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A Simple Equation of State for Nonspherical and Associating Molecules

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A simple semiempirical model is presented that gives an accurate representation of the thermodynamic properties for hydrogen bonding and nonspherical molecules. The model is shown to provide a good representation of available molecular simulation data for hard chains, hard spherocylinders, square-well spheres, Lennard-Jones chains, and dimerizing spheres. The simplicity of the model leads to an equation of state that can be applied easily and generally via corresponding states. The equation of state is cubic for nonassociating fluids and has only three real roots for associating fluids. Analysis of hydrogen-bonding systems shows that specifically accounting for molecular association clearly improves the equation's ability to represent mixture phase equilibrium data.

Introduction

A number of thermodynamic models can be used to make accurate predictions of the vapor-liquid equilibria for nonpolar and weakly polar compounds. Methods based on a corresponding states approach, such as the Soave (1972) equation or Peng-Robinson (1976) equation, have been remarkably successful for nonassociating mixtures. For example, Elliott and Daubert (1985) have reported an accurate representation of vapor-liquid equilibria with the Soave equation for a large number of binary systems containing hydrocarbons, hydrogen, nitrogen, hydrogen sulfide, carbon monoxide, and carbon dioxide. Elliott and Daubert (1987) also have shown that vapor-liquid critical properties can be predicted accurately for these systems. Michelsen (1986) has obtained a remarkably detailed representation of multiphase and tricritical phenomena. These results extend over a wide range of temperatures and pressures and treat multicomponent as well as binary mixtures.

However, no simple generalized theory is available for associating systems as yet. Components like water and ethanol tend to self-associate, mutually associate, and multiply associate to form trimers, tetramers, etc. The complexity of these associations makes it difficult to characterize such mixtures even with sophisticated analytical chemistry. Furthermore, the types of phase behavior exhibited by these mixtures are difficult to describe quantitatively. For example, liquid-liquid immiscibilities are common in mixtures containing a hydrogen-bonding component. Such systems are more difficult to represent than systems that exhibit vapor-liquid equilibria. The desire to accurately predict such multiphase equilibria over wide ranges of temperature and pressure makes it necessary to develop models that take into account the physical and chemical interactions that make these mixtures distinctly different from nonassociating mixtures.

Counter to the need for representing these complex molecular interactions, simplicity is essential when considering engineering applications. The heart of most engineering applications is the fugacity evaluation. This must be repeated over and over, and it must never fail. This

necessity for simplicity is the reason many recent advances in molecular physics have not made their way into routine engineering calculations. The purpose of this paper is to partially resolve the difference between these two competing needs. Hence, we present expressions that accurately mimic the results of molecular physics and maintain a clear physical interpretation but are simple enough to allow repetitive fugacity evaluations. We concentrate on three molecular attributes that are important to the chemical industries. These are (1) the effect of non-sphericity on repulsive forces, (2) the effects of attractive dispersion forces, and (3) the effects of molecular association. Slight modifications of available theories are presented that yield simple forms and yet lead to a generalized cubic equation of state. The simple forms are compared to the results of molecular simulations and fundamental theories to show that they accurately mimic the relevant physics. The resulting final equation is compared to the Soave equation of state to show how a realistic physical model improves the ability to represent experimental data with little penalty in computational complexity.

Repulsive Forces

Several approaches are available for representing the contributions of repulsive forces in the equation of state. We would like to present a method that is capable of representing the essential features of the various approaches while retaining the simplicity of popular engineering equations.

There are two well-developed but distinctly different approaches to the treatment of repulsive forces for nonspherical molecules: convex-body models and chain-molecule models. In both cases, the equations reduce to the Carnahan-Starling equation (1969) for spherical molecules. The convex-body models are typified by the works of Nezbeda and Boublik (1978) and co-workers and are closely related to scaled particle theory. These models have the limitation that the molecules are treated as rigid. This tends to be a poor approximation for larger molecules. Studies of chain molecules relax the assumption of rigidity

but are somewhat limited in that little has been done to account for branching. The theories of chain molecules are typified by the works of Prigogine (1957) and Flory (1965). Our investigations show that the simulation results from both the convex-body and flexible-chain approaches are adequately represented for most practical conditions by the relatively simple form,

$$Z^{\text{rep}} = \frac{4c\eta}{1 - 1.9\eta} \quad (1)$$

where Z^{rep} is the repulsive contribution to the compressibility factor according to

$$\frac{PV}{NkT} = 1 + Z^{\text{rep}} + Z^{\text{att}}$$

c is the shape factor, η is the reduced number density $\equiv Nv^*/V$, v^* is the characteristic size parameter, N is the number of molecules, and V is the volume of the container. This form represents a compromise between the form used in the Generalized Flory theory (Dickman and Hall, 1986), the Perturbed Hard Chain (PHC) theory (Donohue and Prausnitz, 1978), the Cubic Chain of Rotators (CCOR) theory (Kim et al., 1986), the simple van der Waals repulsive form assumed in the Soave equation, and the recent results by Tobochnik and Chapin (1988). For hard spheres, eq 1 is exact for the second virial coefficient and accurate for densities up to $\eta < 0.4$. Like the original van der Waals repulsive term used in the Soave and Peng-Robinson equations, it identifies the divergence of pressure to be first order (as opposed to third order in the Carnahan-Starling form). Recent results by Tobochnik and Chapin (1988) indicate that this divergence is first order. However, in the random close packed limit, eq 1 leads to $\eta_{\text{rcp}} = 0.53$ (where η_{rcp} is the reduced density at the random closed packed limit) versus the value of $\eta_{\text{rcp}} = 0.68$ determined by Tobochnik and Chapin (1988). This discrepancy is necessary to compensate for the inaccurate higher virial coefficients implied by the simple form of eq 1. For nonspherical molecules, shape effects are represented as in Generalized Flory theory (Dickman and Hall, 1986) and PHC theory (Donohue and Prausnitz, 1978). Dickman and Hall (1986) obtained an accurate representation of simulation data for hard chains by assuming that Z^{rep} can be represented by the Carnahan-Starling result multiplied by a single characteristic parameter. This assumption is consistent with the result from PHC theory for the repulsive term. Equation 1 applies the analogous approach to our hard sphere equation. Because of the inaccuracy in η_{rcp} , the range of application for eq 1 must be limited to $\eta < 0.4$, but this is adequate for saturated liquids at reduced temperatures of $T_r > 0.45$. Equations like the Soave (1972) equation also are limited to $T_r > 0.45$, and this is rarely a practical limitation for many engineering calculations. Figure 1a compares eq 1 to the molecular simulation data (Erpenpeck and Wood, 1984) for spheres and to the van der Waals repulsive term that is used in the Soave equation. Figure 1b compares eq 1 to molecular simulation data (Nezbeda and Boublik, 1978) for hard spherocylinders. Figure 1c compares eq 1 to the molecular simulation data (Dickman and Hall, 1988) for chain molecules. These figures show that eq 1 gives a reasonable representation for all these simulation results. Equation 1 also has the advantage of leading to a cubic equation of state when combined with the attractive term described in the following section.

In summary, the nature of these repulsive forces and the effects of shape are fairly well understood and should be implemented in engineering equations. By invoking a

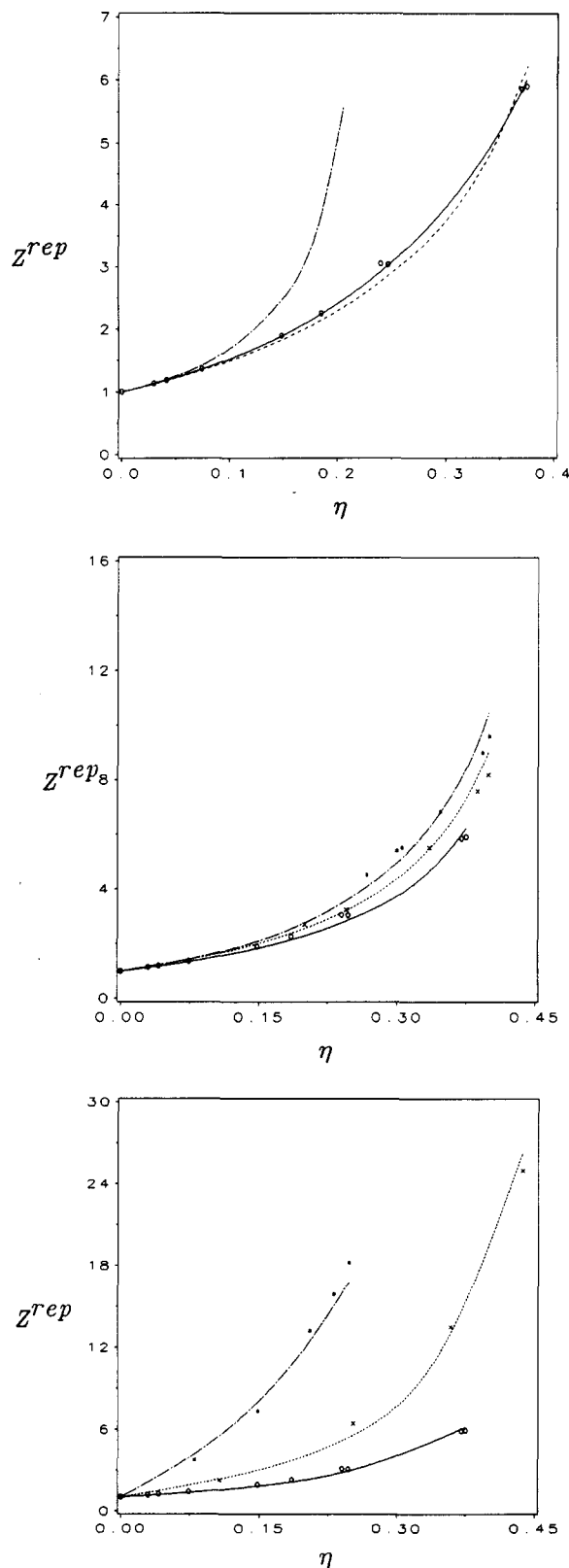


Figure 1. (a, top) Repulsive contribution to compressibility factor for spheres. (—) Carnahan-Starling (1969) equation, (---) eq 1, (---) van der Waals equation, (O) simulation data from Erpenpeck and Wood (1984). (b, middle) Repulsive contribution to compressibility factor for hard spherocylinders. (—, O) $L/B = 1$, (---, X) $L/B = 2$, (---, *) $L/B = 3$ where $L/B = \text{length/breadth}$. Simulation data are from Nezbeda and Boublik (1978). Calculations were made by using eq 1 with $c = 1.0 + 0.2(L/B - 1)$. (c, bottom) Repulsive contribution to compressibility factor for hard tangent sphere chains. (—, O) $N_s = 1$ (spheres), (---, X) $N_s = 4$, (---, *) $N_s = 16$ where N_s is the number of segments in a chain. Simulation data are from Dickman and Hall (1988). Calculations were made by using eq 1 with $c = 1 + (N_s - 1)/2$.

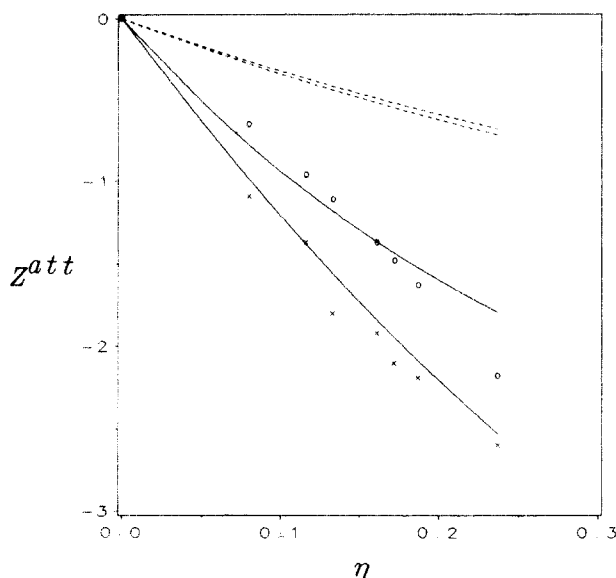


Figure 2. Attractive contribution to compressibility factor for Lennard-Jones chains. (O) Spheres (Nicolas et al., 1979), (X) *n*-butane (Vimalchand and Donohue, 1989), (---) Soave equation, (—) eq 2 computed at $T_r = 1.2$. $c = 1$ for Lennard-Jones spheres and $c = 1.7024$ for Lennard-Jones butane, consistent with eq 3.

simple equation that accurately mimics these contributions, engineering developments can approach a more fundamental physical basis with little practical penalty.

Attractive Dispersion Forces

The approaches for analyzing the contributions of attractive dispersion forces are similar to those for repulsive forces, but fewer simulation data exist that specifically address the attractive forces. Sandler and co-workers (cf. Sandler and Lee, 1986) have developed simple and accurate equations for the spherical square-well potential based on comparisons with molecular simulation data. For other spherical potentials, however, no simple results are available. Thus, we would like to adapt the results of Sandler and Lee and extend them to nonspherical molecules in a manner that is similar to our adaptation of the repulsive forces. For the attractive contribution of nonspherical molecules, the best available analysis is that of Vimalchand and Donohue (1989). Vimalchand and Donohue (1989) isolated the attractive contribution by subtracting the contribution due to repulsive forces from the overall compressibility factor in a simulation of *n*-butane. Figure 2 shows a comparison of their results and the results for spherical Lennard-Jones molecules from Nicolas et al. (1979) at roughly equal reduced temperatures of $T_r = 1.2$. What is encouraging about Figure 2 is that it suggests that the nonspherical contribution can be represented by a simple factor multiplying the spherical contribution. This observation is analogous to the result for repulsive forces shown by the Generalized Flory theory, PHC theory, and eq 1. The curves in Figure 2 correspond to the results of our generalized theory and the Soave (1972) equation of state, but the details behind generating these results must be discussed first.

One question that remains is how the shape affects the attractive term relative to the repulsive term. The PHC theory of Donohue and Prausnitz (1978) assumes that the magnitude of the shape effect is the same for each term. Pavlicek and Boublik (1981) obtained a relation by assuming perturbation theory applied to hard convex bodies. Here we relax a priori assumptions about the relative magnitudes of shape effects. We obtain the relation be-

Table I. Vapor Pressure Analysis for Pure Hydrocarbon Compounds

family	no. of compds	%AAD ^a	
		Soave	eq 3
paraffins	44	1.74	1.89
olefins	14	2.99	2.55
naphthenes	20	4.24	3.25
aromatics	25	4.00	4.36
overall	103	2.79	2.87

^a %AAD = percent average absolute deviation.

tween the attractive and repulsive terms by determining q in the equation below:

$$Z^{\text{att}} = -\frac{z_m q \eta Y}{1 + k_1 \eta Y} \quad (2)$$

where q is the parameter that accounts for the effect of shape on the attractive part of Z , $Y \equiv \exp(\beta\epsilon) - k_2$, $\beta \equiv 1/(kT)$, ϵ is the depth of the square-well potential, and z_m , k_1 , k_2 , and k_3 are constants in the equation of state.

For spheres, the shape parameters, q and c , are both equal to unity. Based on our vapor pressure analysis of spherical molecules, where $c = 1$, the following values for k_1 , k_2 , and z_m were obtained: $k_1 = 1.7745$, $k_2 = 1.0617$, $z_m = 9.49$. k_3 is the parameter that accounts for the effect of shape on the attractive part of the compressibility factor. To determine a reasonable value for k_3 , we performed an analysis of vapor pressure data for 102 hydrocarbon compounds based on the compilation by the American Petroleum Institute Technical Data Book Project. The analysis required values of $\{\epsilon/k, v^*, c\}$ for each compound. Since we were interested in a generalized engineering equation, we obtained these values in direct analogy with the method used by Soave (1972) to determine $\{a, b, m\}$ in his equation. By applying $(\partial P/\partial V) = 0$ and $(\partial^2 P/\partial V^2) = 0$ at T_c and P_c , we obtained values for ϵ/k and v^* at any given value of c . The value of c was then adjusted until the vapor pressure of the equation of state was equal to the true vapor pressure at a reduced temperature of $T_r = 0.7$. For example, a value of c equal to unity yielded a reduced vapor pressure of 0.1 for the equation of state, leading to $w = 0$. The parameters c , v^* , and ϵ were found to be related to the critical properties T_c and P_c and the acentric factor, w , as follows:

$$c = 1.0 + 3.535w + 0.533w^2 \quad (3)$$

$$\frac{\epsilon}{k} = T_c \frac{1.000 + 0.945(c - 1) + 0.134(c - 1)^2}{1.023 + 2.225(c - 1) + 0.478(c - 1)^2} \quad (4)$$

$$v^* = \frac{kT_c}{P_c} \frac{0.0312 + 0.087(c - 1) + 0.008(c - 1)^2}{1.0000 + 2.455(c - 1) + 0.732(c - 1)^2} \quad (5)$$

where k is Boltzmann's constant.

In this way, the value of k_3 was the only adjustable parameter for all 102 compounds for vapor pressures over the range $T_r = [0.45, 1.0]$. The optimum value of k_3 was determined to be 1.92. However, accurate results were obtained for k_3 values between 1.9 and 1.95. For reasons explained later, a value of $k_3 = 1.90476$ was chosen. Table I shows that for $k_3 = 1.90476$, a generalized equation of state is obtained that has an accuracy comparable to the Soave equation.

Returning to the comparisons with simulation results, Figure 2 compares the results of eq 2, the attractive term in the Soave equation of state, and the simulation results for Lennard-Jones spheres and *n*-butane at a $T_r = 1.05$. For the spheres, $c = 1$, and for butane, $c = 1.7024$, in accord with eq 3 obtained from the generalized analysis. The

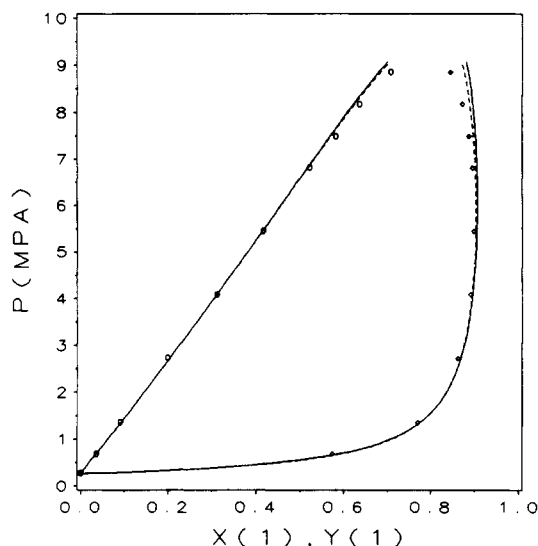


Figure 3. P (MPa) vs x, y for methane + propane at 255.3 K. (○) Wichterle et al. (1972), (---) Soave equation, (—) eq 6.

inaccuracy evident in the approximation can be explained partly by the fact that it was developed from simulation data for square-well fluids and here it is compared with simulation data on Lennard-Jones fluids. Furthermore, simulation data for internal energy were considered in developing the form of eq 2 (Sandler and Lee, 1986), and fitting the internal energy and pressure simultaneously is somewhat difficult. The inaccuracy apparent in Figure 2 is compensated, however, by the notable simplicity of eq 2.

Mixtures of Nonassociating Components

The equation of state for a nonassociating mixture can be written as follows:

$$\frac{PV}{NkT} = 1 + \frac{\langle 4c\eta \rangle}{1 - 1.9\eta} - \frac{z_m \langle q\eta Y \rangle}{1 + k_1 \langle \eta Y \rangle} \quad (6)$$

where

$$\begin{aligned} \eta &\equiv \frac{N}{V} \sum x_i v_i^* \\ \langle 4c\eta \rangle &\equiv 4 \frac{N}{V} \sum \sum x_i x_j (c v^*)_{ij} \\ \langle q\eta Y \rangle &\equiv \frac{N}{V} \sum \sum x_i x_j (q v^*)_{ij} Y_{ij} \\ (c v^*)_{ij} &\equiv (c_i v_j^* + c_j v_i^*)/2 \\ (q v^*)_{ij} &\equiv (q_i v_j^* + q_j v_i^*)/2 \\ \epsilon_{ij} &\equiv (\epsilon_{ii} \epsilon_{jj})^{1/2} (1 - k_{ij}) \\ Y_{ij} &\equiv \exp(\beta \epsilon_{ij}) - k_2 \\ \langle \eta Y \rangle &\equiv \langle q\eta Y \rangle / \sum x_i q_i \end{aligned}$$

N is the number of molecules, i and j are the i th and j th species, and k_{ij} is the binary interaction coefficient. These mixing rules are fairly close to the typical Lorentz-Berthelot approach and similar to the rules used in COM-PACT (Ikononou and Donohue, 1987). Figure 3 shows that the extension to nonassociating mixtures such as the methane-propane system yields results that are comparable to those obtained from the Soave equation.

These results establish that this simple equation is capable of mimicking the important aspects of both the

molecular physics and real experimental data for nonassociating molecules in a simple and general form. While this strong physical interpretation is not necessary for representing vapor-liquid equilibria (VLE) of nonassociating components (as demonstrated by the success of the Soave (1972) equation), it is necessary for developing a consistent theory of associating mixtures and their multiphase equilibria over broad ranges of temperature and pressure.

Extension to Associating Components

A recent result in molecular physics is the analytical solution of the statistical mechanics of a model potential that would be expected to mimic hydrogen bonding. This development is reviewed and extended in the papers by Jackson et al. (1988) and Chapman et al. (1988). In our analysis below, we show how to reproduce the results of Jackson et al. for spherical molecules and extend the analysis to nonspherical molecules by applying a reaction equilibrium approach. In the reaction equilibrium approach that we adopt, the extension to nonspheres is straightforward and we maintain a simple, generalized approach.

An important feature of the results of Jackson et al. is that an analytical solution is obtained for the mole fraction of monomer as a function of temperature and density. Knowing the composition, the rest of the thermodynamic properties can be computed with relative ease. Their analysis applies to molecules with two bonding sites, as well as one bonding site, and this configuration results in higher order oligomers being formed as well as dimers. Still, they obtain an analytical solution for the composition of the fluid. On the basis of this analytical solution, Jackson et al. show how the composition changes with density and how association affects the critical point and the vapor pressure curve.

Jackson et al. introduce association effects by choosing a potential function that would be expected to mimic hydrogen bonding. A more traditional alternative is to express the association by a reaction equilibrium. For example, Anderko (1989) has pursued this approach by adding reaction equilibrium to equations of state like the Soave equation. However, the resulting equations are coupled in a complicated way that would not be any simpler than the method we present in this paper. And the number of parameters and their relationship to meaningful quantities are somewhat less clear. The approach described below yields only one adjustable parameter per pure associating component to account for the distinction between chemical association effects relative to physical shape effects.

The reaction equilibrium approach for the case of dimerization leads to an approximate analysis when higher order oligomers are considered. By adapting the results of Ikononou and Donohue (1987), we show below that the reaction equilibrium approach can also yield a simple analytical solution for the mole fraction of monomer using our equation of state and that this solution coincides very nearly with the solution of Jackson et al. We use our solution in corresponding states to show how shape and association affect the vapor pressure curve differently and how to characterize the differences between shape effects and association effects using readily available engineering data for pure fluids. Finally, we show how the results for pure associating fluids extend to associating mixtures and improve the ability to represent the thermodynamics of associating mixtures.

In any system, which exhibits association, even a pure component becomes a mixture of the monomers with the

dimers, trimers, tetramers, etc. To apply our theory to such a system, we must treat it as a mixture using the true mole fractions in the system. Then the equation of state is

$$\frac{PV}{N_T kT} = 1 + \frac{\langle 4c\eta \rangle}{1 - 1.9\eta} - \frac{z_m \langle q\eta Y \rangle}{1 + k_1 \langle \eta Y \rangle} \quad (7)$$

where

$$\begin{aligned} \eta &\equiv \frac{N_T}{V} \sum x_i v_i^* \\ \langle 4c\eta \rangle &\equiv 4 \frac{N_T}{V} \sum \sum (c v^*)_{ij} x_i x_j \\ \langle q\eta Y \rangle &\equiv \frac{N_T}{V} \sum \sum x_i x_j (q v^*)_{ij} Y_{ij} \\ (c v^*)_{ij} &\equiv (c_i v_j^* + c_j v_i^*)/2 \\ (q v^*)_{ij} &\equiv (q_i v_j^* + q_j v_i^*)/2 \\ \epsilon_{ij} &\equiv (\epsilon_{ii} \epsilon_{jj})^{1/2} (1 - k_{ij}) \\ \langle \eta Y \rangle &\equiv \langle q\eta Y \rangle / \sum x_i q_i \end{aligned}$$

N_T is the true number of molecules present after accounting for association. The value of k_{ij} for oligomer-oligomer interaction is assumed to be zero. Hence, for a pure associating component,

$$\epsilon_{ij} \equiv (\epsilon_{ii} \epsilon_{jj})^{1/2}$$

Returning to the problem of reaction equilibrium and considering dimerization as an example, we seek a solution to the problem

$$K = \frac{\Phi_D}{\Phi_M^2} \frac{x_D}{x_M^2} \frac{1}{P}$$

where Φ_i is the fugacity coefficient of component i and K is the reaction equilibrium constant for dimerization. This solution is not immediate because Φ_D and Φ_M are functions of temperature and density according to the equation of state. If we take the log of the fugacity coefficient ratio, we find

$$\ln \Phi_D - 2 \ln \Phi_M = \ln \Phi_D^{\text{sp}} + \ln \Phi_M^{\text{tt}} - \ln (PV/N_T kT) - 2[\ln \Phi_M^{\text{sp}} + \ln \Phi_M^{\text{tt}} - \ln (PV/N_T kT)] \quad (8)$$

Following Heidemann and Prausnitz (1976), the attractive contributions will cancel if $(q\eta Y)_{DD} = 4(q\eta Y)_{MM}$. The effective shape of the dimer cannot be assessed, but it is reasonable to assume that $\epsilon_{DD} = \epsilon_{MM}$ and $v_D^* = 2v_M^*$, giving $q_D = 2q_M$. Since $q = 1 + k_3(c - 1)$, then $c_D = 2c_M - (k_3 - 1)/k_3$. Substituting

$$\begin{aligned} \ln \Phi_D - 2 \ln \Phi_M &= -\frac{4.0}{1.9} c_D \ln(1 - 1.9\eta) + \\ &\frac{N_T}{V} \frac{4c v_D^*}{1 - 1.9\eta} - \ln \left(\frac{PV}{N_T kT} \right) - \\ &2 \left[-\frac{4.0}{1.9} c_M \ln(1 - 1.9\eta) + \right. \\ &\left. \frac{N_T}{V} \frac{4c v_M^*}{1 - 1.9\eta} - \ln \left(\frac{PV}{N_T kT} \right) \right] = \\ &-\frac{4.0}{1.9} (c_D - 2c_M) \ln(1 - 1.9\eta) + \ln \left(\frac{PV}{N_T kT} \right) \quad (9) \end{aligned}$$

Substituting

$$\frac{x_D}{x_M^2} = (1 - 1.9\eta)^{-4.0(k_3-1)/1.9k_3} N_T \frac{kT}{V} K \quad (10)$$

At this point, we note that a much more convenient expression would be obtained if $4.0(k_3 - 1)/1.9k_3$ were equal to an integer. In our analysis of vapor pressure, which determined k_3 , we found that the quantity $4.0(k_3 - 1)/1.9k_3$ was nearly equal to unity and that choosing k_3 to make it exactly equal to unity had little detrimental effect. The value of $k_3 = 1.90476$ was thus chosen such that

$$\frac{x_D}{x_M^2} = (1 - 1.9\eta)^{-1} N_T \frac{kT}{V} K \equiv \alpha \frac{N_T}{N_0} \quad (11)$$

where

$$\alpha = (1 - 1.9\eta)^{-1} N_0 \frac{kT}{V} K = \frac{\eta}{1 - 1.9\eta} \left(\frac{K k T_c T_r}{v^*} \right)$$

and N_0 is the number of molecules imagined if association was ignored. To solve for x_M and N_T/N_0 , we shall consider the mass balance equations:

$$x_M + x_D = 1 = x_M(1 + \alpha x_M N_T/N_0) \quad (12)$$

$$x_M + 2x_D = \frac{N_0}{N_T} = x_M(1 + 2\alpha x_M N_T/N_0) \quad (13)$$

From eqs 11-13, we obtain the relation

$$x_M = \frac{(1 + 8\alpha)^{1/2} - 3}{2(\alpha - 1)} \quad (14)$$

and the equation of state reduces to

$$\frac{PV}{N_0 kT} = \frac{N_T}{N_0} + \frac{\langle 4c\eta \rangle_0}{1 - 1.9\eta_0} - \frac{z_m \langle q\eta Y \rangle_0}{1 + k_1 \langle Y \rangle_0} \quad (15)$$

where

$$\frac{N_T}{N_0} = \frac{2(\alpha - 1)}{4\alpha - 1 - (8\alpha + 1)^{1/2}} \quad \boxed{= 1/(2 - x_M)}$$

The subscript 0 implies that all properties of these terms can be evaluated as if association is ignored. For example, $\eta_0 = N_0 v_M^*/V$. The solution of Jackson et al. is

$$x_M = \frac{(1 + 4\rho\Delta)^{1/2} - 1}{2\rho\Delta} \quad (16)$$

where

$$\rho\Delta \equiv \frac{24\eta(1 - \eta/2)}{(1 - \eta)^3} K^* [\exp(\beta\epsilon_{\text{site}}) - 1]$$

The density dependence of these two functions is compared graphically in Figure 4. The figure shows that the density dependence of the monomer fraction is nearly the same for eq 14 as for the values of Jackson et al. It should be noted that the denominator, $1 - 1.9\eta$, is a result of not assuming the c_D equal to $2c_M$ as assumed by Ikononou and Donohue (1987). This increases the complexity of the equations somewhat but leads to better agreement with molecular simulations as shown in Figure 4.

This agreement with the molecular simulations is strongly encouraging because the reaction equilibrium approach can be extended readily to nonspherical molecules. This permits one to analyze the interaction between shape and association. On the other hand, the extension of association theory to nonspherical molecules by Chapman et al. (1988) requires neglecting the "correlation hole" effect of chain molecules. Curro and Schweizer (1987)

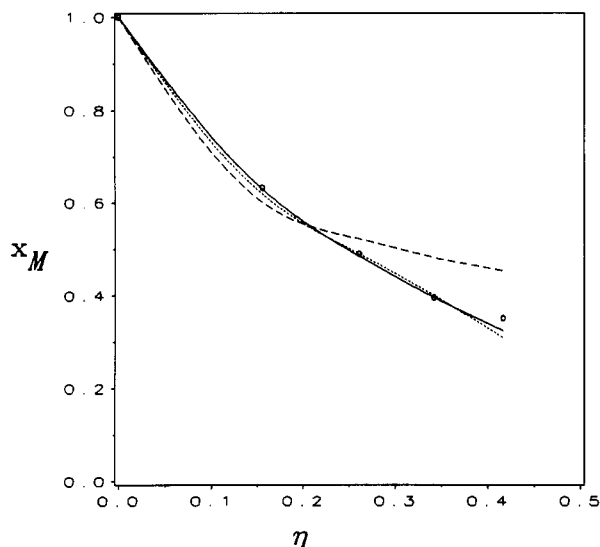


Figure 4. Mole fraction of monomer in a dimerizing mixture vs dimensionless density. (—) Jackson et al. (1988), (---) COMPACT (Ikonomou and Donohue, 1987), (-.-) eq 14, (O) simulation data from Jackson et al. (1988).

Table II. Effect of the Association at the Critical Point for Acetic Acid on the Value of Z_c^a

α_c	Z_c	α_c	Z_c
0	0.342	4	0.260
1	0.270	5	0.253
3.5	0.264	6	0.247

^a $\Delta H^\circ/RT_c$ was set at a value of 5.

show that this effect can be a factor of 10 or more. Honnell and Hall (1986) presented simulations on relatively short chains that verified the strong effect of the correlation hole. While the reaction equilibrium approach involves several approximations, it is important to realize that these simple approximations lead to accurate results.

To obtain a generalized analysis of molecular association with the minimum number of adjustable parameters, it is necessary to recognize several distinctive effects of association. One effect of association demonstrated by Jackson et al. (1988) and Heidemann and Prausnitz (1976) is the depression of the critical compressibility factor, Z_c . Z_c is available for many common compounds, and we would like to use it as a measure of the effect of association at the critical temperature. In this way, the number of adjustable parameters for a "pure associating component" can be reduced. The Z_c of our nonassociating equation of state has a value of roughly 0.34 for all shape factors. A constant value of Z_c for nonassociating compounds is obtained with other simple equations of state as well. For example, the value of Z_c as predicted by the Soave equation of state is 0.33 and that predicted by the Peng-Robinson (1976) equation is 0.31. In contrast to the shape effect, we find that hydrogen bonding has a strong effect on the value of Z_c in our equation of state as shown in Table II. Jackson et al. (1988) noted a similar effect on Z_c in their analysis. We have made use of this distinction between the shape effect and the hydrogen bonding effect to characterize the extent of association at the critical point. We have obtained success with the relation $Z_c/Z_c^{\text{HOMO}} = Z_c^{\text{EOS}}/0.34$, where Z_c^{HOMO} is the Z_c of a nonassociating homomorph with the same shape (e.g., the homomorph of ethanol is propane; the homomorph of acetic acid is isobutylene). The values of Z_c , Z_c^{EOS} , and Z_c^{HOMO} for some associating components are given in Table III. This relation establishes the measure of association at T_c . The temperature

Table III. Effect of the Association on the Critical Compressibility Factor as Compared to the Effect of Nonsphericity Shape as Exemplified by Shape Homologues^a

compd	homologue	Z_c	Z_c^{HOMO}	Z_c^{EOS}
acetic acid	isobutylene	0.200	0.275	0.244
ethanol	propane	0.248	0.280	0.305
methanol	ethane	0.224	0.280	0.271
water	methane	0.233	0.288	0.278

^a $Z_c^{\text{NA}} \approx 0.34$ for all nonassociating compounds according to eq 1.

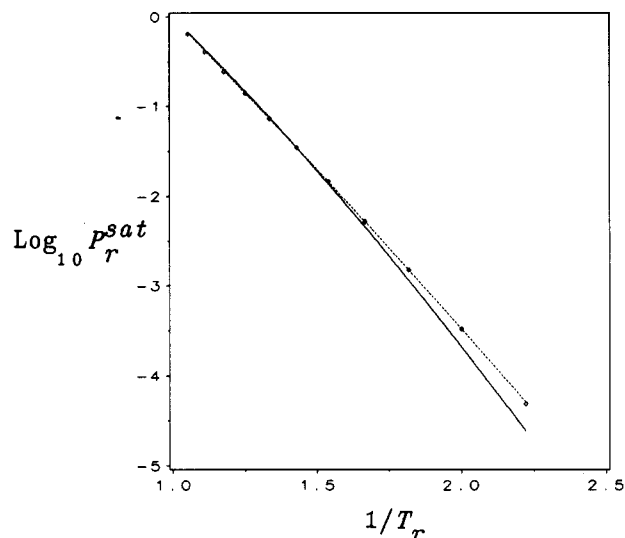


Figure 5. Logarithm of reduced vapor pressure of acetic acid vs inverse reduced temperature. (O) Vargaftik (1975), (—) no association, (---) association effects included. Both curves are fit at the critical point and at $T_r = 0.7$.

dependence of the association constant, K , can be expressed as follows:

$$\ln K = \frac{-\Delta H^\circ + \Delta C_p^\circ T_0}{RT} + \frac{1}{R} [\Delta S^\circ - \Delta C_p^\circ - \Delta C_p^\circ \ln T_0] + \frac{\Delta C_p^\circ}{R} \ln T$$

where ΔH° , ΔS° , and ΔC_p° are the standard enthalpy, entropy, and heat capacity of association at the temperature $T_0 = 273.15$ K, respectively. Setting $\Delta C_p^\circ/R = -1$, we obtain the relation

$$KT_r = K_c \exp[H(1 - 1/T_r)] \quad (17)$$

where

$$H = \frac{\Delta H^\circ}{RT_c} - \frac{\Delta C_p^\circ}{R}$$

K_c is a measure of association at T_c and is eventually lumped into α_c , which is the value of α at the critical point.

It should be noted that for $\Delta C_p^\circ/R > -1$, the extent of association diverges at high temperature. The enthalpy of hydrogen bonding is thus the only parameter that can be adjusted to obtain the best fit of the vapor pressure for reduced temperatures ranging from $T_r = 0.95$ to 0.45. For a given value of ΔH° , the method of obtaining c is entirely analogous to the procedure described for nonassociating compounds. Thus, the value of c is determined directly from the value of the acentric factor, and it is not adjustable. Since changes in the value of ΔH° affect the shape of the vapor pressure curve, a single value of ΔH° can be obtained that provides the best match for that shape. The nature of this change in shape is illustrated in Figure 5. Nonspherical shape depresses the vapor pressure more at low temperatures than does hydrogen

Table IV. Vapor Pressure Analysis for Acetic Acid where α_c Was Determined According to the Procedure Outlined in the Text and Other Parameters Were Established by Corresponding States

α_c	$-\Delta H^\circ/RT_c$	Z_c^{EOS}	$Z^V(413)^a$	%AADP	c
6.5	2	0.245	0.896	4.1	2.81
	4	0.245	0.829	4.7	2.22
	6	0.245	0.747	8.0	1.76
	8	0.244	0.669	9.1	1.44
	10	0.244	0.606	3.3	1.21
	10.4	0.244	0.596	1.9	1.18
	11.0	0.244	0.581	4.3	1.13
desired		0.244	0.596		

^a $Z^V(413)$ is the apparent compressibility factor of the saturated vapor at 413 K and is closely related to the mole fraction of monomer in the saturated vapor.

Table V. Values of ϵ (Joules/Molecule), v^* (Cubic Meter/Molecule), c , $\Delta H^\circ/RT_c$, and α_c of Some Associating Compounds

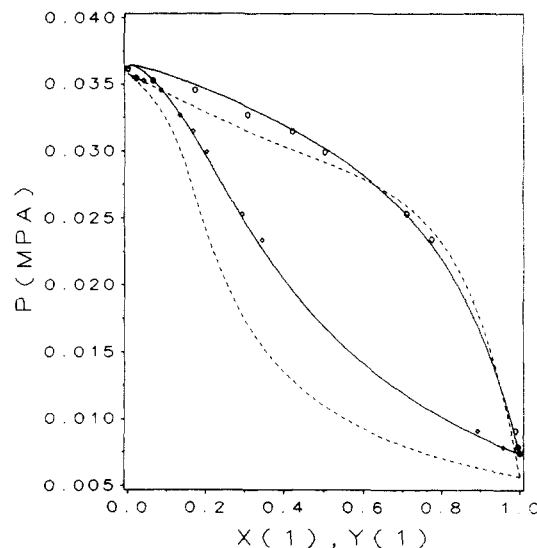
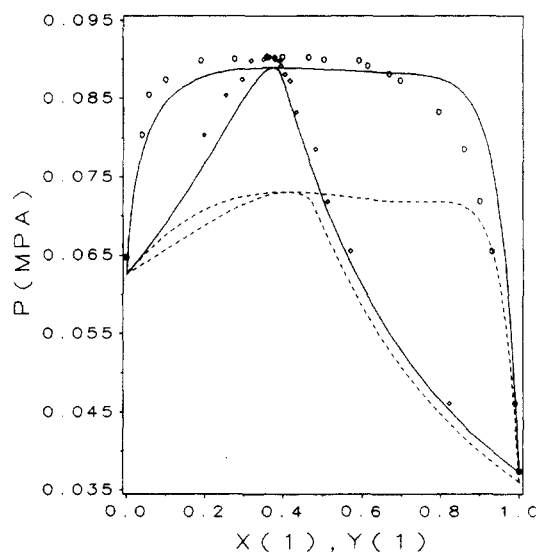
	ethanol	water	acetic acid	methanol
$10^{21}\epsilon$	2.850	3.572	4.971	2.720
$10^{29}v^*$	2.586	0.864	3.220	1.700
c	2.500	2.134	1.190	2.349
$\Delta H^\circ/RT_c$	4.350	3.160	10.400	4.250
α_c	1.010	1.700	6.600	1.880

bonding. For acetic acid, Table IV illustrates the trade-off between these two effects: shape characterized by c and association characterized by ΔH° . At a given value of c , association is expected to decrease the vapor pressure. But, for a particular compound, increasing the enthalpy of hydrogen bonding necessitates a decrease in the value of c to maintain the value of acentric factor obtained from the vapor pressure at $T_r = 0.7$. As $\Delta H^\circ/RT_c$ is increased from 2 to 12, the error in vapor pressure first rises then decreases to a minimum. We find that this minimum corresponds to a case where the mole fraction of monomer in the saturated vapor phase is small at low temperatures as observed for acetic acid. The other minimum corresponds to large mole fractions of vapor-phase monomer at low temperatures as observed for alcohols. We feel that this observation enables us to roughly characterize the effects of association by using only *PVT* data. The values of ΔH° , α_c , ϵ , c , and v^* are shown in Table V for some associating components.

It can be argued that evaluating molecular parameters from critical data is deficient in that the critical region is not well-represented by such a simple equation of state. While this is true, it is important in mixture calculations that the parameters for all species be evaluated in a consistent way. As the errors introduced are systematic and apply to all components in the same way, the ready availability of critical constants (actual or estimated) more than compensates for the errors introduced. By building qualitatively correct physics into the model, as verified by comparison with molecular simulations, we expect that better representation of fugacity with respect to temperature, density, and composition will be obtained despite this deficiency. Alternative methods can be used to evaluate the molecular parameters, and clarification of better alternatives should result from future studies. But it is important in all cases to keep the number of adjustable parameters to a minimum.

Results for Mixtures Containing a Single Associating Species

To test our theory, we have applied it to several binary mixtures containing one associating component and one nonassociating diluent. Since only one component asso-

**Figure 6.** Pressure (MPa) vs mole fraction diagram for acetic acid (1) + benzene (2) at 323 K. (O) Zawidzki (1982), (—) this work (Dimer Model), (---) Soave equation result, constrained to yield a stable, single phase.**Figure 7.** Pressure (MPa) vs mole fraction diagram for ethanol (1) + *n*-hexane (2) at 328 K. (O) Kudrayavtseva and Susarev (1977), (—) this work (Infinite Equilibrium Model), (---) The Soave equation or nonassociating model are roughly equivalent, constrained to yield a stable, single phase.

ciates, cross association between the two components is not present in the mixtures. Figure 6 compares our results to the Soave equation for acetic acid + benzene. The improvement is small but significant. Figure 7 shows results obtained for the ethanol + *n*-hexane system. It should be noted that the extension to alcohols requires recognizing the formation of higher oligomers, and this makes the derivatives of the theory more complicated than those presented above for dimers. We have adapted the Infinite Equilibrium Model as described by Ikononou and Donohue (1987) as an approximate way of treating higher oligomer formation. Although the derivatives are more complicated, the final equations are just as simple. For example, the expressions we obtain for N_T/N_0 and x_M are as follows:

$$\frac{N_T}{N_0} = \frac{-1 + (1 + 4\alpha)^{1/2}}{2\alpha} = x_M \quad (18)$$

where α is given by eq 11.

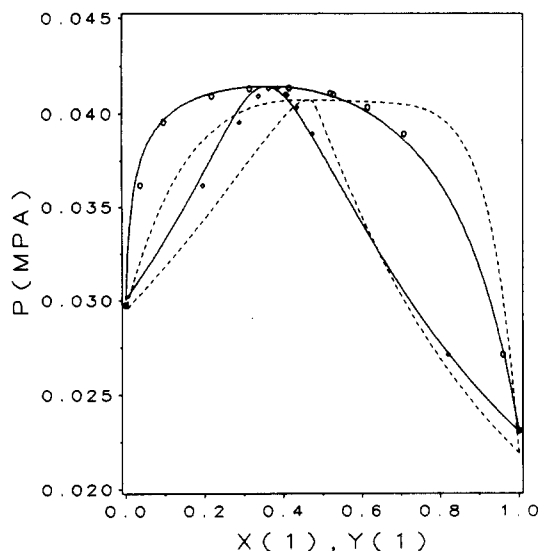


Figure 8. Pressure (MPa) vs mole fraction diagram for ethanol (1) + benzene (2) at 318 K. (O) Brown and Smith (1977), (—) this work (Infinite Equilibrium Model). (---) The Soave equation or nonassociating model are roughly equivalent, constrained to yield a stable, single phase.

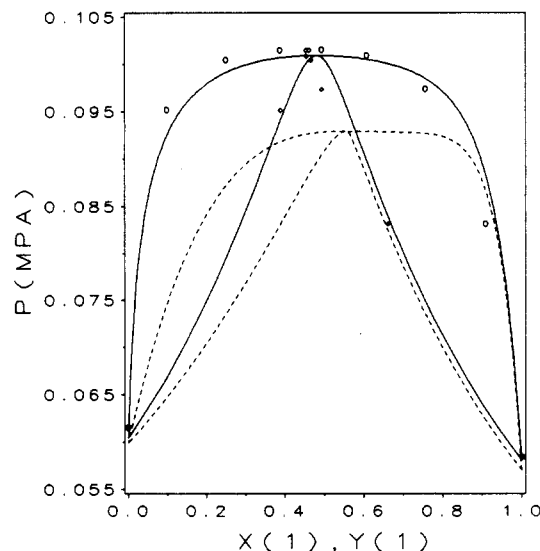


Figure 9. Pressure (MPa) vs mole fraction diagram for ethanol (1) + cyclohexane (2) at 338 K. (O) Scatchard and Sathkiewicz (1977), (—) this work (Infinite Equilibrium Model). (---) The Soave equation or nonassociating model are roughly equivalent, constrained to yield a stable, single phase.

The lower curve in Figure 7 is the best possible result using the Soave equation constrained to yield single-phase behavior. The results of our equation with no association roughly coincide with this lower curve. When we recognize the self-association of ethanol, we obtain the upper curve with a significant improvement in accuracy. Other binary mixture results are shown in Figures 8–10. It is evident from Figures 7, 9, and 10 that while the vapor pressures are matched accurately by both the Soave equation of state and the association model, the mixtures are better represented by the association model. This means that the improvement is not simply a manifestation of improving the vapor pressure accuracy but is clearly a result of recognizing the role of association in these mixtures. We also have studied several other systems of one associating component, obtaining similar results. Table VI compares the average errors in the bubble point pressure for these systems when applying the Soave equation (one adjustable parameter), our analysis (one adjustable parameter) and

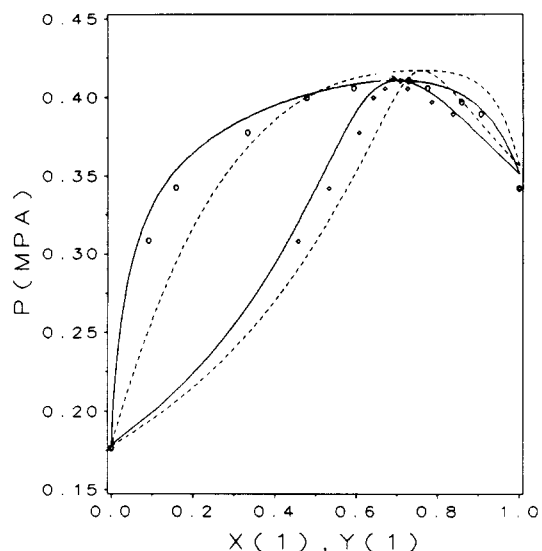


Figure 10. Pressure (MPa) vs mole fraction diagram for methanol (1) + benzene (2) at 373 K. (O) Schmidt (1977), (—) this work (Infinite Equilibrium Model). (---) The Soave equation or nonassociating model are roughly equivalent, constrained to yield a stable, single phase.

Table VI. Values of Bubble Point Pressure Percent Errors as Generated by the Wilson Equation, the Soave Equation, and Our Analysis

	T, K	our analysis	Soave eq	Wilson eq
ethanol-benzene	318	0.69	4.50	0.27
ethanol-hexane	328	3.96	14.70	0.70
ethanol-cyclohexane	338	1.74	8.40	0.27
methanol-benzene	373	1.73	4.65	0.70
acetic acid-benzene	323	1.39	6.93	3.50
total		1.90	7.84	1.10

Table VII. Values of the Binary Interaction Parameter (k_{ij}) for the Soave Equation and Our Analysis for Different Binary Mixtures

	T, K	our analysis	Soave eq
ethanol-benzene	318	0.0460	0.10
ethanol-hexane	328	0.0650	0.04
ethanol-cyclohexane	338	0.0770	0.10
methanol-benzene	373	0.0840	0.11
acetic acid-benzene	323	0.0320	0.07

the Wilson equation (two adjustable parameters). The adjustable parameter utilized for the Soave equation and our analysis is the binary interaction parameter (k_{ij}). The values of this parameter for various mixtures are shown in Table VII.

Conclusions

We have developed a generalized theory of associating mixtures that is consistent with molecular simulation results while maintaining the simplicity essential for engineering applications. The resulting equation of state matches available simulation results for spherocylinders, hard chains, the square-well fluid, Lennard-Jones chains, and dimerizing spheres. The shape parameter, c , for a dimer is not twice that for a monomer as assumed by Ikononou and Donohue (1987). This leads to much more accurate agreement with molecular simulation results for dimerizing fluids. Having established a simple and accurate basis for the equation of state from molecular simulations, we applied this equation to real fluids by evaluating the molecular parameters from real fluid properties. To obtain maximum utility, we use the readily available critical properties of real fluids to evaluate the molecular parameters in direct analogy with current engineering

methods. Comparison to experimental results for real associating fluids appears to justify this simple corresponding states approach. Doing so permits an approximate analysis of associating mixtures without the need of extensive spectroscopic data. Future work will focus on multiple associating components. Ikononou and Donohue (1988) have described this extension in the context of the Associated Perturbed Anisotropic Chain Theory, which is a somewhat more complicated theory. Their analysis shows that the extension is difficult but it can be made. Simplifying the generalizing the analysis via our equation should make these results more accessible for engineering applications.

Nomenclature

c = quantity representing shape effect on repulsive term of Z
 ΔC_p° = standard heat capacity change of hydrogen bond formation
 ΔG° = standard free energy change of hydrogen bond formation
 ΔH° = standard enthalpy change of hydrogen bond formation
 $H = \Delta H^\circ/RT_c - \Delta C_p^\circ/R$ = parameter characterizing temperature dependency of association
 k = Boltzmann's constant
 K = reaction equilibrium constant for hydrogen bond formation
 k_{ij} = binary interaction parameter in a mixture
 k_1, k_2, k_3 = constants in the equation of state
 K^* = dimensionless bonding volume (Jackson et al., 1988)
 N_s = number of segments in a chain
 N = number of molecules
 N_0 = number of molecules imagined if association is ignored
 N_T = true number of molecules after accounting for association
 P = pressure
 q = quantity representing the shape effect on the attractive term of Z
 ΔS° = standard entropy change of hydrogen bond formation
 T = temperature
 V = total volume
 v^* = characteristic size parameter = $\Pi/6\sigma^3$
 x = mole fraction
 Y = attractive energy parameter = $\exp(\epsilon/kT) - k_2$
 Y_{ij} = attractive energy parameter for the interaction between the i th and the j th molecules
 Z^{rep} = repulsive contribution to the compressibility factor
 Z^{att} = attractive contribution to the compressibility factor
 z_m = constant in the equation of state

Greek Letters

$\alpha = [\eta/(1 - 1.9\eta)][(KkT_cT)/v^*]$
 $\beta = 1/(kT)$
 ϵ = potential energy well depth
 Φ = fugacity coefficient
 η = reduced number density
 σ = effective molecular diameter

Subscripts

c = critical property
 D = dimer
 i = i th associating species
 M = monomer
 r = reduced property
 rcp = random close packed limit
 rxn = reaction
 T = quantity is calculated after accounting for association
 0 = quantity is independent of association

Superscripts

EOS = equation of state
HOMO = homomorph
V = vapor phase

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Sample Calculation for Acetic acid at 300K

$$\alpha = \alpha_{\text{ac}} \exp[-H(1-1/T_r)]$$

$$x_M = [\sqrt{1+8\alpha} - 3] / [2(\alpha - 1)]$$

$$z_{\text{Chem}} = 1 - nT/n_0 = 1 - 1/(2 - x_M)$$

$$x_A = (-1 + \sqrt{1 + 4\alpha}) / (2\alpha)$$

$$z_{\text{Assoc}} = 0.5(1 - x_C) / (1 - 1.9 \cdot 0.44)$$

$$a_{\text{Assoc}} = \ln(x_C) + (1 - x_C)/2$$

T(K)	α	x_M	nT/n_0	z_{Chem}	a_{Chem}	x_C	z_{Assoc}	a_{Assoc}	f_{Assoc}
300	62094	0.00565	0.501	-0.4985	-5.176	0.00401	-3.0367	-5.02	0.998
592	6.6	0.387	0.620	-0.380	-0.949	0.3208	-2.071	-0.797	0.824

Alternative approach:

Suppose