A Modified van der Waals Mixture Theory
for Associating Fluids:
Application to Ternary Aqueous Mixtures

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ABSTRACT: *In this study a simple and general chemical association theory is introduced. The concept of infinite equilibrium model is re-examined and true mole fractions of associated species are calculated. The theory is applied to derive the distribution function of associated species. As a severe test the application of presented theory to the van der Waals mixture model is introduced in order to perform Vapor-Liquid Equilibrium (VLE) calculations of aqueous ternary mixtures. The calculations are shown to be consistently improving the prediction over the non-associating case. Also, well known empirical models of NRTL and UNIQUAC are applied on the studied systems and their results are compared with proposed model.*

KEY WORDS: *Association, van der Waals, van Laar, NRTL, UNIQUAC, VLE.*

INTRODUCTION

Thermodynamic properties of pure associating fluids and their mixtures are significantly different from non-associated solutions, due to strong attractive (chemical) interactions. The well known molecular association is hydrogen bonding. Considerable theoretical and experimental studies have been devoted to association because it affects the physical and chemical properties of pure fluids and their mixtures [1-3]. Hydrogen bonding causes the special properties of water on which the life is based on. As water is the most common solvent in chemical,

biochemical, and environmental processes, for predicting its properties, more information about hydrogen bonding is required [4,5]. In the 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 an associating fluid can be regarded as a mixture of associated species with different sizes or degree of association [6-9]. In dealing with associating fluids, the main problem has been calculation 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 [7,8,10,11]. Several models have been proposed to describe the thermodynamic properties of associating solutions [7]. Probably the oldest of such models is the chemical theory of *Dolzalek* in 1908 [7]. According to this theory a pure associated fluid is considered as an ideal solution of the monomer and higher associated species. In other words, all the non-ideality of the system is described by the chemical effects due to hydrogen bonding. Dolzalek's theory was successful in describing solution properties for many real systems. New versions of the chemical theory are also used to model the associated systems in which physical forces are appreciable [5,7,8,12]. *Breitholz et al.*, examined the nonrandom lattice equation of state (NLF-HB EOS) with hydrogen bonding to correlate Liquid-Liquid Equilibrium (LLE) of binary alcohol and hydrocarbon system. They compared the accuracy of this model with those of PR equation of state. The results showed that both equations of state had similar degree of accuracies while NLF-HB EOS had fewer adjustable parameters [13]. *Perfetti et al.* proposed an Equation Of State (EOS) based on statistical association fluid theory and mean spherical approximation to model liquid-vapor-equilibrium of pure water and hydrogen sulfide. They took into account the association by hydrogen bonding and dipolar interactions. Their results showed good agreement with experimental data [14]. *Nickmand & Aghamiri* modified van Laar theory and derived a general model for binary associating fluids. In this modifications they added two new steps to van Laar cycle. They simplified their model for two interesting cases: (i) just one fluid is associating, (ii) two fluids are associating but only self-associated species exist in the mixture. They used the new model for VLE calculation of 16 binary associating systems. Their results showed that the new model was much better than van Laar model for VLE prediction [15]. Also a new association term for SAFT equation of state was presented by *Nickmand & Aghamiri* in 2010. The new equation of state was named CSAFT. They investigated performance of CSAFT by PVT calculations of pure associating fluids and LLE calculations of binary and ternary associating mixtures. Their results showed that the accuracy of CSAFT model to correlate vapor pressure and liquid density data of pure associating fluids and for LLE prediction of associating mixtures is higher than original SAFT equation of state [16].

The chemical theory of association

The main assumption in present theory is that only linear association species are present in an associating fluid. Association in a pure fluid may be described by the following set of reactions, according to chemical theory, for molecules with at least two bonding sites:

$$p_1 + p_{i-1} \quad \Leftarrow K_{pi} \Rightarrow \quad pi \qquad i=2, 3, \dots L_{ap} \qquad (1)$$
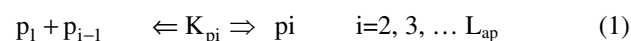
In the above equations P_i is the i-th associated species (containing i monomers) and $K_{pi}(T)$ is the equilibrium constant for association of (i-1) molecules of p with one molecule (monomer) of p. It should be pointed out that K_{p1} defined as unity $\left(K_{p1} \equiv 1\right)$. According to the set of reactions (1), a pure associating compound actually consists of a mixture of various species with different associated compounds. Considering the above set of reaction for systems when non-idealities are due to the physical as well as chemical interactions, K_{pi} may be written in terms of the chemical activities of the species [7-9,17,18].

$$K_{pi}(T) = \frac{x_{pi}^T}{x_{pi-1}^T x_{p1}^T} \frac{\gamma_{pi}}{\gamma_{pi-1}\gamma_{p1}} \qquad i= 2, 3, 4, \dots, L_{ap} \qquad (2)$$

Where x_{pi}^T and γ_{pi} are true mole fraction and activity coefficient of *i-th* associated species, respectively. This definition is general enough to be applied to all possible classes of associations. By rearranging Eq. (2), one can obtain the following expression for the *true* mole fraction of *i*-th associated species:

$$x_{pi}^T = K_{pi}(T) x_{pi-1}^T \gamma_{pi-1} x_{p1}^T \gamma_{p1} / \gamma_{pi} \qquad (3)$$
$$i= 2, 3, 4, \dots, L_{ap}$$

When the above equation is applied to the all associated species, the following equation results:

$$x_{pi}^T = \left[\prod_{j=1}^{i} K_{pj}(T)\right]\left(x_{p1}^T \gamma_{p1}\right)^i / \gamma_{pi} \qquad (4)$$
$$i= 2, 3, 4, \dots, L_{ap}$$

In principle, the ratio $\left(\gamma_{p1}\right)^i \Big/ \gamma_{pi}$ is a function of temperature, pressure and composition in the system. This ratio may be calculated using an expression of the excess Gibbs function. But for a pure associating fluid, the composition of associated species is a function of temperature and pressure, only. Therefore, the ratio $\left(\gamma_{p1}\right)^i \Big/ \gamma_{pi}$ in Eq. (4) can be defined by $\Gamma_p\left(T,P\right)^{i-1}$ in the following form:

$$\Gamma_p\left(T,P\right)^{i-1} \equiv \left(\gamma_{p1}\right)^i \Big/ \gamma_{pi} \tag{5}$$

In Eq. (4) the true mole fraction of all associated species are expressed with respect to the true mole fraction of monomer species x_{p1}^T. Therefore by substituting Eq. (5) in Eq. (4) and considering the normalizing condition, $\sum_{i=1}^{Lap} x_{pi}^T = 1$, we get:

$$x_{p1}^T = \left[\sum_{i=1}^{Lap} \left\{ \left[\prod_{j=1}^{i} K_{pj}\left(T\right) \right] \left[x_{p1}^T \Gamma_p\left(T,P\right) \right]^{i-1} \right\} \right]^{-1} \tag{6}$$

Eq. (6) can be solved for x_{p1}^T provided the functionalities of $K_{pj}(T)$ for $j \geq 2$ with (j) are known $\left(K_{p1} \equiv 1\right)$. It needs to be pointed out that $K_{pj}(T)$ is a function of temperature and the number of the same monomers in an associated species (j):

$$K_{pj}(T) = K_p(j,T) \qquad j = 2, 3, 4, \ldots, L_{ap} \tag{7}$$

When Eq. (7) is joined with Eq. (6) one can solve the latter equation for x_{p1}^T. One special case of interest is when the limit of association approaches infinity, which, in this case Eq. (6) can be written as the following:

$$x_{p1}^T = \left[\sum_{i=1}^{\infty} \left\{ \left[\prod_{j=1}^{i} K_{pj}\left(T\right) \right] \left[x_{p1}^T \Gamma_p\left(T,P\right) \right]^{i-1} \right\} \right]^{-1} \tag{8}$$

There is no simple general analytic solution for this equation. However, it can be solved analytically, when is assumed that all equilibrium constants of association reactions are the same, $K_{pj} = K_p(T)$ for $j \geq 2$. Therefore Eq. (8) reduces to the following equation:

$$x_{p1}^T = \left[\sum_{i=1}^{\infty} \left[K_p\left(T\right) \Gamma_p\left(T,P\right) x_{p1}^T \right]^{i-1} \right]^{-1} \tag{9}$$

The summation in Eq. (9), for $\left[K_p\left(T\right)\Gamma_p\left(T,P\right)x_{p1}^T \right] < 1$, converges to the following simple expressions:

$$x_{p1}^T = \left[1 + K_p\left(T\right)\Gamma_p\left(T,P\right) \right]^{-1} \tag{10}$$

The assumption of infinite equilibrium model has been used widely in chemical theories of associating fluids [7,8,18] because of its mathematical simplicity.

In the following section, the van der Waals theory of mixture (van Laar equations) which is essentially a non-associating theory will be applied to associating fluids.

The van der Waals theory of mixture (van Laar equations)

According to the van der Waals model, the configurational Helmholtz free energy of a non-associating mixture, A_{conf}, is [19]:

$$A_{conf}/RT = \ln\left(N_A \Big/ V\right) - 1 + \sum_p x_p \ln x_p^A + \tag{11}$$
$$\ln\left[V/(V - b_m) \right] - a_m/VRT$$

Where N_A is the Avogadro's number, x_p is the mole fraction of component p, and R is the universal gas constant. The well known van der Waals mixture parameters "a_m" and "b_m" are defined as the following:

$$a_m = \sum_p \sum_q x_p x_q a_{pq}(1 - \lambda_{pq}) = \tag{12}$$
$$\sum_p \sum_q x_p x_q \left(a_{pp}.a_{qq}\right)^{1/2}\left(1 - \lambda_{pq}\right)$$

$$b_m = \sum_p \sum_q x_p x_q b_{pq} = \tag{13}$$
$$\sum_p \sum_q x_p x_q \left(b_{pp} + b_{qq}\right)\Big/2$$

Where summations in the above equations are extended over all components in the mixture, and λ_{pq} isthe coupling parameter. The pure component parameters a_{pp} and b_{pp} can be calculated from pure fluid critical properties of component p,

$$a_{pp} = 27R^2 T_{cp}^2 \Big/ \left(64 P_{cp}\right) \tag{14}$$

$$b_{pp} = RT_{cp} \big/ \left(8P_{cp}\right) \tag{15}$$

Where T_{ci} and P_{ci} are the critical temperature and pressure of pure component i, respectively. According to van Laar, van der Waals mixture model yields the following expression for the molar excess Gibbs function of a multi component mixture, G^E, over the ideal solution at constant pressure and temperature.

$$G^E = G - \sum_p x_p G_p - RT \sum x_p \ln x_p = \tag{16}$$

$$\sum \left(x_p a_{pp} / b_{pp}\right) - a_m / b_m$$

Where G is the molar Gibbs free energy of the mixture and G_p is the molar Gibbs function of component p in pure state at the same pressure and temperature as the mixture system. This equation, known as the van Laar equation, can be used to derive activity coefficient, γ_p, of component p in a mixture by the following relation [20]:

$$\ln \gamma_p = G^E - \sum_{k \neq p} x_k \left(\frac{\partial G^E}{\partial x_k^A}\right)_{T,P,x_{q \neq p,k}^A} \tag{17}$$

$$p = 1,2,\ldots, c$$

In the case when one or more components of the mixture are associating, in accordance with the present association theory, every component also will constitute a mixture of associated species (monomer, dimer, . . etc.). According to the van der Waals mixing rules, Eqs. (12) and (13), assuming $\lambda_{pij} = 0$, parameters "a_{pp}" and "b_{pp}" of associating component p can be expressed by the following relations, respectively:

$$a_{pp} = \sum_i \sum_j x_{pi}^T x_{pj}^T a_{pij} = \tag{18}$$

$$\sum_i \sum_j x_{pi}^T x_{pj}^T \left(a_{pii} a_{pjj}\right)^{1/2} = \left(\sum_i x_{pi}^T a_{pi}^{1/2}\right)^2$$

$$b_{qq} = \sum_i \sum_j x_{pi}^T x_{pj}^T b_{pij} = \tag{19}$$

$$\sum_i \sum_j x_{pi}^T x_{pj}^T \left(b_{pii} + b_{pjj}\right)\big/2 = \sum_i x_{pi}^T b_{pi}$$

Where x_{pi}^T is the true mole fraction of associated-species p_i, also a_{pi} and b_{pi} are the parameters of the i-th associated species formed from i monomers of molecule p. Now, by considering the case when the limit of association, L_{ap}, approaches infinity, the true composition of an associated fluid may be described by a distribution

function $\chi_p \left(I\right)$ where I is the continuous version of discrete variable (i). This distribution function must satisfy the following normalization conditions:

$$\int_0^\infty \chi_p \left(I\right) \, dI = 1 \tag{20}$$

For a mixture in which equilibrium constants of association are independent of composition, the following distribution function can be proposed:

$$\chi_p \left(I\right) = \chi_{op} \, \mathbf{X}_{pi}^T \tag{21}$$

Where $\mathbf{X}_{pi}^T$ is the true mole fraction of the *i*-th associated species, and χ_{op} is the normalization factor which can be computed by substituting Eqs. (4) and (21) in Eq. (20), and considering the case that ($K_{pj}=K_p$, j=1, 2, …, Lap) and (Lap $\longrightarrow \infty$):

$$\chi_{op} = -\ln \left(K_p \Gamma_p X_I^T\right)^i \tag{22}$$

Where $\mathbf{X}_{pl}^T$ is given by Eq. (10). Now, summations Eqs. (18) and (19) can be replaced with the following integral forms:

$$a_{pp} = \left(\int_0^\infty \chi_p \left(I\right) \left[a_p \left(I\right)\right]^{1/2} dI\right)^2 \tag{23}$$

$$b_{pp} = \int_0^\infty \chi_p \left(I\right) b_p \left(I\right) dI \tag{24}$$

In order to solve integrals appearing in Eqs. (23) and (24) we need to have in hand analytic expressions for $a\left(I\right)$ and $b\left(I\right)$ of with respect to I. *Touba & Mansoori* (1996) and *Aghamiri et al.* (1998) proposed the following expressions for a(I) and b(I) of an associating component [7,18]:

$$a_p \left(I\right)^{1/2} = a_{po}^{1/2} + a_{p1}^{1/2} I \tag{25}$$

$$b_p \left(I\right)^{1/3} = b_{p1}^{1/3} I \tag{26}$$

Where a_{po}, a_{p1} and b_{p1} are constants. By inserting Eqs. (21), (25), and (26) in Eqs. (23) and (24) it can be shown that the expressions for parameters a_{pp} and b_{pp} reduce to the following:

$$a_{pp} = 27R^2 T_{cp}^2 \big/ \left(64P_{cp}\right) = a_{cp} \tag{27}$$

$$b_{pp} = \xi_p^3 RT_{cp} \big/ \left(8P_{cp}\right) = \xi_p^3 . b_{cp} \qquad (28)$$

Where

$$\xi_p \equiv \frac{\ln(K_p \Gamma_p x_{p_1}^T)_{Tc}}{\ln(K_p \Gamma_p x_{p_1}^T)} \qquad (29)$$

Also in Eq. (29) the subscript T_c refers to critical temperature and it means that this expression should be calculated at critical temperature. Equations (27) and (28) represent the van der Waals parameters a_{pp} and b_{pp} of an associating component. By substituting x_{p1}^T from Eq. (10) in Eq. (29), we will get:

$$\xi_p = \frac{\ln(\frac{\kappa}{1+\kappa})_{Tc}}{\ln(\frac{\kappa}{1+\kappa})} \qquad (30)$$

In the following section the van der Waals theory of mixture of associating fluids is applied to calculate and predict the phase behavior of various ternary associating mixtures.

RESULTS AND DISCUSSIONS

In this section we utilize the association theory presented above for property calculation of ternary aqueous mixtures. The most important associating fluid is water. Aqueous mixtures of organic components belong to the most complicated mixtures. Therefore we applied the presented associated theory in this work to ternary aqueous mixtures of organic components. Calculations were done for 7 different ternary systems. Components of each system have been introduced by Table 1. For these ternary mixtures the Vapor-Liquid Equilibrium (VLE) data and pure vapor pressure data are taken from reference [22]. The VLE data are P-x-y data at constant T and low pressure. Therefore vapor phase can be regarded as ideal gas. In this case pressure and vapor phase mole fractions are obtained by the following equations, respectively:

$$P = \Sigma \, x_p \, \gamma_p \, P_p^{sat} \qquad (31)$$

$$y_p = (\, x_p \, \gamma_p \, P_p^{sat})/P \qquad (32)$$

Where y_p, P, x_p, γ_p, and, P_p^{sat} are vapor mole fraction, pressure, liquid mole fraction, activity coefficient in liquid phase, and saturation vapor pressure at the system temperature, respectively. The customary bubble-P calculations are employed to investigate presented theory.

In this calculations activity coefficients are obtained through equations (A-5 to A-7). Results of the VLE calculations have been reported in Table 1 for 7 ternary systems. This table includes the average square absolute deviation in predicting the total pressure (ΔP), and average square absolute error in predicting the mole fraction of components in the vapor phase defined as:

$$\Delta P = \frac{1}{n_d} \sum_{i=1}^{n_d} \Big[(P_{exp} - P_{cal})^2 \Big]_i \qquad (33\text{-}a)$$

$$\Delta y = \frac{1}{2n_d} \sum_{i=1}^{n_d} \Big[(y_{1cal} - y_{1exp})^2 + (y_{2cal} - y_{2exp})^2 \Big]_i \qquad (33\text{-}b)$$

Also reported in Table 1 are the results of the calculations if the original non-associating van der Waals property calculation model (the van Laar equation) was used. Similarly, Table 1 compares results of this work with NRTL and UNIQUAC (as two important correlative activity coefficients models) for studied systems. Parameters of these models (NRTL and UNIQUAC) have been obtained by minimizing of equations (33-a, b). Regarding NRTL has 7 and UNIQUAC has 6 parameters; presented model has only two adjustable parameters. Also in this work, temperature dependency of parameters has been given. It should be pointed that parameters of NRTL and UNIQUAC have been obtained by correlating the models to experimental data.

According to this table, with the application of the proposed association theory predictions of the mixture VLE are appreciably improved over the non-associating model. It should be pointed out that in applying the presented theory for ternary aqueous mixtures we have to specify ξ_p, the association parameter of association component (water) as defined by Eq. (30). Provided experimental data for association equilibrium constant K and Γ are available, Eq. (30) can be used to calculate ξ_p. However, due to the lack of such data this parameter is obtained by correlating the experimental VLE data. Therefore numerical values of ξ_p for water have been calculated from various ternary mixture data and reported in Table 1. According to Eq. (30) parameter ξ_p depends on temperature, because K is the equilibrium constant of association, and can be defined as follows:

$$K = \exp\left(\frac{-\Delta G_o}{RT}\right) = \exp\left(\frac{-\Delta H_o + T\Delta S_o}{RT}\right) \qquad (34)$$

Table 1: Association parameter (ξ_p) of water and (ΔP, and Δy^*) of various ternary systems.

Components			T (°C)	ξ_p	Δy^*				ΔP				Ref.
1	2	3			This work	van Laar	NRTL	UNIQUAC	This work	van Laar	NRTL	UNIQUAC	
1-butanol	2-Methyl-1-propanol	Water	35	1.217	2.6E-3	2.3E-2	8.4E-3	1.2E-2	1.5E-1	1.0E10	1.39	1.77	[22]
2-propanol	Acetone	Water	75	1.066	2.8E-3	1.5E-2	3.0E-3	4.2E-3	3.2E-1	5.0E5	17.99	11.19	[22]
Acetone	Methanol	Water	100	1.072	3.1E-3	1.1E-3	2.1E-2	1.9E-2	4E0	8.2E2	64.72	104.61	[22]
Benzene	2Propanol	Water	40	1.080	1.1E-1	2.9E-1	1.0E-2	2.3E-2	4.5E0	7.0E5	6.35	14.03	[22]
Benzene	1Propanol	Water	30	1.097	4.1E-2	4.9E-2	2.3E-2	2.4E-2	1.50E-2	1.6E-2	3.39	6.38	[22]
			60	1.108	2.0E-2	3.1E-2	1.1E-2	1.4E-2	1.10E-1	1.5E-1	13.43	13.00	
Benzene	Ethanol	Water	35	1.113	1.4E-1	1.2E-1	1.7E-2	2.5E-2	1.72E-1	9.7E3	8.95	11.36	[22]
			45	1.111	1.3E-1	1.2E-1	1.4E-2	3.3E-2	1.50E-1	1.4E4	15.68	20.12	
			55	1.111	1.0E-1	1.1E-1	2.7E-2	2.5E-2	2.14E-1	2.2E4	22.17	27.52	
			64	1.108	9.0E-2	1.3E-1	2.2E-2	2.7E-2	3.38E-1	2.0E4	35.11	44.47	
Ethanol	Water	Ethyl acetate	50	1.051	4.5E-3	1.7E-2	1.1E-2	1.0E-2	8.60E-2	3.6E6	3.61	4.73	[22]
			80	1.063	9.3E-3	1.3E-2	9.0E-3	9.4E-3	2.29E-1	4.7E6	7.95	7.89	
Average					5.44E-2	7.66E-2	2.11E-2	1.88E-2		8.34E8	16.73	22.26	

*Δy is average deviation of vapor mole fractions of component 1 and 2

Table 2: Enthalpy and Entropy of association of water molecules.

$\Delta H'/R$	$\Delta S_o/R$
-119.66	-1.56

Where ΔG_o, ΔH_o and ΔS_o are standard Gibbs free energy, standard enthalpy and standard entropy of association, respectively. Also, according to Eq. (5), Γ is the ratio of activity coefficient of associated species, a measure of interaction between these species. In the case of consideration (dense fluid) Γ can be described as a function of T only. Therefore the following simple relation is introduced for it here:

$$\Gamma = \exp\left(-\frac{\alpha}{RT}\right) \tag{35}$$

By combination of Eqs. (34) and (35) with the definition of κ ($\kappa = \Gamma K$), we can obtain:

$$\kappa = \exp\left(\frac{-\Delta G_o - \alpha}{RT}\right) = \exp\left(\frac{-(\Delta H' + \alpha) + T\Delta S_o}{RT}\right) \tag{36}$$

Where for simplicity $\Delta H' = \Delta H_o + \alpha$. Eqs. (30) and (36) and values of ξ_p from Table 1, can be used to evaluate $\Delta H'$ and ΔS_o. Results have been given in Table 2.

CONCLUSIONS

In this work the van der Waals mixture model (van Laar equations) was extended to associating mixtures by using an improved chemical theory of association. VLE calculations were done for 7 aqueous ternary mixtures in different temperatures, where water was regarded as the only associating fluid. The introduced model was compared with original van Laar model, and well known empirical models of NRTL and UNIQUAC. The results showed superior agreement of proposed model with experimental VLE data in comparison with original van Laar model. Also, our model and empirical models had similar accuracies; although, NRTL and UNIQUAC had 6 adjustable parameters and the modified model had only one adjustable parameter.

Nomenclature

a	van der Waals equation of state parameter
b	van der Waals equation of state parameter
A	Molar Helmholtz free energy
G	Molar Gibbs free energy
H	Enthalpy
I	Number of same monomers in an associated species
I	Continuous variable version of (i) defined above
K	Equilibrium constant of association
L	The limit of association
n	Number of moles
N_A	Avogadro number
p	Component p
p_i	Associated species formed from i molecules of component p
P	Pressure
R	Universal gas constant
S	Entropy
T	Absolute temperature
x	Liquid phase mole fraction
$\chi(I)$	Distribution function
χ_o	Distribution function normalizing factor
y	Vapor phase mole fraction

Greece Letters

Δ	Deviation
γ	Activity coefficient
Γ	Function of T and P, defined by Eq. (5)
κ	$= K \Gamma$

Superscript

T	True

Subscript

calc	Calculated
exp	Experimental
conf	Configurational
m	Mixture
p	Associated component p
p_i	Associated species formed from i molecules (monomers) of p

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