical state of random mixing; in the case of large η_{AB} and small η_{AR}, η_{BR}, it can be neglected in first approximation. If constant η_{AB} grows to infinity, quantities y_{AR} and y_{BR} decrease to zero even at nonzero η_{AR}, η_{BR}, and $\chi_{\mathrm{sc}}^{\mathrm{I}}$ parameter diverges to infinitely negative values. On the other hand, if η_{AB}^{-1} and ψ are small quantities of the same order of magnitude as η_{AR} and η_{BR}, the frequency of the "thermodynamically high-quality" A–B contacts decreases in favour of the formation of lower-quality A–R and B–R contacts. Thus the absolute value of $\chi_{\mathrm{sc}}^{\mathrm{I}}$ will be strongly reduced by increasing η_{AR} and/or η_{BR}.

Course of Spinodal in the Temperature versus Composition Diagram

An interesting conclusion concerning the form of the spinodal curve in the phase diagram temperature-composition follows from equations derived for systems with small values of $1/\eta_{\mathrm{AB}}$, η_{AR} and η_{BR}. We start from expressions for the second derivative of the Gibbs energy with respect to composition and denote

$$Z = \left[\partial^2(\Delta G_{\mathrm{N}}/\boldsymbol{R}T)/\partial\phi_1^2\right]_T\,. \tag{36}$$

The equation $Z = 0$ must be fulfilled in every point of the spinodal curve and the change in composition with temperature is thus given by the relation

$$\left(\frac{\partial\theta_1}{\partial T}\right) = -\frac{\left(\partial Z / \partial T\right)_{\theta_1}}{\left(\partial Z / \partial\theta_1\right)_T} \;. \qquad (37)$$

It follows from Eqs (*13*) and (*26*) that

$$Z = Z^{\mathrm{c}} - 2\left(\chi^{\mathrm{I}}_{\mathrm{sc}}\right)_{\infty} - \langle s\rangle\left[\eta_{\mathrm{AR}}Q_{\mathrm{AR}} + (\eta_{\mathrm{BR}} / \eta_{\mathrm{AB}})Q_{\mathrm{BR}} + \eta^{-2}_{\mathrm{AB}}Q_{\mathrm{AB}}\right] , \qquad (38)$$

where Z^{c} is a combinatorial term and the second term on the right-hand side is given by Eq. (*24*). For our system, both these expressions are dominant terms on the right-hand side of Eq. (*38*) and are independent of temperature. The change of Z with temperature is then given by the equation

$$\frac{\partial Z}{\partial T} = \frac{\langle s\rangle}{\boldsymbol{R}T^2}\left[-h_{\mathrm{AR}}\eta_{\mathrm{AR}}Q_{\mathrm{AR}} + 2h_{\mathrm{AB}}\eta^{-2}_{\mathrm{AB}}Q_{\mathrm{AB}} + \left(h_{\mathrm{AB}} - h_{\mathrm{BR}}\right)\left(\eta_{\mathrm{BR}} / \eta_{\mathrm{AB}}\right)Q_{\mathrm{BR}}\right] , \qquad (39)$$

where h_{KL} is the change of enthalpy associated with formation of one KL-type contact. It is obvious that for small values of η_{AR}, η_{BR} and η^{-1}_{AB}, this derivative is negligible. On the other hand, by differentiation of Eq. (*38*) with respect to θ_1, the first two terms on the right-hand side of the equation do not vanish. Then the denominator on the right-hand side of Eq. (*37*) usually attains reasonable values, so that the spinodal composition is almost independent of temperature and both branches of the spinodal curve are almost vertical straight lines. The only exception is in the vicinity of the critical point where

$$\left(\partial Z/\partial\theta_1\right)_T = 0 \;. \qquad (40)$$

The slope of the spinodal is thus finite in the vicinity of the critical point, and it is zero in the critical point itself.

Effect of Difference in Nonpolar Groups

The phase separation in systems so far studied with complexation of components was conditioned by inequality of relative areas of polar groups ($\alpha_{\mathrm{A}} \neq \alpha_{\mathrm{B}}$). It follows from Eq. (*13*) that the phase instability can be also brought about by a sufficiently great difference in molecular surface-

-to-volume ratios, s_1–s_2. Finally, it is necessary to take into account that our calculations were made under the assumption that nonpolar groups R are of the same nature in both components. Let us admit that they are different and denote polar groups in components 1 and 2 as P and Q, respectively. An exact solution would result in a much more complicated expression than that included in the right-hand side of Eq. (*16*); therefore, we assume that

$$\eta_{AP} = \eta_{AQ} \ , \tag{41a}$$

$$\eta_{BP} = \eta_{BQ} \ , \tag{41b}$$

but

$$\eta_{PQ} = 1 - \delta\eta \ , \tag{42}$$

where $\delta\eta$ is sufficiently low to permit a perturbation procedure of solution. We obtain thus the correction for parameter χ^{I}_{sc}

$$\delta\chi^{I}_{sc} = -(\delta\eta/2)\frac{\partial^2 (y_P y_Q)}{\partial\theta_1^2} \tag{43}$$

which is to be added to the original value of χ^{I}_{sc}. The correction can be expressed simply in some limit cases only; for instance, if all four parameters of interactions of polar with nonpolar groups (*i.e.*, η_{AP}, η_{AQ}, η_{BP}, η_{BQ}) are zero, then we have

$$\delta\chi^{I}_{sc} = \frac{(1-\alpha_A)^2\ (1-\alpha_B)^2}{[(1-\alpha_A)\theta_1 + (1-\alpha_B)\theta_2]^3}\delta\eta \ . \tag{44}$$

Accordingly, if $\eta_{PQ} < 1$, $\delta\eta$ is positive and the contribution of this term to the value of the second derivative of *G* is negative. Thus, for sufficiently great $\delta\eta$, phase instability may arise even for $\alpha_A = \alpha_B$ as a consequence of unfavourable P–Q interaction, as was assumed by authors who solved this problem by the method of association equilibria[2–5].

Let us discuss the symmetry of curves in Fig. 1, where $\alpha_A = \alpha_B$. The negative contribution of the P–Q interaction will be concentration-independent, so that the curve for the second derivative of the Gibbs energy is shifted without deformation toward lower values and two regions of phase instability are formed on both sides of the vertical symmetry axis ($\phi_2 = 1/2$). Accordingly, in the phase diagram $T(\phi_2)$, two symmetrically placed spinodal curves appear, which in general case may, but not necessarily, mean an occurrence of two symmetrically placed binodals (*cf.* refs[2–5]).

DISCUSSION

Using several graphs, we will show an influence of different factors on the sign and value of the second derivative of the Gibbs energy with respect to composition. First, let us show the unimportance of the athermal contribution in Eq. (*13*). The first two terms on its right-hand side correspond to the Flory–Huggins equation and, for long chains (r of the order 10^3 and higher), they have negligible values with the exception of narrow intervals at the margins of the graph (for $\phi_1 \to 0$ and $\phi_2 \to 0$). The third term is negative and follows from the difference in molecular surface-to-volume ratios of both components. In our graphs, this term does not play any role be-

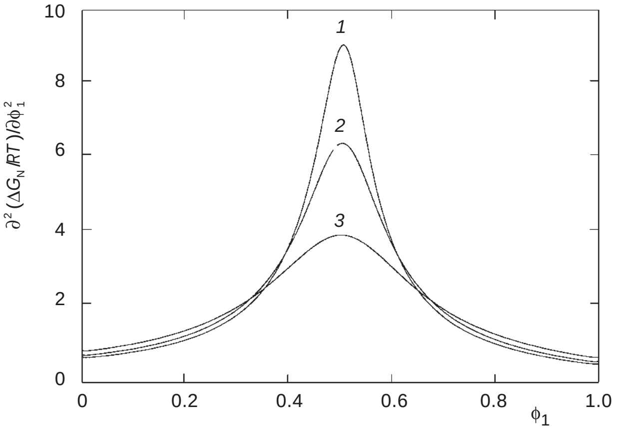

FIG. 1
The second derivative of the Gibbs energy of mixing with respect to composition in its compositional dependence: the influence of η_{BR} parameter if $\eta_{AR} = \eta_{BR}$. $\alpha_A = \alpha_B = 0.25$; $\eta_{AB} = 10$. Curves: *1* $\eta_{AR} = 0$, *2* $\eta_{AR} = 0.1$, *3* $\eta_{AR} = 0.3$

cause we have chosen $s_1 = s_2$ and thus also $\theta_1 = \phi_1$. It is then only the interaction term which becomes operative in the whole range of composition:

$$\partial^2 \Delta G_{\mathrm{N}} \,/\, \partial\varphi_1^2 \cong -2\boldsymbol{R}T\chi_{\mathrm{sc}}^{\mathrm{I}} \ . \tag{45}$$

In Fig. 1, the system with a great affinity to polymer–polymer association (η_{AB} = 10) is shown for different values of the interaction parameter η_{AR}, which are the same also for the parameter η_{BR}. We observe dramatic differences between the second derivative of G in the middle (the maximum corresponds to condition $\psi_A = \psi_B$) and in the border regions of composition, but the second derivative does not sink into negative values and the system is phase-stable in the whole range of composition. The order of curves in the middle region is opposite to that at the borders. For instance, at the right border, an influence of thermodynamic quality of A–R contacts becomes operative, the Q_{AR} term in Eq. (*26*) prevails over the Q_{BR} term and the second derivative increases with η_{AR}. On the other hand, competition of contacts A–R and/or B–R with A–B contacts prevails in the middle region. This can be seen more clearly in Fig. 2 where the influence of A–R contacts is eliminated and the curves only differ in the η_{BR} parameter. At an excess of groups B (small ϕ_1), the quality of B–R contacts plays a dominant role,

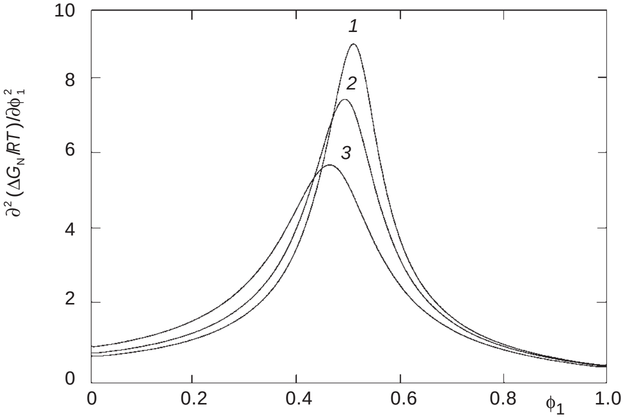

FIG. 2

The second derivative of the Gibbs energy of mixing with respect to composition in its compositional dependence: the influence of η_{BR} parameter if $\eta_{AR} = 0$. $\alpha_A = \alpha_B = 0.25$; $\eta_{AB} = 10$. Curves: *1* $\eta_{BR} = 0$, *2* $\eta_{BR} = 0.1$, *3* $\eta_{BR} = 0.3$

while at their lack ($\phi_1 > 1/2$), the order of curves is governed by an unfavorable influence of the competition of B–R and A–B contacts.

The influence of increasing difference in the relative area of polar groups is noticeable in Fig. 3. If we let increase α_A and, to the same extent, decrease α_B, then, according to Eq. (*29*), the value of θ_1, at which the equivalence of surface sites A and B is reached, decreases and so does the value of ψ. Accordingly, the maxima of curves are shifted to the left (somewhat more quickly than the mentioned value of θ_1) and, according to Eqs (*34*) and (*35*), the value of $(-\chi^{\mathrm{I}}_{\mathrm{sc}})$ increases with decreasing ψ, the value of the second derivative in its maximum also increasing. On the left-hand side, we observe an increase in the second derivative with increasing difference ($\alpha_A - \alpha_B$). On the contrary, a decrease at the right-hand side is evident; at sufficiently great difference in α's (curve *4*), the sought-after region of phase instability even appears. The phase separation of blends of two strongly interacting polymers can thus appear if the content of polar group A along the chain differs significantly from that of group B. In this manner (in sufficient distance from the equivalence composition), "unfavorable" contacts between polar groups in excess (in Fig. 3, groups A) and nonpolar groups are forced. The mixture responds by forming another phase where the excessive molecules of component 1 concentrate.

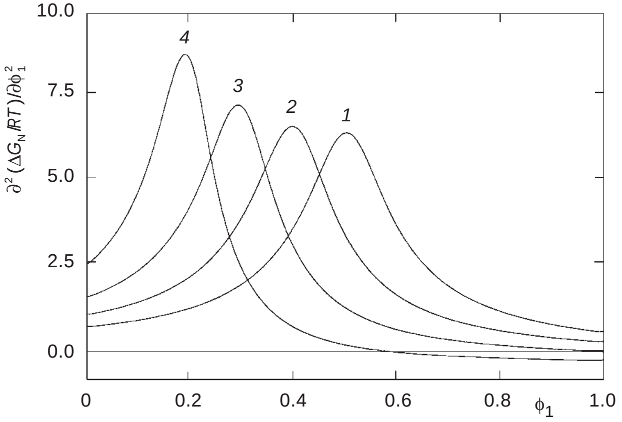

FIG. 3
The second derivative of the Gibbs energy of mixing with respect to composition in its compositional dependence: the influence of the difference $\alpha_A - \alpha_B$. $\alpha_A + \alpha_B = 0.5$; $\eta_{AB} = 10$, $\eta_{AR} = \eta_{BR} = 0.1$. Curves: *1* $\Delta\alpha = 0$, *2* $\Delta\alpha = 0.1$, *3* $\Delta\alpha = 0.2$, *4* $\Delta\alpha = 0.3$ ($\Delta\alpha = \alpha_A - \alpha_B$)

In Fig. 4, a similar system with $\alpha_A > \alpha_B$ is studied in dependence on decreasing strength of A–B interactions. As it is seen, the maximum of the second derivative decreases and shifts left. In the same direction, the region of negative values becomes wider and the minimum deepens. In Fig. 4, we put

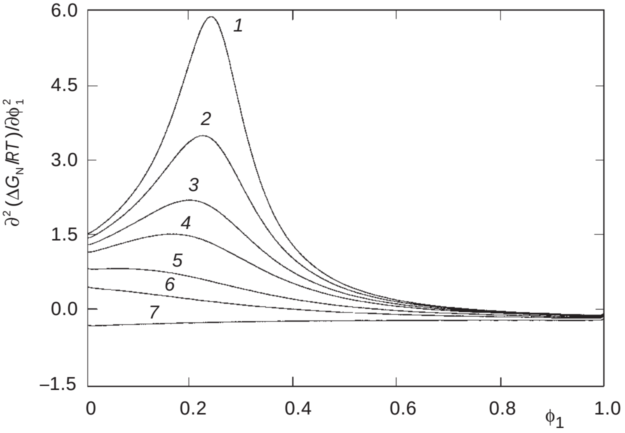

FIG. 4

The second derivative of the Gibbs energy of mixing with respect to composition in its compositional dependence: the influence of η_{AB} parameter. $\alpha_A = 0.3$, $\alpha_B = 0.1$; $\eta_{AR} = \eta_{BR} = 0.1$. Curves: *1* $\eta_{AB} = 10$, *2* $\eta_{AB} = 6$, *3* $\eta_{AB} = 4$, *4* $\eta_{AB} = 3$, *5* $\eta_{AB} = 2$, *6* $\eta_{AB} = 1.5$, *7* $\eta_{AB} = 1$

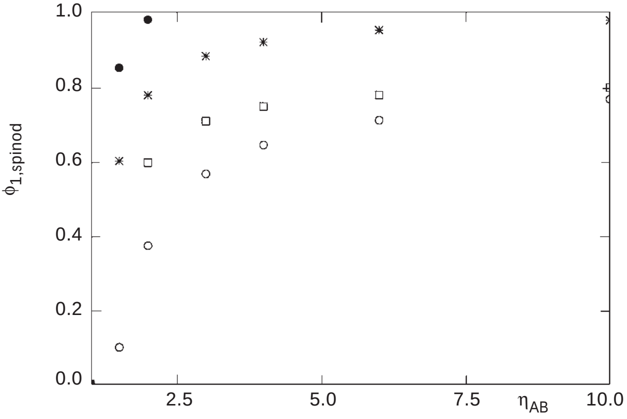

FIG. 5

The position, $\phi_{1,spinod}$, of the left margin of the phase instability region in the dependence on η_{AB} for different values of η_{AR} and η_{BR} parameters (the right margin lies in close vicinity of $\phi_1 = 1$). $\alpha_A = 0.3$, $\alpha_B = 0.1$. Curves: ○ $\eta_{AR} = 0.1$, $\eta_{BR} = 0.3$; □ $\eta_{AR} = \eta_{BR} = 0.1$; ∗ $\eta_{AR} = 0.2$, $\eta_{BR} = 0.1$; ● $\eta_{AR} = 0.3$, $\eta_{BR} = 0.1$

$\eta_{AR} = \eta_{BR}$. An inequality of these constants may influence the region of thermodynamic instability in different directions, as it is shown in Fig. 5. There, the dependence of composition corresponding to the left-hand spinodal point *versus* the η_{AB} constant is plotted (the right-hand spinodal point lies near to $\theta_1 = 1$). It is obvious that the composition range of instability widens if the polar group with greater α has smaller tendency to enter into contacts with the nonpolar group R (*e.g.*, when $\alpha_A > \alpha_B$, $\eta_{AR} < \eta_{BR}$); in the opposite case, the region becomes smaller and it may not appear at all (*e.g.*, for $\eta_{AR} = 0.3$, $\eta_{BR} = 0.1$, if $\eta_{AB} > 2$).

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