Polymer Journal, Vol. 13, No. 4, pp 399—406 (1981)

Quasi-Chemical Treatment of the Hole Theory for *r*-Mers. I. Pure Liquids

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(Received October 23, 1980)

ABSTRACT: The quasi-chemical or first approximation proposed by Guggenheim was applied to the hole theory with fixed cell volume (the lattice fluid theory), in order to investigate effects of the nonrandom distribution of free volume in a liquid. These effects consisted in the differences between the first and zeroth approximations. The partition function for a pure liquid of an *r*-mer was derived, and the equation of state, saturated vapor pressures and orthobaric densities were calculated numerically for various values of *r* so as to investigate the effect of nonrandomness on these quantities. We also discuss the differences between the lattice fluid theory, the zeroth and first approximations.

KEY WORDS Hole Theory / Liquid / Quasi-Chemical Approximation / *r*-Mer / Hole Distribution /

The free-volume theory for dense fluids of *r*-mers[1-6] has proved successful in explaining thermodynamic behavior qualitatively. This theory, however, contains several assumptions which are not always acceptable. Recently, Renuncio and Prausnitz[7] suggested that one limitation of Flory's equation[1-3] for fluid mixtures might be due, in part, to the random-mixing assumption. They modified Flory's partition function by an intuitive concept of local composition, introduced first by Wilson,[8] to take into account the nonrandomness in fluid mixtures. Brandani[9] extended their treatment using a two-fluid theory and derived an equation of state similar to Flory's having an additional term arising from abandonment of the random-mixing assumption. In a mixture, the average distribution of vacant space (holes) around one molecular species should be different from that around the other species. Furthermore, in a liquid, molecules are not dispersed uniformly in space. Therefore, it is necessary to consider nonrandomness of the free-volume distribution as well as the nonrandom mixing of component molecules. However, the two theories mentioned above consider only the nonrandom mixing of component molecules and ignore nonrandomness of the free-volume distribution. Thus an equal free volume is assigned to each molecule. Nonrandomness (nonuniformity) of the free-volume distribution may seriously effect solution properties, since it is well known that free volume plays an important role in the thermodynamic properties of polymer solutions.[10]

In this paper, we apply the quasi-chemical treatment (the first approximation) to the lattice fluid theory[11-14] in order to take into account the nonrandomness of free-volume distribution and derive a partition function for a pure liquid of an *r*-mer. The lattice fluid theory is a sort of hole theory with fixed cell volume. In it, the volume change of a system is expressed by the change in the number of holes and the holes play the same role as does the free volume. The nonrandom distribution of free volume can be expressed by a nonuniform distribution of holes on a lattice. This is why we adopt the lattice fluid theory here. The present treatment is an extension of the old work of Toda,[15] who treated the special case of $r=1$. We discuss the influence of the nonrandom distribution of holes on the thermodynamic quantities and investigate the difference between the lattice fluid theory and the present theory. Extension to multicomponent systems will be made in the following paper.

THEORY

Partition Function[16-18]

We assume the existence of a lattice of coordination number z, and consider a system of N molecules and N_0 vacant lattice sites (holes). Each molecule occupies r lattice sites (r-mer), and is characterized by a flexibility parameter δ and a symmetry number σ. The parameter δ is defined as the number of ways in which an r-mer can be arranged after one of its end segments has been placed in a lattice site. It is convenient to introduce the following notations:

$$qz = r(z-2)+2 \tag{1}$$

$$N_r = N_0 + rN \tag{2}$$

$$N_q = N_0 + qN \tag{3}$$

$$Q = zN_q/2 \tag{4}$$

The quantity qz represents the number of contact pairs per molecule exclusive of chemically bonded pairs, N_r is the total number of lattice sites, and Q is the total number of contacts between nonbonded pairs when a hole is treated as a monomer. We also introduce the following abbreviations:

$$u = qN/N_q\,, \qquad v = N_0/N_q = 1-u \tag{5}$$

We assign $-2\varepsilon^*/z$ to the configurational potential energy of a contact between segments of r-mers, and the value zero to that of a contact with a hole. Let the number of contacts between a segment and a hole be represented by $2Qy$. Then the numbers of contacts between segments and between holes are $Q(u-y)$ and $Q(v-y)$, respectively.

The configurational partition function Ω is given by,

$$\Omega = \sum_{Qy} g(N_0, N, Qy) \exp\,[2Q(u-y)\varepsilon^*/zkT] \tag{6}$$

where k is Boltzmann's constant and T is the absolute temperature. The summation is performed for all possible values of y. The number of configurations g cannot be obtained exactly, but Guggenheim presented an approximate expression eq 7 by adopting the quasi-chemical treatment,[16,17]

$$g(N_0, N, Qy) = \left(\frac{\delta}{\sigma}\right)^N \frac{N_r!}{N_0!N!}\left(\frac{N_q!}{N_r!}\right)^{z/2} \times \frac{(Qu-Qy^*)!(Qy^*)!(Qy^*)!(Qv-Qy^*)!}{(Qu-Qy)!(Qy)!(Qy)!(Qv-Qy)!} \tag{7}$$

In this equation, two $(Qy)!$ were inserted instead of one $(2Qy)!$, since a distinction was made between the segment-hole and hole-segment pairs. The numerator of eq 7 is the normalization factor introduced to compensate for overestimation of the denominator. Thus y^* stands for the random-mixing value of y and is given by,

$$y^* = uv \tag{8}$$

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

$$\begin{aligned} -F/kT &= \ln \Omega \\ &= \frac{2Q(u-y)\varepsilon^*}{zkT} + N \ln \frac{\delta}{\sigma} - N_0 \ln N_0 \\ &\quad - N \ln N - \left(\frac{z}{2}-1\right) N_r \ln N_r \\ &\quad + \frac{z}{2} N_q \ln N_q - Qu\frac{u-y}{u^2} - Qv \ln \frac{v-y}{v^2} \\ &\quad + Qy \ln \frac{(u-y)(v-y)}{y^2} \end{aligned} \tag{9}$$

The value of y which gives the maximum term is determined by,

$$(\partial F/\partial y)_{T,N_0,N} = 0 \tag{10}$$

which yields

$$(u-y)(v-y)/y^2 = \exp\,(2\varepsilon^*/zkT) \equiv \eta^2 \tag{11}$$

The solution of this quadratic equation is,

$$y = 2uv/(\beta+1) \tag{12}$$

where

$$\beta \equiv [1+4uv(\eta^2-1)]^{1/2} \tag{13}$$

Using eq 11, we can rewrite eq 9 as,

$$\begin{aligned} -F/kT &= \frac{2Qu\varepsilon^*}{zkT} + N \ln \frac{\delta}{\sigma} - N_0 \ln N_0 \\ &\quad - N \ln N - \left(\frac{z}{2}-1\right) N_r \ln N_r \\ &\quad + \frac{z}{2} N_q \ln N_q - Qu \ln \frac{u-y}{u^2} - Qv \ln \frac{v-y}{v^2} \end{aligned} \tag{9$'$}$$

Equation of State

Let the volume of a lattice site be denoted by v^*. Then the volume V of the system is represented by,

$$V=(N_0+rN)v^* \tag{14}$$

On assuming that v^* is independent of temperature T and pressure P, the equation of state is derived from the free energy as,

$$P=-(\partial F/\partial V)_{T,N}=-(\partial F/\partial N_0)_{T,N}/v^* \tag{15}$$

Regarding F as a function of Qy and N_0 and using eq 10, we have,

$$\begin{aligned}(\partial F/\partial N_0)_{T,N}&=(\partial F/\partial N_0)_{T,N,Qy}\\&\quad+(\partial F/\partial Qy)_{T,N,N_0}(\partial Qy/\partial N_0)_{T,N}\\&=(\partial F/\partial N_0)_{T,N,Qy}\end{aligned} \tag{16}$$

From eq 9, 15, and 16, we have,

$$Pv^*/kT=(z/2-1)\ln(N_0/N_r)-(z/2)\ln(1-y/v) \tag{17}$$

The equation of state in the reduced form is given by,

$$\tilde{P}/\tilde{T}=(z/2-1)\ln(1-1/\tilde{V})-(z/2)\ln(1-y/v) \tag{18}$$

where

$$y=y(\tilde{V},\tilde{T},r) \qquad v=v(\tilde{V},\tilde{T},r)$$

and the reduced quantities are defined by,

$$\tilde{P}=P/P^* \qquad \tilde{T}=T/T^* \qquad \tilde{V}=V/V^* \tag{19}$$

where

$$P^*=\varepsilon^*/v^* \qquad T^*=\varepsilon^*/k \qquad V^*=rNv^* \tag{20}$$

The characteristic volume parameter V^* corresponds to the occupied volume of the system.

Internal Energy and Chemical Potential

Internal energy U is calculated from eq 9 and 10 to be,

$$\begin{aligned}U&=kT^2(\partial\ln\Omega/\partial T)_{V,N}=kT^2(\partial\ln\Omega/\partial T)_{N_0,N,Qy}\\&=-2Q(u-y)\varepsilon^*/z\end{aligned} \tag{21}$$

Chemical potential μ is expressed, using eq 17, by,

$$\begin{aligned}\mu&=(F+PV)/N\\&=-q\varepsilon^*-kT\{\ln(\delta/\sigma)-\ln N\\&\quad+(1-z/2)r\ln N_r+(z/2)q\ln N_q\\&\quad+(z/2)q\ln[u^2/(u-y)]\}+Prv^*\end{aligned} \tag{22}$$

Vapor–Liquid Equilibrium and Critical Point

The saturated vapor pressure and the densities of the gas and liquid phases in equilibrium at temperature T are calculated from the equation of state and the equilibrium condition,

$$\mu_g(T,P,\rho_g)=\mu_l(T,P,\rho_l) \tag{23}$$

where ρ is the density and the subscripts g and l denote the gas and liquid phases respectively.

The critical point for the gas-liquid phase transition is determined from the conditions,

$$(\partial P/\partial V)_T=0\,, \qquad (\partial^2P/\partial V^2)_T=0 \tag{24}$$

Substituting eq 17, we obtain the reduced expressions for the critical volume $\tilde{V}_c$ and temperature $\tilde{T}_c$ as,

$$\tilde{V}_c=1+q[(z-1)/(qz-1)]^{1/2}\equiv 1/\tilde{\rho}_c \tag{25}$$

$$\eta_c^2=\exp(2/z\tilde{T}_c)=(1/2)\{1+ab+[(a^2-1)(b^2-1)]^{1/2}\} \tag{26}$$

where

$$a=z/(z-2) \quad\text{and}\quad b=qz/(qz-2)=qz/r(z-2) \tag{27}$$

The critical pressure $\tilde{P}_c$ is obtained by substituting eq 25 and 26 into eq 18.

NUMERICAL RESULTS AND DISCUSSION

General Features of the Theory

When the contact energy between segments ε^* vanishes, random mixing is established and eq 8 is deduced from eq 12. If random mixing is assumed even for a nonzero value of ε^*, $y=uv$, which when substituted into eq 6 and 7 gives,

$$\Omega=\left(\frac{\delta}{\sigma}\right)^N\frac{N_r!}{N_0!N!}\left(\frac{N_q!}{N_r!}\right)^{z/2}\exp\frac{2Qu^2\varepsilon^*}{zkT} \tag{28}$$

This is referred to as the zeroth approximation, while the quasi-chemical approximation presented above is referred to as the first approximation. Equations 11—13 suggest that the zeroth approximation is obtained mathematically by letting z be infinitely large only in the thermal term η, while ignoring the z-dependence of u and v. In fact, the zeroth approximation formulae for various thermodynamic quantities can be derived from the first approximation formulae by the above manipulation. Thus, we expand eq 12 in powers of $1/z$ and

retain the first order term,

$$y = uv(1 - 2uv\varepsilon^*/zkT) \tag{29}$$

Then we substitute eq 29 into the formulae of the first approximation and retain the same order terms to obtain those of the zeroth approximation. For example, substituting eq 29 into eq 17, we have,

$$Pv^*/kT = (z/2 - 1)\ \ln\ (N_0/N_r) - (z/2)\ \ln\ v - u^2\varepsilon^*/kT \tag{30}$$

which is the same as those derived directly from eq 28 in the conventional way. Here we must notice that the above procedure is only formal and that the random-mixing value of y is not given by eq 29.

As a rougher approximation, we make $z \to \infty$ not only in the thermal terms but also in the other terms. This approximation, referred to as Flory's approximation, leads to the lattice fluid theory proposed by Sanchez and Lacombe. Thus, using Stirling's approximation, we obtain from eq 6,

$$\Omega = \left(\frac{1}{f_0}\right)^{N_0}\left(\frac{\omega}{f}\right)^{N} \exp\frac{N_r f^2 \varepsilon^*}{kT} \tag{31}$$

where

$$f_0 \equiv N_0/N_r\,, \qquad f \equiv rN/N_r \quad \text{and} \quad \omega \equiv \delta r/\sigma e^{r-1}$$

The theory presented above is very similar to Guggenheim's theory for two-component systems, while the lattice fluid theory is very similar to the Flory–Huggins theory for polymer solutions, if a liquid is considered as a mixture of molecules and holes in the hole theory. Therefore, various quantities of pure liquids derived from the lattice fluid theory or the present theory correspond to certain quantities of binary systems derived from Guggenheim's theory. For example, making $z \to \infty$ in eq 25 and 26, we have,

$$\tilde{\rho}_c = 1/(1+\sqrt{r})\,, \qquad \tilde{T}_c = 2/(1+1/\sqrt{r})^2 \tag{32}$$

The right-hand sides of these equations are the same as the expressions for the segment fraction ϕ_c and the parameter $1/\chi_c$ at the critical point in the Flory–Huggins theory. This enables us to interpret the thermodynamic behavior of a fluid of a chain molecule in terms of the theoretical predictions for solution properties which have been fully investigated.

In the reduced equation of state, eq 18, y and v depend not only on the reduced quantities but also on r. Therefore, the principle of corresponding states[19] holds not generally but only for the molecules of the same size (the same r). The failure of the corresponding states principle for liquids with different chain lengths may be essential, considering the above-mentioned analogy between a liquid and a two-component system, since the asymmetric shape of the phase diagram, which depends on the chain length r, is essential in polymer solutions.

Numerical Results and Discussion

By comparing the results calculated from the first-approximation formulae with those from the zeroth-approximation formulae, we can examine the influence of nonrandom distribution of holes on various quantities.

V–T relations. Figure 1 shows the reduced volume–temperature relations and the boiling points calculated from various approximations for $r = 2$, 5 and ∞ at $\tilde{P} = 3 \times 10^{-4}$, which is roughly the atmospheric pressure for most organic compounds.[12] We put $z = 12$ for both the zeroth and first approximations, which are abbreviated below as the 0th and 1st, respectively. The reduced volume of the 1st is expanded more than that of the zeroth when compared at the same reduced temperature. This result is reasonable, since nonrandomness suppresses the contribution from the energy difference between holes and segments. The boiling temperature is scarcely affected by nonrandomness, while the volume at the boiling point is significantly affected. The volume difference between $r = 5$ and ∞ at the same T is slightly larger in the 1st than in the 0th. The V–T curve for the lattice fluid theory (LF) crosses that of the 1st, while the volume of LF is expanded more than that of the 0th throughout the entire temperature range. The boiling point of LF is at a higher temperature than those in other cases.

Saturated Vapor Pressures and Orthobaric Densities. Figure 2 shows the saturated vapor pressure curves for different r, which terminate at critical points. The influence of nonrandomness depends on r. That is, for $r = 1$ and 2 the vapor pressures of the 1st are higher than those of the 0th, while the tendency is reversed for $r = 5$ and higher r, (only the case of $r = 5$ is shown in the figure). The vapor pressure of LF is always lower than those in the two other cases and the difference is larger for higher r. This behavior can be explained by the fact that the available surface area of a molecule depends

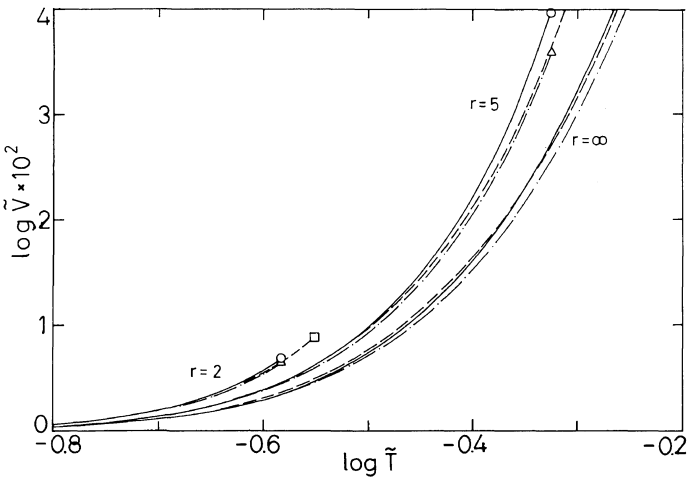

Figure 1. Reduced volume–temperature relations and boiling points at $\tilde{P}=3\times10^{-4}$: —— (○), 1st approximation; — · — · — (△), 0th approximation; — — — (□), lattice fluid theory.

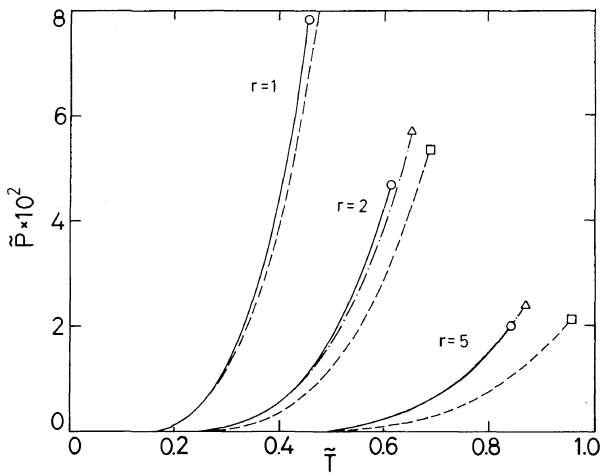

Figure 2. Saturated vapor pressures and critical points for $r=1$, 2 and 5. Symbols are the same as in Figure 1.

on z. Thus, the surface of an r-mer on a lattice of finite z is q/r ($\leqq 1$) that on a lattice of infinite z which corresponds to LF. Therefore, even for a molecule characterized by the same T^* or ε^*, the total contact energy per molecule is larger in the case of LF, being proportional to the surface area of the molecule.

Although the vapor pressure for $r=5$ is not seriously affected by the nonrandom distribution of free volume, orthobaric density curves are more sensitive to nonrandomness as illustrated in Figure 3. For $r=5$, the curve of the 1st appears inside that of the 0th, but this is not always true for other r, since the relative positions of the critical points for different approximations vary with r, as shown in the next section. The reduced density at the same boiling temperature is largely affected by the position of the critical point.

Critical Points. Figure 4 shows the relation between the critical density and critical temperature, where the critical points for the first ten integers of r are illustrated by symbols. As r increases, $\tilde{\rho}_c$ decreases to zero at $r=\infty$, and $\tilde{T}_c$ increases

monotonically to a finite value at $r=\infty$. For $r=1$, $\tilde{\rho}_c$ is 0.5, irrespective of the kind of approximation. In the case of LF, $\tilde{T}_c$ is given by eq 32, which reduces to $\tilde{T}_c=2$ as $r\rightarrow\infty$, and this plot is quite similar to the Flory–Shultz plot for polymer solutions, which allows the Θ-point to be determined as the critical point of an infinitely large molecule. $\tilde{T}_c$ of the 0th approaches 5/3 as $r\rightarrow\infty$, which is equal to the value of LF multiplied by the decrement of the available surface q/r. $\tilde{T}_c$ of the 1st for infinite r is calculated from eq 26 to be,

$$\tilde{T}_c=2/\{z \ln [(z-1)/(z-2)]\} \tag{33}$$

It is interesting that $\tilde{T}_c$ of the 1st has a limiting value at $r=\infty$ different from that of the 0th, in spite of $\tilde{\rho}_c=0$ in both cases. $\tilde{T}_c$ of the 1st is lower than that of the 0th for smaller r, and becomes closer as r increases, and exceeds that of the 0th in the case of larger molecules.

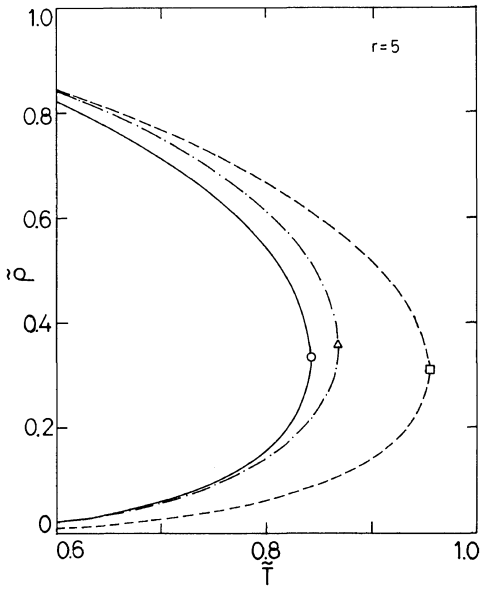

Figure 3. Orthobaric densities and critical point for $r=5$. Symbols are the same as in Figure 1.

Number of Contacts. Figure 5 shows, for $r=2$ and ∞, the temperature dependence at $\tilde{P}=3\times10^{-4}$ of the number of contacts between segments $Q(u-y)$, that between holes $Q(v-y)$, and that between holes and segments Qy, normalized by the random-mixing values Qu^2, Qv^2, and Quv, respectively. At low temperature the deviation of the number of contacts between holes from the random-mixing value is large, while the corresponding deviations for other types of contacts are small. The reduced volume of the system at low temperature is small and nearly equal to unity; thus, the system can be regarded as a dilute solution of holes in a solvent of chain segments. In this situation, though the energy difference is enhanced at low temperature as can be seen from eq 11, the nonrandom effect does not appear in $Q(u-y)$ or Qy, and it is appreciable only in $Q(v-y)$. However, at much lower temperature, the nonrandom effect on $Q(v-y)$ is considered to diminish, as is the case in which an infinitely small

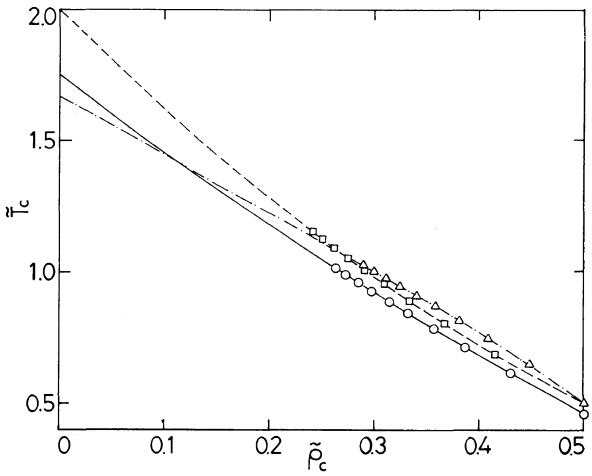

Figure 4. Relation between critical temperature and density, Symbols are the same as in Figure 1 except that ○, △, and □ represent the critical points for $r=1, 2, \cdots, 10$.

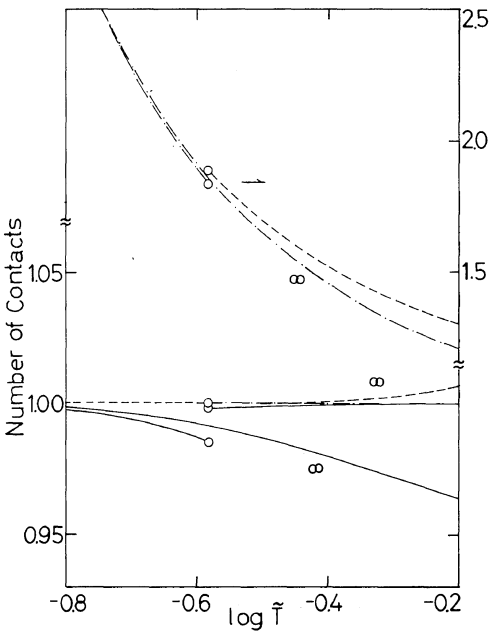

Figure 5. Numbers of contacts between various pairs, normalized by random-mixing values, for $r=2$ and ∞ at $\tilde{P}=3\times10^{-4}$. ○ shows the boiling point of $r=2$. —·—·—, hole–hole pair; – – –, segment–segment pair; ——, hole–segment pair.

amount of a solute can be dissolved even in an extremely poor solvent. As the temperature is raised, the amount of holes increases and the deviation of $Q(u-y)$ and Qy from unity is also enhanced at least in the liquid phase which is not so expanded, while that of $Q(v-y)$ from unity decreases since the energy difference becomes less important. As r gets larger, the system condenses more and the deviation of $Q(u-y)$ and Qy becomes smaller. There exists a discontinuity at the boiling point, as can be seen for $r=2$. Above the boiling point, *i.e.*, in the gas state, the number of segments is very small compared with that of holes. Further, the energy difference is less effective at high temperature. As a result, in this range, deviation from random mixing decreases with increasing temperature.

Values of Parameters

Values of the molecular parameters used in comparing theory with experiment are often determined so that the theory reproduces experimental data. To see how much the parameters evaluated in this way depends on the approximation of the theory, we estimated the difference in the parameters between LF and the 1st, obtaining the same V–T relation. Thus, we evaluated the LF parameters which allowed us to reproduce the V–T relation under $P=0$ that was calculated from the first approximation, using given values of the parameters. By applying the conventional nonlinear least-squares method with V^* fixed over a temperature range 10—70°C, we obtained $r=8.00$ and $T^*=524$ K for LF so as to reproduce the V–T relation of the 1st with $z=12$, $r=24$, and $T^*=508$ K. These values are nearly equal to those for benzene according to Sanchez *et al.*[12] If we treat V^* as a variable, we obtain $V^*=7.86\times10^{-5}$ $m^3\,mol^{-1}$, $r=7.89$, and $T^*=523$ K for LF from the 1st with $z=12$, $V^*=7.88\times10^{-5}$ $m^3\,mol^{-1}$, $r=18$, and $T^*=516$ K. Of course, the change in the parameter with degree of approximation depends on the physical properties involved in determining it. For example, if we use saturated vapor pressure instead of the V–T relation, we obtain results different from the above. However, the difference may not be large. We may conclude that the parameters of the same order as those of LF can be used in the 1st when making theoretical predictions for liquid properties.

CONCLUSION

We applied the quasi-chemical or first approximation to the lattice fluid theory and presented a new formulation for a pure liquid of an r-mer, which takes into account the nonrandom distribution of free volume in a liquid. We also presented a more crude formulation referred to as the zeroth approximation, in which we assumed the random distribution of free volume for a finite coordination number. On making a comparison of the numerical results from these two approximations, we found appreciable differences caused by nonrandomness. Thus, at a fixed temperature the volume of a liquid is always more expanded if nonrandomness is taken into account. With regard to saturated vapor pressure and the critical quantities, the influence of nonrandomness depends on the chain length r. The value of r at which the mode of the influence changes depends on the thermodynamic quantity considered.

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