INTRODUCTION

It is well known that the existing theories of thermodynamics have not been capable of predicting the thermodynamic properties of associating fluids with reasonable accuracy. To improve the applicability of theories for such compounds, a statistical polydisperse theory of characterizing the molecular association effects has been developed. By the application of the theories of polydisperse fluids, it has become possible to develop accurate and analytic equations of state for associating fluids. In order to demonstrate the reliability of the theory it is applied for four different kinds of associating fluids; namely water, ammonia, methanol and hydrogen sulfide over wide ranges of temperature and pressure with success.

ABSTRACT

It is well known that the existing theories of thermodynamics have not been capable of predicting the thermodynamic properties of associating fluids with reasonable accuracy. Development of an accurate theory for associating fluids has been a challenging problem and remains an active field of research in thermodynamics. Hydrogen bonding and charge transfer are the cases of such chemical associations between molecules, in which monomers are linked to form dimers, trimers and other association species. Equilibrium between these associating species makes thermodynamic properties, and specifically the phase behavior, somehow complicated and it causes large deviation from ideality.

Review of Previous Studies

Although many previous studies using an equation of state (EOS) showed trends of phase equilibria consistent with the experimental data (Heidemann and Prausnitz 1976), it failed to match the experimental data unless a term
representing partial association was included. Both physical and chemical interactions exist simultaneously in associated systems and interrelate each other, which would make it difficult to obtain physical and chemical parameters uniquely. In addition, the assignment of probable associated species is arbitrary. Since the proposed models can not take into account the complex behavior of associating fluids into EOS, the adjustable parameters are essentially empirical with little physical significance.

Any serious development of equation of states (EOS’s) for correlating fluid-phase equilibria of associating fluids needs a rigorous statistical mechanical basis as well as the identification of the dominant source of nonideality (Mansoori 1986, Haile and Mansoori 1983). In recent years a number of statistical mechanics theories have been also formulated and applied towards a better representation of non-associating or associating fluids (Hamad and Mansoori 1990, Matteoli and Lepori 1984, Wertheim 1986). The pure fluids and mixtures to be studied consist of aqueous and other associating solutions of compounds for which, generally, intermolecular potential energy functions are not accurately known. As a result, conventional statistical mechanical theories of mixtures have failed to predict behavior of such fluids.

**Polydisperse Thermodynamics**

The failure to find a satisfactory analytic theory for associating fluids arises from the lack of information at the molecular level about the appropriate mathematical functions in characterizing these fluids. Due to the formation of different molecular aggregates within an associating fluid and in order to account for these different aggregates, thermodynamic characterization of such associating fluids would be better represented by polydisperse thermodynamics. This will provide a full description of all possible associating species that constitute an individual polar fluid. Two classes of multicomponent fluid mixtures (Prausnitz 1983) have to be distinguished here:

Class 1: A mixture of chemically identifiable nonelectrolyte components

Class 2: A mixture of chemically non-identifiable nonelectrolyte components.

A number of investigators have established a consistent groundwork of polydisperse thermodynamics theory using probability distribution functions (Salacuse and Stell 1982, Du and Mansoori 1989). The class 2 mixtures,
mentioned above, have been analyzed extensively through polydisperse thermodynamics. However none of polydisperse thermodynamics have been applied on the class 1 mixtures. The simple nature of class 2 mixtures is frequently encountered in the petroleum industry. Due to the complexity of class 1 mixtures, we do not have a clear understanding of associating phenomena within this class.

The abnormal behavior of polar fluids in view of their low molecular weights is due, largely, to such group formation, and deviation of solution of polar fluids from ideality often is the result of association. Therefore, a polar fluid is basically a collective mixture of these different groups which differ in size, shape, and structure. These groups are classified chemically as monomers, dimers, trimers, etc. In this case, we apply the theory of polydisperse thermodynamics to associating fluids because the association species may be approximated as a polydisperse system and modify an existing mathematical model of the thermodynamic EOS for such fluids. As it is shown in this work both repulsive and attractive terms of an EOS are modified by considering the principle of polydisperse thermodynamics.

Development of Statistical Polydisperse Theory

From statistical mechanics, the canonical-ensemble partition function \( Q \) in a \( C \)-component system composed of total \( N \) particles

\[
\sum_{i} N_i = N, \text{ an assembly of } N_a \text{ molecules of species } a, N_b \text{ molecules of species } b, \text{ etc.} \]

is given by McQuarrie (1975):

\[
Q(N, V, T) = Q_{\text{mol}}(N, T) Q_{\text{conf}}(N, V, T) \tag{1}
\]

where \( N, V \) and \( T \) are the thermodynamic state variables. \( Q_{\text{mol}} \) is the partition function related to the translation and intramolecular energies (rotation, vibration, etc.) and \( Q_{\text{conf}} \) is the configurational integral from the contribution of the intermolecular energy. The configurational integral of mixtures with noncentral forces has the following form

\[
Q_{\text{conf}} = \frac{1}{\Omega} \int \cdots e^{-\phi/kT} \, dV_1 \ldots dV_N \, d\omega_1 \ldots d\omega_N \tag{2}
\]

where \( k \) is Boltzmann's constant, \( \Omega = \int d\omega \), and \( d\omega \) represents the appropriate differential of angular coordinates for molecule \( i \). \( \phi \) is the (microscopic) intermolecular potential energy function which may be greatly simplified if it is a sum of pair potentials

\[
\phi = \sum_{i=1}^{C} \sum_{j=1}^{C} \left( \sum_{k > 1}^{N_i} \sum_{l=1}^{N_j} \phi_{ij}^{(kl)} \right) \tag{3}
\]
where \( k \) and \( l \) denote a pair of molecules of any species. Note that there is little or no information available about intermolecular interaction parameters of the various kinds of associating fluids.

**Conformal Solution Theory**

The conformal solution theory assumes that there exists a pure hypothetical fluid that the same properties as those of the mixture at the same density and temperature. Since it has a theoretical framework which is not tied to any physical model, the conformal solution theory seems to offer a practical and accurate approach to develop proper mixing rules for associating fluids. It is known that the concept of the conformal solution is suited to polydisperse system (Dickinson 1980).

For simple spherically symmetric molecules obeying a two parameter conformal function, we have (Brown 1957).

\[
\phi = f_{ij} \phi_\infty \left( f/h_{ij}^{1/3} \right)
\]

where subscripts (oo) denote the reference fluids and the parameters \( f_{ij} \) and \( h_{ij} \) represent the molecular conformal energy and volume parameter, respectively. The mixture theory is considered very important in extending the applicability from pure fluids to fluid mixtures. Mansoori (1986) developed proper mixture theories which correctly utilize the conformal solution theory of statistical mechanics for discrete mixtures.

The combining rules for unlike-interaction potential parameters are usually expressed by the following expressions

\[
f_{ij} = (1 - k_{ij}) (f_{ii} f_{jj})^{1/2}
\]

\[
h_{ij} = (1 - l_{ij}) \left[ (h_{ii}^{1/3} + h_{jj}^{1/3})/2 \right]^3
\]

where \( k_{ij} \) and \( l_{ij} \) are binary interaction parameters of an unlike pair of molecules \( i \) and \( j \), and are equal to zero between the same molecules (e.g. monomers vs. dimers of an associating fluid here).

Among the statistical mechanical conformal solution theories of mixtures, one-fluid van der Waals theory is simple to use and accurate enough with the following form:

\[
f_m f_m = \sum_i \sum_j x_i x_j f_{ij} h_{ij}
\]

\[
h_m = \sum_i \sum_j x_i x_j h_{ij}
\]

We can relate \( f_{ij} h_{ij} \) term in Eq. (7) to \( f_{ii} h_{ii} \) (single component properties) by substituting Eqs. (5)-(6) into Eq. (7) and obtain

\[
f_{ij} h_{ij} = \left( f_{ii} h_{ii} f_{jj} h_{jj} \right)^{1/2} \left[ \frac{1}{2} \left( \frac{h_{ij}}{h_{jj}} \right)^{1/2} + \frac{1}{3} \left( \frac{h_{ij}}{h_{jj}} \right)^{1/6} \right]
\]
The bracket $[\{\}]$ in the above equation is due to the correction of the molecular size differences between an unlike pair of molecules $i$ and $j$. This size difference effect is similar in the polydisperse mixture between two different association species.

If the polydisperse mixture exhibits a narrow distribution, the above correction term is close to unity and Eq. (7) reduces to

$$f_m h_m = \left( \sum_i x_i (f_{ii} h_{ii})^{1/2} \right)^2$$  \hspace{1cm} (10)

Next, for the sake of simplicity it is suggested by Chen et al. (1973)

$$h_{ij} = (1 - 1_{ij}) (h_{ii} + h_{jj}) / 2$$  \hspace{1cm} (11)

Substituting Eq. (11) into (8), we obtain

$$h_m = \sum_i x_i h_{ii}$$  \hspace{1cm} (12)

Eqs. (10) and (12) are the mixing rules for the discrete mixtures.

Now we will show how to extend these mixing rules to the polydisperse mixture. In order to extend conformal solution mixture theories to a polydisperse mixture, we need to introduce a mole fraction distribution function to characterize the polydisperse fluids instead of using a set of mole fractions describing the amounts of each species present in a multi-component system (Gualtieri 1993).

**Distribution function**

Statistical concepts related to random variables are directly applicable to the modeling of the polydisperse mixture. In the case of narrow distributions, the thermodynamic properties of the mixture can be related to those of the most predominant species plus correction terms in powers of the variance of the distribution. Considering an associating fluid to be a polydisperse mixture of different aggregates i.e. monomers, dimers, trimers, and so on., we may assume that the associating fluid follows an exponential decay distribution function. This distribution can be written as

$$F(I) = \frac{1}{\eta} \exp \left( \frac{- (I - I_0)/\eta} {\eta} \right)$$  \hspace{1cm} (13)

where the distributed variable $I$ represents the chain length (index of distribution) with $I_0$ of the predominant association species.

In the vapor phase the molecules existing as monomers make up the major part of the total number of molecules, and chains of 2, 3, 4, etc. molecules are present in diminishing amounts. While the composition or the distribution of these components varies appreciably with temperatures and pressures, the concentration of monomers and the smaller chains are much

higher than those of the larger chain groups at moderate temperatures and pressures. In other words, the probability of finding monomers and dimers in an associating fluid is much higher than that of trimers and larger chains at moderate temperatures and pressures. This suggests an exponential decay distribution of the associating species should be obtained in the vapor phase.

However, the hypothesis of applying an exponential decay distribution function may be valid only to regions above the normal boiling point temperature of a polar fluid. At temperatures near the vicinity or below the normal boiling point temperature of a polar fluid higher associating species have more significant contributions to the whole structure of a polar fluid. Therefore, an exponential decay distribution function would not be valid at those low temperature regions. Since the proportions of chains composed of multiple molecules are widely spread at low temperatures, a different distribution function (i.e., gamma distribution function) which is able to characterize the molecular association, is required.

In this case, we may assume a gamma distribution function to represent the scatter of associated components which can be written as

\[
F(I) = \frac{(I - I_c)^{\kappa-1}\exp\left[-(I - I_c)/\eta\right]}{\eta^\kappa \Gamma(\kappa)}
\]

(14)

where \(\kappa\) and \(\eta\) are distribution parameters. In the case of gamma distribution function, variance is defined as \(\kappa\eta^2\). In case of \(\kappa = 1\), we have a single variable exponential-decay distribution which describes the chain length of the associating species.

Substituting \(F(I)\) for \(x_i\), Eqs. (10) and (12) are replaced by the following expressions for the polydisperse mixture:

\[
f h = \left\{ \int F(I) \left[ f(I) h(I) \right]^{\kappa/2} \mathrm{d}I \right\}^{1/\kappa}
\]

(15)

\[
h = \int F(I) h(I) \mathrm{d}I
\]

(16)

where \(F(I)\) is normalized such that

\[
\int F(I) \mathrm{d}I = 1
\]

(17)

over the entire range of \(I\) starting from \(I_0\).

Eqs. (15) and (16) are the mixing rules applied to the polydisperse mixture based on the conformal solution mixing rules and a distribution function. Before using this set of mixing rules for a mathematical model one has to express the constant parameters with respect to the molecular conformal parameters \(f\) and \(h\).
**Theory of associating fluids**

Functional Form of Variance

Since bonding strength between different aggregates of molecules may be influenced by a change in the system under consideration, the distribution variance of molecules present, to a great extent, is a measure of such influence in their conditions. An increase in temperature usually results in a breakdown of chain of molecules which in turn leads to a lower degree of association and a smaller variance of distribution. The extent of association is expected to be lower for vapor phase compared to that of liquid phase and has an influence on the range of vapor-liquid coexistence.

However, this behavior is quite different in the liquid phase, of which the proportion of longer chains in the liquid at coexistence increases as the temperature is decreased according to computer simulation studies. In addition, the molecular bonding strength is also enhanced by the available volume. Molecules have very low tendency of forming high molecular aggregates at larger volumes, whereas their tendency of forming high molecular aggregates is very smaller volumes. As a result, the distribution variance is expected to increase at small volumes and decrease at large volumes. Therefore, temperature dependence of the association is more important for dense or liquid-like phases and less extent of association is obtained when volume increases.

For a full representation of both vapor and liquid phases variance ($\eta$) may also be expressed in a function of temperature and volume as:

$$\eta = f \left( \frac{1}{T}, \frac{1}{V} \right)$$

This approach transforms the variance of a distribution function of the associating species in the microscopic system into thermodynamic state variables of the real bulk fluids in the macroscopic state. The bulk parameters, $(f)(h)$ and $(h)$, given in Eqs. (15) and (16) now depend on state variables (temperature and volume), and they can be related to $\eta$.

Different functional forms of $\eta$ have been tried in our search for the appropriate functional form of $\eta$. Among all the possible forms of $\eta$ that have been examined, we recommend the following dimensionless form:

$$\eta = \eta_c T_r^{C_1} V_r^{C_2}$$

where $\eta_c$ is $\eta$ at $T = T_c$ and $V = V_c$, $T_r$ is the reduced temperature, $V_r$ is the reduced molar volume, and $C_1$, $C_2$ are constants. For a term for high temperature and volume dependence on the low-temperature liquid phase, we propose

$$\kappa = 1 - \frac{(1 - \eta_c)}{T_r}$$

when constant $K_c$ becomes unity, it reduces to the case of exponential decay distribution function. Since it is our aim to describe the complete range of fluid behavior, the choice of a functional form is not entirely arbitrary.

**Derivation of Polydisperse Model**

The molecular (or microscopic) partition function is related to the thermodynamic (or macroscopic) functions in statistical mechanics. For the case of Helmholtz free energy ($A$), it is related to the canonical partition function ($Q$) by

$$A = -kT \ln Q \quad (20)$$

From Eqs. (1) and (20), the total thermodynamic functions of a substance is the sum of the molecular functions and the configurational functions; for example the Helmholtz free energy is given as

$$A = A_{mol} + A_{conf} \quad (21)$$

where the molecular Helmholtz free energy $A_{mol}$ is independent of volume.

As pointed out by Brown (1957), it is not possible to relate the thermodynamic functions of a conformal solution, whose intermolecular energies are given by Eq. (4), exactly to those of a reference solution in a similar fashion. Therefore we utilize a model molar configurational Helmholtz free energy determined from classical thermodynamics instead of relating the molar configurational Helmholtz free energy of a family of conformal substances to that of the reference substances through statistical thermodynamics.

The difference between the molar configurational Helmholtz free energy and its ideal gas value can be written as

$$\frac{A_{conf} - A_{conf}^o}{RT} = \int_V (Z - 1) \frac{dV}{V} \quad (22)$$

where superscript $o$ denotes the ideal gas state.

This is the expression for residual Helmholtz energy. Given the residual Helmholtz free energy, which is specified by the thermodynamic state variables $T$ and $V$, we can calculate other thermodynamic functions by simple mathematical manipulation or by differentiation. For a pressure-explicit form of EOS, we have

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\left[\left(\frac{\partial A_{conf}}{\partial V}\right)_{T,\eta} + \left(\frac{\partial A_{conf}}{\partial \eta}\right)_{T,V}\frac{\partial \eta}{\partial V}\right] \quad (23)$$

Using the principles of polydisperse thermodynamics, we can extend an existing model of non-associating fluids to the case of associating fluids.
**Theory of associating fluids**

**Application of Theory**

We now illustrate the utility of this statistical polydisperse theory on a generalization of a well-known mathematical model of the thermodynamic equation of state - vdW-EOS. The reason for the choice of the vdW-EOS is its simplicity and the fact that van der Waals mixing rules are quite accurate. vdW-EOS is written as

\[ Z = \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{VRT} \]  

(24)

Defining \( V_r = \frac{V}{V_c}, T_r = \frac{T}{T_c}, b_r = \frac{b}{V_c} \) and \( a_r = \frac{a}{RT_cV_c} \), \( Z \) of vdW-EOS will be in a reduced form of the following:

\[ Z = \frac{V_r}{T_r \cdot b_r} - \frac{a_r}{V_r} \]  

(25)

An EOS can be represented in general by the sum of two terms: repulsive and attractive. For the compressibility factor we can write

\[ Z = Z_{\text{repulsive}} + Z_{\text{attractive}} \]

Previous efforts to improve the performance of vdW family of EOS's empirically have been directed towards proposing the arbitrary temperature-dependency models of attractive term for cubic EOS's. In cubic EOS's the repulsive term of the van der Waals equation of state, \( V/(V-b) \), is retained in its original form, while their attractive terms are modified to different forms. For instance, the Peng-Robinson (PR) EOS is expressed as (Peng, and Robinson 1976).

\[ Z = \frac{V}{(V-b)} - \frac{a(T)}{[V(V+b) + (b/V)(V-b)]} \]  

(26)

In the present work we will limit our calculations and discussion to PR-EOS with the understanding that similar manipulations can be performed on other cubic EOS's.

Owing to the general behavior of cubic EOS's, an improvement in their representation of one particular property may adversely affect their representation of another property. For instance, the selection of the functional form of parameter \( (a) \) to fit pure component vapor pressures results in poor representation of other features of the EOS such as PVT surface, or enthalpy. This arises because of theoretical flaws in the van der Waals family of equations, primarily in the repulsive (Leland 1980), hard-sphere pressure term \( RT/(V-b) \).

Heidmann and Prausnitz (1976) proposed an EOS for associating fluids and applied it to the phase behavior of pure substances. Assuming that the attractive term of an EOS does not contribute to the chemical equilibrium of associating mixtures, their expression leads to the modification of repulsive term. Our present
work differs from these studies in a number of ways. In this work we modify both terms of the original vdW-EOS by following the principle of polydisperse thermodynamics. Rather than trying to develop completely new EOS, it was attempted to improve existing equations based on theoretical concepts and test the resulting EOS to other thermodynamic properties. It will be shown here that the temperature and volume dependence of parameters (a) and (b) must meet certain limitations if thermodynamic consistency is to be maintained.

To develop an accurate EOS, we start with the residual Helmholtz energy function. We have a residual Helmholtz free energy for the vdW-EOS from Eq. (22),

$$\frac{A_{\text{conf}} - A_{\text{conf}}^0}{RT} = \ln \frac{V_r}{V_r - b_r} - \frac{a_r}{T_r V_r}$$  \hspace{1cm} (27)

From Eqs. (15) and (16), we obtain parameters of the polydisperse mixture:

$$\alpha^{1/2} = \int F(I) a_r(I)^{1/2}\, dI$$ \hspace{1cm} (28)

$$\beta = \int F(I) b_r(I)\, dI$$ \hspace{1cm} (29)

We relate molecular conformal parameters $\alpha$ and $\beta$ to be a linear polynomials of the distribution index $I$ of polar fluids in the following forms:

$$a_r^{1/2} = A_o + A_1 I + \ldots$$ \hspace{1cm} (30)

$$b_r = B_o + B_1 I + \ldots$$ \hspace{1cm} (31)

The continuous distribution can be approximated with a discrete number of pseudocomponents for which mole fraction and molecular weight are determined. Applying the Gaussian quadrature method to the distribution functions, we have

$$\int e^{-x} f(x)\, dx = \sum_{i=1}^{N} w_i f(x_i)$$ \hspace{1cm} (32)

where $x_i$ are a number of quadrature points and $w_i$ are weighing factors. These are determined from a class of Laguerre polynomials which are tabulated for various numbers of quadrature points $N$.

Generally, the success of the various polydisperse (continuous) thermodynamics methods depends on (1) the composition which is characterized experimentally and (2) the suggested theory which can use this information. Unfortunately, the problem of associating fluids is not the case. Since all the necessary information for associating fluids are not available, we can not apply the Gaussian
quadrature method to associating fluids (Class 1 mixtures).

If a gamma distribution function is used, analytic results can be obtained by integration. The bulk parameters \( \alpha \) and \( \beta \) of the polydisperse mixture can be represented as the following forms:

\[
\alpha^{1/2} = A_0 + A_1 (I_0 + \eta) + \ldots . \tag{33}
\]

\[
\beta = B_0 + B_1 (I_0 + \eta) + \ldots \tag{34}
\]

In the case of \( \kappa = 1 \), the functional forms of \( \alpha \) and \( \beta \) are reduced to the case of exponential decay form.

\[
\alpha^{1/2} = A_0 + A_1 (I_0 + \eta) + \ldots \tag{35}
\]

\[
\beta = B_0 + B_1 (I_0 + \eta) + \ldots \tag{36}
\]

The bulk parameters \( \alpha \) and \( \beta \) of the associating fluids depend on state variables: temperature and volume, and they can be related to \( \eta \) through Eqs. (33) - (36).

Now we are ready to derive polydisperse generalized model of the vdW-EOS for associating fluids. The configurational properties of the ideal gas mixture are obtained from Eq. (2) for \( \Phi = 0 \), by using Stirling's approximation for \( \ln N_i! \):

\[
\ln Q_{\text{def}}^0 = N \ln V - \sum_i C_i (\ln x_i - 1) \tag{37}
\]

It follows that the molar configurational Helmholtz free energy of the ideal gas mixture is

\[
A_{\text{def}}^0 = RT \left( \ln \frac{N_A}{V} - 1 \right) + \sum_i x_i \ln x_i \tag{38}
\]

where \( R \) is the universal gas constant, \( V \) is molar volume, \( N_A \) is Avogadro's number, and \( x_i \) is mole fraction. Substituting Eq. (38) into Eq. (27), we obtain the molar configurational Helmholtz free energy of associating fluids.

Differentiating the resulting equation and considering \( \alpha \) and \( \beta \) to be functions of volume and temperature (they are constants for non-associating fluids), it can be shown that the polydisperse generalized model for pure associating fluids has the following form:

\[
Z = \frac{V_T}{V_r} \left( 1 - \frac{\partial \beta}{\partial V_T} \right) - \frac{1}{T_r} \left( \frac{\alpha}{V_r} - \frac{\partial \alpha}{\partial V_T} \right) \tag{39}
\]

where

\[
\left( \frac{\partial \beta}{\partial V_T} \right) = \kappa B_1 \left( \frac{\partial \eta}{\partial V_T} \right) \tag{40}
\]

\[
\left( \frac{\partial \alpha}{\partial V_T} \right) = 2 \kappa \alpha^{1/2} \left( \frac{\partial \eta}{\partial V_T} \right) \tag{41}
\]
All the thermodynamic functions derived from this polydisperse model have analytic expressions. To reduce the number of adjustable parameters, $A_1$ and $B_1$ for pure associating fluids at this stage may be determined by procedures similar to those of Du and Mansoori (1989). In describing the slope of associating fluids, the slopes of $a^{1/2}$ and $\beta$ from cyclic hydrocarbon compounds are used.

**Applications and Results**

*Optimization of Equation of State Parameters*

Three different experimental isothermal data for water (Haar et al. 1984), ammonia (Haar and Gallagher 1978), methanol (Goodwin 1987) and hydrogen sulfide (Goodwin 1983), respectively, to search for the unknown parameters in our proposed EOS.

The three different isotherms are chosen to have a reduced temperature range of around 0.70, 1.00, 1.20 and a reduced pressure range of up to around 2.50, 3.50 and 4.50, respectively, which cover both vapor and liquid phases equally. The following objective function is used to search for the optimal set of the parameters:

$$O. F. = \sum_{i=1}^{M} \left( \frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2$$

(42)

where $M$ is the number of experimental data considered, and $P_{\text{exp}}$ and $P_{\text{cal}}$ are the experimental and calculated pressures, respectively. Argon was chosen as a reference fluid since it is monoatomic, spherically symmetric and nonpolar. The use of argon as a reference substance has been useful as most systems have converged by using its parameters as a reference.

Tables 1 shows the estimated parameters for associating fluids using the above three isotherms. Once parameters have been obtained for different associating fluids, the parameters were used to evaluate thermodynamic properties such as saturated densities. It would be important to test the predictive capabilities of the model with other thermodynamic properties that are not included in the optimization of the parameters.

**TABLE 1**

PARAMETERS OF THE PROPOSED MODEL FROM EQ. (39)

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$A_0$</th>
<th>$B_0$</th>
<th>$\eta_c$</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$\kappa_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.6796</td>
<td>0.015E-2</td>
<td>13.1038</td>
<td>0.6676</td>
<td>0.4994</td>
<td>-0.4140</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.8446</td>
<td>0.106E-2</td>
<td>15.7261</td>
<td>0.6787</td>
<td>0.5178</td>
<td>-0.1807</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.8231</td>
<td>0.047E-2</td>
<td>13.2112</td>
<td>0.6668</td>
<td>0.5195</td>
<td>-0.5113</td>
</tr>
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</table>
Prediction of Saturated Density

It has been often stated that the predictions of the current vdW-like cubic EOS's are frequently poor for saturated liquid density, even for one-component fluids. It is well known that it is difficult to predict even the single-phase density of highly polar compounds without a large number of constants. We have performed phase equilibria calculations for this associating fluid model of pure fluids. For a specified temperature the saturated liquid density \( \rho_L \) and the corresponding vapor pressure \( P^S \), and the saturated vapor density \( \rho_V \) are calculated from a mathematical model of the thermodynamic EOS by solving the following two equations simultaneously:

\[
G^R = G^R_0
\]

\[
P^I = P^D
\]

where

\[
\frac{G^R}{RT} = \frac{A_{off} - A_{off}^0}{RT} + (Z-1) + \ln (\rho RT)
\]

\( G^R \) is residual Gibbs free energy relative to the ideal-gas state at unit pressure and superscript 0 is in an ideal-gas state. A closed-form approximation can be obtained in solving the liquid and vapor densities, \( \rho_L \) and \( \rho_V \), applying the above definition of \( G^R \).

The predicted saturated liquid densities for three different kinds of associating fluids using the optimized parameters obtained from the gamma distribution are given in Tables 2-4. These predicted results from our proposed
model are improved significantly compared to those calculated from original models, which are also listed in these Tables for comparison. The appreciable improved performance of the proposed EOS for associating fluids is obvious. Figures 1-3 illustrate the ability of the proposed equation to predict PVT behavior as well as densities of associating fluids. The reliability of the predictions is considered to be very satisfactory.

**Prediction of Critical Compressibility Factor**

The critical compressibility factor predicted by vdW-EOS and other cubic EOS's is constant for all components. This may be verified by comparing the compressibility factor \( Z \) of the vdW-EOS with experimental data for a variety of fluids. At the critical point,

\[
Z_{c,vdW} = \frac{P_c V_c}{RT_c} = 0.375
\]

while for the most fluids the critical compressibility \( Z_c \) is in the range 0.23 to 0.31. It

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<table>
<thead>
<tr>
<th>T (K)</th>
<th>( r_{\text{exp}} \cdot r_{\text{cal}} )</th>
<th>( r_{\text{exp}} \cdot r_{\text{cal, vdw}} )</th>
<th>( r_{\text{exp}} \cdot r_{\text{cal, PR}} )</th>
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<tr>
<td>330.0</td>
<td>0.7434</td>
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<td>52.13</td>
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<td>355.0</td>
<td>1.9316</td>
<td>0.02</td>
<td>52.53</td>
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<td>5.0689</td>
<td>0.01</td>
<td>53.26</td>
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<tr>
<td>405.0</td>
<td>8.8354</td>
<td>0.24</td>
<td>53.98</td>
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<td>430.0</td>
<td>16.3463</td>
<td>0.69</td>
<td>55.39</td>
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<tr>
<td>450.0</td>
<td>28.1354</td>
<td>1.23</td>
<td>59.05</td>
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<tr>
<td>475.0</td>
<td>41.6498</td>
<td>1.62</td>
<td>176.11</td>
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<tr>
<td>500.0</td>
<td>62.2850</td>
<td>3.35</td>
<td>134.02</td>
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---

**Figure 1.** P-V diagram for water at different isotherms and saturated region. The curves are calculated from the proposed model, Eq. (39). The points with different symbols are experimental data.

**Figure 2.** P-V diagram for ammonia at different isotherms and saturated region. The curves are calculated from the proposed model, Eq. (39). The points with different symbols are experimental data.
was believed that the proposed model should result in the improved performance for predicting $Z_c$. According to Table 5, the performance of the proposed model for predicting the critical compressibility is satisfactory. Compared with cubic EOS's our proposed EOS produces a substance dependent value for $Z_c$.

**Prediction of PVT behavior**

Using optimized parameters, attempts have been made to predict the PVT behavior for three different isotherms of corresponding fluids with reduced temperature of around 0.80, 0.90 and 1.35 and a reduced pressure up to around 2.50, 3.0 and 4.50, respectively. Results have been obtained using parameters from a gamma distribution function.

Figures 4-7 illustrate the ability of the proposed model to predict the compressibility of associating fluids. Compared to the original vdW-EOS and PR-EOS, the agreements between the predicted and experimental compressibilities are good. The values inside parenthesis indicate the absolute deviation error percentage.

<table>
<thead>
<tr>
<th></th>
<th>$Z_c$</th>
<th>vdW-$Z_c$</th>
<th>PR-$Z_c$</th>
<th>$Z_c$ from Eq. (39)</th>
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</thead>
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<tr>
<td>Water</td>
<td>0.235</td>
<td>0.375</td>
<td>0.307</td>
<td>0.308</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(59.8)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.244</td>
<td>0.375</td>
<td>0.307</td>
<td>0.262</td>
</tr>
<tr>
<td></td>
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<td>(53.7)</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.224</td>
<td>0.375</td>
<td>0.307</td>
<td>0.294</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(67.4)</td>
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<tr>
<td>Hydrogen</td>
<td>0.283</td>
<td>0.375</td>
<td>0.307</td>
<td>0.283</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(32.5)</td>
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<tr>
<td>Sulfide</td>
<td></td>
<td></td>
<td></td>
<td>(8.5)</td>
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Figure 4. Prediction of compressibility for water
for associating fluids are obvious. It can be seen that the interpolated pressure predictions among these isotherms over broad range of volume have similar high accuracy. In the case of methanol, the extrapolation of this proposed model to high temperatures does not give very good predictions in the vapor phase. The phenomena may be attributed to the high association in the vapor phase at high temperatures.

**Discussion of Association**

The value of variance increases in dense fluids from the thermodynamic points of view. The higher value of variance suggests wider distribution, which in turn indicates higher association in fluid behavior. As variance being a reflection of association phenomenon in associating fluids, the ratio of variance over variance at the critical point is plotted in Figure 8 for water.

Similar trends are observed for other associating fluids. Variance has a higher value...
in dense fluids and less association is obtained when volume increases. Figure 8 shows a distinctive trend of variance for vapor and liquid phases, whereas variance increases as temperature decreases for liquid phase, variance decreases as temperature decreases for vapor phase. Similar findings have been reported where the results are indicated that while the proportion of longer chains in the liquid increases as the temperature decreases, the behaviour is quite different in the vapor phase where the fraction of monomer molecules in the vapor increases with decreasing temperatures (Kataoka 1984, Frank and Reid 1973).

The ratio of variance at critical isotherm for four different fluids is shown in Figure 9. Figure 9 indicates that methanol has a highest variance which apparently suggests that methanol has the highest degree of association among three associating fluids. It may be concluded that the pattern of hydrogen bonding in methanol is very different from that found in water or ammonia. Since the ammonia molecule resembles that of water in being small and polar, we expect to obtain similar molecular associations for these two components. It can be seen that hydrogen sulfide has smaller association effect than that of ammonia.

Conclusions

A statistical theory for deriving an analytical theory for associating fluids is presented. The utilization of polydisperse thermodynamics has provided us with a strong tool for improving the predictive capabilities of the existing empirical engineering thermodynamic models. This theory provides a predictive method for the calculation of thermodynamic properties, which all have analytical expressions, of the associating fluids with high accuracy. This theory allows us to extend an existing model of non-associating fluids to the case of associating fluids.

Overall, this theory is general and may be applied as well to any EOS's. The techniques described are illustrated with reference to the vdW-EOS. The application of this theory has led to an improvement in predicting PVT behavior compared to existing models for
associating fluids. It has been shown to be successful for prediction of saturated properties, and most regions of the volumetric properties including both liquid and vapor phases. The present approach also provides detailed insights into the peculiar behavior of associating fluids.

REFERENCES


