Thermodynamics of Hydrogen-Bonded Molecules: The Associated Perturbed Anisotropic Chain Theory

The perturbed anisotropic chain theory (PACT) developed by Vimalchand and Donohue has been generalized to treat pure fluids that associate through hydrogen bonding, as well as mixtures of one associating component and several diluents. Using an approach similar to that of Heidemann and Prausnitz, a closed-form equation of state has been derived. It is applicable to simple as well as complex molecules at both gas and liquidlike densities and takes into account dipole and/or quadrupole moments. Molecular parameters were obtained by fitting the equation to experimental liquid density and vapor pressure data.

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Introduction

Many industrially important systems contain molecules that exhibit hydrogen bonding. Although there are many empirical and theoretical correlations that can be used to predict phase behavior, few give accurate results for hydrogen-bonded molecules. In these systems, nonidealities result from both van der Waals interactions and from "chemical" association. Therefore, to predict thermodynamic properties of such systems, equations must be written for both the phase equilibria and the "chemical" equilibria. Once this is done, the result is a complicated set of equations that must be solved simultaneously by trial and error; this is tedious and expensive.

The trial-and-error approach has been used by many investigators. Weihe (1967) used a continuous association model with the Flory-Huggins athermal solution theory to treat alcohol-hydrocarbon binaries. Neau and Peneloux (1979) proposed a chemical-reticular model for activity coefficients using a monomer-dimer association equilibrium. Nagata (1985) extended the UNIQUAC activity coefficient model to treat alcohol-hydrocarbon, alcohol-alcohol binary and ternary mixtures by including a continuous association model in the phase equilibrium calculations.

There also have been several applications of trial-and-error methods for calculating combined chemical/physical equilibria using equations of state. Baumgaertner et. al. (1980) used a cubic equation of state to solve binary phase equilibria assuming a continuous association model and the existence of a cross-dimer. Baumgaertner et al. (1979) calculated carboxylic acid binary phase equilibria with the Redlich-Kwong equation of state and a monomer-dimer-trimer association model. Gmehling, et al. (1979) used the perturbed hard-chain theory (PHCT) and a monomer-dimer association model to calculate alcohol-hydrocarbon binary phase equilibria. Although such methods give satisfactory results in some cases, they have proved to be cumbersome to use and have not been sufficiently accurate to justify the complexity involved. For these reasons, experimental data usually are correlated with equations that do not explicitly account for the presence of hydrogen bonding. For example, Peng and Robinson (1980) used their equation of state to calculate phase equilibria for binary mixtures containing water.

As an alternative to trial-and-error solution, a particularly simple and elegant approach for pure components was derived by Heidemann and Prausnitz (1976). In their paper it is shown that it is possible to arrive at a closed-form equation of state that takes into account the existence of hydrogen bonding. This equation of state then can be used to solve the phase equilibrium equations for the desired properties. Unfortunately, the particular equation of state that Heidemann and Prausnitz used in their approach is not adequate for systems encountered in the chemical industry. Heidemann's method was used later by Hu et. al. (1984), who presented equations that allow treatment of mixtures of an associating component and a diluent. However, they found that the Carnahan-Starling/Redlich-Kwong equation of state used in their calculations did not give satisfactory results for binaries such as water-benzene in which components differ markedly in size.

The usefulness of this approach would be greatly increased by using a more powerful equation of state. The perturbed anisotropic chain theory (PACT) provides such an equation (Vimal-

chand and Donohue, 1985). PACT is a theoretically based equation that takes into account molecular motions due to rotational and vibrational as well as translational degrees of freedom. Anisotropic forces due to dipoles and quadrupoles are accounted for with the theory of Gubbins and Twu (1979). Because of the unique treatment in PACT, the resulting equations are valid for large and small molecules, for nonpolar and polar molecules, and at all fluid densities. The theory can be applied to fluid mixtures with high accuracy because the mixing rules are derived from statistical mechanics. Because of the proven effectiveness of PACT, it is used here to arrive at a closed-form equation of state that also takes into account hydrogen bonding. This is done by superimposing two association models upon PACT: an infinite equilibria model, and a monomer-dimer model using the approach of Heidemann and Prausnitz.

Theory

Hydrogen bonding arises when an electron-rich group, for example, a terminal oxygen of an alcohol, interacts with an electron-deficient group, such as the hydrogen in a water molecule. By delocalizing the electrons, a weak chemical bond (15 to 30 KJ/gmol) is formed and the associated molecules lower their free energy.

Once the assumption that new chemical species are formed is accepted, the inevitable consequence is that a pure compound is really a mixture of these associated species. Moreover, the actual number of moles of all species present in such a mixture is lower than what would exist in the absence of hydrogen bonding.

In the derivations that follow, the important assumption is made that the effect hydrogen bonding has on a collection of molecules is to change the actual number of molecules present. To see this, consider acetic acid vapor at ideal gas conditions (for example, at 400 K and 1 atm). If it were not for the presence of dimerization, the ideal gas law could be used to describe the properties of this system. However, at these conditions, about 80% of the acetic acid molecules exist as dimers. As a result, the appropriate correction to the equation of state (the ideal gas law) would be to replace the number of molecules, N, by $[0.20 + 0.80(1/2)]\ N$. At different conditions, where more sophisticated equations of state must be used, the number of moles must be replaced by the true number of moles of all chemical species present and mixing rules must be written to arrive at an equation for the mixture.

In the present analysis, a pure component is considered to be a mixture containing monomers, dimers, trimers, etc. The stoichiometry in such a mixture is determined by defining n_T, the total number of moles of all chemical species, and n_0, the number of moles that would exist in the absence of hydrogen bonding. By using an association model that determines the identity of the species present in this mixture and superimposing it on PACT, a closed-form equation of state that takes into account hydrogen bonding is derived.

For such a mixture of hydrogen-bonded species, an equation of state may be written in which the total number of moles is n_T and the mole fractions of its components are $z_1, z_2, z_3, \ldots$:

$$\frac{PV}{n_T RT} = 1 + Z^{\text{rep}} + Z^{\text{att}} \tag{1}$$

In this equation, n_T appears in all the terms and depends on temperature, density, and the equilibrium constant for hydrogen-bond formation. In order to reduce this equation to a usable form, an expression for n_T as a function of temperature and density must be found and then substituted into Eq. 1. In the following sections, this is done for two association models, the infinite equilibria model, and the monomer-dimer model.

Pure Components

Infinite equilibria model

The infinite equilibria model is useful in modeling the hydrogen bonding of molecules that form linear association products such as the aliphatic alcohols and water. In this model, linear association polymers are assumed to form via an infinite number of equilibria as follows:

$$\begin{aligned} A_1 + A_1 &\rightarrow A_2 \\ A_1 + A_2 &\rightarrow A_3 \\ &\vdots \\ A_1 + A_j &\rightarrow A_{j+1} \end{aligned} \tag{2}$$

The true number of moles, n_T, and the number of moles that would exist in the absence of association, n_0, are given by:

$$n_T = n_1 + n_2 + n_3 + \cdots = \sum_{j=1}^{\infty} n_j \tag{3}$$

$$n_0 = n_1 + 2n_2 + 3n_3 + \cdots = \sum_{j=1}^{\infty} j\, n_j \tag{4}$$

where n_1 is the number of moles of monomer, n_2 the number of moles of dimer, etc. True mole fractions in terms of association species are defined as follows:

$$z_j = n_j / n_T \tag{5}$$

A quantity of interest emerging from these definitions is the ratio n_T/n_0, the extent of association. It is unity when there is no association, and approaches zero when there is complete association. In order to solve for the extent of association and for the true mole fractions, the following equations are used:

$$\frac{n_0}{n_T} = \sum_{j=1}^{\infty} j\, z_j \tag{6}$$

$$\sum_{j=1}^{\infty} z_j = 1 \tag{7}$$

$$K_j = \frac{\phi_{j+1}}{\phi_j \phi_1 P} \frac{z_{j+1}}{z_j z_1} \tag{8}$$

where ϕ is the fugacity coefficient. Equation 6 is a material balance; Eq. 7 is the constraint that the true mole fractions must sum to 1; Eq. 8 is the jth canonical equilibrium expression for the assumed chemical association equilibria.

The fugacity coefficients in Eq. 8 are obtained from classical

thermodynamics as follows:

$$RT \ln \phi_j = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_j} \right)_{T,V,n_{i \neq j}} + \frac{RT}{V} \right] - RT \ln Z \qquad (9)$$

In this expression, the partial derivative of P with respect to N must be evaluated; in order to do that one needs the equation of state. The coupled nature of the problem is evident at this point: while n_T/n_0 is necessary before a closed-form equation of state can be determined, the equation of state is needed to determine n_T/n_0.

The expression for P given by PACT is written keeping in mind that the quantity n_T appearing in it is still unknown. The expression for pressure of a mixture is:

$$\frac{PV}{n_T RT} = 1 + Z^{\text{rep}} + Z^{\text{att}} \qquad (10)$$

The repulsive term is given by:

$$Z^{\text{rep}} = \langle c \rangle \frac{\xi(4 - 2\xi)}{(1 - \xi)^2} \qquad (11)$$

Here, $\langle c \rangle$ is the number of external (density-dependent) degrees of freedom and the reduced density, ξ, is given by:

$$\xi = \frac{\tau}{\langle \upsilon \rangle} = \frac{\tau \langle \upsilon^* \rangle}{V/n_T} \qquad (12)$$

All quantities in angular brackets, $\langle \cdots \rangle$, are mixture properties. The attractive term is a sum of two perturbation expansions, the first for Lennard-Jones interactions and the second for anisotropic interactions:

$$Z^{\text{att}} = Z_1^{\text{LJ}} + Z_2^{\text{LJ}} + \cdots + Z_2^{\text{ani}} + Z_3^{\text{ani}} + \cdots \qquad (13)$$

The first-order Lennard-Jones term is given by:

$$Z_1^{\text{LJ}} = \frac{1}{T} \sum_{m=1}^{6} \frac{m A_{1m} \langle cT^* \upsilon^* \rangle \langle \upsilon^* \rangle^{m-1}}{\left(\frac{V}{n_T} \right)^m} \qquad (14)$$

where

$$\langle c \rangle = \sum_{j=1}^{\infty} z_j c_j$$

$$\langle \upsilon^* \rangle = \sum_{j=1}^{\infty} z_j \upsilon_j^*$$

$$\langle cT^* \upsilon^* \rangle = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} z_i z_j \left(\frac{\epsilon_{ij} q_i}{c_i k} \right)^n \frac{r_j \sigma_{ji}^3}{\sqrt{2}}$$

Higher order Lennard-Jones terms are given by similar yet somewhat more involved expressions (Morris, 1984, 1986). Anisotropic terms are given by Vimalchand and Donohue (1985). In all these terms, the reduced density, ξ, and all mixture properties contain the ratio n_T/n_0, which is an unknown quantity. The molecular parameters appearing in this equation are: ϵ, the intersegment potential energy well depth; σ, the segmental radius; c, the external degrees of freedom per molecule; r, the number of segments in a molecule; and q, the surface area of a molecule relative to a spherical segment.

In the mixture under consideration, the parameters for the monomer are different from those of the dimer, trimer, etc. To make an analytic solution possible, it is necessary to relate the molecular parameters for each j-mer (i.e., each product of association) to those of the monomer. A simple set of such relations is used here and is similar to those used by Heidemann. They are:

$$\begin{aligned} \epsilon_{ij} &= \epsilon_{11} \\ \sigma_{ij}^3 &= \sigma_{11}^3 \\ c_j &= j\, c_1 \\ r_j &= j\, r_1 \\ q_j &= j\, q_1 \end{aligned} \qquad (15)$$

In these relations, subscript 1 refers to monomer. When they are substituted into the equation of state, two important simplifications result. First, the reduced density becomes independent of association and is given by:

$$\xi_0 = \frac{\tau \langle \upsilon^* \rangle}{V/n_0} \qquad (16)$$

Second, the repulsive term as well as all the attractive terms becomes independent of association because n_T cancels out of all of them. This fortunate outcome simplifies the final result greatly, as will become apparent.

To solve for n_T/n_0, the ratio of fugacities in Eq. 8 is evaluated and Eqs. 6, 7, and 8 are solved. Details of the solution are given by Heidemann and Prausnitz, and the result is:

$$\frac{n_T}{n_0} = z_1 = \frac{2}{1 + \sqrt{S}} \qquad (17)$$

where $S = 1 + 4KRTe^g/\upsilon_0$ with $\upsilon_0 = V/n_0$ and $e^g = 1$. Here, the result that e^g is identically 1 is a consequence of the equation of state and the mixing rules used, Eq. 15. For other equations of state or for other mixing rules, more complicated expressions for e^g result.

Finally, the closed-form equation of state is given by:

$$\frac{PV}{n_0 RT} = \frac{n_T}{n_0} + Z^{\text{rep}} + Z_1^{\text{LJ}} + Z_2^{\text{LJ}} + \cdots + Z_2^{\text{ani}} + Z_3^{\text{ani}} + \cdots \qquad (18)$$

The interesting result is that in this equation, the only term that depends on the association is the ideal gas term. All other terms depend only on n_0, and the mixture properties reduce to quantities that contain molecular parameters of the monomer alone. Specifically, the repulsive term is:

$$Z^{\text{rep}} = c_1 \frac{\xi_0(4 - 2\xi_0)}{(1 - \xi_0)^2} \qquad (19)$$

In this equation, the subscript 0 is used as a reminder that the

reduced density depends on n_0 and is independent of n_T. The first-order Lennard-Jones term is:

$$Z_1^{LJ} = \frac{c_1 T_1^*}{T} \sum_{m=1}^{6} \frac{m A_{1m}}{m} \tag{20}$$

where

$$T_1^* = \frac{\epsilon q_1}{c_1 k}$$

$$\tilde{v} = \frac{V/n_0}{v_1^*}$$

It is easily shown that higher order Lennard-Jones and anisotropic terms also reduce to expressions involving the monomer only. They are given elsewhere (Morris, 1984). Thus, the repulsive and attractive terms in the original equation of state written for a mixture of association species have reduced to those for the monomer.

To summarize, a closed-form equation of state has been derived to take into account hydrogen bonding. For PACT, the perturbed anisotropic chain theory, the equation of state depends on the extent of association through the ideal gas term only.

Monomer-dimer model

Another association model useful for molecules that exhibit strong dimerization is the monomer-dimer model. It has been used extensively to model the behavior of acetic acid and it results in a simple algebraic equation that can be solved easily. A dimerization equilibrium is assumed as follows:

$$A_1 + A_1 \rightarrow A_2^c \tag{21}$$

Where the superscript c denotes the cyclic (doubly bonded) dimer. The material balance constraint is:

$$\frac{n_0}{n_T} = z_1 + 2 z_2^c \tag{22}$$

where

$$z_2^c = \frac{n_2^c}{n_T} \tag{23}$$

All true mole fractions again must sum to 1:

$$1 = z_1 + z_2^c \tag{24}$$

The equilibrium expression for cyclic dimer formation is:

$$K_2^c = \frac{\phi_2^c}{\phi_1^2 P} \frac{z_2^c}{z_1^2} \tag{25}$$

where K_2^c is the equilibrium constant. It can be shown that the equation of state in this case is the same as in the infinite equilibria model and e^g again is unity. However, n_T/n_0 is different. To solve for n_T/n_0, the fugacity coefficient ratio of Eq. 25 is evaluated using Eq. 9 and the equation of state, Eqs. 10–14. The result is substituted in Eq. 25, which, upon rearrangement gives:

$$z_2^c = \frac{K_2^c RT}{V/n_0} z_1^2 (n_T/n_0) \tag{26}$$

This expression for z_2^c is substituted into Eqs. 22 and 24 to give a set of two algebraic equations in n_T/n_0 and z_1. Upon solution, this gives:

$$\frac{n_T}{n_0} = \frac{2(\alpha - 1)}{4\alpha - 1 - \sqrt{(8\alpha + 1)}} \tag{27}$$

where

$$\alpha = \frac{K_2^c RT}{V/n_0}$$

and

$$z_1 = 2 - \frac{1}{n_T/n_0} \tag{28}$$

The closed-form equation of state in this case is Eq. 18 with n_T/n_0 given by Eq. 27.

Mixtures

One associating component and one or more diluents

By generalizing the preceding analysis, an equation of state is derived for a mixture of an associating component and one or more diluents. Here a diluent is defined as a component that does not hydrogen-bond with itself or with the other components in the mixture. Aliphatic hydrocarbons are examples of diluents.

The stoichiometry in this case is defined in a slightly different manner. The total number of moles, n_T, is the sum of moles of diluent, n_D, plus the moles of all association species, n_{TA}, i.e.,

$$n_T = n_D + n_{TA} \tag{29}$$

where

$$n_{TA} = \sum_{j=1}^{\infty} n_{Aj} \tag{30}$$

Here, n_{Aj} is the number of moles of the jth species in the association equilibria described in the previous sections. Dividing through by n_{TA} in Eq. 30, one obtains:

$$1 = \sum_{j=1}^{\infty} z_{Aj} \tag{31}$$

where z_{Aj}, the mole fraction of the jth species, is:

$$z_{Aj} = \frac{n_{Aj}}{n_{TA}} \tag{32}$$

Division of both sides of Eq. 29 by n_0, gives the extent of associa-

tion in a mixture:

$$\frac{n_T}{n_0} = \frac{n_D}{n_0} + \frac{n_{A0}}{n_0}\frac{n_{TA}}{n_{A0}} = x_D + x_{A0}\frac{n_{TA}}{n_{A0}} \tag{33}$$

Here, the superficial mole fraction of A is defined by introducing the quantity n_{A0}, the number of moles of A that would exist in the mixture if there were no hydrogen bonding. It is given by:

$$x_{A0} = n_{A0}/n_0 = n_{A0}/(n_{A0} + n_D) \tag{34}$$

The extent of association, n_T/n_0, is the quantity that appears in the equation of state for the mixture under consideration.

The last stoichiometric equation is the material balance for n_{A0}:

$$\frac{n_{A0}}{n_{TA}} = \sum_{j=1}^{\infty} j\, z_{Aj} \tag{35}$$

Equations 31 and 35 are the same as Eqs. 7 and 6. The equilibrium expression for the formation of the jth species in the mixture is:

$$K_j = \frac{\phi_{A(j+1)}}{\phi_{Aj}\phi_{A1}P}\frac{z_{A(j+1)}}{z_{Aj}\,z_{A1}}\frac{1}{x_{A0}} \tag{36}$$

Solution of Eqs. 31, 35, and 36 is the same as for the infinite equilibria model, and the expression for n_{TA}/n_{A0} is given by:

$$\frac{n_{TA}}{n_{A0}} = z_{A1} = \frac{2}{1 + \sqrt{S}} \tag{37}$$

where

$$S = 1 + 4KRTe^{\varepsilon}x_{A0}/v_0$$

Once again, e^{ε} is unity and the only term that depends on association in the equation of state is the ideal gas term. This is a direct consequence of the assumptions made to relate the molecular parameters of the jth species in the association equilibria to the parameters of the monomer. The equation of state for a mixture of an associating component and a diluent is:

$$\frac{PV}{n_0RT} = \frac{n_T}{n_0} + Z^{\text{rep}}_{\text{mix}} + Z^{\text{att}}_{\text{mix}} \tag{38}$$

In this equation, the mixture repulsive and attractive terms are given by Vimalchand and Donohue and depend on the superficial mole fractions of A and diluent. The parameters that appear in these terms are those of the diluent and the monomer of component A. For the infinite equilibria model, the extent of association that appears in the ideal gas term is given by Eqs. 33 and 37.

For the monomer-dimer model, an expression for the extent of association is obtained with a procedure similar to the one above. The result for n_{TA}/n_{A0} is:

$$\frac{n_{TA}}{n_{A0}} = \frac{2(\alpha - 1)}{4\alpha - 1 - \sqrt{(8\alpha + 1)}} \tag{39}$$

where

$$\alpha = \frac{K_2^c RTx_{A0}}{V/n_0}$$

Results

The associated perturbed anisotropic chain theory (APACT) has been applied to methyl and ethyl alcohol, water, acetic acid, and to mixtures of these compounds with aliphatic and aromatic hydrocarbons. Thermodynamic properties were calculated using temperature-independent, pure-component parameters evaluated by fitting the theory to experimental data.

APACT has five molecular parameters for each pure component. In addition to ΔH^0 and ΔS^0, the standard enthalpy and entropy of hydrogen-bond formation, they are T^*, a characteristic energy parameter, v^*, a characteristic size parameter, and c, the number of degrees of freedom. Values for ΔH^0 and ΔS^0 are reported in the literature but they are not unique (Pimentel and McClellan, 1960; Vinogradov and Linnell, 1971). The most reliable ΔH^0 values are those obtained using spectroscopic methods, infrared being the most common. These values, however, depend on the assignment of absorption peaks to particular association species and not all investigators agree on what species are present. There is much controversy over the existence of dimers and whether they are linear or cyclic, and on the identity of higher order species. As a result, literature values for ΔH^0 range from 14.6 to 25 KJ/gmol for the alcohols, and from 25 to 33 KJ/gmol for acetic acid (Pimentel and McClellan, 1960). Values for ΔS^0 are rarely reported and are not very reliable. Because of this uncertainty, literature values for ΔH^0 and ΔS^0 were used only as initial estimates and subsequently were fitted to experimental data.

Pure-component parameters in APACT were evaluated by fitting the theory to vapor pressure data and liquid density data. Initially, ΔH^0 and ΔS^0 were set to values that make the equilibrium constant essentially zero and the remaining parameters were evaluated using a nonlinear regression routine. Next, by incrementing ΔH^0 and ΔS^0 by small amounts and repeating the regression, nonzero values of K were reached. Then, ΔH^0 and ΔS^0 were varied until a minimum in the sum of squares of the errors was achieved. The resulting values for ΔH^0 are comparable to those reported in the literature and are given in Table 1.

Tables 2 and 3 give pure-component parameters obtained for APACT and PACT for the molecules considered. Table 4 gives the values of dipole and quadrupole moments used. Comparison of pure-component liquid densities and vapor pressures for ethyl alcohol calculated with PACT and with APACT are shown in Figures 1 and 2. It can be seen that APACT fits the data closely.

Table 1. Association Constants Used in APACT

Molecule	ΔH^0 J/mol	$\Delta S^0/R$
Methanol	−1,331	−10.32
Ethanol	−1,479	−11.57
Water	−1,243	−9.94
Acetic acid, liquid	−1,374	−10.13
Acetic acid, vapor	−3,203	−17.73

Table 2. Pure-Component Parameters for APACT

Molecule	T^* K	v^* m³/mol	c	ϵ/k K
Methanol	231.2	23.24	1.080	161
Ethanol	277.5	34.20	1.220	161
Water	117.7	11.46	1.000	350
Acetic acid	344.6	33.94	1.673	238

Moreover, the parameters obtained for APACT are more realistic than those obtained using PACT. Consider, for example, the value of c for ethyl alcohol given in Tables 2 and 3. It can be seen that APACT fits the data with a value of 1.22, while PACT requires a value of 2.94. Since the ethyl alcohol monomer is a chain equivalent to approximately three CH_2 groups, a value of c comparable to that of propane should be expected. A comparison may be made with the results of Morris (1984), who has correlated molecular parameters with carbon number. According to the correlations of Morris c for propane is about 1.3, whereas a value of c equal to 2.94 corresponds to carbon number 12. This indicates that the effective chain length of the ethanol molecule predicted by APACT is more realistic than that predicted by PACT. Similar arguments could be made for T^* and v^*.

Figure 3 shows the distribution of association species as a function of superficial alcohol mole fraction for ethanol-toluene at two different temperatures. At 0°C, a sharp drop in monomer concentration is predicted at very low alcohol mole fraction, indicating that higher order species form rapidly when alcohol is added to pure toluene. At 50°C, the associated species form at higher alcohol mole fractions because of the increase in kinetic energy. When molecules possess more kinetic energy, the chemical equilibria (Eq. 2) shift to favor monomers, thus retarding the formation of dimers, trimers, etc.

Binary mixture results are given in Figures 4 through 7. Figure 4 shows ethanol binaries with *n*-hexane, benzene, and *n*-octane. For the ethanol-hexane system, PACT predicts liquid-liquid phase separation, while APACT fits the data well with a binary interaction parameter, k_{ij}, of zero. For the ethanol-benzene and ethanol-octane systems, neither theory predicts phase separation, but APACT fits the data more closely. For these systems, the calculations for both theories are with nonzero values of k_{ij}. Table 5 gives the values of k_{ij} for the binary systems studied.

In Figures 5 and 6, comparisons of APACT and PACT for binary mixtures of water in various diluents are shown. With alkanes as diluents, PACT gives large deviations in the vapor phase, as shown in Figure 5. These are corrected when APACT is used. This improvement is typical when a model that accounts for hydrogen bonding is used in place of one that does not (Baumgaertner et al., 1980, Figure 8). With benzene (a quadrupolar fluid) as diluent, the predictions of APACT again are an improvement over those of PACT. This is especially evident in the case of water-benzene at 306°C, in which PACT predicts an azeotrope while APACT gives the correct phase behavior.

Table 3. Pure-Component Parameters for PACT

Molecule	T^* K	v^* m³/mol	c	ϵ/k K
Methanol	309.2	21.55	2.328	128
Ethanol	285.9	29.41	2.961	128
Water	367.2	11.80	1.289	110
Acetic acid	400.9	36.42	1.662	220

Table 4. Anisotropic Constants Used in APACT and PACT

Molecule	Dipole Moment, Debyes	Polarizability, A³
Methanol	1.71	3.28
Ethanol	1.73	5.11
Acetic acid	1.90	5.26
Water	1.82	1.47

Unlike the alcohols, acetic acid dimerizes to a large extent in the vapor phase because the cyclic dimer is unusually stable. However, it is not clear that cyclic dimers are the only associated species, or even the predominant species in the liquid phase; it is quite likely that higher order species (both cyclic and linear) are present in the liquid. For this reason, many investigators report that better fits of spectroscopic results are obtained when the values of ΔH^0 and ΔS^0 used for liquid acetic acid are different from those used for the vapor (Jenkins, 1979). In fitting the APACT equation of state to pure acetic acid data, it also was found that better results were obtained when ΔH^0 and ΔS^0 values used for the vapor were different from those used for the liquid. In our calculations, vapor phase ΔH^0 and ΔS^0 were similar to those used by Jenkins while liquid phase ΔH^0 and ΔS^0 were fitted to liquid density data and vapor pressure data as described above. While it is possible that the data for acetic acid could be fit with single values for ΔH^0 and ΔS^0 if these other species were accounted for, there necessarily are trade-offs between mathematical simplicity and the accuracy of the model.

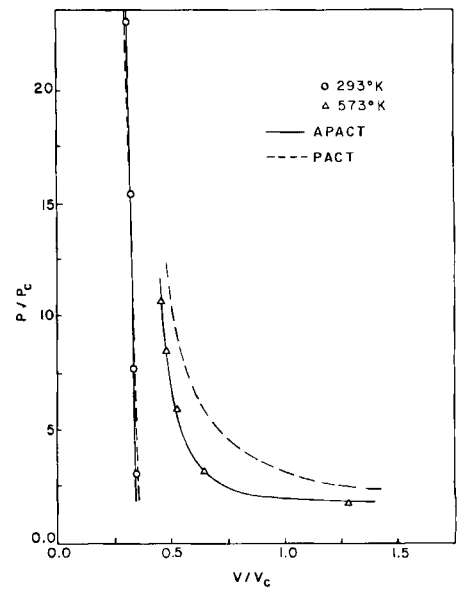

Figure 1. Comparison of predicted fluid densities for ethanol.

Experimental data of Bridgman (1912) and Lo and Stiel (1969). Parameters obtained by fitting both liquid densities and vapor pressures.

Both equations do well at 293 K (below critical temperature), but APACT gives significant improvement at 573 K (above critical temperature).

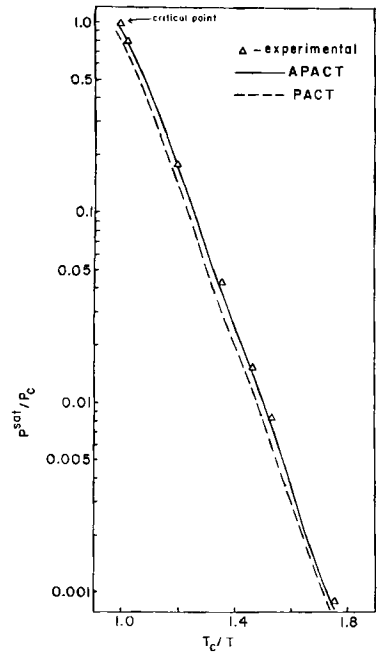

Figure 2. Comparison of predicted vapor pressures for ethanol from triple point to critical point.
Experimental data of Ambrose et al. (1975).

Figure 7 gives phase equilibria for acetic acid binaries with heptane and benzene. For these systems APACT gives better predictions than PACT. For acetic acid-heptane, a small systematic deviation is seen. Similar discrepancies are found in the literature where monomer-dimer equilibria are used to treat acetic acid. For example, Jenkins (1979) claims that such discrepancies in acetic acid-hydrocarbon binaries are due to the presence of trimer and tetramer in the liquid, while Ritter and Simmons (1945) present evidence for the existence of planar trimer and three-dimensional tetramer in liquid acetic acid. Baumgaertner et al. (1979) obtained good results using a monomer-dimer-trimer association model for the liquid phase.

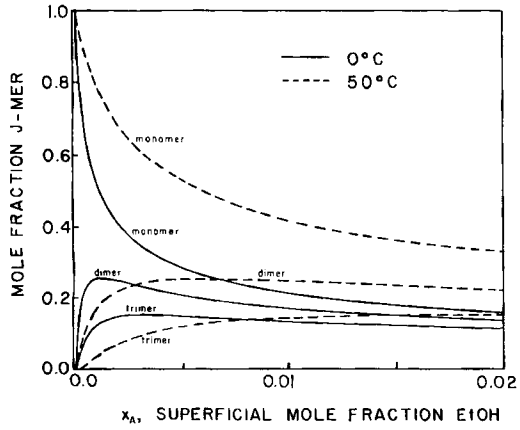

Figure 3. Association species distribution for infinite equilibria model calculated for ethanol-toluene at two temperatures.
50°C: Monomer dominates. 0°C: Significant amounts of dimer, trimer, etc. are present.

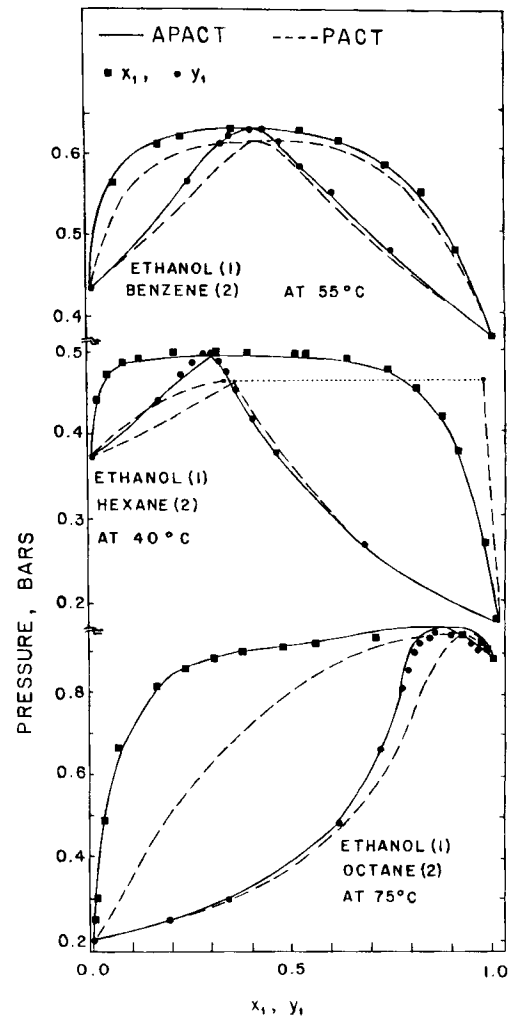

Figure 4. Prediction of phase equilibria for three ethanol systems.
Ethanol-benzene, data of Ho and Lu (1963).
Ethanol-hexane, data of Ho and Lu (1963). PACT predicts liquid-liquid phase separation; APACT predicts correct phase behavior.
Ethanol-octane, data of Boublikova and Lu (1969). Both equations predict an azeotrope, but APACT gives a much better prediction.
Table 5 gives values of k_{ij}.

Table 5. Binary Interaction Parameters Used in Mixture Calculations

System	$k_{ij} \times 100$ APACT	$k_{ij} \times 100$ PACT
Ethanol-hexane	0.0	0.0
Ethanol-benzene	−1.2	3.1
Acetic acid-heptane	0.0	0.0
Acetic acid-benzene	−0.5	−0.6
Water-methane	−12.0	−1.2
Water-butane	0.0	0.0
Water-benzene, 225°C	10.0	11.0
Water-benzene, 306°C	8.0	9.0

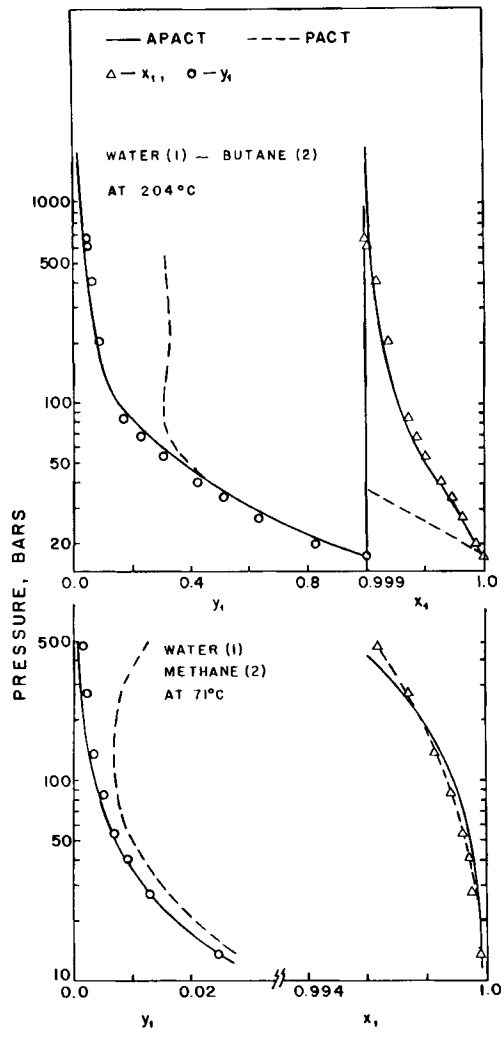

Figure 5. Prediction of phase equilibria for two water systems.

Water-butane, data of Sage and Lacey (1955).
Water-methane, data of Olds et al. (1942) and Culbertson and McKetta (1951).
Both systems: PACT predictions good for P-x line, poor for P-y line; APACT predictions good for both phases.
Table 5 gives values of k_{ij}.

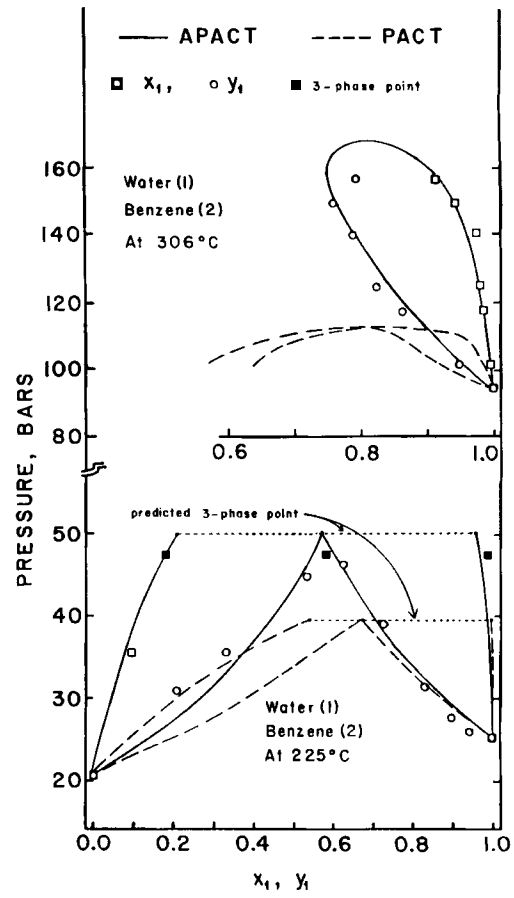

Figure 6. Prediction of phase equilibria for water-benzene at two temperatures.

Data of Rebert and Kay (1959).
225°C: Both equations predict phase separation, but APACT is much closer to the experimental data.
306°C: PACT predicts wrong phase behavior; APACT gives correct representation.
Table 5 gives values of k_{ij}.

In the case of APACT, incorporation of such a model would increase the complexity of the equation of state to an extent that its use may no longer be justified. In view of the simplicity of the hydrogen bonding model, the accuracy is remarkable.

To demonstrate the accuracy of APACT, comparisons have been made with the predictions of other commonly used equations of state. One such equation is the Peng-Robinson equation of state, which has been used with some success to treat hydrogen-bonded systems (Peng and Robinson, 1980). Figure 8 shows the best fit of K factors for ethanol-hexane using the Peng-Robinson equation and APACT. The Peng-Robinson equation gives the best fit with a k_{12} of 0.02; a higher k_{12} incorrectly predicts liquid-liquid phase separation. For this system, APACT fits the experimental data very closely. Figure 9 shows activity coefficients as a function of concentration for ethanol-cyclohexane using a modified Gubbins-Gray-Perturbation Theory (GGPT; Moser and Kistenmacher, 1985), the Redlich-Kwong equation of state (RK-EOS), and APACT. APACT gives a much better representation of the data with a zero value of k_{ij}.

Discussion

The one very important result obtained in this work is that APACT is only slightly more complex than PACT, since the hydrogen bonding corrections involve the ideal gas term only and the repulsive and attractive terms are not affected. In the various figures it is shown that PACT, a theory that explicitly accounts for polar forces, is not adequate for associating fluids, while APACT, which corrects for both polarity and hydrogen bonding, represents an improvement. However, since both equations are rather lengthy and complex in form, one might wonder whether the association corrections alone are adequate to model phase behavior in these systems. To test this hypothesis, Eq. 38 was used with the anisotropic terms, Z^{att}_{mix}, set equal to zero. Note that the attractive term Z^{att}_{mix} is the sum of the Lennard-Jones and the anisotropic terms, ie., $Z^{att}_{mix} = Z^{LJ}_{mix} + Z^{ani}_{mix}$. The result is that this equation, although simpler than APACT, does not give

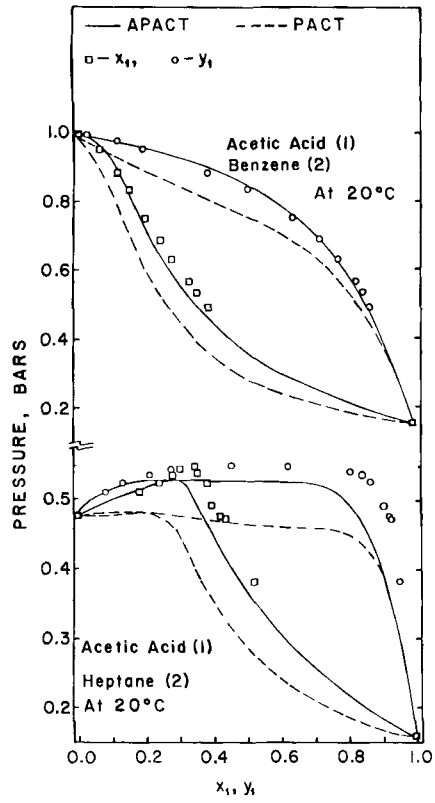

Figure 7. Prediction of phase equilibria for two acetic acid systems with monomer-dimer model.

Acetic acid-benzene, data of Werner (1965).
Acetic acid-heptane, data of Werner (1965) and Markuzin and Pavlova (1971). Both equations predict an azetrope, but APACT is much closer to the experimental data.
Table 5 gives values of k_{ij}.

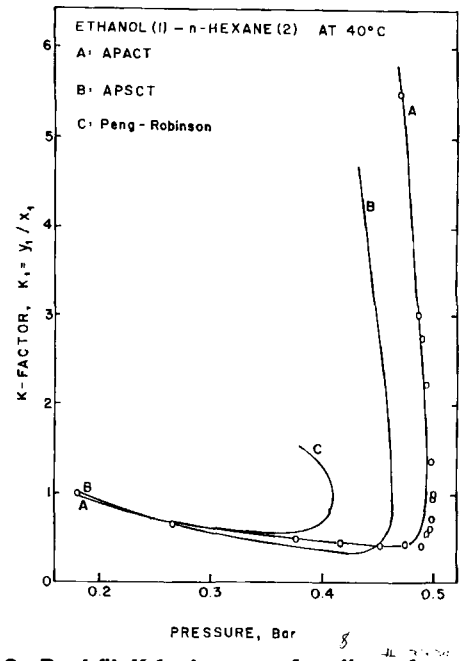

Figure 8. Best-fit *K* factor as a function of pressure for ethanol–*n*-hexane.

Binary interaction parameters: Peng-Robinson EOS, 0.02; APACT, 0.
Curve B (APSCT) is given by Eqs. 38 and 39 with Z^{ani}_{mix} set to 0 (with refitted pure-component parameters) with $k_{ij} = 0$.

adequate results for some hydrogen bonding systems. An example is shown in Figure 8, where the phase behavior of ethanol-hexane can be fitted well by APACT, but when the anisotropic terms are omitted there is considerable loss in accuracy. This indicates that association corrections alone are in some cases not enough to give the accuracy required in engineering calculations. In general, it is necessary to include corrections for both polar forces and chemical association if the system contains molecules that are both polar and associate.

One final comparison that deserves to be made is with the technique of Gmehling et al. (1979) in which the separate expressions for chemical equilibria and phase equilibria are solved simultaneoulsy by trial and error. Since only monomers and dimers are considered, this method has the advantage that it can be generalized to multicomponent mixtures. However, in practice the method of Gmehling is quite demanding computationally. Further, the results above suggest that APACT, although computationally simpler than the method of Gmehling et al., should give better results since that work was based on the perturbed hard chain theory, which does not include the effects of molecular polarity.

While APACT is shown here to work well for several hydrogen bonding systems, there are limitations that should be pointed out. One obvious shortcoming is the crudness of the infinite equilibria model, which assumes linear equilibrium species. Stable cyclic species have been found to exist in significant amounts for some some molecules (Pimentel and McClellan 1960) and APACT does not take them into account. While it is possible to account for both linear and cyclic species, the equations become significantly more complex. Another limitation of the theory in its present form is that it cannot be applied to mixtures in which more than one component associates. To treat such mixtures, assumptions must be made about the nature and composition of cross-dimers, trimers, etc., present in the mixture. Substantial progress has been made toward a more general equation and these results will be presented in forthcoming publications.

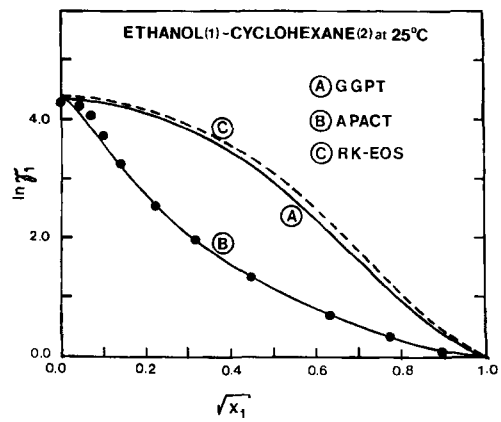

Figure 9. Prediction of phase equilibria for ethanol-cyclohexane.

GGPTh, modified Gubbins-Gray perturbation theory (Moser and Kistenmacher, 1985).
RK-EOS, Redlich-Kwong equation of state.
$k_{ij} = 0$ for all three equations.

Acknowledgment

Support of this research by the Division of Chemical Sciences of the Office of Basic Energy Sciences, U.S. Department of Energy under contract number DE-AC02-81ER10982 is gratefully acknowledged. The authors wish to thank the The Johns Hopkins University Computing Center and the Engineering Computing Facility for the use of their facilities. Discussions with H. F. Kistenmacher of Linde A. G. led us to attack this problem.

Notation

A_{1m} = constants in attractive terms of PACT
c = 1/3 number of external (density-independent) degrees of freedom
ΔH^0 = standard enthalpy of hydrogen bond formation
N = number of molecules
n = number of moles
P = pressure
q = surface area of a molecule relative to a spherical segment
R = gas constant
ΔS^0 = standard entropy of hydrogen bond formation
r = segmental radius
T = temperature
V = total volume
v = molar volume
x = mole fraction calculated ignoring association
Z = compressibility
z = true mole fraction

Greek letters

ϵ = intersegmental potential energy well depth
ξ = reduced density
σ = segmental radius
$\tau = \pi, \sqrt{2}/6$
ϕ = fugacity coefficient

Subscripts

A = component exhibiting association
D = diluent
j = jth association species
mix = mixture
T = true association species
0 = quantity calculated ignoring association
1, 2, 3, . . . = attractive terms in perturbation expansion

Superscripts

ani = anisotropic attractions
att = attractive
rep = repulsive
LJ = Lennard-Jones attractions

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Manuscript received Sept. 30, 1985, and revision received Mar. 14, 1986.