PHASE STABILITY OF HYDROGEN-BONDED POLYMER MIXTURES: APPLICATION OF THE QUASICHEMICAL THEORY

Julius POUCHLY, Antonin ZIVNY and Antonin SIKORA

Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

Received May 3, 1995
Accepted June 22, 1995

Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

Expressions for the second derivative of Gibbs energy of mixing with respect to composition and/or the corresponding Flory–Huggins interaction parameter are derived using the Barker–Guggenheim quasichemical theory. The calculation is performed first for a system of compounds with a homogeneous molecular surface, then for a binary mixture of molecules the surface of which consists of various kinds of contact sites. The result is expressed in terms of "indexes of nonrandomness", the factors which characterize deviations of individual types of contact pairs from random mixing at a given composition. Main attention is paid to a mixture of substances, each of which contains a different type of polar groups and a nonpolar residue which is similar for both components. Translucent relations are obtained in two limit cases, namely for small deviations from random mixing and for small attraction between polar and nonpolar groups. The effect of the relative size of the polar groups and of the affinity to formation of various heterocontacts is illustrated using the limit relations derived, as well as by means of model calculations.

The probability that two polymers can coexist in a homogeneous phase is very limited. This is due to very small combinatorial entropy of mixing found in a system of long chain molecules, displaying low freedom of translational motion. Thus the small tendency to mixing is easily overcome by a small positive enthalpy change.

The miscibility of polymers can be enhanced by introducing polar groups into the macromolecules in such a way that hydrogen bonding (or another type of specific interaction) occurs between the two components of the mixture. Part of the theories describing this effect treat formation of hydrogen bonds as a chemical process, the contribution of which is added to the energy term originating from physical (van der Waals) interactions. A system with hydrogen bonds can be handled as a multicomponent mixture of association species, which are in chemical equilibrium. Indeed, if proton acceptor and proton donor groups are present simultaneously in a molecule, chainlike or branched complex structures or even association networks originate. This is true mainly in polymers and polymer mixtures (Coleman and Painter[1–3]). Enumeration and weighting of all possible structures is then a difficult combinatorial problem. Therefore Veytsman[4] proposes to disregard individual structures and to consider the global equilibrium between hydrogen-bonded group pairs and "unreacted" proton donor and acceptor groups. This approach is more transparent at the cost of losing the possibility of expressing correlation between the hydrogen-bonding affinities of two groups belonging to the same molecule (or to the same complex). Panayiotou and Sanchez[5] elaborated Veytsman's idea in developing their LFAS (lattice-fluid associated solutions) model, in which the existence of vacancies is also taken into account and thus, besides specific interaction, the free-volume effects are included.

In presence of polar groups, interactions (e.g. dipole–dipole) also occur which may exhibit a lower energetic effect than hydrogen bonding but a higher one than the dispersive forces. The separation of the "chemical" from the "physical" contribution to the Gibbs energy of mixing is then questionable. This problem does not appear in the Barker–Guggenheim theory[6] in which all kinds of pair contacts are treated in the same way irrespective of their Gibbs energy: A quasichemical equilibrium is supposed to exist between like–unlike contacts (heterocontacts) and corresponding like–like contacts (homocontacts) for each pair of different molecular contact sites. In accord with a commonly respected view, the interaction effects are expressed in terms of surface concentrations of molecules and/or their interaction sites. Thus the quasichemical theory is a good alternative to hydrogen-bonding theories in studying systems with strongly interacting groups. It has been used, e.g., by Kehiaian[7] as a basis for construction of his system of group contributions for small molecule mixtures. Barlow and Paul[8] used a similar procedure for prediction of miscibility of polymer pairs, based on enthalpy of mixing of model compounds.

Our aim is to use the quasichemical theory to the discussion of the influence exerted by polar groups (their relative surface extent and their interaction "strength") on the phase stability of a mixture of polymers. A convenient criterion of stability is found in the second derivative of Gibbs energy with respect to composition. This quantity vanishes at the spinodal; besides, it governs the extent of concentration fluctuations and the intensity of radiation scattering. Therefore we focused on the Flory–Huggins interaction parameter, χ_{sc}, redefined on the basis of the second derivative mentioned[9,10]. In some limit cases only, χ_{sc} can be expressed directly in terms of the parameters of the Barker theory (i.e., relative size of interacting groups and quasichemical equilibrium constants). Generally, the Flory–Huggins parameter is expressed by means of "indexes of nonrandomness" of various contact pairs, which are concentration-dependent and indicate the statistical preference of a given type of pair, compared to the case of random mixing. Although the Barker–Guggenheim theory is approximate only, we believe that the equations derived may be used for a discussion of semiquantitative relations between χ_{sc}, the nonrandomness indexes and the Barker theory parameters.

GENERAL RELATIONS

The Flory–Huggins expression for the Gibbs energy of mixing can be decomposed into the athermal or combinatorial part (A) and the residual part (R)

$$\Delta G_N = \Delta G_N^A + \Delta G_N^R \tag{1}$$

$$\Delta G_N^A = RT[(\phi_1/r_1) \ln \phi_1 + (\phi_2/r_2) \ln \phi_2] \tag{2}$$

$$\Delta G_N^R = RT\chi\phi_1\phi_2 \quad , \tag{3}$$

where ΔG_N and the interaction parameter χ are related to one mole of segments, r_1 and r_2 give the numbers of segments in molecules of components 1 and 2, and ϕ_1, ϕ_2 are the segment or volume fractions. The second derivative of Gibbs energy with respect to composition is expressed according to Flory and Huggins as

$$\frac{\partial^2 \Delta G_N}{\partial \phi_1^2} = RT\left(\frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} - 2\chi_{sc}\right) . \tag{4}$$

The sign of this quantity is decisive for the thermodynamic stability of a binary mixture. The right-hand side of Eq. (*4*) represents the well-known de Gennes expression of the static structure factor in the limit of zero scattering angle. The parameter χ_{sc} is defined by

$$RT\chi_{sc} = -(1/2)(\partial^2 \Delta G_N^R/\partial \phi_1^2) \tag{5}$$

and is identical with χ in Eq. (*3*) only if it is independent of the composition ϕ_1. The relation of the two interaction parameters[9,10] is described by

$$\chi_{sc} = \chi + (\phi_1 - \phi_2)(\partial\chi/\partial\phi_1) - (1/2)\phi_1\phi_2(\partial^2\chi/\partial\phi_1^2) \quad . \tag{6}$$

Our attention will be paid to χ_{sc}, as it is relevant in the discussion of phase stability and in the analysis of light scattering.

In the Barker theory[6] the Gibbs energy of mixing is a sum of the combinatorial term in Miller–Guggenheim form and an interaction contribution ΔG^{I} resulting from nonrandom mixing. The Barker relation can then be expressed as

$$\Delta G_{\mathrm{N}} = \Delta G_{\mathrm{N}}^{\mathrm{A}} + \Delta G_{\mathrm{N}}^{\mathrm{A}'} + \Delta G_{\mathrm{N}}^{\mathrm{I}} \ . \qquad (7)$$

Here $\Delta G_{\mathrm{N}}^{\mathrm{A}}$ is given by Eq. (*2*), $\Delta G_{\mathrm{N}}^{\mathrm{A}'}$ is a complement to combinatorial term

$$\Delta G_{\mathrm{N}}^{\mathrm{A}'} = (RT/2) \sum_i s_i\phi_i \ln (s_i / \sum_j s_j\phi_j) \ , \qquad (8)$$

where the subscripts *i, j* relate to the components 1 or 2; s_i is indicative of the molecular surface-to-volume ratio of the component *i*:

$$s_i = zq_i/r_i \ , \qquad (9)$$

zq_i gives the number of contact interaction sites on the molecular surface of *i*. The complementary term, Eq. (*8*), vanishes if $s_1 = s_2$.

Our goal is the double differentiation of Eq. (*7*) with respect to composition. Due to the general favour enjoyed by the Flory–Huggins equation it will be desirable to present the results in form of a parameter like χ_{sc}, as a function of composition and of the Barker parameters. Therefore we define the parameters χ^{I}

$$\chi^{\mathrm{I}} = \Delta G_{\mathrm{N}}^{\mathrm{I}}/(RT\phi_1\phi_2) \qquad (10)$$

and $\chi_{\mathrm{sc}}^{\mathrm{I}}$

$$\chi_{\mathrm{sc}}^{\mathrm{I}} = -(1/2RT)(\partial^2\Delta G_{\mathrm{N}}^{\mathrm{I}}/\partial\phi_1^2) \ . \qquad (11)$$

A complete Gibbs energy expression is then

$$\partial^2\Delta G_{\mathrm{N}}/\partial\phi_1^2 = RT[1/(r_1\phi_1) + 1/(r_2\phi_2) - (1/2)(s_1 - s_2)^2/(\sum_i s_i\phi_i) - 2\chi_{\mathrm{sc}}^{\mathrm{I}}] \ . \qquad (12)$$

The third term on the right-hand side arises by double differentiation of Eq. (*8*). From Eq. (*12*) we see that if the chains are very long and $s_1 = s_2$, then the phase stability exists at negative values of $\chi^{\mathrm{I}}_{\mathrm{sc}}$ only.

The Barker interaction term is handled more easily, if related to a unit amount of contact interaction sites. We introduce

$$\Delta G^{\mathrm{I}}_s = \Delta G^{\mathrm{I}}_{\mathrm{N}} / \sum_i s_i \phi_i \quad . \tag{13}$$

The sum $\sum_i s_i \phi_i$ gives the average amount of interaction sites per one segment in the mixture. As will be shown later, the dependence of ΔG^{I}_s on composition can be unambiguously expressed using the interaction site fraction (or surface fraction), defined by

$$\theta_1 = \frac{s_1 \phi_1}{\sum_i s_i \phi_i} \quad . \tag{14}$$

From Eq. (*13*) we can obtain

$$\partial^2 \Delta G^{\mathrm{I}}_{\mathrm{N}} / \partial \phi_1^2 = \langle s \rangle \, . \, (\partial^2 \Delta G^{\mathrm{I}}_s / \partial \theta_1^2) \quad , \tag{15}$$

where

$$\langle s \rangle = \frac{s_1^2 s_2^2}{(\sum_i s_i \phi_i)^3} \quad . \tag{16}$$

The latter expression is a function of composition unless $s_1 = s_2 = \langle s \rangle$ holds.

Therefore $\chi^{\mathrm{I}}_{\mathrm{sc}}$ will be calculated using Eq. (*17*) rather than the definition relation (Eq. (*11*)):

$$\chi^{\mathrm{I}}_{\mathrm{sc}} = -\frac{\langle s \rangle}{2RT} \left(\frac{\partial^2 \Delta G^{\mathrm{I}}_s}{\partial^2 \theta_1^2} \right) \quad . \tag{17}$$

Mixture of Components with a Homogeneous Molecular Surface (Guggenheim Model)

First, let us turn our attention to a system of molecules, of which each contains one type of contact interaction sites only. The subscript of a given surface group will thus be identical with that of the respective component (1 or 2). We give full treatment of this simple case in order to illustrate our way of handling more complicated systems.

If a molecule of component i can enter into zq_i binary contacts with other molecules then the following balance equations apply for a binary mixture

$$2n_{11} + n_{12} = zq_1n_1 \tag{18a}$$

$$n_{12} + 2n_{22} = zq_2n_2 \ , \tag{18b}$$

where n_{ij}(in moles) stands for the amount of contacts between molecules i and j. According to the Guggenheim quasichemical equilibrium theory the frequencies of different types of contacts follow the relation

$$n_{12}^2 = 4\eta^2 n_{11}n_{22} \ , \tag{19}$$

where η is constant at given temperature. The expression for the non-athermal part of the Gibbs energy of mixing is

$$\Delta G^{\mathrm{I}}/RT = (z/2)[q_1n_1 \ln (n_{11}/n_{11}^*) + q_2n_2 \ln (n_{22}/n_{22}^*)] \ , \tag{20}$$

where the asterisk relates to random mixing, i.e., to a hypothetical case with η = 1. We introduce

$$y_{ij} = \frac{(1+\delta_{ij})n_{ij}}{z(q_1n_1 + q_2n_2)} \qquad (i = 1, 2, \ \ j = 1, 2) \ , \tag{21}$$

where δ_{ij} is the Kronecker delta. For like–like contacts ($i \equiv j$), y_{ii} is the fraction of i–i contacts. On the other hand, y_{12} is half the fraction of 1–2 contacts. The Gibbs energy per mole of contact sites (see Eq. (*13*)) is

$$\Delta G_s^{\mathrm{I}} = \frac{\Delta G^{\mathrm{I}}}{z(q_1n_1 + q_2n_2)} \ . \tag{22}$$

We define y_i by the relation

$$y_{ii} = y_i^2 \quad (i = 1, 2) \ . \tag{23}$$

Then we obtain from Eqs (*18a*) and (*18b*)

$$y_{11} + y_{12} = \theta_1 \tag{24a}$$

$$y_{12} + y_{22} = \theta_2 \tag{24b}$$

and from Eq. (*19*)

$$y_{12} = \eta y_1 y_2 \ . \tag{25}$$

Substituting from (*23*) and (*25*) into (*24a*) and (*24b*) we have

$$y_1^2 + \eta y_1 y_2 = \theta_1 \tag{26a}$$

$$\eta y_1 y_2 + y_2^2 = \theta_2 \tag{26b}$$

and from (*20*) and (*22*)

$$\Delta G_s^{\mathrm{I}}/RT = \theta_1 \ln (y_1/y_1^*) + \theta_2 \ln (y_2/y_2^*) \ , \tag{27}$$

where

$$y_i^* = \theta_i \quad (i = 1, 2) \tag{28}$$

as it follows from Eqs (*26a*) and (*26b*) when we put $\eta = 1$. From Eqs (*26*), (*27*) and (*28*) we see that $\Delta G_s^{\mathrm{I}}/RT$ is fully determined by the values of η and θ_1.

In order to obtain the second derivative of the non-athermal term we start by differentiating Eqs (*23*) and (*25*); we get

$$\mathrm{d}y_{ij} = y_{ij}(\mathrm{d}\ln y_i + \mathrm{d}\ln y_j) \quad (i, j = 1, 2) \ . \tag{29}$$

Summing and differentiating Eqs (*24a*) and (*24b*) and substituting from (*29*) we obtain

$$\theta_1 \mathrm{d}\ln y_1 + \theta_2 \mathrm{d}\ln y_2 = 0 \ . \tag{30}$$

By double differentiation of Eq. (*27*) and using Eqs (*28*) and (*30*) we get

$$\frac{\partial^2(\Delta G_s^{\mathrm{I}}/RT)}{\partial\theta_1^2} = \frac{\partial \ln (y_1/\theta_1)}{\partial\theta_1} - \frac{\partial \ln (y_2/\theta_2)}{\partial\theta_1} \ . \tag{31}$$

The derivatives on the right-hand side can be obtained from the contact balance. We differentiate Eqs (*24a*) and (*24b*) and substitute from Eq. (*30*) to obtain

$$(y_{11} + \theta_1)\ \mathrm{d}\ln y_1 + y_{12}\ \mathrm{d}\ln y_2 = \mathrm{d}\theta_1 \tag{32a}$$

$$y_{12}\ \mathrm{d}\ln y_1 + (y_{22} + \theta_2)\ \mathrm{d}\ln y_2 = \mathrm{d}\theta_2 \ . \tag{32b}$$

Equation (*32a*) can be rearranged to

$$(y_{11} + \theta_1)\ \mathrm{d}\ln (y_1/\theta_1) + y_{12}\ \mathrm{d}\ln (y_2/\theta_2) = [-(y_{11}/\theta_1) + (y_{12}/\theta_2)]\ \mathrm{d}\theta_1 \ . \tag{33}$$

Now we put

$$y_{ij} = (1 + g_{ij})\theta_i\theta_j \quad (i, j = 1, 2) \ . \tag{34}$$

The parameters g_{ij} describe deviations from random mixing; for $\eta = 1$ we have $g_{ij}^* = 0$ (see Eq. (*20*)) for all types of binary contacts. On substitution from Eq. (*34*) into Eqs (*24a*) and (*24b*) we get

$$g_{11}\theta_1 + g_{12}\theta_2 = 0 \tag{35a}$$

$$g_{12}\theta_1 + g_{22}\theta_2 = 0 \quad . \tag{35b}$$

Using Eqs (*34*) and (*35a*) the right-hand side of Eq. (*33*) can be written as $g_{12}\,\mathrm{d}\theta_1$.

In an analogous way we deal with Eq. (*32b*). We thus obtain relations

$$(y_{11} + \theta_1)Y_1 + y_{12}Y_2 = g_{12} \tag{36a}$$

$$y_{12}Y_1 + (y_{22} + \theta_2)Y_2 = -g_{12} \tag{36b}$$

with

$$Y_i = \frac{\partial \ln (y_i/\theta_i)}{\partial\theta_1} \quad . \tag{37}$$

Except for $\theta_1 = 0$ and $\theta_1 = 1$, Eqs (*36a*) and (*36b*) can be solved using determinants

$$Y_i = -D_i/D_0 \quad (i = 1, 2) \quad , \tag{38}$$

where

$$D_k = \begin{vmatrix} \delta_{k0} & \delta_{k1} & \delta_{k2} \\ g_{12} & y_{11} + \theta_1 & y_{12} \\ -g_{12} & y_{12} & y_{22} + \theta_2 \end{vmatrix} \qquad (k = 0, 1, 2) \quad . \tag{39}$$

From Eq. (*31*) we have

$$\frac{\partial^2(\Delta G_s^{\mathrm{I}}/RT)}{\partial\theta_1^2} = \frac{D_2 - D_1}{D_0} \quad . \tag{40}$$

We eliminate y_{11} and y_{12} from Eq. (*39*) using Eqs (*24a*) and (*24b*) and expand the determinants to get

$$\frac{\partial^2(\Delta G_s^{\mathrm{I}}/RT)}{\partial\theta_1^2} = \frac{g_{12}}{2\theta_1\theta_2 - y_{12}} \quad . \tag{41}$$

We finally arrive at the interaction parameter, Eq. (*17*)

$$\chi_{\mathrm{sc}}^{\mathrm{I}} = -\frac{\langle s\rangle}{2}\,\frac{y_{12}-\theta_1\theta_2}{\theta_1\theta_2(2\theta_1\theta_2-y_{12})} = -\frac{\langle s\rangle}{2\theta_1\theta_2}\,\frac{g_{12}}{1-g_{12}} \quad . \tag{42}$$

The index of nonrandomness g_{12} can be calculated from

$$g_{12} = y_{12}/(\theta_1\theta_2) - 1 \quad , \tag{43}$$

where

$$y_{12} = \frac{1-\sqrt{1-4(1-\eta^{-2})\theta_1\theta_2}}{2(1-\eta^{-2})} \quad . \tag{44}$$

The last relation follows from solving Eqs (*26a*) and (*26b*).

Mixture of Components with a Heterogeneous Molecular Surface (Barker Model)

Now we acknowledge that the molecules consist of various groups so that their surface contains various types of contact sites (surface groups), e.g. A, B, R, S... For each type of surface site a balance relation similar to Eq. (*18a*) is valid. If c types of contact sites can be distinguished, we have $c(c–1)/2$ types of binary contacts between unlike groups (e.g. A–B) and c types of contacts between like groups (e.g. A–A). The Barker theory implies that for each pair of dissimilar groups an equation like Eq. (*19*) holds with a constant η dependent on the chemical character of interacting groups. The expression for ΔG^{I} is then a sum of contributions of all kinds of like–like contacts. A given type of group may be built into molecules of both components but we assume that all groups of the same kind interact to the same extent. Then the respective constant η is the same whether the interacting sites belong to component 1 or 2.

Let the molecule of component i contain q_{Ki} contact sites of type K (K = A, B, R, S…). Then the total number of sites per molecule is

$$q_i = \sum_K q_{Ki} \tag{45}$$

and the expression

$$\alpha_{Ki} = q_{Ki}/q_i \tag{46}$$

gives the fraction of contact sites of type *K* in the surface of molecule *i*. The surface fraction of sites *K* in the whole system is given by

$$\psi_K = \frac{q_{K1}n_1 + q_{K2}n_2}{q_1 n_1 + q_2 n_2} \tag{47}$$

or

$$\psi_K = \alpha_{K1}\theta_1 + \alpha_{K2}\theta_2 \ . \tag{48}$$

Further we define

$$y_{KL} = \frac{(1+\delta_{KL})n_{KL}}{z(q_1 n_1 + q_2 n_2)} \quad (\mathrm{K, L = A, B, R, S\ldots}) \ , \tag{49}$$

where n_{KL} is the amount of contacts between groups of types *K* and *L*, and

$$y_K = y_{KK}^{1/2} \ . \tag{50}$$

Then we have a set of *c* balance equations, to be compared with Eqs (*24a*) and (*24b*)

$$\sum_L y_{KL} = \psi_K \tag{51}$$

and a set of $c(c–1)/2$ equilibrium relations

$$y_{KL} = \eta_{KL} y_K y_L \ . \tag{52}$$

By substitution from Eq. (*52*), the set (*51*) transforms into

$$\sum_L \eta_{KL} y_K y_L = \psi_K \ , \tag{53}$$

where indeed η_{KL} = 1 for *K* = *L*. For the non-athermal part of Gibbs energy we have

$$\Delta G_s^{\mathrm{I}}/RT = \sum_L \psi_L \ln (y_L/\psi_L) - \sum_i \theta_i (G_s^{\mathrm{I}})_i^0/RT \ , \tag{54}$$

where $(G_s^{\mathrm{I}})_i^0$ refers to pure liquid component i; the respective terms will vanish after double differentiation with respect to θ_1. Again, looking at Eqs (*52*) and (*53*), we can state that $\Delta G_s^{\mathrm{I}}/RT$ is fully determined by θ_1 at given molecular and interaction parameters. In a way analogous with that used in the case of homogeneous molecular surface we get

$$\sum_L \psi_L \,\mathrm{d} \ln y_L = 0 \tag{55}$$

and

$$\frac{\partial^2 (\Delta G_s^{\mathrm{I}}/RT)}{\partial \theta_1^2} = \sum_L \psi_L' Y_L \tag{56}$$

with

$$\psi_L' = \partial \psi_L/\partial \theta_1 = \alpha_{L1} - \alpha_{L2} \tag{57}$$

$$Y_L = \frac{\partial \ln (y_L/\psi_L)}{\partial \theta_1} \ . \tag{58}$$

Now we differentiate the set (*51*) in a way used in Eq. (*29*) and we obtain a set

$$\sum_L y_{KL} \,\mathrm{d} \ln y_L + \psi_K \,\mathrm{d} \ln y_K = \mathrm{d}\psi_K \ . \tag{59}$$

On both sides we subtract $\sum_L y_{KL} \,\mathrm{d} \ln \psi_L + \mathrm{d}\psi_K$ and on the right-hand side we substitute

$$y_{KL} = (1 + g_{KL}) \psi_K \psi_L \ . \tag{60}$$

The set (*59*) assumes the form

$$\sum_L (y_{KL} + \delta_{KL} \psi_K) Y_L = -\sum_L g_{KL} \psi_K \psi_L' \ . \tag{61}$$

Finally we use the relation

$$\sum_L g_{KL}\psi_L = 0 \tag{62}$$

and Eqs (*48*) and (*57*) to obtain

$$\sum_L (y_{KL} + \delta_{KL}\psi_K)Y_L = \sum_L (\alpha_{K1}\alpha_{L2} - \alpha_{K2}\alpha_{L1})g_{KL} \ . \tag{63}$$

As $K \equiv$ (A, B, R, S…) the relations (*63*) represent a set of c equations, which can be solved for Y_K's; substituting the results into Eq. (*56*) we get

$$\frac{\partial^2(\Delta G_s^{\mathrm{I}}/RT)}{\partial\theta_1^2} = -\frac{D}{D_0} \ . \tag{64}$$

Here D_0 is the determinant of a $c \times c$ matrix $\boldsymbol{D}_0$ whose elements are

$$(d_0)_{KL} = y_{KL} + \delta_{KL}\psi_K \ .$$

D is the determinant of a square matrix $\boldsymbol{D}$

$$\boldsymbol{D} = \begin{bmatrix} 0 & \boldsymbol{A} \\ \boldsymbol{G} & \boldsymbol{D}_0 \end{bmatrix} , \tag{65}$$

where $\boldsymbol{A}$ is a row matrix ($1 \times c$) of elements

$$A_L = \alpha_{L1} - \alpha_{L2} \quad (L \equiv \mathrm{A, B, R, S}\ldots)$$

and $\boldsymbol{G}$ is a column matrix ($c \times 1$) of elements

$$G_K = \sum_L (\alpha_{K1}\alpha_{L2} - \alpha_{L1}\alpha_{K2})g_{KL} \quad (K, L \equiv \mathrm{A, B, R, S}\ldots) \ .$$

Evidently it holds

$$\chi_{\mathrm{sc}}^{\mathrm{I}} = \frac{\langle s\rangle}{2}\frac{D}{D_0} \ . \tag{66}$$

In the following, Eq. (*66*) will be applied to a special type of systems.

A Mixture of Two Components with a Similar Nonpolar Residue

Let us suppose that the molecules of component 1 consist of polar groups A and a nonpolar residue R1; the component 2 contains a chemically similar nonpolar residue R2, but different polar groups B. We then put

$$\alpha_{A1} \equiv \alpha_A \quad \alpha_{B1} \equiv 0 \quad \alpha_{R1} \equiv 1 - \alpha_A \tag{67a}$$

$$\alpha_{A2} \equiv 0 \quad \alpha_{B2} \equiv \alpha_B \quad \alpha_{R2} \equiv 1 - \alpha_B \tag{67b}$$

and we have

$$\psi_A = \alpha_A \theta_1 \quad \psi_B = \alpha_B \theta_2 \quad \psi_R = 1 - (\psi_A + \psi_B)\ . \tag{68}$$

The determinant D is, after modification of the last row (column) by addition of two preceding ones,

$$D = \begin{vmatrix} 0 & \alpha_A & -\alpha_B & 0 \\ \alpha_A\,[\alpha_B g_{AB} + (1-\alpha_B) g_{AR}] & y_{AA} + \psi_A & y_{AB} & 2\psi_A \\ -\alpha_B\,[\alpha_A g_{AB} + (1-\alpha_A) g_{BR}] & y_{AB} & y_{BB} + \psi_B & 2\psi_B \\ 0 & 2\psi_A & 2\psi_B & 2 \end{vmatrix}\ , \tag{69}$$

where

$$g_{KL} = \eta_{KL} y_K y_L / (\psi_K \psi_L) - 1 \tag{70}$$

and y_A, y_B, y_R are obtained by numerical solution of the set of equations

$$y_A^2 + \eta_{AB} y_A y_B + \eta_{AR} y_A y_R = \psi_A \tag{71a}$$

$$\eta_{AB} y_A y_B + y_B^2 + \eta_{BR} y_B y_R = \psi_B \tag{71b}$$

$$\eta_{AR} y_A y_R + \eta_{BR} y_B y_R + y_R^2 = \psi_R \ . \qquad (71c)$$

Expanding the determinant D and its subdeterminant D_0 and substituting into Eq. (*66*) we obtain a relationship for the interaction parameter

$$\chi_{sc}^{I} = -\langle s \rangle P/(2Q\theta_1\theta_2\psi_R) \ , \qquad (72)$$

where

$$P = \alpha_A \alpha_B g_{AB} \psi_R + \alpha_A (1 - \alpha_B)^2 g_{AR} \theta_2 + \alpha_B (1 - \alpha_A)^2 g_{BR} \theta_1 - (\alpha_A \theta_2 + \alpha_B \theta_1 - \alpha_A \alpha_B) S \qquad (73a)$$

$$Q = 1 - g_{AB}(\psi_A + \psi_B) - g_{AR}(\psi_A + \psi_R) - g_{BR}(\psi_B + \psi_R) + S \qquad (73b)$$

$$S = g_{AB} g_{AR} \psi_A + g_{AB} g_{BR} \psi_B + g_{AR} g_{BR} \psi_R \ . \qquad (73c)$$

An alternative form of the relationship can be obtained if the main term in Eq. (*54*) is separated into two parts, corresponding to non-random and random mixing

$$\sum_L \psi_L \ln (y_L/\psi_L) = \sum_L \psi_L \ln y_L - \sum_L \psi_L \ln \psi_L \qquad (74)$$

and each part is submitted to double differentiation with respect to composition. The final result is

$$\chi_{sc}^{I} = -\frac{\langle s \rangle}{2} \left[\frac{(\alpha_A - \alpha_B)^2 D_{AB} + \alpha_B^2 D_{AR} + \alpha_A^2 D_{BR}}{D_{AB} D_{AR} + D_{AB} D_{BR} + D_{AR} D_{BR}} - \frac{\alpha_A \theta_2 + \alpha_B \theta_1 - \alpha_A \alpha_B}{\theta_1 \theta_2 \psi_R} \right] , \qquad (75)$$

where

$$D_{KL} = 2\psi_K \psi_L - y_{KL} \qquad (K, L \equiv \mathrm{A, B, R}) \ . \qquad (76)$$

The second term in square brackets in Eq. (*75*) represents the limit of the first term for the hypothetical state of random mixing, where $D_{KL} = \psi_K \psi_L$. Equations (*72*) and (*74*) are invalid for $\theta_1 = 0$ and $\theta_1 = 1$.

The set of Eqs (*72*) and (*73a*)–(*73c*) expresses the interaction parameter in terms of indexes of nonrandomness g_{KL}. At small deviations from random mixing the *S*-term can be neglected in the expression for *P*, while *Q* is not far from unity. Then the parameter $\chi^{\mathrm{I}}_{\mathrm{SC}}$ decreases linearly with growing g_{AB}, g_{AR} and g_{BR}, i.e., with increasing frequency of heterocontacts. Indeed, a given g_{KL} is a function of all three η constants; e.g. the relative frequency of A–B contacts is influenced not only by interaction in A–B pairs, but also by that in pairs A–R and B–R. We see that the functional dependence of the Flory–Huggins parameter on η_{AB}, η_{AR} and η_{BR} is rather involved in general case; however, it can be expressed explicitly in some limit cases which will be studied in the following sections.

Small Deviations from Random Mixing (Linear Approximation)

Let us define

$$\gamma_{KL} = \eta_{KL} - 1 \quad (K, L = \mathrm{A, B, R}) \tag{77}$$

and consider the case of small γ_{AB}, γ_{AR} and γ_{BR}. Then, $\zeta_K = y_K - \psi_K$ (K = A, B, R) are also small and, in the first approximation, Eqs (*71a*)–(*71c*) can be transformed into a set of linear equations. We solve them for ζ_{A}, ζ_{B} and ζ_{R} and substitute for *y*'s into Eq. (*70*). In the same approximation we obtain

$$g_{\mathrm{AA}}/2 = -\gamma_{\mathrm{AB}}(1-\psi_{\mathrm{A}})\psi_{\mathrm{B}} - \gamma_{\mathrm{AR}}(1-\psi_{\mathrm{A}})\psi_{\mathrm{R}} + \gamma_{\mathrm{BR}}\psi_{\mathrm{B}}\psi_{\mathrm{R}} \tag{78a}$$

$$g_{\mathrm{BB}}/2 = -\gamma_{\mathrm{AB}}\psi_{\mathrm{A}}(1-\psi_{\mathrm{B}}) + \gamma_{\mathrm{AR}}\psi_{\mathrm{A}}\psi_{\mathrm{R}} - \gamma_{\mathrm{BR}}(1-\psi_{\mathrm{B}})\psi_{\mathrm{R}} \tag{78b}$$

$$g_{\mathrm{RR}}/2 = \gamma_{\mathrm{AB}}\psi_{\mathrm{A}}\psi_{\mathrm{B}} - \gamma_{\mathrm{AR}}\psi_{\mathrm{A}}(1-\psi_{\mathrm{R}}) - \gamma_{\mathrm{BR}}\psi_{\mathrm{B}}(1-\psi_{\mathrm{R}}) \tag{78c}$$

and

$$g_{\mathrm{AB}} = \gamma_{\mathrm{AB}}(\psi_{\mathrm{R}} + 2\psi_{\mathrm{A}}\psi_{\mathrm{B}}) - \gamma_{\mathrm{AR}}(1-2\psi_{\mathrm{A}})\psi_{\mathrm{R}} - \gamma_{\mathrm{BR}}(1-2\psi_{\mathrm{B}})\psi_{\mathrm{R}} \tag{79a}$$

$$g_{AR} = -\gamma_{AB}(1 - 2\psi_A)\psi_B + \gamma_{AR}(\psi_B + 2\psi_A\psi_R) - \gamma_{BR}\psi_B(1 - 2\psi_R) \qquad (79b)$$

$$g_{BR} = -\gamma_{AB}(1 - 2\psi_B)\psi_A - \gamma_{AR}\psi_A(1 - 2\psi_R) + \gamma_{BR}(\psi_A + 2\psi_B\psi_R) \ . \qquad (79c)$$

In the further text our consideration will be limited to a class of systems exhibiting following properties:

1) Polar groups A and B, nonpolar R; specific interaction between A and B. This means

$$\gamma_{AB} > 0 \quad \gamma_{AR} < 0 \quad \gamma_{BR} < 0 \ . \qquad (80)$$

2) Prevailing surface of nonpolar groups in both kinds of molecules, i.e.

$$\alpha_A < 0.5 \quad \alpha_B < 0.5 \ . \qquad (81)$$

Let us first consider the nonrandomness of homocontacts; e.g. the index g_{AA} characterizes the self-aggregation of groups A. From Eq. (*78a*) we see that this factor decreases with increasing constants η_{AB} and η_{AR}, as expected; however it grows with η_{BR}, as at higher η_{BR} fewer groups B and R are left for a contact with A, so that the latter groups prefer to interact among themselves. For our class of systems, g_{AA} and g_{BB} can assume either sign according to circumstances, but g_{RR} is always positive.

For a discussion of the frequency of heterocontacts at small values of γ_{KL} the following relation is useful:

$$g_{KL} = \gamma_{KL} + \frac{1}{2}(g_{KK} + g_{LL}) \ . \qquad (82)$$

For instance, the number of A–B contacts grows with increasing constant η_{AB} and with the frequencies of A–A and B–B contacts. The latter depend on η_{AR} and η_{BR}; for example, with increasing η_{AR} the frequency of A–A contacts diminishes, but g_{BB} increases according to Eqs (*78a*) and (*78b*). Therefore the final influence of η_{AR} on g_{AB} is ambiguous in general and its sense is determined by the sign of the expression $(1 - 2\psi_A)$ in Eq. (*79a*). However, in our class of systems, the latter expression is always positive and g_{AB} diminishes with η_{AR}, and, by analogous reasoning, also with η_{BR}.

For our class of systems, all terms on the right-hand sides of Eqs (*79a*)–(*79c*) are of the same sign, and we always have

$$g_{\mathrm{AB}} > 0 \quad g_{\mathrm{AR}} < 0 \quad g_{\mathrm{BR}} < 0 \ . \tag{83}$$

This involves preference of A–B contacts and reluctance to form A–R and B–R contacts in comparison with the random mixing case. The Flory–Huggins parameter is expressed in a surprisingly simple way in linear approximation:

$$\chi^{\mathrm{I}}_{\mathrm{sc}}/\langle s\rangle = -\alpha_{\mathrm{A}}\alpha_{\mathrm{B}}\gamma_{\mathrm{AB}} + (\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}})(\alpha_{\mathrm{A}}\gamma_{\mathrm{AR}} - \alpha_{\mathrm{B}}\gamma_{\mathrm{BR}}) \ . \tag{84}$$

As expected, the specific interactions between A and B groups result in a negative contribution to χ. The contributions of the “repulsive” interactions A–R and B–R compensate each other if we have either $\alpha_{\mathrm{A}} = \alpha_{\mathrm{B}}$ or $\alpha_{\mathrm{A}}\gamma_{\mathrm{AR}} = \alpha_{\mathrm{B}}\gamma_{\mathrm{BR}}$. If α_{A} is different from α_{B}, but $\gamma_{\mathrm{AR}} = \gamma_{\mathrm{BR}}$, the combined contribution of the two interactions is positive. It can become negative if the group with higher α has a greater tendency to enter into contacts with R (e.g. if $\alpha_{\mathrm{B}} > \alpha_{\mathrm{A}}$ and simultaneously $\eta_{\mathrm{BR}} > \eta_{\mathrm{AR}}$). This change of sign is the easier the smaller the relative difference of the α’s is. In general, it is apparent that the disparity in the surface fractions of polar groups A and B affects the value of the γ-parameter more strongly than the difference in their interaction with the nonpolar residues.

Small Deviations from Random Mixing (Quadratic Approximation)

Starting from the linear approximation we can arrive at a quadratic expansion of the interaction parameter χ. For this purpose, we express the enthalpy of the mixture per mole of surface sites in terms of contributions of individual kinds of heterocontacts

$$H_s = h_{\mathrm{AB}}y_{\mathrm{AB}} + h_{\mathrm{AR}}y_{\mathrm{AR}} + h_{\mathrm{BR}}y_{\mathrm{BR}} \ , \tag{85}$$

where h_{KL} is the enthalpy of a contact K–L related to that of respective homocontacts; if $\tau = 1/RT$, we have

$$h_{KL} = -\left(\frac{\partial \ln \eta_{KL}}{\partial \tau}\right) \quad (K, L \equiv \mathrm{A, B, R}) \ . \tag{86}$$

We express the *y*'s in Eq. (*85*) in terms of linear expansions with respect to γ_{AB}, γ_{AR} and γ_{BR} and we calculate the interaction Gibbs energy on integrating H_s according to the formula

$$G_s^{I} = \int_0^{\tau} H_s \, d\tau \quad . \tag{87}$$

On performing the integration we use formulae valid for small γ's

$$\int_0^{\tau} h_{KL} \, d\tau = -\gamma_{KL} + \gamma_{KL}^2/2 \tag{88a}$$

$$\int_0^{\tau} (h_{KL}\gamma_{K'L'} + h_{K'L'}\gamma_{KL}) \, d\tau = -\gamma_{KL}\gamma_{K'L'} \quad . \tag{88b}$$

The resulting expression for G_s^{I} is subject to double differentiation with respect to composition and a rather complex equation for χ_{sc}^{I} is obtained. It becomes much simpler if we put $\theta_1 = \theta_2 = 0.5$ and $\alpha_A = \alpha_B$; therefore we give a linear expansion in the vicinity of this point:

$$\chi_{sc}^{I}/\langle s \rangle = M_0 + M_1(\theta_2 - \theta_1) + M_2(\alpha_B - \alpha_A) \tag{89}$$

with

$$M_0 = \alpha^2[-\gamma_{AB} + \frac{1}{2}\alpha(1-\alpha)\gamma_{AB}^2 + (1-\alpha)^2\gamma_{AB}(\gamma_{AR} + \gamma_{BR})] + \\ + \frac{1}{2}\alpha^2(1-\alpha)(1-2\alpha)(\gamma_{AR} - \gamma_{BR})^2 \tag{89a}$$

$$M_1 = 3\alpha^3(1-\alpha)\gamma_{AB}(\gamma_{AR} - \gamma_{BR}) \tag{89b}$$

$$M_2 = \alpha(\gamma_{AR} - \gamma_{BR})\left\{1 + \frac{\alpha^2}{2}\gamma_{AB} - \frac{1}{2}[1 - 4\alpha(1-\alpha)](\gamma_{AR} + \gamma_{BR})\right\} , \tag{89c}$$

where we might put $\alpha = (\alpha_A + \alpha_B)/2$.

The two terms of Eq. (*84*) reappear approximately in expressions for M_0 and M_2 as first terms. We may remember that according to Eq. (*84*) the interaction parameter is independent of composition, so that M_1 contains no term linear in γ. From (*89a*) we see that in our class of systems the change of χ with γ_{AB} slows down with increasing γ_{AB}; on the other hand, the effect of A–B interaction is amplified by an indirect influence of the interactions A–R and B–R. We also find the missing contribution of the diference $\eta_{AR} - \eta_{BR}$; this term is positive and is not bound to a disparity of the α values. The difference of η_{AR} from η_{BR} is essential for the appearance of the M_1 and M_2 terms, which indeed change their signs at $\theta_2 = 0.5$ and $\alpha_A = \alpha_B$.

Very Small Attraction Between Polar and Nonpolar Groups

The hypothetical case of

$$\eta_{AR} = 0 \quad \eta_{BR} = 0 \quad \eta_{AB} = 1 \tag{90}$$

can be described by simple analytical expressions. On substituting from Eq. (*90*) into Eqs (*71a*)–(*71c*), the resulting equations can be solved to obtain

$$y_{AA} = \psi_A^2/\psi_S \quad y_{AB} = \psi_A\psi_B/\psi_S \quad y_{BB} = \psi_B^2/\psi_S \tag{91a}$$

$$y_{AR} = 0 \quad y_{BR} = 0 \quad y_{RR} = \psi_R \tag{91b}$$

with

$$\psi_S = \psi_A + \psi_B = 1 - \psi_R \ . \tag{92}$$

We see that the frequencies of pairs A–A, A–B and B–B are in the same relative proportions as in the case of random mixing, but they are higher by a factor $(\psi_A + \psi_B)^{-1}$ due to the fact that no pairs A–R and B–R can originate. For the indexes of nonrandomness we have

$$g_{AA} = g_{AB} = g_{BB} = \psi_R/\psi_S \tag{93a}$$

$$g_{AR} = g_{BR} = -1 \quad g_{RR} = \psi_S/\psi_R \tag{93b}$$

and the interaction parameter is

$$\chi^{\mathrm{I}}_{\mathrm{sc}}/\langle s\rangle = (\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})^2/(4\psi_{\mathrm{R}}\psi_{\mathrm{S}}) \ . \tag{94}$$

As expected $\chi^{\mathrm{I}}_{\mathrm{sc}}$ is positive in this case and results from unequal fractions of polar contact sites in molecules of diferent kind.

If the quasiequilibrium constants are not too much different from the set of values $\eta_{\mathrm{AR}} = 0$; $\eta_{\mathrm{BR}} = 0$; $\eta_{\mathrm{AB}} = 1$, a linear expansion can be performed in a similar way as in the case of small deviations from universal random mixing. Compared to the latter case, the expressions for the nonrandomness indexes contain essentially the same qualitative information concerning the dependences of g's on η's in our class of systems. Therefore we give the equation for the interaction parameter only:

$$\chi^{\mathrm{I}}_{\mathrm{sc}}/\langle s\rangle = \frac{(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})^2}{4\psi_{\mathrm{R}}\psi_{\mathrm{S}}} + \frac{(\alpha_{\mathrm{A}}\alpha_{\mathrm{B}})^2}{\psi_{\mathrm{S}}^3}(1 - \eta_{\mathrm{AB}}) + \\ + \frac{\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}}}{2\psi_{\mathrm{R}}^{3/2}\psi_{\mathrm{S}}^{5/2}}\left[\alpha_{\mathrm{A}}\alpha_{\mathrm{B}}(\eta_{\mathrm{AR}} - \eta_{\mathrm{BR}})\psi_{\mathrm{R}} - \frac{\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}}}{4}(\eta_{\mathrm{AR}}\psi_{\mathrm{A}} + \eta_{\mathrm{BR}}\psi_{\mathrm{B}})\right] . \tag{95}$$

The first term corresponds to the limit equation (*94*). It may be useful to compare the other terms with the respective terms in Eq. (*84*), valid for small δ_{KL}. Those in Eq. (*95*) are more involved, but we can see that the interaction A–B contributes in a similar way in both cases, and that again, the interactions A–R and B–R manifest themselves only if α_{A} is different from α_{B}, no matter whether η_{AR} equals η_{BR} or not. Indeed, unlike in Eq. (*84*), all contributing terms are composition-dependent.

DISCUSSION

The relations derived will be illustrated by means of simple models. Let us first consider a mixture of components the molecules of which display the same surface fractions of polar groups and the same parameters of polar–nonpolar interaction ($\alpha_{\mathrm{A}} = \alpha_{\mathrm{B}}$; $\eta_{\mathrm{AR}} = \eta_{\mathrm{BR}}$). If we have $\theta_1 = 0.5$, the system is symmetrical, i.e. components 1 and 2 are interchangeable. Then $g_{\mathrm{AA}} = g_{\mathrm{BB}}$, $g_{\mathrm{AR}} = g_{\mathrm{BR}}$ holds. The indices of nonrandomness are shown in dependence on the quasiequilibrium constants in Figs 1 and 2*a*. We see from Fig. 1 that g_{AR} becomes negative and decreases if η_{AR} diminishes (direct influence) or if η_{AB} increases (competition effect). The parameter g_{RR} shows opposite behaviour. If $\eta_{\mathrm{AB}} = 1$, then g_{AA}, g_{BB} and g_{AB} obey the same curve (curve *1* in Fig. 2*a*). With growing η_{AB} the index g_{AB} increases, while g_{AA} and g_{BB} decrease, so that they can assume negative values for large η_{AB}. All three indexes in Fig. 2*a* increase if η_{AR} and η_{BR} decrease, i.e. with diminishing competition of A–R and B–R contacts. The Flory–Huggins interaction parameter (full curves in Fig. 3*a*) decreases with η_{AB} and grows with η_{AR}. On passing from $\eta_{AB} = 1$ to larger values, the slope of the curves increases, which may be characterized as synergism of η_{AB} with η_{AR} in affecting χ and which corresponds qualitatively to the third term on the right-hand side of Eq. (*89a*). All the plots discussed so far have been computed for $\alpha_A = \alpha_B = 0.3$; calculations performed for symmetric sys-

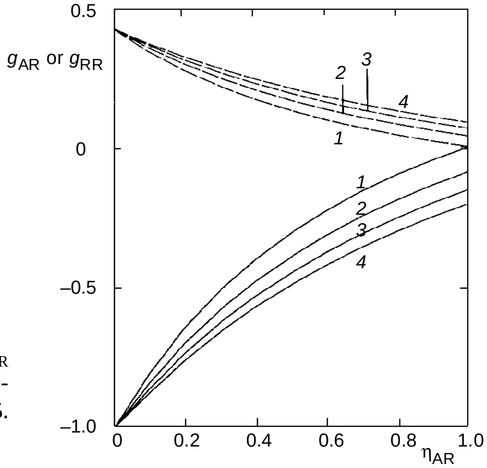


FIG. 1
Indexes of nonrandomness g_{KL} as functions of η_{AR} (at $\eta_{AR} = \eta_{BR}$). The curves are labelled with η_{AB}-values. $\alpha_A = \alpha_B = 0.3$; $\theta_2 = 0.5$, i.e. $\psi_A = \psi_B = 0.15$. Full lines: g_{AR}(= g_{BR}); broken lines: g_{RR}

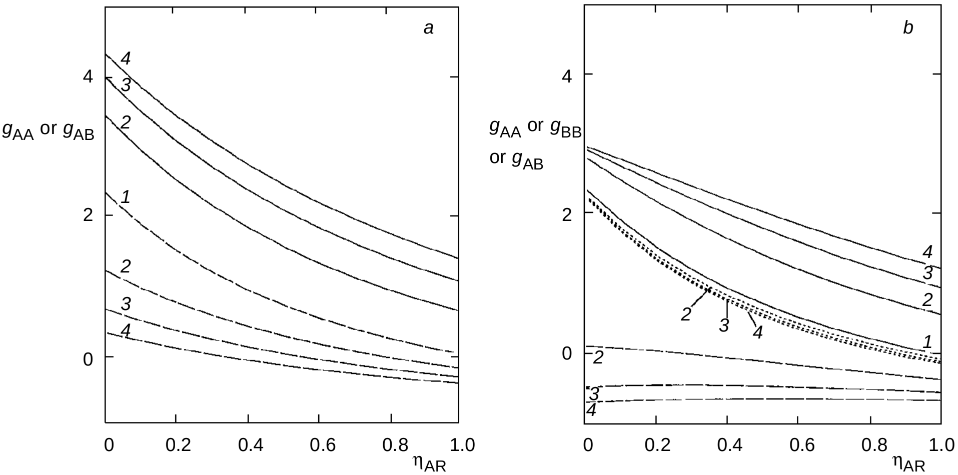


FIG. 2
Indexes of nonrandomness g_{KL} as functions of η_{AR} (at $\eta_{AR} = \eta_{BR}$). The curves are labelled with η_{AB}-values. At $\eta_{AB} = 1$, $g_{AA} = g_{BB} = g_{AB}$ holds. *a* $\alpha_A = \alpha_B = 0.3$; $\theta_2 = 0.5$, i.e. $\psi_A = \psi_B = 0.15$. Broken lines: g_{AA}(= g_{BB}), full lines: g_{AB}. *b* $\alpha_A = \alpha_B = 0.3$; $\theta_2 = 5/6$ (also $\alpha_A = 0.1$; $\alpha_B = 0.5$; $\theta_2 = 0.5$), i.e. $\psi_A = 0.05$; $\psi_B = 0.25$. Broken lines: g_{AA}; dotted lines: g_{BB}; full lines: g_{AB}

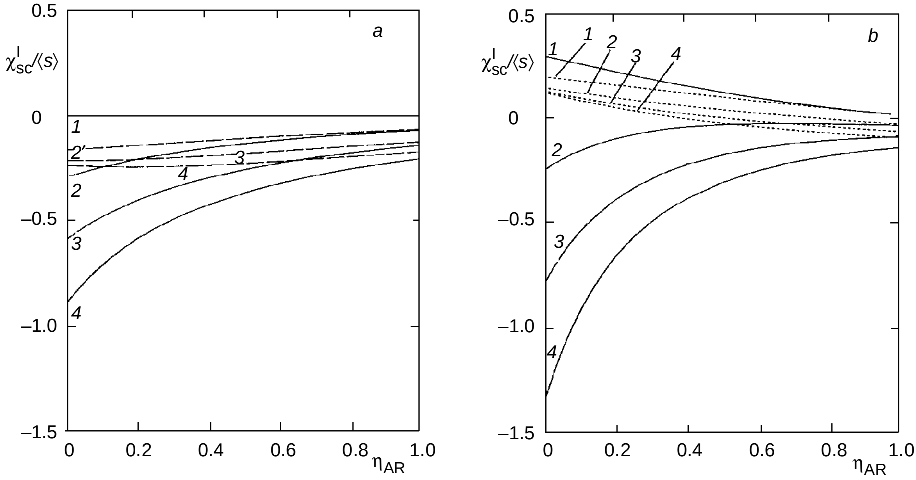
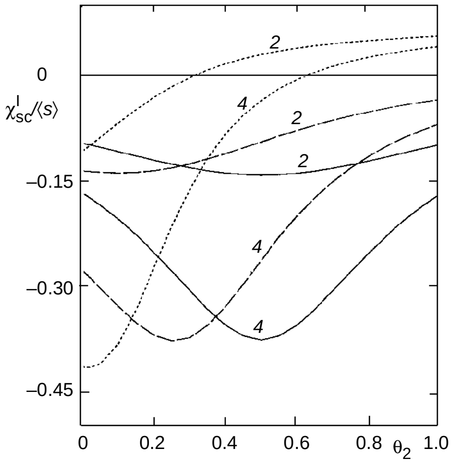


FIG. 3

Flory–Huggins interaction parameter as a function of η_{AR} (at $\eta_{AR} = \eta_{BR}$). The curves are labelled with η_{AB}-values. *a* $\alpha_A = \alpha_B = 0.3$; full lines: $\theta_2 = 0.5$, i.e., $\psi_A = \psi_B = 0.15$; broken lines: $\theta_2 = 5/6$, i.e., $\psi_A = 0.05$; $\psi_B = 0.25$. At $\eta_{AB} = 1$ the full and broken lines coincide. *b* $\alpha_A = 0.1$; $\alpha_B = 0.5$; full lines: $\theta_2 = 1/6$, i.e., $\psi_A = \psi_B = 1/12$; dotted lines: $\theta_1 = 0.5$, i.e., $\psi_A = 0.05$; $\psi_B = 0.25$



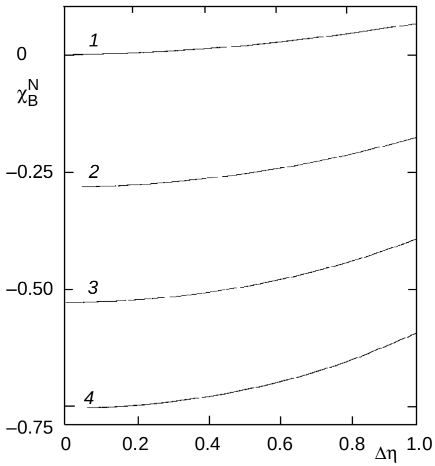


FIG. 4

Flory–Huggins interaction parameter as a function of composition. The curves are labelled with η_{AB}-values. $\eta_{AR} = \eta_{BR} = 0.5$; full lines: $\alpha_A = \alpha_B = 0.3$; broken lines: $\alpha_A = 0.2$; $\alpha_B = 0.4$; dotted lines: $\alpha_A = 0.1$; $\alpha_B = 0.5$

FIG. 5

Flory–Huggins interaction parameter as a function of $\Delta\eta$ (where $\Delta\eta = \eta_{AR} - \eta_{BR}$ at $\eta_{AR} + \eta_{BR} = 1$). The curves are labelled with η_{AB}-values. $\alpha_A = \alpha_B = 0.3$; $\theta_2 = 0.5$

tems with different α values confirm the expectation that the effects described grow with increasing extent of the polar groups.

If $\theta_2 > \theta_1$ at $\alpha_A = \alpha_B$, the group B is in excess with respect to A; hence, more groups B than A are left outside the A–B interaction (Fig. 2*b*). Then the index g_{BB} depends very little on η_{AB} and is larger than at $\theta_1 = 0.5$ (cf. Fig. 2*a*). Indexes g_{AA} and g_{AB} are considerably smaller than in the symmetrical case, due to the unequal population of groups A and B. In these circumstances the parameter χ is less negative and less dependent on η_{AB} and η_{AR} (Fig. 3*a*, broken curves).

Now we turn our attention to systems with components which differ in their content of polar groups in molecule. For instance, if we put $\alpha_A = 0.1$, $\alpha_B = 0.5$, then at $\theta_2 = 0.5$ we have the same group concentrations $\psi_A = 0.05$, $\psi_B = 0.25$ as in the case $\alpha_A = \alpha_B = 0.3$; $\theta_2 = 5/6$, shown in Fig. 2*b*. As the indexes of nonrandomness depend on ψ_A and ψ_B only at given η's, we can use the latter figure again. This is not the case for the Flory–Huggins parameter, which is determined not only by the concentrations of A and B groups in the system but also by the distribution of these groups among the molecules of individual components. Therefore, the χ-values are different for the two systems under consideration; at the same ψ_A and ψ_B, the symmetrical system ($\alpha_A = \alpha_B$; broken curves in Fig. 3*a*) displays lower χ-values than the strongly assymmetric system with $\alpha_A << \alpha_B$ (Fig. 3*b*, dotted curves). In a mixture with $\alpha_A = 0.1$, $\alpha_B = 0.5$, an equal concentration of groups A and B ($\psi_A = \psi_B = 0.015$) is attained at $\theta_2 = 1/6$ (full curves in Fig. 3*b*); then the interaction parameter is considerably lower than at $\theta_2 = 0.5$. There is evident analogy of Fig. 3*a* with Fig. 3*b* if the curves are distinguished according to whether $\psi_A = \psi_B$ (full lines) or not.

From the above discussion it is seen that the Flory–Huggins parameter must be composition-dependent. Symmetric systems, in which the interactions A–R and B–R are mutually compensated, exhibit a minimum for $\theta_2 = 0.5$, the depth of which increases with η_{AB} (Fig. 4, full curves). In dissymmetric systems ($\alpha_A < \alpha_B$), the minimum shifts toward smaller values of θ_2 until it disappears at a large disparity of the α-values. Then χ increases monotonously with θ_2 and the sign can be switched at some composition (dotted curves in Fig. 4). The minimum discussed above should not be confused with that of the dependence of ΔG_s^I on composition. The latter minimum occurs in all systems with prevailing specific interaction A–B. With increasing η_{AB}, this minimum becomes deeper and the corresponding composition approaches the value $\theta_2 = \alpha_A/(\alpha_A + \alpha_B)$, at which $\psi_A = \psi_B$.

So far we have assumed that both types of polar groups have the same interaction with the nonpolar one ($\eta_{AR} = \eta_{BR}$). In Fig. 5 the parameter χ_{sc} is plotted as a function of the difference $\eta_{AR} - \eta_{BR} = \Delta\eta$ assuming that $\eta_{AR} + \eta_{BR} = 1$. Then

$$\eta_{AR} = (1 + \Delta\eta)/2 \qquad \eta_{BR} = (1 - \Delta\eta)/2$$

holds. Further it is assumed that $\alpha_A = \alpha_B$. In these circumstances the interaction parameter shifts moderately toward less negative values with increasing the difference $\eta_{AR} - \eta_{BR}$; the effect of this difference, however, is much smaller than that of the disparity in the content of the polar groups A and B discussed above. Such a conclusion also follows from Eqs (*84*) and (*95*), derived for some other cases; according to these equations the difference $\eta_{AR} - \eta_{BR}$ exerts no influence if $\alpha_A = \alpha_B$.

The authors are indebted to the Grant Agency of the Academy of Sciences of the Czech Republic for financial support of this work (Grant No. A450102).

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