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Quasi-Chemical Approximation for Nonrandomness in the Hole Theory of Polymeric Fluids. 2. Miscibility Behavior of Binary Systems: Polystyrene in Cyclohexane or Methyl Acetate

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ABSTRACT: The nonrandom mixing version of the Holey Huggins theory for pure components presented in a previous paper is extended to binary mixtures and is applied to the miscibility behavior of the systems polystyrene/methyl acetate and polystyrene/cyclohexane. Comparison with the experimental data shows that the present theory is successful in predicting the miscibility behavior and its pressure dependence for these two systems. For polystyrene/cyclohexane the results of the random mixing and nonrandom mixing theory are comparable. For this system one indeed does not expect that nonrandomness will be very important. For the system polystyrene/methyl acetate the agreement between theory and experiment improves by applying the nonrandom mixing theory, indicating that nonrandom effects are of importance.

I. Introduction

In a previous paper the effects of nonrandom mixing of polymer segments with holes in the Holey Huggins (HH) theory was accounted for by application of the quasi-chemical approximation of Guggenheims. The purpose of this paper is to report on (1) a generalization of the theory to polymer blends and polymer solutions and (2) the application to the miscibility behavior of binary systems. The theory is compared to experimental miscibility data at atmospheric and elevated pressure for solutions of polystyrene in methyl acetate and polystyrene in cyclohexane. The results show that the present theory is as good as, or in some respects, better than the original HH and SS theories.

The present theory is regarded as an intermediate but necessary step toward the establishment of an equation of state theory involving polymer systems with, e.g., strong directional interactions. In these systems, considerable deviation from complete randomness may be expected, and this can be handled in a similar fashion as discussed presently. So far, the present theory has already been extended to random copolymer systems and homopolymer/random copolymer blends, which will be presented in a forthcoming paper. The development of an equation of state theory for self-associated polymer systems in which very strong specific interactions play an important role is in progress.

II. Theory

(a) Model System. Consider a binary mixture of monodisperse components A and B. The following parameters characterize the system: \( N_A \) (\( N_B \)), the number of molecules of component A (B); \( s_A \) (\( s_B \)), the number of segments of each molecule A (B); \( c_A \) (\( c_B \)), the number of external degrees of freedom of a molecule A (B); \( M_{60A} \) (\( M_{60B} \)), the molar mass of component A (B); \( P \), \( V \), and \( T \), the pressure, total volume, and temperature of the system. For the sake of convenience, we introduce some other parameters as given below.

\[
\begin{align*}
N & \quad \text{the total number of molecules} \\
n & \quad \text{the total number of moles of the mixture} \\
N_B & \quad \text{the number of holes on the lattice} \\
z & \quad \text{the coordination number of the lattice} \\
y & \quad \text{the occupied site fraction, } y = (N_A s_A + N_B s_B) / (N_A s_A + N_B s_B + N_h) \\
\phi_A & \quad \text{the segment fraction of component A (B), } \phi_A = (N_A s_A) / (N_A s_A + N_B s_B + N_h) \\
\phi_B & \quad \text{the segment fraction of component B (A), } \phi_B = (N_B s_B) / (N_A s_A + N_B s_B + N_h) \\
c_{A/segment} & \quad \text{the flexibility parameter per segment, } c_{iA} = c_i / s_i \quad (i = A, B) \\
\langle zq_A \rangle & \quad \text{the number of external contact sites of each molecule A (B), } zq_i = s_i (z - 2) + 2 \quad (i = A, B) \\
\langle s \rangle & \quad \text{the average number of segments, } \langle s \rangle = (\phi_A s_A + \phi_B s_B)^{-1} \\
\langle c_s \rangle & \quad \text{the average flexibility parameter, } \langle c_s \rangle = \phi_A c_{iA} + \phi_B c_{iB} \\
\langle M_0 \rangle & \quad \text{the average molar mass, } \langle M_0 \rangle = \phi_A M_{60A} + \phi_B M_{60B} \\
\langle u \rangle & \quad \text{the contact site fraction of component A, } u = N_A zq_A / (N_A zq_A + N_B zq_B + z N_h) \\
\langle v \rangle & \quad \text{the contact site fraction of component B, } v = N_B zq_B / (N_A zq_A + N_B zq_B + z N_h) \\
q & \quad \text{the total contact site fraction of components A and B, } q = u + v \\
Q & \quad \text{the total number of external contact pairs, } Q = (N_A zq_A + N_B zq_B + z N_h) / 2
\end{align*}
\]

To take nonrandomness of the system into account, we need extra microscopic parameters to describe the number of contacts between different species. For a binary mixture, there are six different kinds of contacts; thus three extra parameters, denoted by \( X_1 \), \( X_2 \), and \( X_3 \), are necessary. Their meanings are self-evident when one looks at the number of different kinds of contacts as cited in Table I.

The derivation of the theory is quite similar to that for pure components and is discussed in detail in the Appendix. Here only the main result of the derivation, i.e., the expression for the Helmholtz free energy of the system is presented.

(b) The Helmholtz Free Energy. According to the present theory, the free energy of the system is given by

\[
\begin{align*}
\Delta F & = \sum_{i<j} N_i N_j \psi_{ij} - \sum_{i} \sum_{j} N_i \phi_i (N_j \phi_j) \langle s \rangle \\
\psi_{ij} & = \begin{cases} 0, & i = j \text{ or } (i, j) \text{ not allowed} \\
B_{ij} \exp(-\beta \phi_i (N_j \phi_j)), & \text{otherwise}
\end{cases}
\end{align*}
\]
from the Helmholtz free energy, all other thermodynamic
properties, e.g., the equation of state and miscibility
even though in the relevant paper it has not been shown
previously. The parameters

111.

Methyl Acetate and Its Pressure Dependence. Poly-
Applications

A/n(s)RT = φ_A \ln n_A/s_A + φ_B \ln n_B/s_B +
\frac{1}{\langle s \rangle} \ln y + \frac{1}{\langle s \rangle} \ln (1 - y) - \frac{1 - \langle \alpha \rangle}{\langle s \rangle} \ln (1 - \langle \alpha \rangle) y -
\frac{2q}{q} [2u \ln w + 2v \ln v + 2w \ln w - (u - X_1 - X_3) \ln (u - X_1 - X_3) -
(w - X_2 - X_3) \ln (w - X_2 - X_3) - 2X_1 \ln X_1 - 2X_2 \ln X_2 -
2X_3 \ln X_3] +
\frac{\langle c_1 \rangle}{2T} \left( \frac{1 - \langle X \rangle}{q} (A \omega^4 - 2B \omega^{-2}) + k_1 \langle c_1 \rangle \right) \in (k_2(M_0)T)

In eq 1, the first five terms on the right-hand side account
for the combinatorial entropy of mixing randomly holes and segments of both components. The following terms
in the square brackets are extra contributions due to
nonrandom mixing, where X_1, X_2, and X_3 are the values of X_1, X_2, and X_3 derived by the maximization condition
in a similar manner as for pure component systems (see
Appendix). The next two terms are contributions from
the free volume and internal energy. The last term, derived
from the kinetic part of the partition function, was
originally introduced by Jain and Simha\(^6\) to account for
the influence of mixing on the external degrees of freedom
of the system. This term is also present in the HH theory,
even though in the relevant paper it has not been shown
explicitly.\(^3\) The parameters k_1 and k_2 are numerical
constants, and (M_0) is the average molar mass. Starting
from the Helfandt free energy, all other thermodynamic
properties, e.g., the equation of state and miscibility
behavior, can be derived in a straightforward way.

III. Applications

(a) Miscibility Behavior of the System Polystyrene/
Methyl Acetate and Its Pressure Dependence. Poly-
styrene (PS)/methyl acetate (MeOAc) is an interesting
system which shows an upper critical miscibility temper-
ature (UCMT) at low temperatures as well as a lower
critical miscibility temperature (LCMT) at high temper-
atures.\(^6\) The relative location of the LCMT miscibility
gap with respect to the UCMT miscibility gap ensures
that the LCMT is governed by free volume parameters
and therefore can be explained by hole theories. The
miscibility behavior of this system according to the HH
theory has been studied earlier.\(^6\) In that study, the pure
component parameters are obtained from the experimental
equation of state data of both components, and the
intermolecular parameters are determined from a single
experimental UCMT critical point.\(^7\) With these param-
eters, not only a satisfactory description of both UCMT
and LCMT phase behavior is obtained but also the pressure
dependences of UCMT and LCMT consolute states are
predicted, at least qualitatively. Here, the same analysis
is presented for the nonrandom mixing theory and the
results are compared to those of the HH theory. The pure

| Table I
| Enumeration of Contacts in Mixture |
| kind of contact pair | no. of contact pairs |
| segments a-b or b-a | QX |
| segment b-hole or hole-segment b | QX |
| segment a-hole or hole-segment a | Q(u - X_1 - X_3) |
| segments a-a | Q(w - X_1 - X_3) |
| hole-hole | Q(w - X_2 - X_3) |

| Table II
<p>| Molecular Parameters for PS and MeOAc According to the Present Theory and the HH Theory |</p>
<table>
<thead>
<tr>
<th>theory</th>
<th>(\gamma^*)</th>
<th>(\gamma^*)</th>
<th>(M_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>present</td>
<td>5471.4</td>
<td>7.068</td>
</tr>
<tr>
<td></td>
<td>HH</td>
<td>5454.9</td>
<td>8.159</td>
</tr>
<tr>
<td>MeOAc</td>
<td>present</td>
<td>6083.6</td>
<td>6.8225</td>
</tr>
<tr>
<td></td>
<td>HH</td>
<td>5243.3</td>
<td>6.6813</td>
</tr>
</tbody>
</table>

\(*\) Experimental data taken from refs 13 and 14.

| Table III
<p>| Intermolecular Parameters Determined from the UCMT Critical Point of PS(M=179 kg/mol)/MeOAc |</p>
<table>
<thead>
<tr>
<th>theory</th>
<th>(d_{c1})</th>
<th>(d_{c2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>present</td>
<td>1.022 815 3</td>
<td>0.996 371 05</td>
</tr>
<tr>
<td>HH</td>
<td>1.029 971 5</td>
<td>0.990 110 00</td>
</tr>
</tbody>
</table>

\(*\) Experimental data taken from ref 7.\(^6\) By definition, \(\gamma^* = \delta_{c1}(\gamma_{c1}^{1/2} + \gamma_{c2}^{1/2})/2\)\(^6\).
primary interest is the pressure dependence of the critical points, since the HH theory has proven successful in this respect. The predicted and experimental pressure dependence of the LCMT and UCMT critical temperatures is shown in Figures 2 and 3. It may be seen that both theories can predict reasonably the pressure dependence of both LCMT and UCMT critical temperatures. In the case of the LCMT critical temperature, the prediction made by the present theory is almost quantitative. Also for the UCMT critical temperature, the present theory gives a better prediction of the pressure dependence, especially at higher molar masses. For the low molar masses, the pressure dependence is not reproduced exactly. Nevertheless the significant change in pressure dependence observed experimentally is also observed theoretically, although at a much lower molar mass. Thus the molar mass dependence is predicted qualitatively. In comparison, the predictions concerning the molar mass dependence according to the HH theory can be regarded to be less satisfactory.

(b) Pressure Dependence of the UCMT Critical Temperature of the System Polystyrene/Cyclohexane. As another example of the application of the present theory, we will discuss briefly the system PS/cyclohexane (CH). As mentioned before, the HH theory is very successful in predicting the subtle changes in the UCMT critical temperature with pressure of the system PS/CH. The same is true for the present theory. Here, we follow exactly the same procedure as in ref 3. The molecular parameters for the pure components obtained from equation of state data and the intermolecular parameters obtained from a single UCMT consolute point \( (M_{PS} = 520 \text{ kg/mol}) \) are summarized in Tables IV and V. In this case, the segmental molar mass of PS can be taken equal to that of the chemical repeat unit, because the characteristic volumes of PS and CH are almost equal. The predicted pressure dependence of the UCMT critical temperature is shown in Figure 4 in comparison with the experimental data of Wolf and Geerissen. At first inspection it appears that the nonrandom mixing HH (NRMHH) theory does not predict the UCMT pressure dependence as good as the random mixing theory. However, it should be noted that for the HH theory some extra adjustment has been done. To obtain spinodal curves in better agreement with experimental data, the number of external degrees of freedom for cyclohexane was increased to \( c_{CH} = 1.8 \). For the NRMHH theory no such adjustment was introduced. Much better agreement between theory and experiment can be expected if some adjustment of the \( c \) parameter is
simulated results. Presently, the hole model has not been the subject of such a study. However, for the simple lattice–fluid model in which cell contributions are neglected a comparison with MC results is in progress. The preliminary results show that the quasi-chemical approach presents a very accurate approximation to the exact partition function at densities relevant for pure polymers and mixtures. This is reflected in a successful prediction of, e.g., equation of state behavior and the number and type of segmental contacts. A more detailed comparison will be the subject of a forthcoming paper.

Finally, we remark once more that the present theory is regarded as a starting point for a theory of associating systems. The ultimate aim there is the establishment of connections between thermodynamic equilibrium constants and the equation of state.

Appendix: Derivation of the Theory for Binary Mixtures

(1) Partition Function. The partition function of the system is given by

$$Z(N,\phi_A,\gamma, V, T) = \sum_{X_i} Z_i(N,\phi_A, \gamma, V, T, X_1, X_2, X_3) \quad (A.1)$$

where the summation runs over the three $X_i$ parameters. The partition function of the subsystem $X_i$ can be factorized:

$$Z_X = g_i^N \left( \begin{array}{c} c_i \end{array} \right)^N \exp\left( -E_i / kT \right) \quad (A.2)$$

where the parameters $c_i$ and $s$ in the pure component theory have been replaced by their average values $\langle c_i \rangle$ and $\langle s \rangle$. According to Guggenheim, the combinatorial factor $g$ reads

$$g = \frac{N_{hh} \sum_{X_1 X_2 X_3} \left[ (Q(u_{X_1} - X_{1})! (Q(u_{X_2} - X_{2})! (Q(u_{X_3} - X_{3})! \right]}{\sum_{X_1 X_2 X_3} \left[ (Q(u_{X_1} - X_{1})! (Q(u_{X_2} - X_{2})! (Q(u_{X_3} - X_{3})! \right]} \quad (A.3)$$

where $X_i$ ($i = 1, 2, 3$) are the corresponding values of $X_i$ in case of random mixing. The expression for the segmental free length takes almost the same form as for pure components, if only we define $X$ to be the sum of $X_2$ and $X_3$.

$$l_r = \left( \frac{X_2 + X_3}{1 - \omega} \right) \langle l_4 \rangle + \frac{X_2 + X_3}{\omega} \langle l_4 \rangle = \left( 1 - \frac{X}{q} \right) \langle l_4 \rangle + \frac{X}{q} \langle l_4 \rangle \quad (A.4)$$

Also, the definitions of the solid-like and gas-like free lengths ($l_4$) and ($l_4$) are similar to those in the pure component theory, viz.

$$\langle l_4 \rangle = \omega^{1/3} - \gamma^{1/3} \omega^{1/3} = \langle l_4 \rangle \quad (A.5)$$

$$\langle l_4 \rangle = \omega^{1/3} \langle \omega^* \rangle \quad (A.6)$$

where $\omega = \gamma / \omega^*$ is the reduced cell volume, and $\gamma = V / N(s)$ is the volume per segment. The internal energy
$E_0$ now becomes

$$E_0 = Q(u - X_1 - X_2)\epsilon_{aa} + Q(u - X_1 - X_2)\epsilon_{bb} + 2QX_1\epsilon_{ab}$$

(A.7)

or

$$E_0 = Qu_{aa} + Qu_{bb} + Q(2\epsilon_{ab} - \epsilon_{aa} - \epsilon_{bb})X_1 - 3Q_{ab}X_2 - q0X_3$$

(A.8)

If we define

$$\epsilon_1 = 2\epsilon_{ab} - \epsilon_{aa} - \epsilon_{bb}$$

(A.9)

$$\epsilon_2 = -\epsilon_{bb}$$

(A.10)

$$\epsilon_3 = -\epsilon_{aa}$$

(A.11)

then the internal energy can be expressed as

$$E_0 = Qu_{aa} + Qu_{bb} + Q(\epsilon_1X_1 + \epsilon_2X_2 + \epsilon_3X_3)$$

(A.12)

In the above equations, $\epsilon_{aa}$, $\epsilon_{bb}$, and $\epsilon_{ab}$ obey Lennard-Jones 6-12 potentials

$$\epsilon_{aa} = 4(A\rho_{aa}^{-1} - 2B\rho_{aa}^{-2})$$

(A.13)

$$\epsilon_{bb} = 4(A\rho_{bb}^{-1} - 2B\rho_{bb}^{-2})$$

(A.14)

$$\epsilon_{ab} = 4(A\rho_{ab}^{-1} - 2B\rho_{ab}^{-2})$$

(A.15)

The different indices in $\omega_i$ ($i = a, b, ab$) in the above equations indicate that these volumes are reduced with respect to different kinds of hard-core volumes.

(2) Maximization of $Z_X$. If we denote the values of $X_i$ ($i = 1, 2, 3$) which make $Z_X$ maximum by $\bar{X}_i$, we have

$$Z(N,\phi_A, Y, V, T) = Z(\bar{N}, \phi_A, V, T, \bar{X}_1, \bar{X}_2, \bar{X}_3)$$

(A.16)

where $\bar{X}_i$ ($i = 1, 3$) are determined by

$$\frac{\partial \ln Z_X}{\partial \bar{X}_i} = 0$$

(A.17)

The logarithm of $Z_X$ reads

$$\ln Z_X = \ln [Q(u - X_1 - X_3)]! + \ln [Q(u - X_1 - X_2)]! + \ln [Q(w - X_3 - X_2)]! + 2 \ln (QX_1)! + 2 \ln (QX_2)! + 2 \ln (QX_3)! + constant$$

(A.18)

where $\beta = 2^{-1/2}\omega^{-1/3}$. Note that $\beta$ (or, more exactly, $\langle u^* \rangle$) is a function of $X_1$, $X_2$, and $X_3$ as may be seen later. Combination of eqs A.17 and A.18 yields the following set of equations which determine the values of $\bar{X}_1$, $\bar{X}_2$, and $\bar{X}_3$:

$$(\bar{X}_1\eta_1)^2 = (u - X_1 - X_3)(w - X_1 - X_2)\eta_1$$

$$(\bar{X}_2\eta_2)^2 = (u - X_1 - X_3)(w - X_2 - X_3)\eta_2$$

$$(\bar{X}_3\eta_3)^2 = (u - X_1 - X_3)(w - X_2 - X_3)\eta_3$$

(A.19)

where $\eta_i$ ($i = 1, 2, 3$) are given by $\eta_i = \exp(\epsilon_i/2kT)$ and $\eta_1$ through $\eta_3$ are defined as

$$\eta_1 = \exp\left[\frac{2(\epsilon_{ci})}{z(1 - \langle u \rangle)} \frac{\beta(1 - \frac{X}{q})}{1 - \beta(1 - \frac{X}{q})} \frac{\partial \ln \langle u^* \rangle}{\partial X_1}\right]$$

(A.20)

$$\eta_2 = \exp\left[\frac{2(\epsilon_{ii})}{z(1 - \langle u \rangle)} \frac{\beta(1 - \frac{X}{q})}{1 - \beta(1 - \frac{X}{q})} \frac{\partial \ln \langle u^* \rangle}{\partial X_2}\right]$$

(A.21)

$$\eta_3 = \exp\left[\frac{2(\epsilon_{ei})}{z(1 - \langle u \rangle)} \frac{\beta(1 - \frac{X}{q})}{1 - \beta(1 - \frac{X}{q})} \frac{\partial \ln \langle u^* \rangle}{\partial X_3}\right]$$

(A.22)

where $\langle \kappa \rangle = (1 - 1/\langle u \rangle)$, $\gamma = 2/\langle u \rangle$, and $l_\gamma = l_\gamma/\langle u^* \rangle^{1/3}$ is the reduced free length. The partial derivatives $\partial \ln \langle u^* \rangle/\partial X_i$ in the above equations may be calculated from the definition of $\langle u^* \rangle$ (cf. eq A.35).

(3) Determination of $X_i^{*}$. Following Guggenheim, $X_1^*$, $X_2^*$, and $X_3^*$ are determined from the minimization condition

$$\partial Z_X^{(0)}/\partial X_i = 0 \quad (i = 1, 2, 3)$$

(A.23)

where

$$\ln Z_X^{(0)} = \ln [Q(u - X_1 - X_3)!] + \ln [Q(u - X_1 - X_2)!] + \ln [Q(w - X_3 - X_2)!] + 2 \ln (QX_1)! + 2 \ln (QX_2)!$$

(A.24)

The resulting equations for the $X_i^*$'s are

$$X_1^* = (u - X_1^* - X_3^*)(w - X_1^* - X_2^*)$$

$$X_2^* = (w - X_1^* - X_2^*)(w - X_2^* - X_3^*)$$

$$X_3^* = (u - X_1^* - X_3^*)(w - X_2^* - X_3^*)$$

(A.25)

or equivalently

$$[w - (u + v)]X_1^* + [(u + v) - u]X_2^* = u(w - u)$$

$$[w - (u + v)]X_1^* + [(u + v) - u]X_3^* = u(w - u)$$

$$[u - (u + v)]X_2^* + [(u + v) - u]X_3^* = w(u - v)$$

(A.26)

From the above set of linear equations we obtain the following expressions for $X_2^*$ and $X_3^*$ in terms of $X_1^*$

$$X_2^* = \frac{u(w - u) + [(u + v) - w]X_1^*}{(w + u) - u}$$

$$X_3^* = \frac{u(w - w) + [(u + v) - w]X_1^*}{(u + w) - v}$$

(A.27)

Notice that, since the determinant of the set of linear equations (eq A.26) equals zero, there are an infinite number of solutions for $X_1^*$. However, if we consider the total fraction of segment–hole contacts $X^*$ ($X^* = X_1^* + X_2^*$) and the total contact fraction of polymer segments $q$ ($X_1^*$ may be determined by the requirement that the relationship between $X^*$ and $q$ should be the same as that for the pure component. In other words, when we consider the polymer as a whole entity, we should have $X^* = q(1 - q)$, as in the pure component theory. At present, $q = u$
+ v and 1 - q = w, so we have
\[ X^* = \frac{w^2(u + v) - w(u + v') + 2w(u + v - w)X_1^*}{(v + w - u)(u + w - v)} \]

From eq A.28, we obtain \( X_1^* = uv \) and, thereafter, \( X_2^* = uw \) and \( X_3^* = uw \).

(4) Appropriate Partition Function. Combination of eqs A.16 and A.2 gives the configurational partition function of the system
\[ Z_{conf} = g(N, \phi_A, \gamma, X_1, X_2, X_3)[l_1(\phi_A, \gamma, X_1, X_2, X_3)]^3 \times \exp[-E_0/N, \phi_A, \gamma, X_1, X_2, X_3]/kT] \]

The combinatorial factor \( g \) has the form
\[ g = \frac{N_{bb}}{(Q(u - X_1^* - X_3^*))![(Q(u - X_1^* - X_3^*))!(Q(u - X_3^* - X_1^*))!] \times \frac{[(QX_1^*)![(QX_2^*)![(QX_3^*)!]^{3}}{(QX_1^!)[(QX_2^!)[(QX_3^!)!]^{3}} \]

According to HH theory, \( \psi \) we have
\[ \ln N_{bb} = N(s) \left[ -\phi_A \ln \phi_A/s_A - \phi_B \ln \phi_B/s_B - \phi_1 \right] \ln y - \frac{1 - \gamma}{y} \ln (1 - y) + \frac{1}{\gamma} \ln (1 - (\langle \alpha \rangle y) \ln (1 - (\langle \alpha \rangle y) \right] \]

and the free length per segment is
\[ l_1(\phi_A, \gamma, X_1, X_2, X_3) = \bar{\omega}^{1/3} \left[ 1 - \beta \left( 1 - \frac{X_1^*}{q} \right) \right]^{(\psi) 1/3} \]

The expression for the internal energy reads
\[ -E_0/N, \phi_A, \gamma, X_1, X_2, X_3)/kT = \]

\[ -\frac{N(s)z(1 - (\langle \alpha \rangle y)}{2qRT} [(u - X_1 - X_3) \xi_{ab}^* (A\tilde{\omega}^{a^4 - 2B\tilde{omega}^{-2}}) + (u - X_1 - X_3) \xi_{bb}^* (A\tilde{\omega}^{b^4 - 2B\tilde{omega}^{-2}}) + 2X_1 \xi_{ab}^* (A\tilde{\omega}^{a^4 - 2B\tilde{omega}^{-2}})] \]

Comparing eq A.33 with the corresponding formulas for the pure component
\[ -E_0/kT = -N(s)(1 - (\langle \alpha \rangle y)}{2qRT} \psi \]

we obtain the mixing rules:
\[ (u - X_1 - X_3) \xi_{ab}^* (v_{as}^{a^4 + (u - X_1 - X_3) \xi_{bb}^* (v_{bb}^{b^4 + 2X_1 \xi_{ab}^* (v_{ab}^{a^4 = (q - X)(\psi) (\psi)^4 \right] \]

\[ (u - X_1 - X_3) \xi_{ab}^* (v_{as}^{a^2 + (u - X_1 - X_3) \xi_{bb}^* (v_{bb}^{b^2 + 2X_1 \xi_{ab}^* (v_{ab}^{a^2 = (q - X)(\psi) (\psi)^2 \right] \]

where \( \xi_{ab}^* \) and \( \xi_{bb}^* \) are related to the interaction between segments of identical molecules, \( \xi_{ab}^* \) and \( \xi_{bb}^* \) are cross interaction parameters related to the interaction between A-B segments, and \( X = X_2 + X_3 \). Note that if we let \( X_i = X_i^* (i = 1, 2, 3) \) eq A.35 recovers the mixing rules in the HH theory. Using \( (e^*) \) and \( (u^*) \) defined by eq A.35, the internal energy of the system may be written simply as
\[ -E_0/kT = -N(s) \left( \frac{c_j}{2T} \right) \left[ \left( 1 - \frac{X_1}{q} \right) (A\tilde{\omega}^{a^4 - 2B\tilde{omega}^{-2}}) \right] \]

where \( T = T/T^* \) is the reduced temperature and
\[ T^* = z(1 - (\langle \alpha \rangle y)) (\psi) / ((c_j) R) \]

Finally, the logarithm of the partition function of the system is given by
\[ \ln Z_{conf} = N(s) - \phi_A \ln \phi_A/s_A - \phi_B \ln \phi_B/s_B - \gamma \ln y - \frac{1 - \gamma}{\gamma} \ln (1 - y) + \frac{1 - (\alpha y)}{\gamma} \ln (1 - (\alpha y)) - \frac{z(1 - (\langle \alpha \rangle y)}{2q} (2u ln u + 2v ln v + 2w ln w - (u - X_1 - X_3) - (u - X_1 - X_3) ln (u - X_1 - X_3) - (u - X_1 - X_3) ln (w - X_2 - X_3) - 2X_1 ln X_1 - 2X_2 ln X_2 - 2X_3 ln X_3) + (c_j) ln (\psi) \right] \]

(5) Helmholtz Free Energy and Equation of State. The free energy of the system is given by
\[ A/n(s)RT = \psi_A ln \phi_A/s_A + \psi_B ln \phi_B/s_B + \frac{1}{\psi} \ln y + \frac{1 - \gamma}{\gamma} \ln (1 - y) - \frac{1 - (\alpha y)}{\gamma} \ln (1 - (\alpha y)) - \frac{z(1 - (\alpha y)}{2q} (2u ln u + 2v ln v + 2w ln w - (u - X_1 - X_3) ln (u - X_1 - X_3) - (u - X_1 - X_3) ln (w - X_2 - X_3) - 2X_1 ln X_1 - 2X_2 ln X_2 - 2X_3 ln X_3) - (c_j) ln \left( \psi \right) \left[ 1 - \beta \left( 1 - \frac{X_1}{q} \right) \right] \]

where the last term on the right-hand side of the equation comes from the kinetic part of the partition function.\(^5\)

The equilibrium value of the occupied site fraction \( y \) is determined by the minimization condition
\[ \frac{\partial A}{\partial y} = 0 \]

and the equation of state of the binary system is given by
\[ P = -\frac{\partial A}{\partial y} \]

Formally, eqs A.40 and A.41 are quite similar to the corresponding equations in the pure component theory. However, in the present case, the partial derivatives are much more complicated. Especially, one must be cautious about the reduced parameters, since now \( (\psi) \) and \( (\psi) \) are functions of \( X_i \) \( (i = 1, 2, 3) \) and \( y \), whereas the \( X_i \)'s themselves are functions of \( y \) and \( v \).
By straightforward algebra, one obtains the equation of state of the system in its reduced form

\[
\frac{P_0}{T} = \frac{1}{1 - \beta \left(1 - \frac{X}{q}\right)} + \frac{2}{T} \left(1 - \frac{X}{q}\right)(A\omega^4 - B\omega^{-2}) + \frac{m_{11} + m_{33} + \frac{m_{43}}{T} b \frac{\partial X_3}{\partial \theta}}{\partial \theta^{\infty}} (A.42)
\]

where

\[
m_{21} = -\frac{z(1 - \langle \alpha \rangle)}{2q \langle c_s \rangle} \ln \left[ \frac{(X_1)^2}{(u - X_1 - X_3)(u - X_1 - X_2)} \right]
\]

\[
m_{22} = -\frac{z(1 - \langle \alpha \rangle)}{2q \langle c_s \rangle} \ln \left[ \frac{(X_2)^2}{(u - X_1 - X_2)(u - X_2 - X_3)} \right]
\]

\[
m_{23} = -\frac{z(1 - \langle \alpha \rangle)}{2q \langle c_s \rangle} \ln \left[ \frac{(X_3)^2}{(u - X_1 - X_3)(u - X_2 - X_3)} \right]
\]

\[
m_{31} = -\frac{1}{1 - \beta \left(1 - \frac{X}{q}\right)} \left[ 3\theta \left(1 - \frac{X}{q}\right) \log (\tilde{\epsilon}_s) \right]
\]

\[
m_{32} = -\frac{1}{1 - \beta \left(1 - \frac{X}{q}\right)} \left[ 3\theta \left(1 - \frac{X}{q}\right) \log (\tilde{\epsilon}_s) \right]
\]

\[
m_{33} = -\frac{1}{1 - \beta \left(1 - \frac{X}{q}\right)} \left[ 3\theta \left(1 - \frac{X}{q}\right) \log (\tilde{\epsilon}_s) \right]
\]

\[
m_{41} = -\frac{1}{2} \left(1 - \frac{X}{q}\right) \left( A\omega^4 - 2B\omega^{-2} \right) + 4(A\omega^4 - B\omega^{-2}) \frac{\partial \ln (\epsilon_s)}{\partial X_1}
\]

The partial derivatives in the above equations may be obtained either analytically or numerically. The way to proceed analytically has been explained in the previous publication. In the present applications these derivatives were obtained numerically with the aid from a computer algorithm to determine derivatives of functions. The derivatives \(\partial X_i/\partial \theta\), \(\partial (\epsilon_s)/\partial X_i\), and \(\partial (\epsilon_s)/\partial X_i\) for \(i = 1-3\) are obtained from eqs A.19 and A.35, respectively, keeping the relevant parameters constant.

Notice that although the above theory is derived for a binary mixture of homopolymers, it is also valid for polymer solutions.

**References and Notes**

(6) Myrat, C. D.; Rowlinson, J. S. *Polymer* 1965, 6, 645.
(16) E.g.: (a) NAG Routine D04AAF, NAG Fortran Library Manual, Mark 15, NAG Ltd., Oxford, U.K. or (b) IMSL Routine Dderv, IMSL Mathematical Library, IMSL, Houston, TX.