

A New Theoretical Approach to the Hydrogen-Bonded Fluids Based on the Conformal Solution Concept

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In this work, a new generalized chemical theory of association is developed and is used to derive the distribution function of associated species formed due to hydrogen bonding in a pure associating fluid. The concepts of conformal solution theory are extended to consider the pure associating fluids, and the derived distribution function is used to obtain the conformal parameters. A general procedure is proposed for computing the parameters of any cubic equation of state based on the conformal solution theory developed in this work. As an example, the parameters of van der Waals equation of state are obtained. The PVT calculations for three associating fluids (water, ammonia, and methanol) substantiate the effectiveness of the proposed approach.

I. Introduction

Thermodynamic properties of pure associating fluids and their mixtures are significantly different from nonassociating solutions, due to strong attractive (chemical) interactions. The well-known molecular association is the hydrogen bonding. Considerable theoretical and experimental studies have been devoted to the hydrogen bonding that affects the physical and chemical properties of pure fluids and their mixtures.^{1–6} The hydrogen bonding causes the special properties of water on which the life is based. As water is the most common solvent in chemical, biochemical, and environmental processes, for predicting its properties, more information about hydrogen bonding is required.^{7–9}

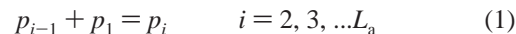
In a pure associating fluid, it is commonly accepted that hydrogen-bonding causes a distribution of associated species formed by self-association between molecules which have at least two bonding sites per molecule. It means that a pure associating fluid can be regarded as a mixture of associated species with different sizes or degrees of association.^{10,11} In dealing with pure associating fluids, the main problem has always been calculations of mole fractions of different species in the mixture, which could be obtained by a suitable chemical associating theory. Therefore, it is usual to use a combination of a well-established mixture theory for thermodynamics properties and a chemical theory for calculating mole fractions of species.^{10–14} In this work, an improved chemical theory is proposed and combined with the conformal solution theory to calculate the thermodynamic properties of pure associating fluids.

The conformal solution theory was first proposed by Longuet-Higgins,¹⁵ for the mixtures in which the intermolecular forces between molecules are similar. Since the energy and structural characteristics of associated species formed from self-association are similar, the mixture of associated species can be considered

as a conformal solution. According to conformal solution theory, it is assumed that the intermolecular pair potential functions are the same for all components, differing only in the magnitude of the potential function parameters. As a result, the excess (nonideal) thermodynamics properties of mixing can be related to these parametric differences.^{15–18} Therefore, a conformal solution is approximated as a perturbed reference system, which the latter can be a real or a hypothetical pure fluid where the intermolecular potential function has the same form as that of the mixture components.

II. Chemical Theory of Association

The widely accepted model for hydrogen bonding between molecules is the chain model.^{10,11} In this model, the molecules are bonded together through their active sites to form a chain. Therefore, the only molecules at the ends of every chain will have unoccupied active sites and will be capable of forming hydrogen bonding with the new molecules. Self-association between molecules may be considered through the following set of chemical reactions:^{10–14}



In this equation, p_i is defined as the i th associated species containing i molecules, and L_a is the limit of association in molecules. In the case that the nonidealities can be related to the physical as well as chemical interactions between associated species, the equilibrium constant K_i for eq 1 may be defined as follows:^{10–14}

$$K_i = \frac{x_i \gamma_i}{(x_{i-1} \gamma_{i-1})(x_1 \gamma_1)} \quad i = 2, 3, \dots \quad (2)$$

Where γ_i is the activity coefficient of the i th associated species. Equation 2 can be rearranged and applied to the all associated species, which will produce the following expression for the mole fraction of the i th associated species:

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$$x_i = \left[\prod_{j=2}^{i-1} (K_j) \right] \frac{(x_1 \gamma_1)^i}{\gamma_i} \quad i = 2, 3, \dots \quad (3)$$

where the constraint that all mole fractions must sum up to unity requires that

$$\sum_{i=1 < \text{bu} > L_a} \left\{ \left[\prod_{j=2}^{i-1} (K_j) \right] \frac{(x_1 \gamma_1)^i}{\gamma_i} \right\} = 1 \quad (4)$$

This equation in general case can be solved for x_1 , provided that the functionality's of $[(\gamma_1)^i/\gamma_i]$ and K_j with respect to the degree of association are known.

In principle, the ratio $[(\gamma_1)^i/\gamma_i]$ is a function of the temperature, pressure, and composition of the system. This ratio may be calculated using an expression of the excess Gibbs energy that expresses the activity coefficients of the components to composition of the solution as well as the state variables. But for a pure associating fluid, the composition of the true associated species is a function of temperature and pressure, only. Therefore, the ratio $[(\gamma_1)^i/\gamma_i]$ in eqs 3 and 4 is actually a function of the state variables and can be replaced by $\Gamma(T,P)$

$$\Gamma(T,P) = [(\gamma_1)^i/\gamma_i] \quad (5)$$

Also, in Table 1, a number of models are reported for $K_i(T)$ which relate the equilibrium constant of formation of the i th associated species to the degree of association. These relations in Table 1 are collected from the literature for various self-association models. Symbolically, all the models appearing in Table 1 can be shown by the following general equation:

$$K_i = K(i,T) \quad i = 2, 3, 4, \dots L_a \quad (6)$$

When eq 6 is joined with eqs 4 and 5, one can solve the former equation for x_1 . In general case, this equation is solved numerically. However, it can be solved analytically when it is assumed that all the equilibrium constants of the association reactions are the same, i.e., $K_j = K(T)$. If $K_j = K(T)$ is substituted in eq 4, it reduces to the following equation:

$$\sum_i [K(T)\Gamma(T,P)]^{i-1} (x_1)^i = 1 \quad (7)$$

The summation in eq 7 for $[K(T)\Gamma(T,P)](x_1) < 1$ converges to the following expression:^{9,10}

$$x_1 \{1 - [K(T)\Gamma(T,P)x_1]^{L_a}\} / \{1 - K(T)\Gamma(T,P)x_1\} = 1 \quad (8)$$

One special case of interest is when the limit of association L_a , approaches infinity, eq 8 simplifies as the following:

$$x_1 = 1/[1 + K(T)\Gamma(T,P)] \quad (9)$$

The above-mentioned assumption has been used widely in chemical theories of associating fluids⁷⁻¹³ because of its mathematical simplicity.

As an important feature of this model, we can obtain the distribution function of associated species. The true composition of an associated fluid may be described by a distribution function $\chi(i)$, where i is the degree of association. The distribution function $\chi(i)$ must satisfy the following normalization condition:¹⁰

$$\int_0^\infty \chi(i) di = 1 \quad (10)$$

TABLE 1: Various Models for the Relation between $K_i(T)$ and the Degree of Association¹⁰

model	range
$K_i(T) = K(T)$	$i = 2, 3, 4, \dots L_a$
$K_i(T) = K(T)^{i-1}$	$i = 2, 3, 4, \dots L_a$
$K_i(T) = K(T)[i/(i-1)]$	$i = 2, 3, 4, \dots L_a$
$K_i(T) = K(T)/i$	$i = 2, 3, 4, \dots L_a$
$K_i(T) = K(T)\alpha^{i-2}/(i-1)!$	$i = 2, 3, 4, \dots L_a$
$K_i(T) = K(T)[1 + \beta(T)(i-1)] / \{[1 + \beta(T)][1 + \beta(T)(i-2)]\}$	$i = 2, 3, 4, \dots L_a$

For an associating fluid which the associated species are formed through the set of reactions (eq 1), the following functionality can be proposed for the distribution function of associated species:¹⁰

$$\chi(i) = \chi_o [K(T)\Gamma(T,P)]^i x_1^{i+1} \quad (11)$$

Where χ_o is the normalizing factor and can be calculated by eq 10. From eqs 9-11, we will get the following expression for $\chi(i)$:

$$\chi(i) = -\ln[\kappa/(1+\kappa)][\kappa/(1+\kappa)]^i \quad (12)$$

where for simplicity, we define

$$\kappa = K(T)\Gamma(T,P) \quad (13)$$

In what follows, the application of presented chemical theory is used to calculate conformal parameters for a pure associating fluid, which is regarded as a mixture of associated species.

III. Conformal Parameters for the Mixture of Associated Species

The configuration integral of the conformal mixture Q_c is related to that of the reference system Q_o by the following expression^{19,20}

$$Q_c(T, V, x) = h_x^N Q_o(V/h_x, T/f_x) \quad (14)$$

where x represents the composition of the mixture, f_x is the energy conformal parameter, and h_x is the size conformal parameter. It should be noted that for the reference system, these parameters are close to unity.^{15,20} The f_x and h_x parameters can be respectively related to the pair energy and size conformal parameters f_{ij} and h_{ij} by the following generalized mixing rules:^{20,21}

$$f_x = \left[\sum_i \sum_j x_i x_j f_{ij}^m h_{ij}^n \right]^{q/(mq-np)} \left[\sum_i \sum_j x_i x_j f_{ij}^p h_{ij}^q \right]^{-n/(mq-np)} \quad (15)$$

$$h_x = \left[\sum_i \sum_j x_i x_j f_{ij}^m h_{ij}^n \right]^{-p/(mq-np)} \left[\sum_i \sum_j x_i x_j f_{ij}^p h_{ij}^q \right]^{m/(mq-np)} \quad (16)$$

where x_i is the mole fraction of component i and the summations are carried out over all components in the mixture. Also, in the above two equations, m , n , p , and q are constants, where, by choosing the proper values for them, one can obtain the different mixing rules. For example, Kwak and Mansoori²¹ derived the van der Waals mixing rules for f_x and h_x for a multicomponent mixture from eq 15 and 16 by inserting $m = 1$, $n = 1$, $p = 0$, and $q = 1$ as follows:

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \quad (17)$$

$$h_x = \sum_i \sum_j x_i x_j h_{ij} \quad (18)$$

In the case of a pure associating fluid, x_i is the mole fraction of the i th associated species calculated by a chemical theory, and the monomer species (the molecules which are not in association with the other molecules) is considered as the reference system.

IV. Equation of State

The equation of state for a mixture, which is a PVT relation with the composition of the system, can be presented as^{15,16,19–20}

$$P(T, V, x) = (f_x/h_x)P_o(T_o, V_o) \quad (19)$$

where P_o is the pressure of the reference system and, according to the conformal solution theory, T_o and V_o are defined as follows:²⁰

$$T_o = T/f_x \cdot V_o = V/h_x \quad (20)$$

The other configuration properties of the system can be obtained by starting from eq 19 using suitable thermodynamics relations, provided that the conformal parameters f_x and h_x are known. To compute these parameters by using eqs 17 and 18, we could relate the differing pair conformal parameters f_{ij} and h_{ij} to the similar pair parameters f_{ii} , f_{jj} , h_{ii} , and h_{jj} through the following familiar combining rules:

$$f_{ij} = (1 - k_{ij})(f_{ii}f_{jj})^{1/2} \quad (21)$$

$$h_{ij}^{1/3} = (h_{ii}^{1/3} + h_{jj}^{1/3})/2 \quad (22)$$

where k_{ij} is the differing interaction parameters and is considered as an adjustable parameter. Substituting eqs 21 and 22 in eqs 17 and 18 gives the mixture conformal parameters f_x and h_x as the following:

$$f_x h_x = (1/2) \sum_i \sum_j x_i x_j (1 - k_{ij})(f_{ii}f_{jj})^{1/2} (h_{ii}^{1/3} + h_{jj}^{1/3}) \quad (23)$$

$$h_x = (1/2) \sum_i \sum_j x_i x_j (h_{ii}^{1/3} + h_{jj}^{1/3}) \quad (24)$$

As it is seen from eqs 23 and 24, the conformal parameters f_x and h_x can be calculated, provided that the mole fractions of species i , x_i , and species j , x_j , are available. The mole fractions of associated species x_i and x_j can be obtained from the distribution function presented by eq 12.

Let us reconsider a pure associating fluid as a conformal solution composed of n_1 moles of monomers, n_2 moles of dimers, etc., where $n_1 + n_2 + \dots = n_t$. It is reasonable to assume that the strength of hydrogen bonding interaction is independent of the size of the chain and is only a function of the nature of active sites involved in hydrogen bonding. Therefore, the conformal energy parameter of the i th associated species f_{ii} will be equal to that of the reference (monomer) species f_{oo} , which means that

$$f_{ii} = f_{jj} = f_{ij} = f_{oo} \quad (25)$$

Also, it is evident that upon increasing the size of a chain, the size parameter should increase linearly with the degree of association. Therefore, the size energy parameter of the i th associated species h_{ii} , can be related to that of the reference (monomer) species h_{oo} as follows:

$$h_{ii}^{1/3} = ih_{oo}^{1/3} \quad (26)$$

The differing pair conformal size parameter h_{ij} can be obtained by combining eq 26 with eq 22 as the following:

$$h_{ij}^{1/3} = \frac{1}{2}(i + j)h_{oo} \quad (27)$$

Substituting f_{ij} , h_{ij} , and k_{ij} from eqs 25 and 27 in eqs 17 and 18 and considering that f_{oo} and h_{oo} are close to unity^{14,20} result in the following equations for the conformal parameters f_x and h_x of a pure associating fluid:

$$f_x h_x = (1/8) \sum_i \sum_j x_i x_j (i + j)^3 \quad (28)$$

$$h_x = (1/8) \sum_i \sum_j x_i x_j (i + j)^3 \quad (29)$$

One can conclude from above two equations that

$$f_x = 1 \quad (30)$$

In case when the limit of association L_a (see eq 1) approaches infinity, the summations in eq 29 can be replaced with the integral, and the mole fraction x_i can be replaced by the distribution functions $\chi(i)$ given by eq 12

$$h_x = (1/8) \int \int \chi(i)\chi(j)(i + j)^3 di dj \quad (31)$$

substituting $\chi(i)$ from eq 12 gives

$$h_x = (1/8) \{ \ln \tau \}^2 \int_0^\infty \int_0^\infty \tau^{i+j} (i + j)^3 di dj \quad (32)$$

where for simplicity we define

$$\tau \equiv \kappa/(1 + \kappa) \quad (33)$$

The above integral which is given by eq 32 can be solved analytically, and the resulting equation will be

$$h_x = -3/[\ln \tau]^3 \quad (34)$$

where, in accordance with eq 34, the conformal parameter h_x is a function of temperature and pressure only.

In what follows, the PVT calculations are performed for three pure associating fluids species by combining the associating conformal solution theory presented in this work with a nonassociative equation of state.

V. PVT Calculations (based on the van der Waals equation of state)

Let us consider a pure associating fluid as a mixture of associated species. According to eq 19, we need an equation of state for the reference system in order to calculate thermodynamic properties of the real system. In this work, the reference system is considered as the monomer species, i.e., a nonassociating system. The most widely used equations of state are the cubic equations of state, which are based on the well-known van der Waals equation of state²⁵

$$P = RT/(v - b) - a/v^2 \quad (35)$$

where a and b are the van der Waals parameters and can be calculated in terms of the critical temperature T_c and critical pressure P_c , as the following:

$$a = 0.421875R^2T_c^2/P_c \quad (36)$$

$$b = 0.125RT_c/P_c \quad (37)$$

It should be noted that T_c and P_c in the above equations could be obtained experimentally for pure fluids.

The same procedure for PVT calculations based on the van der Waals equation of state can be applied to other cubic or non cubic equation of state. To proceed with calculations, we first apply the van der Waals equation of state to the reference system, which is assumed to consist of monomer species here, and the pressure of the reference system is evaluated. Then by using eq 19, the pressure for the real system, which is a pure associating fluid consisting of a mixture of associated species, is calculated.

Since the reference system is one mole of hypothetical monomer species, the critical constants for such a system cannot be obtained experimentally, but according to eq 20 of the conformal solution theory, the critical constants for the reference system are

$$T_{co} = T_c/f_{xc}; V_{co} = V_c/h_{xc}; P_{co} = P_c(h_{xc}/f_{xc}) \quad (38)$$

where T_c , V_c , and P_c are critical constants of the real system. In eq 38, f_{xc} and h_{xc} are conformal parameters of the mixture of associated species calculated at the critical temperature of the real system.

On substituting the critical constants of monomer species expressed by eq 38 in eqs 36 and 37 and after rearrangement, the van der Waals EOS parameters a_o and b_o for the reference system will be as follows:

$$a_o = a/(f_{xc}h_{xc}) \quad (39)$$

$$b_o = b/h_{xc} \quad (40)$$

where a and b are given by eqs 36 and 37. It should be noted that T_c and P_c in these equations are the critical constants of the real system.

Now, the reference system pressure P_o at a given temperature T_o can be calculated by eq 35 using the van der Waals parameters given by eqs 39 and 40. Then the pressure of the real system P can be calculated by eq 19.

In the above-mentioned calculations, to calculate conformal parameter h_x through eq 34, we need to have κ . Therefore, according to eq 13, the equilibrium constant $K(T)$ for the association reaction and the ratio of activity coefficient $\Gamma(T,P)$ should also be available. $K(T)$ can be expressed in terms of the enthalpy and entropy of association, ΔH and ΔS , respectively, as follows:

$$K(T) = \exp(-\Delta H/RT + \Delta S/R) \quad (41)$$

where T is the absolute temperature. According to eq 41, $K(T)$ can be calculated, provided that the enthalpy and entropy of association are available.

In this work, the van der Waals EOS is modified for molecular associations in a way that its cubic nature and its number parameters can be conserved. Therefore, it assumed that the equilibrium constant (K) is independent of the degree of association. This simplifying assumption implies that K is the same for the dimer and trimer and other association reactions and then requires a linear association of species rather than formation of a network. However, in the case of water, there is some theoretical and experimental evidence that water molecules have four hydrogen bonding sites per molecule and, thus, it

TABLE 2: Physical Properties of Associating Fluids Which Are Considered in the Work

	$P_c(\text{atm})$	$T_c(K)$
water	217.7	647.1
ammonia	111.3	405.6
methanol	79.9	512.6

forms a network. Network association can create complications in evaluating the equilibrium constants for the cyclic reactions involved. Although, according to eq 41, each equilibrium constant produces two sets of enthalpy and entropy of associations, this in turn provides more adjustable parameters to obtain better agreement with the experimental data. The linear association model is preferred here, since it provides a simple model with the minimum number of adjustable parameters.

To use eq 41, it is convenient to express the temperature functionality of activity coefficients as the exponential forms.²⁵ Therefore, the following functionality can be proposed for $\Gamma(T,P)$, which was previously introduced by eq 5:

$$\Gamma(T,P) = \exp(-\alpha/RT) \quad (42)$$

where α is considered as the interaction energy parameter between two associated species. The proposed functionality for $\Gamma(T,P)$ satisfies the ideal solution limit—that is, as (α) goes to zero or T goes to infinity, $\Gamma(T,P)$ goes to unity. On combining eqs 24, 41 and 42, we get

$$\kappa = \exp(-\Delta H'/RT + \Delta S/R) \quad (43)$$

where, for simplicity, $\Delta H' = \Delta H + \alpha$. Experimental or semiexperimental data are available in the literature for enthalpy and entropy of association.^{26,27} But for different experimental methods such as NMR, UV, IR, etc., different values for enthalpy and entropy of association for a given association fluid have been reported. Therefore, one is left with the ambiguity of choosing the right values for these quantities. This is the reason that in the PVT calculations it is preferred to consider these quantities as adjustable parameters.

It is well accepted that the PVT calculations is a sever test in judging the capability of a solution theory. In the next section, the PVT results will be presented for three associating fluids, obtained on the application of the theory developed in this work.

VI. Results and Discussion

The PVT calculations were done for three associating fluids, water, ammonia, and methanol. The physical properties of these fluids are given in Table 2. Experimental data for water,²⁸ ammonia,²⁹ and methanol³⁰ are obtained from literature. The criterion of phase equilibrium in our PVT calculations was the equality of fugacity coefficients ($\phi^v = \phi^l$). At a given temperature, the saturation pressure (P) and the liquid (v^l) and vapor (v^v) molar volumes were calculated for both the original and modified van der Waals equations. The results indicated that better agreement with the experimental data was obtained for the calculated P , v^v , and v^l using the modified van der Wall EOS for the whole range of temperature variations up to the critical point. However, to optimize the best values for ΔH^o and ΔS^o , we used an objective function in the following form:

$$\text{error} = \alpha \Sigma (P_{\text{exp}} - P_{\text{calc}})^2 + \beta \Sigma (v_{\text{exp}}^l - v_{\text{calc}}^l)^2 + \gamma \Sigma (v_{\text{exp}}^v - v_{\text{calc}}^v)^2 \quad (44)$$

where the constants α , β , and γ were used to weight each deviation in the calculated results with respect to the others, as

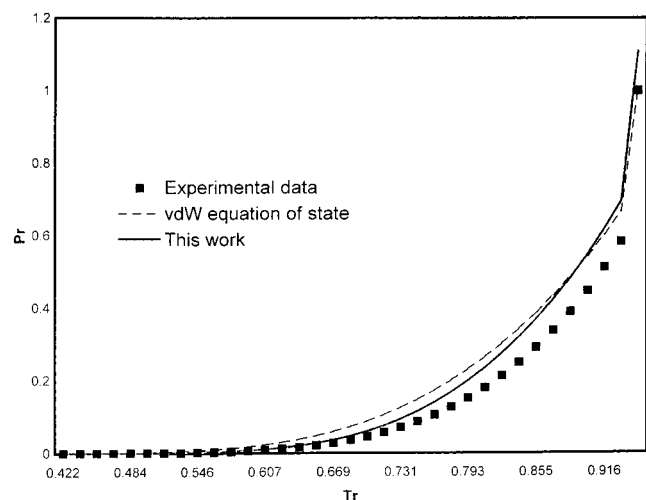


Figure 1. Reduced vapor pressure (P_r) of water vs reduced temperature (T_r).

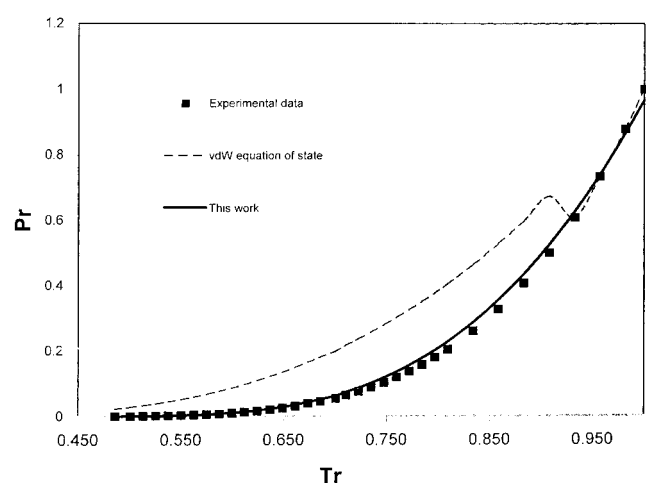


Figure 2. Reduced vapor pressure (P_r) of ammonia vs reduced temperature (T_r).

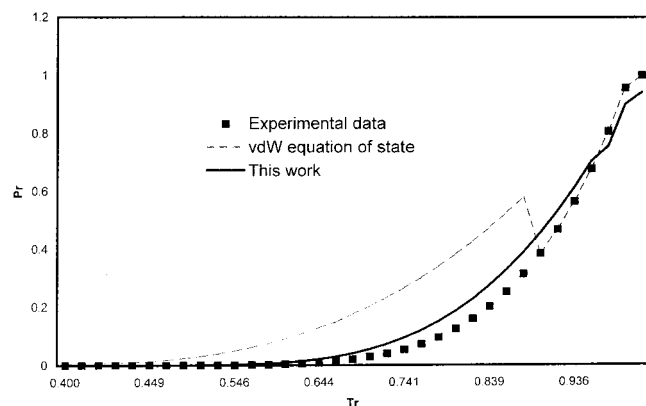


Figure 3. Reduced vapor pressure (P_r) of methanol vs reduced temperature (T_r).

shown in the above equation. In our PVT calculations, by selecting greater value of α , we gave more weight to the accurate calculation of saturation pressure.

The variation of reduced saturation pressure (P_r), with respect to reduced temperature (T_r), up to critical points of water, ammonia, and methanol are shown in Figures 1–3, respectively. Also, in the same figures, experimental data and P_r calculated from the original van der Waals EOS, are given. It is seen that the calculated P_r values obtained from the presented conformal

TABLE 3: Enthalpy and Entropy of Associating Fluids for Three Pure Associating Fluids

	$-\Delta S/R$	$-\Delta H'/R(1/K)$
water	2.75	320
ammonia	2.7	210
methanol	2.75	265

associating solution theory developed in this work are in close agreement with the experimental data compared with the original van der Waals theory.

The values of $\Delta H'$ and ΔS for each fluid calculated by minimization of the relative errors between experimental and calculated pressures are given in Table 3.

As it is shown in Figures 1–3, at low pressures, the predicted results of the original van der Waals equation of state represent small errors in comparison with those of higher pressures expected from the van der Waals equation of state. Also, it is seen that for $P_r > 0.9$, the predicted results by the van der Waals equation of state are in close agreement with the experimental data. The reason for this behavior can be attributed to inability of the van der Waals equation of state in predicting the critical condition.²⁵ This inability causes the molar volumes of liquid and vapor phases to be indistinguishable near the critical point. Therefore, liquid and vapor fugacities will be equal for any given pressure near the critical point, as seen in Figures 1–3. Although near the critical point the experimental and calculated results will eventually coincide, due to the shortcomings of van der Waals EOS in calculating separate values for liquid and vapor volumes, nonsmoothness may appear in the calculated curves, as seen in Figures 2 and 3 near critical regions. However, such a behavior is less prominent in the results of calculations based on a modified van der Waals EOS with the parameters obtained by the approach presented in this work.

VII. Conclusion

In this work, it was described that by using an improved chemical theory and the conformal solution theory, an equation of state, which was essentially a nonassociating equation of state, could be modified to be used for associating fluids. The results demonstrated a good correlation with the experimental data both at low pressures and at high pressures. Also, it was shown that the molar volumes of liquid and vapor phases at pressures near the critical point could be distinguished by the modified van der Waals equation of state. These substantiate the ability of the conformal associating solution theory in developing the van der Waals based cubic equation of state and, therefore, to eliminate their shortcomings in this respect. It should be noted that this method could be applied to the noncubic equation of state as well. However, it is worth noting that the application of this approach to the cubic equation of state doesn't change their cubic nature.

The proposed approach in this work can be extended to the mixtures of associating fluids. The approach can be outlined as follows. The excess properties of a mixture can be calculated from conformal energy and size parameters. Then, to obtain these parameters for a mixture by the appropriate mixing rules proposed in the conformal solution theory, one should evaluate the compositions of associating species. The general theory of association improved by the authors¹⁰ for a mixture containing any number of associating and nonassociating components can be used to calculate the required compositions.

VIII. Nomenclature

a energy parameter in equation of state

b	volume parameter in equation of state
f	conformational parameter of energy
h	conformational parameter of volume
i	number of the same monomers in an associated species, degree of association
K	equilibrium constant of self-association between molecules of component p , which is independent of the degree of association
K_i	equilibrium constant of the formation of the associated species π (can be dependent on the degree of association)
L_a	limit of association in component p
N	number of molecules
P	pressure
Q_c	configuration integral
R	gas constant
T	absolute temperature
V	molar volume
Subscript	
exp	experimental section
o	reference system
l	liquid phase
v	vapor phase
Greek Letters	
ϕ	fugacity
α, β, γ	parameters in eq 44
$\chi(D)$	distribution function
χ_o	normalizing factor
Z	compressibility factor
γ	activity coefficient

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