

does not seem to outweigh the contribution due to the dilution of polar groups by the long hydrocarbon chain in group F, which makes F more positive than G. The systems G and H are less endothermic since both the dipolar contributions and the orientational-order contributions are negligible in these cases.

If the long-chain esters have molecular ordering in the pure state, it is possible to use Kirkwood's parameter  $g$  as an approximate measure of the molecular orientations of these esters. We have calculated  $g$  from eq 9<sup>13</sup> by sub-

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{(n^2 + 2)^2} \frac{M}{d} = \frac{4\pi M_g \mu^2}{9kT} \quad (9)$$

stituting the measured<sup>14</sup> values of dielectric constant  $\epsilon$ , density  $d$ , and refractive index  $n$  of these esters and correlating the interaction parameter  $X_{12}/S_1$  with  $g$  as shown in Figure 2.

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There is a definite trend observed. The value of  $g$  is  $\sim 1$  for ethyl and butyl acetates, indicating that they consist of randomly oriented dipoles, and it systematically decreases for higher esters.

If Kirkwood's parameter bears a correlation with  $\Delta h^M$  and  $X_{12}/S_1$  in the case of ester mixtures, one would expect a similar correlation with alcohol mixtures. In Table III the values of  $\Delta h^M$  and  $X_{12}$  (here  $X_{12}/S_1$  will show the same trend as  $X_{12}$ ) are listed<sup>15,16</sup> at equimolar compositions together with  $\Delta g$  values calculated for aliphatic alcohol mixtures from the literature<sup>3,4</sup> data on  $\epsilon$ ,  $n$ , and  $d$ . Both  $\Delta h^M$  and  $X_{12}$  values systematically increase with  $\Delta g$ .

In conclusion one would say that  $\Delta h^M$  or  $X_{12}/S_1$  variation for the polar systems may be due to two factors: (a) overcoming of dipolar interactions and (b) overcoming of molecular ordering in solvent, solute, or both and bearing a correlation with Kirkwood's parameter.

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## Equilibrium Theory of $r$ -mer Fluids

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In this paper we present a new equation of state for pure  $r$ -mers based on the lattice model. This equation uses the full Guggenheim combinatorial without taking the large coordination number ( $z$ ) limit and is an extension of the Sanchez-Lacombe theory of infinite  $z$ . It is found that the equation is simple in form, predicts a liquid-vapor transition, and gives temperature-dependent virial coefficients.

### Introduction

In 1974, Sanchez and Lacombe<sup>1</sup> (SL) presented a theory of  $r$ -mers based upon a lattice model for liquids. They obtained an equation of state which predicts a liquid-vapor phase transition. Moreover, many trends in physical properties are in qualitative agreement with experiment. Subsequent work<sup>2-4</sup> has used this theory to fit alkane data and treat mixtures. The parameters used by Sanchez and Lacombe are  $\epsilon^* = \epsilon z/2$ , where  $\epsilon$  is the nonbonded mer-mer interaction energy and  $z$  the lattice coordination number;  $v^*$  is the close-packed mer volume and  $r$  the number of mers per  $r$ -mer.

The reduced Gibbs free energy from the SL theory is  $\tilde{G} = G/(Nr\epsilon^*) =$

$$-\bar{p} + \bar{P}\bar{v} + \bar{T} \left[ \frac{(1 - \bar{p})}{\bar{p}} \ln(1 - \bar{p}) + \frac{1}{r} \ln(\bar{p}/\omega) \right] \quad (1)$$

and the equation of state is

$$\bar{p}^2 + \bar{P} + \bar{T}[\ln(1 - \bar{p}) + (1 - 1/r)\bar{p}] = 0 \quad (2)$$

where  $\omega = r\delta/(\sigma e^{r-1})$ ,  $\bar{P} = P/P^*$ ,  $P^* = \epsilon^*/v^*$ ,  $\bar{T} = T/T^*$ ,  $T^* = \epsilon^*/k$ ;  $\bar{v} = 1/\bar{p} = V/(Nr v^*) = V/V^*$  for  $N$   $r$ -mers at pressure  $P$  and temperature  $T$ . The derivation of these equations starts with the Guggenheim<sup>5</sup> combinatorial in the large lattice coordination number ( $z$ ) limit.

We have reexamined the basis upon which eq 1 and 2 rest in the light of the general qualitative success that they display. The motivations of this work are (1) to improve the predictive value of the equation of state and (2) to remove  $r$  as an adjustable parameter. The latter goal is based upon the premise that the length of an  $r$ -mer is essentially fixed such that variations due to vibration are negligible. The available volume per particle in the liquid phase near the melting point is only slightly larger than in the solid. The main difference is that the number of nearest neighbors has a well-defined value in crystals but only some average value in liquids. Moreover, we also seek a theory that is functionally simple.

### Description of the Equation of State

The basis for our treatment is to abandon the large  $z$  limit. In doing so, one needs the ratio of fraction of non-

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bonded pairs  $(z/2)N_q$  to the total number of pairs  $(z/2)N_s$ . Here we specify

$$N_q = N_0 + qN \quad (3)$$

$$N_s = N_0 + rN \quad (4)$$

with, in words,  $qz$  being the number of nonbonded nearest neighbors,  $N_s$  the total number of lattice sites, and  $N_0$  the number of vacant sites. The ratio is

$$N_q/N_s = (1 - \phi\bar{p}) \quad (5)$$

where  $\phi$  is proportional to the fraction of bonded pairs which, for straight or branched  $r$ -mers, is

$$\phi = (2/z)(1 - 1/r) \quad (6)$$

Physically,  $1 - \phi\bar{p} \equiv f_{NB}$  is the fraction of nonbonded pairs in the system and, that being so, it reflects the decrease in the external degrees of freedom of the  $r$ -mers with decreasing numbers of nonbonded pairs (by nonbonded pairs here it is meant hole-hole, hole-mer, and nonbonded mer-mer). It is straightforward to show that  $\phi$  is the ratio of the fraction of bonded  $r$ -mer pairs to the fraction of sites occupied by  $r$ -mers.

We treat  $\phi$  as an adjustable parameter which, for this case of  $r$  fixed, is equivalent to varying  $z$ . The Guggenheim combinatorial becomes with no approximation

$$\Omega(E, V, N) = (\bar{\omega}/f)^N (1/f_0)^{N_0} (1 - \phi f)^{(z/2)N_q} \quad (7)$$

where

$$\bar{p} = f = rN/N_s \quad (8)$$

$$f_0 = 1 - f = N_0/N_s \quad (9)$$

$$\bar{\omega} = r\delta/\sigma \quad (10)$$

where  $\delta$  and  $\sigma$  are a "flexibility parameter" and the symmetry number<sup>2</sup> whose values are of no importance for the equation of state. Use of eq 7 gives

$$\frac{G}{Nr\epsilon^*} = \bar{G} = \frac{-\bar{p}(1 - \phi)^2}{(1 - \phi\bar{p})} + \bar{P}\bar{v} + \bar{T} \left[ \frac{1}{r} \ln(\bar{p}/\bar{\omega}) + (\bar{v} - 1) \ln(1 - \bar{p}) - \left(1 - \frac{1}{r}\right) (\phi)^{-1} \frac{(1 - \phi\bar{p})}{\bar{p}} \ln(1 - \phi\bar{p}) \right] \quad (11)$$

and the equation of state

$$\left[ \bar{p}(1 - \phi)/(1 - \phi\bar{p}) \right]^2 + \bar{P} + \bar{T} [\ln(1 - \bar{p}) - (\phi)^{-1}(1 - 1/r) \ln(1 - \phi\bar{p})] = 0 \quad (12)$$

The set of parameters needed for this theory is  $\epsilon^*$ ,  $V^*$ , and  $\phi$  (or  $z$ ), where  $V^*$  is the total close-packed volume. When  $z \rightarrow \infty$ , eq 12 reduces to the Sanchez-Lacombe equation of state.<sup>2</sup> A similar equation of state has recently been obtained by Vera.<sup>7</sup>

## Discussion

When eq 12 is used, a liquid-vapor transition is predicted similar to SL theory. A numerical technique<sup>6</sup> such as a fixed point iteration method can be used to show this.

In the critical region, the critical compressibility factor is too great, indicating that the theory does not work well there. The spinodal temperature is

$$\bar{T}_s = \frac{2(1 - \phi)^2 \bar{p}_s}{(1 - \phi\bar{p}_s)^3} \left[ \frac{1}{1 - \bar{p}_s} - \left(1 - \frac{1}{r}\right) \frac{1}{1 - \phi\bar{p}_s} \right]^{-1} \quad (13)$$

and the spinodal pressure is

$$P_s = - \left[ \frac{\bar{p}_s(1 - \phi)}{1 - \phi\bar{p}_s} \right]^2 \left\{ 1 + \frac{2(1 - \bar{p}_s)[\ln(1 - \bar{p}_s) - (\phi)^{-1}(1 - 1/r) \ln(1 - \phi\bar{p}_s)]}{\bar{p}_s[(1 - \phi\bar{p}_s) - (1 - 1/r)(1 - \bar{p}_s)]} \right\} \quad (14)$$

while the critical density is the positive root of the cubic

$$(\phi)^3 \bar{p}_c^3 + (1 - 2\phi) \bar{p}_c^2 + \frac{2 - \phi}{r(1 - 1/r - \phi)} \bar{p}_c - \frac{1}{r(1 - 1/r - \phi)} = 0 \quad (15)$$

All of the equations agree with SL theory in the large  $z$  limit. If one uses eq 12, the virial expansion in the density is

$$Z = \frac{PV}{RT} = \frac{\bar{P}\bar{v}}{\bar{T}} r = 1 + B_2(\bar{T})\bar{p} + B_3(\bar{T})\bar{p}^2 + \dots \quad (16)$$

where

$$B_n(\bar{T}) = r \left[ \frac{1}{n} \left( 1 - \left(1 - \frac{1}{r}\right) (\phi)^{n-1} \right) - \frac{n-1}{\bar{T}} (\phi - 1)^2 (\phi)^{n-2} \right] \quad (17)$$

which displays the correct functional form for the second virial coefficient as well as a similar temperature dependence for all of the higher coefficients. This is an improvement over the van der Waals model and SL theory, where  $B_3(\bar{T}) = \text{constant}$ .

The Guggenheim treatment is considered to give the best form of the combinatorial within the lattice model for  $r$ -mers. Assuming this to be so, it is possible to compare the energy and entropy obtained from the exact (finite  $z$ ) and approximate (infinite  $z$ ) combinatorial.

The energy of the lattice depends only on nearest-neighbor interactions. The only nonzero pair interaction energy ( $\epsilon$ ) is the one associated with nonbonded, mer-mer interactions. In the large  $z$  limit approximation, the lattice energy (attractive) is

$$E_{SL} = -z\epsilon N_s (V^*)^2 / (2V^2) \quad (18)$$

which was used<sup>2</sup> to obtain eq 1. With finite  $z$ , this energy is

$$E = -z\epsilon N_s (V^*)^2 (1 - \phi)^2 / [2(V^2 - \phi V V^*)] \quad (19)$$

from which the first term of eq 11 is derived. Comparison between eq 18 and 19 shows that  $E_{SL} < E$ . The effect of using the large  $z$  approximation is that of overestimating the number of effective interactions in the system. As a result the attractive lattice energy is lower than it should be. These two lattice energies give rise to different "energy parts" of the respective equations of state (first term of eq 2 and 12). We believe that the first term of eq 12, if not more simple than in the SL case, gives a better estimation of the "energy part" of the equation of state.

The entropy in SL theory is

$$S_{SL} = R[(1 - \bar{v})r \ln(1 - \bar{p}) + \ln \bar{v}] + R \ln[\delta r / (\sigma e^{r-1})] \quad (20)$$

where eq 7 in the large  $z$  limit is used. If eq 7 is used, it is obtained for the entropy

$$S = R[(1 - \bar{v})r \ln(1 - \bar{p}) + \ln \bar{v} + (z/2)r(\bar{v} - \phi) \ln(1 - \phi\bar{p})] + R \ln(\delta r / \sigma) \quad (21)$$

It is straightforward to show from eq 20 and 21 that  $S_{SL} > S$ . Therefore, neglecting  $f_{NB}$  in the Guggenheim com-

(7) C. Panayiotou and J. H. Vera, presented at the 6th International Conference on Thermodynamics (IUPAC), Merseburg, German Democratic Republic, Aug 1980.

binatory has the effect of increasing the number of configurations and overestimating the entropy. It is interesting to notice that eq 21 shows that the entropy of the present theory depends not only on molecular size through  $r$  but on "lattice composition" through  $f_{NB}$ .

As seen in this work, taking  $z$  finite leads to a functionally simple equation of state, eq 12. Moreover, the chain length  $r$  is removed as an adjustable parameter so that the set required is  $\epsilon^*$ ,  $V^*$ , and  $z$ . The values of  $\epsilon^*$  and  $V^*$  will be, in general, different from the SL theory, and  $r$  will be fixed.

It is left to future work to study specific comparisons with experiment and to assess the numerical advantage of using a finite  $z$  form. Both theories are poor in the

critical region. The finite  $z$  theory improves the temperature dependence of the third virial coefficient. Moreover, using the full Guggenheim combinatorial has a fundamental appeal over the large  $z$  limit. In particular, this permits explicit inclusion of the effects of nonbonded pairs which become negligible in the equation of state as  $z$  increases.

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## Three-Liquid-Phase Equilibrium and Its Tricritical Point in Water-Ethyl Alcohol-*n*-Butyl Alcohol-Isooctane

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The system water-ethyl alcohol-*n*-butyl alcohol-isooctane has been found to have a three-phase region and a tricritical point. The temperature and the composition at the tricritical point are  $T_t = 42 \pm 4$  °C and mass fractions  $W_{H_2O} = 0.24 \pm 0.01$ ,  $W_{EtOH} = 0.22 \pm 0.01$ ,  $W_{n-BuOH} = 0.33 \pm 0.01$ , and  $W_{i-Oc} = 0.21 \pm 0.01$ .

### Introduction

A tricritical point is a thermodynamic state in which three previously distinct coexistent phases become identical. The tricritical point of the system  $(NH_4)_2SO_4$ -water-ethanol-benzene was located by Lang and Widom<sup>1</sup>. More recently, the system water-acetonitrile-benzene-*n*-hexane was studied by Bocko,<sup>2,3</sup> and its tricritical point located. In both of those systems the second component is a good solvent for the first and third, which are relatively insoluble in each other, while the third is a good solvent for the second and fourth, which are also relatively insoluble in each other.

The system water-ethyl alcohol-*n*-butyl alcohol-isooctane was observed in this laboratory to have a three-phase region. This system is similar to the two mentioned above in that the water and the *n*-butyl alcohol are not soluble in each other but are both soluble in ethyl alcohol. However, there is an apparent difference since ethyl alcohol, *n*-butyl alcohol, and isooctane are all soluble in each other over the temperature range in question, -10 to 50 °C, although a solution of ethyl alcohol and isooctane will phase separate below a critical solution temperature of -70 °C.<sup>4</sup>

The system water-ethyl alcohol-*n*-butyl alcohol-isooctane appears to have a tricritical point. We report the preliminary mapping of the three-phase region and an estimate of the tricritical-point temperature and composition.

### Experimental Methods

The three-phase region of the system water-ethyl alcohol-*n*-butyl alcohol-isooctane was examined at -5, 2, 5, 24,

30, 33, 35.6, and 36.1 °C by analyzing mixtures of different gross compositions by gas chromatography. The tricritical point was then determined by extrapolation.

It was necessary to have methods for moving within the three-phase region at a given temperature and for locating three-phase regions at higher temperatures. These techniques have already been described by Lang and Widom,<sup>1</sup> and Bocko,<sup>2,3</sup> and will only be summarized here.

Once a three-phase region has been located at some temperature, it is possible to find all of the composition triangles which compose that region. This is done by making use of the observation that the mass centroids of each triangle (representing mixtures which separate into three phases of equal mass) are nearly collinear for closely spaced triangles. The centroids are used so that the resulting mixtures will have phases of approximately equal volume for ease of analysis. Therefore, if one has a mixture which is three-phase, it is possible to analyze that mixture and construct a line normal to its centroid. Mixtures which lie on this line close to the original triangle will be three-phase. By repeatedly applying this procedure to the newly located triangles, it is possible to traverse the entire three-phase region.

When moving between temperatures, it becomes increasingly difficult to locate the three-phase region as the tricritical point is approached because the three-phase region is both shrinking and translating. An iterative method is used which allows a new mixture to be made

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