

Quasi-Chemical Treatment of the Hole Theory for r -Mers. II. Mixtures

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ABSTRACT: The molecular theory for a pure liquid of r -mers formulated in a previous paper on the basis of the quasi-chemical treatment (the first approximation) has been extended to mixtures. The present theory takes into account nonrandom mixing of both holes and component molecules. A more crude formulation of a mixture based on the zeroth approximation is also presented for comparison. The expressions for the equation of state, chemical potential and internal energy are derived for the mixture. The excess functions of mixing have been numerically calculated so as to investigate the effect of nonrandom mixing on these quantities by comparing the first and zeroth approximations.

KEY WORDS Hole Theory / Quasi-Chemical Approximation / r -Mer /
Mixtures / Excess Functions / Nonrandomness / Hole Distribution /

In a previous paper,¹ we applied the quasi-chemical treatment to the lattice fluid theory²⁻⁶ and presented a new formulation for a pure liquid of r -mer. The lattice fluid theory is a simple type of hole theory where the cell volume is fixed, and its calculation method is very similar to that of the Flory-Huggins theory.⁷ In the hole theory, a hole is treated as if it were a monomer, but it can be created or destroyed according to thermodynamic conditions, and this results in a change in the volume of the system. The hole has the same role as the free volume. In addition, in the lattice fluid theory, the coordination number is taken infinitely large (the Flory approximation), so that a random mixing of holes and molecules is assumed. However, we abandoned this assumption and took into consideration the nonrandom distribution of holes on the lattice with a finite coordination number.

According to the free volume theory presented by Prigogine,⁸⁻¹⁰ Flory,¹¹⁻¹³ and their coworkers, the thermodynamic properties of polymer solutions are very much affected by the difference in free volume or the equation of state of the pure components. Since, as we have found,¹ the nonrandom distribution of holes influences appreciably the equation of state of pure liquids, the thermodynamic quan-

ties of a mixture should be also influenced. Furthermore, in a mixture, the hole distribution around one molecular species should be different from that around another species, depending on their cohesive energy densities. This was ignored by Renuncio and Prausnitz¹⁴ and Brandani.¹⁵ They modified the Flory theory by using the local composition concept introduced by Wilson¹⁶ so as to take into account the nonrandom mixing of component molecules having the same amount of free volume.

From these viewpoints, we extend the treatment presented in a previous paper to binary systems, and discuss the influence of the nonrandom mixing of both holes and molecules on the thermodynamic behavior of binary systems.

GENERAL THEORY

*Partition Function*¹⁷⁻¹⁹

We assume the existence of a lattice of coordination number z , and consider a system of N_i molecules of species i ($i = 1, 2, \dots, n$) and N_0 vacant lattice sites or holes. Each molecule of species i occupies r_i lattice sites and is characterized by a flexibility parameter δ_i and a symmetry number σ_i .

The following notations are introduced:

$$q_i z = r_i(z-2) + 2 \quad (1)$$

$$N_r = \sum_{k=0}^n r_k N_k \quad (2)$$

$$N_q = \sum_{k=0}^n q_k N_k \quad (3)$$

$$Q = z N_q / 2 \quad (4)$$

$$u_i = q_i N_i / N_q \quad (5)$$

where the subscript 0 represents a hole, and $q_0 = r_0 = 1$ is assumed. The meaning of the above notations is the same as those for pure liquids presented in a previous paper.¹ Note that u_i satisfies the following condition,

$$\sum_{k=0}^n u_k = 1 \quad (6)$$

We denote the configurational potential energy of a contact between the segments of species i and j by $-2\varepsilon_{ij}^*/z$, and assign the value zero to that of a contact with a hole; $\varepsilon_{ij}^* = 0$ when either i or j is 0. Let the number of contacts between the segments of species i and j be represented by $Q y_{ij}$, which satisfies the symmetrical condition $y_{ij} = y_{ji}$. The following equation holds for the total number of contacts with species i ,

$$\sum_{k=0}^n Q y_{ik} = Q u_i \quad \text{or} \quad Q y_{ii} = Q \left(u_i - \sum_{k \neq i}^n y_{ik} \right) \quad (7)$$

Using eq 7, we obtain the configurational partition function as follows:

$$\Omega = \sum_{y_{ij}} \cdots \sum_{y_{ij}} g(N_i, y_{ij}) \exp \left\{ 2Q \left[\sum_i \left(u_i - \sum_{k \neq i}^n y_{ik} \right) \varepsilon_{ii}^* + \sum_{i \neq j} \sum y_{ij} \varepsilon_{ij}^* \right] / z k T \right\} \quad (8)$$

where k is Boltzmann's constant, T is the absolute temperature, and the summation is performed for all possible sets of y_{ij} ($i \neq j$). Following Guggenheim's treatment,^{17,18} the approximate number of configurations g is obtained as,

$$g(N_i, y_{ij}) = N_r! \left(\frac{N_q!}{N_r!} \right)^{z/2} \times \prod_i \frac{(\delta_i / \sigma_i)^{N_i} \left(Q u_i - \sum_{k \neq i} Q y_{ik}^* \right)!}{N_i! \left(Q u_i - \sum_{k \neq i} Q y_{ik} \right)!} \prod_{i \neq j} \frac{(Q y_{ij}^*)!}{(Q y_{ij})!} \quad (9)$$

where y_{ij}^* stands for the random-mixing value of y_{ij} and is given by the equation,

$$y_{ij}^* = u_i u_j \quad (10)$$

Free Energy

Replacing the sum by its maximum term and using Stirling's approximation, we obtain from eq 8 the configurational Helmholtz free energy F as,

$$\begin{aligned} -F/kT &= \ln \Omega \\ &= 2Q \sum_i \left[\left(u_i - \sum_{k \neq i} y_{ik} \right) \varepsilon_{ii}^* + \sum_{j \neq i} y_{ij} \varepsilon_{ij}^* \right] / z k T \\ &\quad + \sum_i N_i \ln (\delta_i / \sigma_i) - \sum_i N_i \ln N_i \\ &\quad - (z/2 - 1) N_r \ln N_r \\ &\quad + (z/2) N_q \ln N_q \\ &\quad - \sum_i Q u_i \ln \left[\left(u_i - \sum_{k \neq i} y_{ik} \right) / u_i^2 \right] \\ &\quad + \sum_{i \neq j} Q y_{ij} \ln \left[\left(u_i - \sum_{k \neq i} y_{ik} \right) / y_{ij} \right] \quad (11) \end{aligned}$$

The set of values for y_{ij} which gives the maximum term is determined by,

$$\begin{aligned} (\partial \ln \Omega / \partial y_{\alpha\beta})_{T, N_i, y_{ij \neq \alpha\beta}} &= 0 \\ (\alpha, \beta = 0, 1, \dots, n; \alpha \neq \beta) \end{aligned} \quad (12)$$

which yields,

$$\begin{aligned} \left(u_\alpha - \sum_{k \neq \alpha} y_{\alpha k} \right) \left(u_\beta - \sum_{k \neq \beta} y_{\beta k} \right) / y_{\alpha\beta}^2 \\ = \exp [2(\varepsilon_{\alpha\alpha}^* + \varepsilon_{\beta\beta}^* - 2\varepsilon_{\alpha\beta}^*) / z k T] \\ (\alpha, \beta = 0, 1, \dots, n; \alpha \neq \beta) \end{aligned} \quad (13)$$

Since the system has n components, eq 13 constitutes simultaneous equations for $n(n+1)/2$ unknown quantities. Note that the last term of eq 11 can be rewritten, by substituting eq 13, as,

$$\begin{aligned}
 & \sum_{i \neq j} Q y_{ij} \ln \left[\left(u_i - \sum_{k \neq i} y_{ik} \right) / y_{ik} \right] \\
 &= (1/2) \sum_{i \neq j} \sum_{k \neq i} Q y_{ij} \ln \left[\left(u_i - \sum_{k \neq i} y_{ik} \right) \left(u_j - \sum_{k \neq j} y_{jk} \right) / y_{ij}^2 \right] \\
 &= 2Q \sum_{i \neq j} y_{ij} (\varepsilon_{ii}^* - \varepsilon_{ij}^*) / z k T \quad (14)
 \end{aligned}$$

From the Helmholtz free energy, we can derive the other thermodynamic quantities in the conventional way.

BINARY MIXTURES

Equation of State

The volume of a system V is

$$V = N_r v^* = (N_0 + r_1 N_1 + r_2 N_2) v^* \quad (15)$$

with v^* being the volume of a lattice site assumed to be independent of temperature and pressure P . Therefore, the volume change of a system is expressed by the change of number of holes. By using eq 12 and 15 under this assumption, we obtain the equation of state as follows:

$$\begin{aligned}
 P &= -(\partial F / \partial V)_{T, N_1, N_2} \\
 &= -(\partial F / \partial N_0)_{T, N_1, N_2} / v^* \\
 &= -(1/v^*) \{ (\partial F / \partial N_0)_{T, Q y_{ij}, N_1, N_2} \\
 &\quad + \sum_{\alpha < \beta} [(\partial F / \partial Q y_{\alpha\beta})_{T, Q y_{ij \neq \alpha\beta}, N_1, N_2} \\
 &\quad \times (\partial Q y_{\alpha\beta} / \partial N_0)_{T, N_1, N_2}] \} \\
 &= -(1/v^*) (\partial F / \partial N_0)_{T, Q y_{ij}, N_2} \quad (16)
 \end{aligned}$$

Substituting eq 11 to eq 16, we have,

$$\begin{aligned}
 P v^* / k T &= (z/2 - 1) \ln (1 - 1/\tilde{V}) \\
 &\quad - (z/2) \ln (1 - y_{01}/u_0 - y_{02}/u_0) \quad (17)
 \end{aligned}$$

where

$$\tilde{V} = V/V^* \quad \text{and} \quad V^* = (r_1 N_1 + r_2 N_2) v^* \quad (18)$$

The values of y_{01} and y_{02} are determined by the following simultaneous equations deduced from eq 13,

$$(u_0 - y_{01} - y_{02})(u_1 - y_{01} - y_{12})/y_{01}^2 = \exp(2\varepsilon_{11}^*/z k T)$$

$$(u_0 - y_{01} - y_{02})(u_2 - y_{02} - y_{12})/y_{02}^2 = \exp(2\varepsilon_{22}^*/z k T)$$

$$\begin{aligned}
 & (u_1 - y_{01} - y_{12})(u_2 - y_{02} - y_{12})/y_{12}^2 \\
 &= \exp \{ 2(\varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^*)/z k T \} \quad (19)
 \end{aligned}$$

Chemical Potential and Internal Energy

For simplicity, we neglect the lattice deformation in the mixing process and consider a mixture of components having the same z and v^* . In other words, these quantities of pure liquids should be determined so as to have the same values. Therefore z and v^* are independent of composition.

With the above assumption and the aid of eq 15, the chemical potential μ_1 of component 1 is derived as,

$$\begin{aligned}
 \mu_1 &= (\partial F / \partial N_1)_{T, v, N_2} \\
 &= (\partial F / \partial N_1)_{T, N_0, N_2} - r_1 (\partial F / \partial N_0)_{T, N_1, N_2} \\
 &= (\partial F / \partial N_1)_{T, N_0, N_2} + P r_1 v^* \quad (20)
 \end{aligned}$$

Following the same procedure used for the derivation of eq 17, we have,

$$\begin{aligned}
 \mu_1 &= -q_1 \varepsilon_{11}^* - k T \{ \ln (\delta_1 / \sigma_1) - \ln N_1 \\
 &\quad - (z/2 - 1) r_1 \ln N_r + (z/2) q_1 \ln N_q \\
 &\quad - (z/2) q_1 \ln \{ (u_1 - y_{10} - y_{12}) / u_1^2 \} \} + P r_1 v^* \quad (21)
 \end{aligned}$$

The internal energy U is given by,

$$\begin{aligned}
 U &= -T^2 [\partial (F/T) / \partial T]_{v, N_1, N_2} \\
 &= -N_q [(u_1 - y_{10} - y_{12}) \varepsilon_{11}^* \\
 &\quad + (u_2 - y_{20} - y_{21}) \varepsilon_{22}^* + 2y_{12} \varepsilon_{12}^*] \quad (22)
 \end{aligned}$$

Excess Functions of Mixing

Let the reduced volume of the pure component i be denoted by \tilde{V}_i . The excess volume of mixing v^E is expressed in terms of the mole fraction x_i as,

$$v^E = (r_1 x_1 + r_2 x_2) v^* \tilde{V} - x_1 r_1 v^* \tilde{V}_1 - x_2 r_2 v^* \tilde{V}_2 \quad (23)$$

With the ideal volume v_0 of the mixture given by assuming the additivity of the pure component volumes, eq 23 is rewritten as,

$$v^E / v_0 = \tilde{V} / (\phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2) - 1 \quad (24)$$

where ϕ_i is the segment fraction of component i defined by,

$$\phi_i = r_i N_i / (r_1 N_1 + r_2 N_2) = r_i x_i / (r_1 x_1 + r_2 x_2) \quad (25)$$

The excess heat or the excess enthalpy of mixing h^E is,

$$h^E = e - x_1 e_1 - x_2 e_2 + P v^E \quad (26)$$

where e and e_i are molar internal energies of a mixture and a pure liquid of component i , respectively.

ZEROth APPROXIMATION

The lattice fluid theory assumes an infinitely large coordination number, which implies random mixing, while the quasi-chemical treatment assumes a finite coordination number and foregoes the random-mixing assumption. As an intermediate treatment, we may assume the random mixing of components on a lattice of a *finite* coordination number. This treatment takes into account the decrease in the contact surface of a chain molecule caused by the connectivity of the segments; this differs from the lattice fluid theory. This treatment is referred to as the zeroth approximation, while the quasi-chemical treatment is referred to as the first approximation.

The partition function of the zeroth approximation for a binary system is obtained by substituting the random-mixing values $y_{ij} = u_i u_j$ into eq 8 and 9. Thus,

$$\Omega = \left(\frac{\delta_1}{\sigma_1}\right)^{N_1} \left(\frac{\delta_2}{\sigma_2}\right)^{N_2} \frac{N_r!}{N_0! N_1! N_2!} \left(\frac{N_q!}{N_r!}\right)^{z/2} \times \exp [2Q(u_1^2 \varepsilon_{11}^* + u_2^2 \varepsilon_{22}^* + 2u_1 u_2 \varepsilon_{12}^*)] \quad (27)$$

Various thermodynamic quantities are derived from eq 27 in the same way as in the first approximation. Thus, going on the same assumption in the preceding section, we have the following expression for the Helmholtz free energy,

$$\begin{aligned} -F/kT &= 2Q(u_1^2 \varepsilon_{11}^* + u_2^2 \varepsilon_{22}^* + 2u_1 u_2 \varepsilon_{12}^*)/zkT \\ &+ N_1 \ln (\delta_1/\sigma_1) \\ &+ N_2 \ln (\delta_2/\sigma_2) - N_0 \ln N_0 \\ &- N_1 \ln N_1 - N_2 \ln N_2 + (z/2)N_q \ln N_q \\ &- (z/2-1)N_r \ln N_r \end{aligned} \quad (28)$$

For the equation of state,

$$Pv^*/kT = (z/2-1) \ln (1-1/\tilde{V}) - (z/2) \ln u_0 - (u_1^2 \varepsilon_{11}^* + u_2^2 \varepsilon_{22}^* + 2u_1 u_2 \varepsilon_{12}^*)/kT \quad (29)$$

For the chemical potential,

$$\begin{aligned} \mu_1 &= -q_1 \varepsilon_{11}^* + q_1 [(u_1-1)^2 \varepsilon_{11}^* + u_2^2 \varepsilon_{22}^* \\ &+ 2(u_1-1)u_2 \varepsilon_{12}^*] - kT [\ln (\delta_1/\sigma_1) - \ln N_1 \\ &- (z/2-1)r_1 \ln N_r + (z/2)q_1 \ln N_q] + Pr_1 v^* \end{aligned} \quad (30)$$

For the internal energy,

$$U = -N_q(u_1^2 \varepsilon_{11}^* + u_2^2 \varepsilon_{22}^* + 2u_1 u_2 \varepsilon_{12}^*) \quad (31)$$

The equation of state may be rewritten in the following reduced form,

$$\begin{aligned} \tilde{P}/\tilde{T} &= -\ln (1-1/\tilde{V}) - [s/(s-1+\tilde{V})]^2/\tilde{T} \\ &+ (z/2) \ln [1+(s-1)/\tilde{V}] \end{aligned} \quad (32)$$

where

$$s = q/r \quad (33)$$

$$\tilde{P} = P/P^*, \quad P^* = \varepsilon^*/v^* \quad (34)$$

$$\tilde{T} = T/T^*, \quad T^* = \varepsilon^*/k \quad (35)$$

The equation of state for a pure liquid can also be written in the same reduced form as eq 32. The parameters of a mixture are related to those of pure components by the following combining rules,

$$s = \phi_1 s_1 + \phi_2 s_2 \quad (36)$$

$$\begin{aligned} s^2 \varepsilon^* &= (s_1 \phi_1)^2 \varepsilon_{11}^* + (s_2 \phi_2)^2 \varepsilon_{22}^* \\ &+ 2(s_1 \phi_1)(s_2 \phi_2) \varepsilon_{12}^* \end{aligned} \quad (37)$$

where

$$s_i = q_i/r_i \quad (38)$$

NUMERICAL RESULTS AND DISCUSSION

In the following numerical calculations, we set $v^* = 1 \times 10^{-5} \text{ m}^3/\text{mol}$ and $z = 12$ for both the first and zeroth approximations, and $v_1^* = v_2^* = v^*$ for the lattice fluid theory. For the contact energy ε_{12}^*

between the segments of different molecular species, we use the Berthelot-type expression,⁴

$$\epsilon_{12}^* = \zeta(\epsilon_{11}^* \epsilon_{22}^*)^{1/2} \quad (39)$$

where the parameter ζ measures the deviation from the Berthelot rule, which assumes $\zeta=1$. Only one parameter ζ , other than those characterizing a pure component, is necessary for determining the thermodynamic behavior of a mixture.

Excess Functions of Mixing

First, we consider a mixture of components each having the same chain length but different cohesive energies. In this case, the excess quantities arise mainly from an energy difference or a contact energy dissimilarity. Figure 1 shows the excess volumes v^E and excess enthalpies h^E at $T=300$ K and $P=0.1$ MPa for mixtures with $r_1=r_2=10$, $T_1^* \equiv \epsilon_{11}^*/k = 500$ K and $T_2^* \equiv \epsilon_{22}^*/k = 600$ K, and

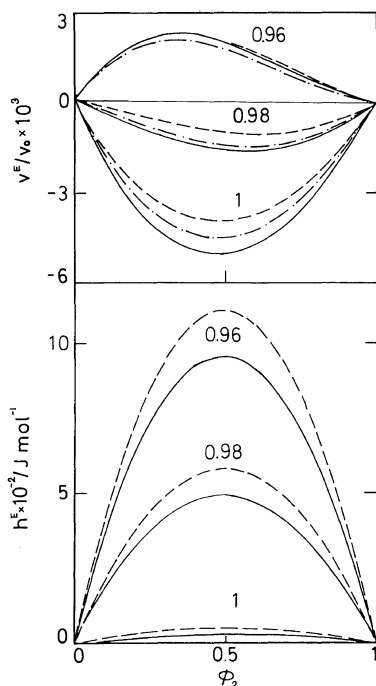


Figure 1. Excess functions at $P=0.1$ MPa and $T=300$ K. Each component is characterized as follows; $r_1=r_2=10$, $T_1^*=500$ K, $T_2^*=600$ K, and $\zeta=0.96, 0.98$, and 1; —, 1st approximation; - - -, 0th approximation; - · - · -, lattice fluid theory; h^E of the 0th approximation falls on the same curve as that of the 1st approximation.

$\zeta=1, 0.98$ or 0.96 . As the contact energy between different molecular species decreases, *i.e.*, as ζ decreases, v^E increases and its sign changes from negative to positive; also, h^E increases. The heat of mixing of the zeroth approximation (0th) is slightly larger than that of the first approximation (1st), but the difference is too small to detect on the scale in this figure. This means that the effect of nonrandom mixing on the heat of mixing is very small in the present case ($r_1=r_2$ and $T_1^* \neq T_2^*$). In other words, the nonrandom mixing of components suppresses the excess enthalpy arising from the contact energy dissimilarity but this is very small. On the other hand, the absolute value of v^E of the 1st approximation is always larger than that of the 0th approximation, indicating that the slope of a $\tilde{V}-\tilde{T}$ curve of the 1st for a pure liquid is steeper than that of the 0th at the same reduced temperature.

The heat of mixing in the lattice fluid theory (LF) is larger than those of the 0th and 1st approximations. This fact is attributable to the difference in

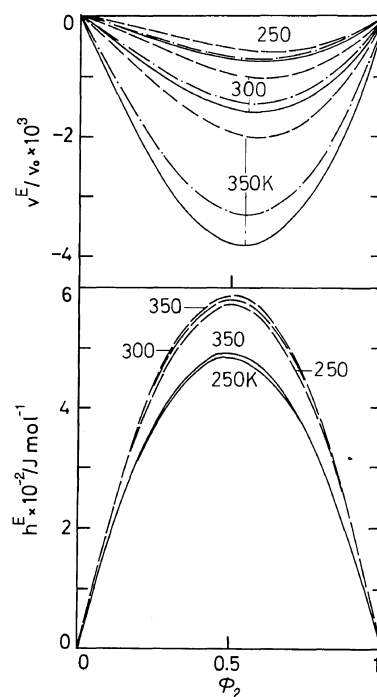


Figure 2. Temperature dependence of excess functions at $P=0.1$ MPa for the system with $\zeta=0.98$ in Figure 1. Curves are the same as in Figure 1. h^E of the 0th and the 1st at various temperatures fall on almost the same curve and are indistinguishable.

the available surface of a chain molecule.¹ The total contact energy per molecule is larger in the case of LF (lattice fluid theory) since the surface area of a molecule in the LF is r/q (≥ 1) of that in the case of the 0th or 1st approximation. In fact, the values of h^E at $\phi_2=0.5$ for $T_1^*=425$ K and $T_2^*=510$ K in LF, which are obtained by multiplying $T_1^*=500$ K and $T_2^*=600$ K by q/r ($=51/60$), are 29.4 ($\zeta=1$), 502 ($\zeta=0.98$), and 976 J/mol ($\zeta=0.96$); these values are almost the same as those of the 0th and 1st for $T_1^*=500$ K and $T_2^*=600$ K, though v^E becomes larger than the values for the 0th and 1st.

Figure 2 shows the temperature dependence of h^E and v^E calculated from various approximations for the system in which $\zeta=0.98$ in Figure 1. It is seen that h^E of both the 0th and 1st are scarcely affected by temperature and fall on the same curve. This shows again that nonrandom mixing has virtually no effect on h^E in this case, since nonrandomness depends essentially on temperature. The absolute value of excess volume v^E increases with temperature because of the large thermal expansion coefficient at higher temperatures.

Figure 3 illustrates the contribution of the free

volume or the equation of state toward the excess functions h^E and v^E , for the case in which components have different chain lengths ($r_1=10$, $r_2=10^2$ or 10^3) but the same characteristic temperatures ($T_1^*=T_2^*=500$ K) and $\zeta=1$. The excess quantities are negative and small compared with those arising from the contact energy dissimilarity (Figure 1). As the difference in r is increased, the equation-of-state difference is also increased and the excess quantities become large. It is interesting that an asymmetric shape of h^E is obtained in spite of using the segment fraction as a composition variable. In contrast to the result in Figure 1, the 0th and 1st give quite different h^E and v^E . Thus we find that the contribution of the free volume to h^E and v^E is appreciably affected by nonrandom mixing.

The temperature dependence of h^E and v^E in the present system is as large as that shown in Figure 4 for $r_1=10$ and $r_2=10^2$. At a higher temperature ($T=350$ K), the free-volume difference is enhanced, resulting in large excess quantities. In particular, h^E is sensitive to temperature, thus differing from the case in which h^E arises from the contact energy

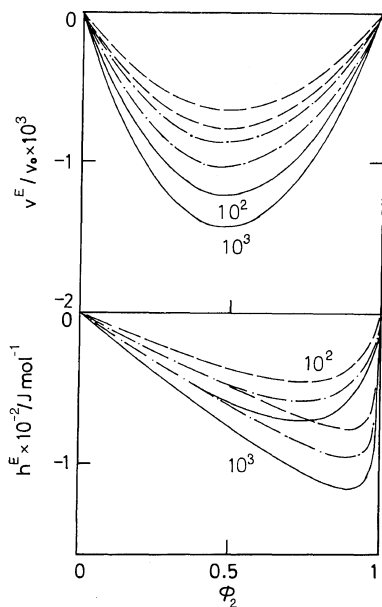


Figure 3. Excess functions at $P=0.1$ MPa and $T=300$ K for mixtures with $r_1=10$, $r_2=100$ or 1000 , $T_1^*=T_2^*=500$ K, and $\zeta=1$. Curves are the same as those in Figure 1.

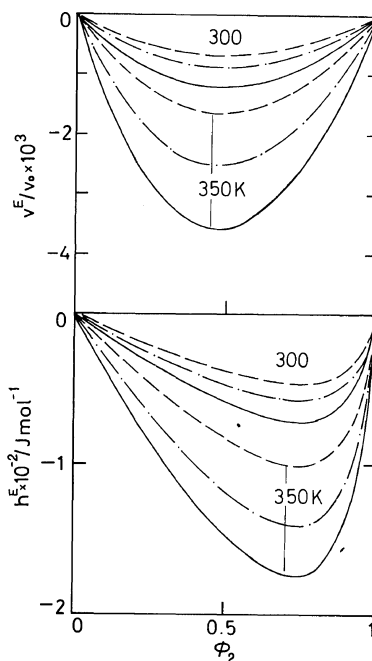


Figure 4. Temperature dependence of excess functions at $P=0.1$ MPa for the system with $r_2=100$ in Figure 3. Curves are the same as in Figure 1.

dissimilarity (Figure 2).

The difference between the 0th and the 1st is larger at higher temperatures, and this is closely related to the fact that the volume of a liquid is always more expanded at the same reduced temperature provided nonrandomness is taken into account. In fact, at $T=300$ K, $\tilde{V}_1=1.164$ and $\tilde{V}_2=1.132$ for the 1st, while $\tilde{V}_1=1.148$ and $\tilde{V}_2=1.121$ for the 0th, and at higher temperatures the difference becomes greater. To compare the 0th with the 1st for systems having the same \tilde{V} -difference, we set $T_1^*=482.7$ K and $T_2^*=484.5$ K for the 0th to obtain the same reduced volumes as those of the 1st at 300 K. We then obtain $v^E/v_0 = -1.18 \times 10^{-3}$ and $h^E = -58.3$ J/mol at $\phi_2=0.5$. These values are close to those of the 1st: $v^E/v_0 = -1.21 \times 10^{-3}$ and $h^E = -58.1$ J/mol. The excess quantities arising only from the free-volume difference are thus determined mainly by nonrandomness in a pure liquid and are virtually independent of nonrandomness in a mixture.

Numbers of Contacts

Figure 5 shows the number of contacts between various pairs in a binary mixture calculated from the first approximation at $\phi_2=0.5$ and $P=0.1$ MPa in a temperature range 200–350 K. We set

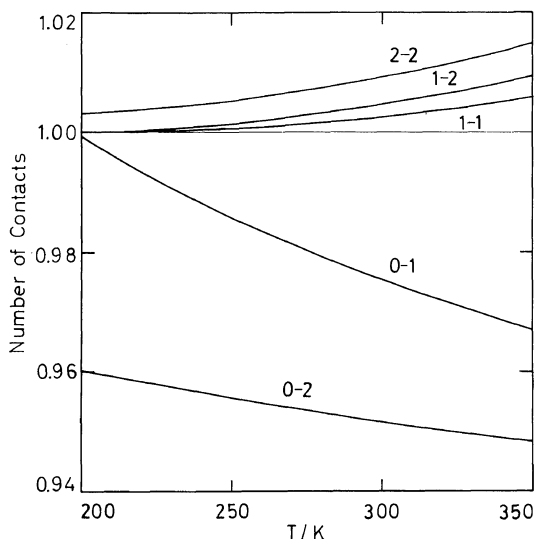


Figure 5. Numbers of contacts between various pairs, which are normalized by the random-mixing values, in the same system as in Figure 1 ($\zeta=1$) at $\phi_2=0.5$ and $P=0.1$ MPa.

$r_1=r_2=10$, $T_1^*=500$ K, $T_2^*=600$ K, and $\zeta=1$. In the figure, a pair of numbers denotes the kind of a contact pair; for example, 0–1 denotes the contact between a hole and component 1. The ordinate is normalized by the random-mixing value, and the derivation from unity measures the degree of nonrandomness.

It is seen that the temperature dependence of the deviation from randomness in a mixture is essentially the same as that in a pure liquid. Thus, the nonrandom distribution is determined by two contributions, that from the energy difference which is a decreasing function of temperature, and that from the number of holes which is an increasing function of temperature. However, the general appearance of the figure is complicated by the existence of an additional component.

The deviation of the 2–2 contact is larger than those of 1–2 and 1–1, which is reasonable, since the 2–2 contact is the most stable among the segment contacts. The value of 2–0 is smaller than that of 1–0 as expected from the fact that $T_2^* > T_1^*$. Since component 2 has a larger cohesive energy, the average distribution of holes around it is less dense than that around component 1, implying that, in a mixture, each component preserves the state of the pure liquid to a certain extent.

CONCLUSION

The quasi-chemical treatment of the hole theory has been extended to binary systems on the basis of the following conditions: the cell volume is fixed and the lattice deformation in the mixing process is not considered. The coordination number and the volume of a lattice site are consequently independent of thermodynamic variables.

The present theory takes into consideration not only the nonrandom mixing of component molecules but also the nonrandom distribution of the free volume. The principle of corresponding states does not hold even for molecules of the same chain length.

We investigated the effect of nonrandom mixing on the excess volume and heat of mixing by comparing the present theory with the more crude zeroth approximation. The excess volume arising from either the equation-of-state difference or the contact energy dissimilarity, always increases as a result of nonrandom mixing. The excess heat arising from

the contact energy dissimilarity is slightly suppressed by nonrandomness, while that arising from the free volume dissimilarity increases. Nonrandom mixing of the component molecules in a mixture is not large enough to affect the excess function, but the nonrandom distribution of holes in a pure liquid contributes very much to this function.

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