Dominant Association Species in Binary Mixtures of Methanol, Ethanol and Propanol in Nonpolar Solvents

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Abstract

The molecular associations in the binary mixtures of (methanol/solvent), (ethanol/solvent) and (propanol/solvent) were studied using NMR, FTIR and VLE data at different temperatures. The activity coefficients as the most important quantities representing the mixture deviation form ideal behavior were evaluated by using various association models to express the physical and chemical contributions of the activity coefficients. The parameters of these models were calculated. The results indicated that for methanol and ethanol the dominant associated species are the tetramer whereas for propanol it is the trimer. The differences between the parameters of activity coefficient models were calculated by considering the physical and chemical contributions separately and were expressed in terms of residual parameters for the activity coefficient models. The parameters of van Laar model were corrected on the basis of the existing dominant species in the associated mixtures and a simple linear relation was obtained for the parameters of the model for the dominant species in terms of the parameters for monomer.

Keywords: Association models; NMR; FTIR; VLE; Activity coefficient models

Introduction

Many industrially important systems contain molecules that exhibit hydrogen bonding. Chemical interactions are dominated in pure and mixtures with hydrogen bonds. The physico-chemical properties of such systems are greatly altered as a result of the hydrogen bonds. The physical properties of hydrogen bonded systems such as melting points, boiling points and heat of vaporization are much higher than expected.

In transitional phases such as melting or boiling, additional energy is required to break the H bonds which lead to unexpected higher values of the enthalpy of transition. Although there are many empirical and theoretical correlations that can be used to predict phase behavior, a few give accurate results for hydrogen-bonding molecules. Viscosity, another physical property, also increases with hydrogen bonding. The increase in molecular structure in hydrogen bonded system, decreases the freedom of molecular motion, causing "entanglements" between molecules and a higher viscosity value.

The development of predictive models for thermodynamic properties of H-bonding solutions

remains a challenge. It is usually agreed, that such a development can only succeed, if besides the physical interactions, the chemical interactions are explicitly taken into account [1].

Hydrogen bonding arises when an electron-rich group, for example, a terminal oxygen of –OH group in an alcohol, interacts with an electron-deficient group, such as the hydrogen in –OH group of another alcohol molecule. By delocalizing the electrons, a weak non-covalent chemical bond (15 to 30 kJ/mol) is formed and the associated molecules lower their free energy [2]. In pharmacological active compounds the non-covalent interactions have been shown to be physiologically important [3]. *ab initio* studies can be of value in describing the competition between inter- and intra molecular hydrogen bonds and the cooperative character of such interactions. Many studies on clusters of molecules capable of intermolecular hydrogen bond formation have been reported [4,5]. A hydrogen bond is considered to be formed when the corresponding inter nuclear distance, is within the sum of van der Waals radii [6].
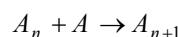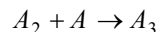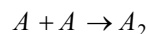
Among other physical-chemical techniques, Nuclear Magnetic Resonance spectroscopy (NMR), Fourier Transfour Infrared spectroscopy (FTIR) and Vapor Liquid Equilibrium (VLE) measurements are the most widely used techniques to study the deviations from ideal behavior in binary mixtures of alcohol/solvent due to hydrogen bonding of alcohol molecules. Various associating models for hydrogen bonding are used to treat the experimental data and to calculate the activity coefficients which are representative of the deviation from ideal behavior of mixtures and are important quantities in thermodynamic calculations [7].

The most commonly used models for calculating the thermodynamic properties of hydrogen bonded mixtures are: the Continuous Linear Association Model (*CLAM*) [8,9], the Linear Association with Cyclic Timer (*LACT*) model [9], the Association with Variable Equilibrium Constant (*AVEC*) model [10].

There are also other association models that could be used to predict solution behavior such as trimer only or tetramer only, but they have limited applications and predication of more sensitive solution properties by them, such as excess enthalpy or LLE, may be very poor.

The Association Model

Flory's treatment [11] clearly shows that the equilibrium constant for the following linear associative reactions:

$$A + A \rightarrow A_2$$

$$A_2 + A \rightarrow A_3$$

$$\cdot \quad \cdot \quad \cdot$$

$$\cdot \quad \cdot \quad \cdot$$

$$\cdot \quad \cdot \quad \cdot$$

$$A_n + A \rightarrow A_{n+1}$$

can be expressed in terms of lattice model for solution polymerization [11,12] as:

$$K_{n+1} = (\frac{\phi_{n+1}}{\phi_1 \phi_n}) \frac{n}{n+1} = (\frac{c_{n+1}}{c_n c_1}) \frac{1}{v_a} \tag{1}$$

where for $n \geq 1$, v_a is the molar volume of alcohol and ϕ_1, ϕ_n are the volume fractions of monomer and *n*-mer, respectively.
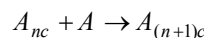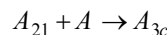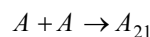
From Equation (1) the volume fraction of linear *n*-mer ϕ_{nl} can be written as:

$$\phi_{nl} = nK_2 K_3 \dots K_n \phi_1^n \qquad (n = 2,3,\dots) \tag{2}$$

Then by assuming $K_1 = K_2 = \dots = K_n$ we will have:

$$\phi_{nl} = nK^{n-1} \phi_1^n \tag{3}$$

For the following cyclic association reactions:

$$A + A \rightarrow A_{21}$$

$$A_{21} + A \rightarrow A_{3c}$$

$$\cdot \quad \cdot \quad \cdot$$

$$\cdot \quad \cdot \quad \cdot$$

$$\cdot \quad \cdot \quad \cdot$$

$$A_{nc} + A \rightarrow A_{(n+1)c}$$

The equilibrium constant, in analogy with Equation (1), can be expressed as:

$$K_{n+1} = \frac{\phi_{c(n+1)}}{\phi_{cn} \phi_1} \frac{n-1}{n} \tag{4}$$

and the volume fraction of cyclic *n*-mer is:

$$\phi_{nc} = 2(n-1)K^{n-1} \phi_1^n \tag{5}$$

The alcohol volume fraction ϕ_a, is given by the following mass balance equation:

$$\phi_a = \phi_1 + \sum_{n=2}^{\infty}(\phi_{nl} + \phi_{nc}) \qquad (6)$$

where, ϕ_1, ϕ_{nl} and ϕ_{nc} are respectively the volume fractions of alcohol as monomer and linear n-mer and cyclic n-mer species.

CLAM

The Continuous Linear Association Model (*CLAM*) used by Krestchmer *et al.* [8] and Renon *et al.* [9] for alcohol-hydrocarbon mixtures, restricted only to formation of linear species, all with equal probability of forming. The CLAM model predicts well the activity coefficients over the entire composition range but it can not able to predict the temperature dependence of the excess enthalpy [8]. For $\phi_{nc} = 0$ and by substitution of Equation (1) in Equation (6):

$$\phi_a = \sum_{n=1}^{\infty} n K^{n-1} \phi_1^n \qquad (7)$$

This equation can be written as:

$$\phi_a = \phi_1(1 + 2K\phi_1 + 3K^2\phi_1^2 + ...) \qquad (8)$$

and then:

$$\phi_a = \phi_1 \left(\frac{d\sum_{n=1}^{\infty}(K\phi_1)^n}{d(K\phi_1)}\right) = \phi_1 \frac{d}{d(K\phi_1)}\left(\frac{1}{1-K\phi_1}\right) \qquad (9)$$
$$= \phi_1 \frac{1}{(1-K\phi_1)^2}$$

The Trimer Model

In this model the trimer is considered as the dominant species at low concentration of alcohols. The presence of linear and cyclic species is considered in this model. The mass balance equation, Equation (6), for this model is:

$$\phi_a = \phi_1 + 7K_3\phi_1^3 \qquad (10)$$

LACT Model

The Linear Association with Cyclic Timer (*LACT*) model [8] was developed for the cyclic trimer. A unique equilibrium constant is assigned to cyclic complex formation and all higher order complexes in the solution are considered linear with equal probability.

$$\phi_a = \phi_1 + \phi_{3c} + \sum_{n=3}^{\infty}\phi_{nl} \qquad (11)$$

Then by substituting from Equation (3) and Equation (5) in Equation (11), it is obtained:

$$\phi_a = \phi_1 + 3K_3\phi_1^3 + 4K_3 K\phi_1^4 + ... + nK_3 K^{n-3}\phi_1^n \qquad (12)$$

Equation (12) can be written as:

$$\phi_a = \phi_1 + K_3 K^{-2}\sum_{m=3}^{n} m K^{m-1}\phi_1^m \qquad (13)$$

Then by using the expression:

$$2x + 3x^2 + ... = \frac{d}{dx}(1 + x^2 + x^3 + ...) \cong \frac{1}{(1-x)^2}$$

Equation (13) becomes:

$$\phi_a = \phi_1 + K_3 K^{-2}\left(\frac{\phi_1}{(1-K\phi_1)^2} - \phi_1 - 2K\phi_1^2\right)$$
$$= \phi_1 + K_3 K^{-2}\left(\frac{3K^2\phi_1^3 - 2K^3\phi_1^4}{(1-K\phi_1)^2}\right) \qquad (14)$$

and after simplification:

$$\phi_a = \phi_1 + \frac{K_3\phi_1^3(3 - 2K\phi_1)}{(1-K\phi_1)^2} \qquad (15)$$

AVEC Model

The Association with Variable Equilibrium Constant (*AVEC*) model is based on the assumption that as temperature of the solution increases, the oligomers breakdown to from the more stable complexes, the trimer or tetramer. The unique feature of this model is that; the probability of forming various species is no longer equal but depends on the size of the complex.

For linear species:

$$\ln K_{nl} = \frac{L_g}{n-1} \qquad (16)$$

where there are (n-1) hydrogen bonds in a complex containing n monomers, with an end proton which is free. L_g is an adjustable chemical model parameter [13].

For cyclic complexes, where there are hydrogen bonds in a complex containing n monomers:

$$\ln K_{nc} = \frac{C_g}{n} \qquad (17)$$

C_g is an adjustable chemical model parameter. It was observed that the two chemical parameters were not independent but instead were interrelated $C_g = (\frac{4}{3})L_g$. The alcohol, or overall species, volume fraction in the mixture is:

$$\phi_a = \phi_1 + 4K_4^3\phi_1^4 \quad \phi_a = \sum_{n=1}^{\infty} nK^{n-1}\phi_1^n + 2(n-1)K^{n-1}\phi_1^n$$

(18)

Activity Coefficient

a. *Chemical Contribution*

The excess Gibbs energy, taken relative to an ideal solution of alcohol and hydrocarbon, can be separated into two contributions, one chemical g_c^E and the other physical g_p^E [14]:

$$g^E = g_c^E + g_p^E$$

(19)

The chemical contribution g_c^E, is obtained from Flory's theory [11]:

$$\frac{g_c^E}{RT} = x_s \ln\frac{\phi_s}{x_s} + x_a\frac{\phi_1}{\phi_1^* x_a} + Kx_a(\phi_1 - \phi_1^*)$$

(20)

where, K is equilibrium constant, assuming that $K_1 = K_2 = ... = K_n = K$. X_a and X_s are respectively the overall (stoichiometric) mole fraction of alcohol and solvent. ϕ_s is the volume fractions solvent and ϕ_1 and ϕ_1^* are the "true" volume fraction of monomer species and the volume fraction of monomer in pure alcohol.

In a mixture the activity coefficient of a component i, γ_i can be obtained by using the following well know equation [15]:

$$RT \ln\gamma_i = (\frac{\partial g^E}{\partial n_i})_{T,P,n_{j\neq i}}$$

(21)

From Equations (20) and (21) by appropriate differentiation relative to mole fraction, the results are [16]:

$$\ln\gamma_a^c = \ln\frac{\phi_1}{\phi_1^* x_a} + \phi_s(1 - \frac{v_a}{v_s}) + K(\phi_a\phi_1 - \phi_1^*)$$

(22)

$$\ln\gamma_s^c = \ln\frac{\phi_s}{x_s} + \phi_a(1 - \frac{v_a}{v_s}) + K(\phi_a\phi_1 - \phi_1^*)$$

(23)

Another of above equations, also based on Flory's theory [11], have been derived [13]:

$$ln\gamma_a^c = ln(\frac{\phi_1}{x_a\phi_1^0}) - \frac{\phi_s v_a}{v_s} + \frac{1}{\overline{X}_n^*} - \frac{\phi_a}{\overline{X}_n}$$

(24)

$$ln\gamma_s^c = ln(\frac{\phi_s}{x_s}) - \phi_a + \frac{\phi_a v_a}{\overline{X}_n v_s}$$

(25)

where, the symbols have the same significance as Equations (24) and (25) and $\overline{X}_n$, $\overline{X}_n^*$ are the average number of segments per n-mer, respectively, in pure alcohol and in mixture and $\overline{X}_n$ can be calculated by the following equation:

$$\overline{X}_n = \phi_a \bigg/ \sum_{n+1}^{\infty} \frac{\phi_n}{n}$$

(26)

b. *Physical Contribution*

Scatchard Hildebrand Equation

The physical contribution g_p^E can be presented by a one-parameter equation as suggested by Scatchard and Hildebrand [16]:

$$g_p^E = \beta\phi_a\phi_s(x_a v_a + x_s v_s)$$

(27)

where v_a and v_s are the liquid molar volumes of alcohol and solvent respectively and β is the physical interaction parameter and is defined as the interaction energy density between solute/solvent pairs [11,17].

$$\beta = (\sigma_s - \sigma_a)^2$$

(28)

In Equation (28), σ_a and σ_s are the Hildebrand solubility parameters of alcohol and solvent respectively [18,19]. The physical contribution of activity coefficient for alcohol, γ_a^P and solvent γ_s^P are:

$$\ln\gamma_a^P = \frac{\beta}{RT}v_a\phi_s^2$$

(29)

$$\ln\gamma_s^P = \frac{\beta}{RT}v_s\phi_a^2$$

(30)

where, β can be considered as the model parameter.

Van Laar Equation [17]

The activity coefficients expressed by van Laar equation for alcohol/solvent mixture is:

$$\ln \gamma_a^P = \frac{A'^P}{(1+\frac{A'^P}{B'^P}\frac{x_a}{x_s})^2} \qquad (31)$$

$$\ln \gamma_s^P = \frac{B'^P}{(1+\frac{B'^P}{A'^P}\frac{x_s}{x_a})^2} \qquad (32)$$

where, A'^P and B'^P are the model parameters.

NMR Spectroscopy

NMR spectroscopy has been used for hydrogen bonding studies. The observed chemical shift δ_0 in NMR spectroscopy has been interpreted by a variety of association models. The chemical shift is the mean number of the chemical shifts of the protons in *OH* groups in different alcohol species existing in the alcohol/solvent mixtures [1]. There are models based on postulating the presence of only one type of associated species or postulating several types of associated species in the mixture [20].

It has been shown that the observed chemical shift for hydrogen bond formation is a weighted average of the chemical shifts of the free and bonded hydrogen, where the weighting factors are the fraction of the total number of bonded hydrogen presents a given state at equilibrium [21]:

$$\delta_0 = [\frac{C_1}{C_a}]\delta_1 + \sum_{n=2}^{\infty} \{[\frac{nC_{nc}}{C_a}]\delta_{nc} \\ +[\frac{(n-1)C_{nl}}{C_a}]\delta_{nl} +[\frac{C_{nl}}{C_a}]\delta_1' \} \qquad (33)$$

The symbols used in the above equations are defined as follows: C_{nc} is the concentration of cyclic *n*-mer, C_{nl} is the concentration of linear *n*-mer, C_a is total concentration of hydrogen/bonding species, δ_1 is chemical shift of the proton on a monomer, δ_1' is chemical shift of the bonded protons on a cyclic *n*-mer. In the NMR model formation it is assumed that $\delta_{nl} = \delta_{nc} = \delta_n = constant$ and the formation of a hydrogen bond causes no volume change and the hydrogen on the end of a linear chain has the same chemical shift as that on a monomer, then the above equation can be rewritten as follows [13, 20]:

$$\Delta_0 = \sum_{n=2}^{\infty} \{[\frac{(n-1)\phi_{nl}}{n\phi_a}]\Delta_{nl} +[\frac{\phi_{nc}}{\phi_a}]\Delta_{nc} \} \qquad (34)$$

where, ϕ_{nc}, ϕ_{nl} and ϕ_a are the volume fractions as defined Equations (3), (5) and (6):

$$\Delta_0 = \delta_0 - \delta_f \; ; \; \Delta_{nl} = \delta_{nl} - \delta_f \; ; \; \Delta_{nc} = \delta_{nc} - \delta_f \qquad (35)$$

with the assumption that only dimers are formed in solution (*Dimer model*) Equation (33) can be presented as:

$$\Delta_0 = \frac{K_2\phi_1^2}{\phi_a}\Delta_2 \qquad (36)$$

Spectroscopic evidence indicates that in certain cases, as in the case of propanol/solvent, linear or cyclic trimer appears to be the dominant hydrogen bonded species (*Trimer model*) therefore Equation (33) will be in the form of [1,13,20]:

$$\Delta_0 = (\frac{3K_3\phi_1^3}{\phi_a})\Delta_3 \qquad (37)$$

For methanol/solvent and ethanol/solvent mixture NMR spectroscopy results have indicated that tetramer is the dominant species, in this case Equation (33) for tetramer model is presented as [1, 22]:

$$\Delta_0 = (\frac{4K_4\phi_1^4}{\phi_a})\Delta_4 \qquad (38)$$

In case that the presented species in the associating mixture are in linear form, continuous association model (*CLAM*) is a good assumption. This is equivalent to assuming that: $K_2 = K_3 = ... = K$. Therefore:

$$\Delta_0 = [\frac{2K\phi_a +1-(4K\phi_a +1)^{0.5}}{2K\phi_a}]\Delta_n \qquad (39)$$

Another association model is the linear association with cyclic trimer (*LACT*) which assumes that the dominant hydrogen bonded species is cyclic trimer:

$$\Delta_0 = [\frac{K_3(K\phi_1)^3(3-3K\phi_1 +(K\phi_1)^2)}{K^3\phi_a(1-K\phi_1)^2}]\Delta_n \qquad (40)$$

In this model K, K_3 and Δ_n are adjustable parameters.

The association model with variable equilibrium constant (*AVEC*) is based on the assumption that all species are present in the mixture. Therefore:

$$\Delta_0 = \sum_{n=2}^{\infty} \{[\frac{(n-1)\phi_{nl}}{n\phi_a}]\Delta_{nl} +[\frac{\phi_{nc}}{\phi_a}]\Delta_{nc} \} \qquad (41)$$

NMR results for the dominant species in alcohol/solvent mixtures are approved by similar results

obtained by FTIR spectroscopy [1].

Correction of van Laar Parameters

In an alcohol/solvent mixture, alcohol is considered as an associating mixture of various associated n-mer. Therefore the parameters a_a and b_a for alcohol can be presented as [23]:

$$a_a = (\sum_n x_{a_n} a_{a_n}^{\frac{1}{2}})^2 \tag{42}$$

$$b_a = \sum_n x_{a_n} b_{a_n} \tag{43}$$

where, x_{a_n} is the mole fraction of associated alcohol in n-mer and a_{a_n}, b_{a_n} are the respective parameters.

a. *The Tetramer Is the Dominant Species*

The experimental and theoretical evidences indicate that, the tetramer as well as the monomer is the dominant species in methanol/solvent and ethanol/solvent mixtures and the amount of the other species are negligible, therefore Equation (42) and (43) can be written as:

$$a_{a_n} \cong [x_{a_1} a_{a_1}^{\frac{1}{2}} + x_{a_4} a_{a_4}^{\frac{1}{2}}]^2 \tag{44}$$

$$b_a \cong [x_{a_1} b_{a_1} + x_{a_4} b_{a_4}] \tag{45}$$

where, a_{a_1}, b_{a_1} and a_{a_4}, b_{a_4} are the parameters, respectively for monomer and tetramer species.

The equilibrium constant for formation of n-mer can be expended as:

$$K_n = \frac{x_{a_n}}{x_{a_{n-1}} x_{a_1}} \frac{\gamma_{a_n}}{\gamma_{a_1} \gamma_{a_{n-1}}} = \frac{x_{a_n}}{x_{a_{n-1}} x_{a_1}} \Gamma_{a_n} \tag{46}$$

where, the activity coefficient ratio $\dfrac{\gamma_{a_n}}{\gamma_{a_1} \gamma_{a_{n-1}}}$ is shown by Γ_{a_n}. A function of association η_{a_n} is defined as:

$$\eta_{a_n} = \frac{K_{a_n}}{\Gamma_{a_n}} = \frac{x_{a_n}}{x_{a_1} x_{a_{n-1}}} \tag{47}$$

Then for dimer:

$$\eta_{a2} = \frac{x_{a2}}{x_{a1}^2}$$
$$x_{a2} = x_{a1}^2 \eta_{a2} \tag{48}$$

for trimer,

$$\eta_{a3} = \frac{x_{a3}}{x_{a1} x_{a2}}$$
$$x_{a3} = x_{a1} x_{a2} \eta_{a3} \tag{49}$$

and for tetramer

$$\eta_{a4} = \frac{x_{a4}}{x_{a1} x_{a3}}$$
$$x_{a4} = x_{a1} x_{a3} \eta_{a4} \tag{50}$$

Form Equations (47),(48) and (49):

$$x_{a4} = x_{a1}^4 \eta_{a2} \eta_{a3} \eta_{a4} \tag{51}$$

Since it is assumed that alcohol constituents are only monomer and tetramer, the following approximation is held:

$$x_a \cong x_{a1} + x_{a4} \tag{52}$$

Then form Equation (52) the following equation is obtained:

$$x_a = x_{a1} + x_{a1}^4 \Theta_{a4} \tag{53}$$

where, $\Theta_{a_4} = \eta_{a2} \eta_{a3} \eta_{a4}$. Equation (53) is a bi-quadratic equation of the form:

$$x_{a1}^4 + \frac{1}{\Theta_{a4}} x_{a1} - \frac{1}{\Theta_{a4}} x_a = 0 \tag{54}$$

and its only acceptable root can be presented as [24]:

$$\begin{aligned}
x_{a1} = [&-0.5(L_1 + L_2)^{0.5} \\
&+0.5(-\frac{1}{2}L_1 - \frac{1}{2}L_2 + 0.8660I(L_1 - L_2))^{0.5} \\
&+0.5(-\frac{1}{2}L_1 - \frac{1}{2}L_2 - 0.8660I(L_1 - L_2))^{0.5}]
\end{aligned} \tag{55}$$

where

$$L_1 = [\frac{1}{128}\frac{x_a}{\Theta_{a4}} + ((\frac{1}{48}\frac{1}{\Theta_{a4}^2} - \frac{1}{12}\frac{x_a}{\Theta_{a4}})^3 + \frac{x_a^2}{16384\Theta_{a4}^4})^{0.5}]^{\frac{1}{3}} \tag{56}$$

$$L_2 = [\frac{1}{128}\frac{x_a}{\Theta_{a4}} - ((\frac{1}{48}\frac{1}{\Theta_{a4}^2} - \frac{1}{12}\frac{x_a}{\Theta_{a4}})^3 + \frac{x_a^2}{16384\Theta_{a4}^4})^{0.5}]^{\frac{1}{3}} \tag{57}$$

In the original van Laar model [25] the parameters a and b are expressed in terms of critical properties of pure component i derived from van der Waals equation.

$$a_i = \frac{27R^2 T_{ci}^2}{64 P_{ci}} \tag{58}$$

$$b_i = \frac{RT_{ci}}{8 P_{ci}} \tag{59}$$

Therefore as alcohol is a mixture of *n*-mer, the parameters of alcohol a_a and b_a are dependent on the mole fraction of *n*-mer species represented by the function $F(x)$ and $G(x)$ in the following form:

$$a_a = a_{ac} F(x) \tag{60}$$

$$b_a = b_{ac} G(x) \tag{61}$$

where, a_{ac} and b_{ac} are the parameters for pure alcohol. By using Equations (48) and (49) in Equations (60) and (61) and then substitution for x_{a_4} from Equation (55) the results will be:

$$F(x) = (x_{a_1} \frac{a_{a_1}^{\frac{1}{2}}}{a_{ac}} + x_{a_1}^4 \Theta_{a4} \frac{a_{a_4}^{\frac{1}{2}}}{a_{ac}})^2 \tag{62}$$
$$= (x_{a_1} A_1 + x_{a_1}^4 \Theta_{a4} A_4)^2$$

$$G(x) = (x_{a_1} \frac{b_{a_1}}{b_{a_c}} + x_{a_1}^4 \Theta_{a4} \frac{b_{a_4}}{b_{ac}}) \tag{63}$$
$$= (x_{a_1} B_1 + x_{a_1}^4 \Theta_{a4} B_4)$$

According to the van Laar model [24] the following expression for the molar excess Gibbs function of alcohol/solvent mixture holds:

$$g^E = \frac{a_a x_a^2}{b_a} + \frac{a_s x_s^2}{b_s} - \frac{a_a x_a^2 + 2 x_a x_s (a_a a_s)^{\frac{1}{2}} + a_s x_s^2}{b_a x_a + b_s x_s} \tag{64}$$

Upon substitution for $F(x)$ and $G(x)$ from Equations (62) and (63) respectively in Equations (52) and (60) and then by substituting for x_{a_1} from Equation (55) in the resulting equations, two equations for expressing the parameters a_a and b_a are obtained. These equations are used in Equation (64) and then by utilizing Equation (21), the following equations for the activity coefficients of alcohol γ_a and solvent γ_s are derived:

$$RT \ln \gamma_a = [\frac{Dx_a}{L_1} + L_2 B_1 + B_4 [L_1 + L_2]^4 + \frac{a_s x_s}{b_s}$$
$$- \frac{Dx_a^2 + 2 x_a x_s (a_s)^{0.5} + a_s x_s^2}{x_a L_1 + L_2 B_1 + B_4 [L_1 + L_2]^4 + x_s b_s}$$
$$- x_a (\frac{Dx_a}{L_1} + L_2 B_1 + B_4 [L_1 + L_2]^4$$
$$+ \frac{a_s x_s}{b_s} - \frac{Dx_a^2 + 2 x_a x_s (Da_s)^{0.5} + a_s x_s^2}{x_a L_1 + L_2 B_1 + B_4 [L_1 + L_2]^4 + x_s b_s})] \tag{65}$$

$$RT \ln \gamma_s = [\frac{Dx_a}{L_1} + L_2 B_1 + B_4 [L_1 + L_2]^4 + \frac{a_s x_s}{b_s}$$
$$- \frac{Dx_a^2 + 2 x_a x_s (Da_s)^{0.5} + a_s x_s^2}{x_a L_1 + L_2 B_1 + B_4 [L_1 + L_2]^4 + x_s b_s}$$
$$- x_s (\frac{a_s}{b_s} - \frac{2 x_a (Da_s)^{0.5} + 2 a_s x_s}{x_a L_1 + L_2 B_1 + B_4 [L_1 + L_2]^4 + x_s b_s}$$
$$+ \frac{(Dx_a^2 + 2 x_a x_s (Da_s)^{0.5} + a_s x_s^2) b_s}{(x_a L_1 + L_2 B_1 + B_4 [L_1 + L_2]^4 + x_s b_s)^2})] \tag{66}$$

where

$$D = ((L_1 + L_2) A_1 + [L_1 + L_2]^4 \Theta_{a4} A_4)^2 x_a \tag{67}$$

and L_1, L_2 and Θ are by Equations (56), (67) and (50).

b. *The Trimer Is the Dominant Species*

The experimental and theoretical evidences prove that the monomer and trimer are the dominant species in propanol/solvent mixtures, therefore from Equations (48) and (49) the mole fraction of trimer is obtained as:

$$x_{a3} = x_{a1}^3 \eta_{a2} \eta_{a3} = x_{a1}^3 \Theta_{a3} \tag{68}$$

and the total alcohol mole fraction is:

$$x_a = x_{a1} + x_{a3} = x_{a1} + x_{a1}^3 \Theta_{a3} \tag{69}$$

Then the parameters a_a and b_b for propanol is expressed as:

$$a_a = (x_{a1} a_{a1}^{\frac{1}{2}} + x_{a1}^3 \Theta_{a3} a_{a3}^{\frac{1}{2}})^2 = a_{ac} F(x) \tag{70}$$

$$b_b = (x_{a1} b_{a1} + x_{a1}^3 \Theta_{a3} b_{a3}) = b_{ac} G(x) \tag{71}$$

Equations (62) and (63) for the case of trimer as the dominant species will be presented as:

$$F(x) = (x_{a_1} \frac{a_{a_1}^{\frac{1}{2}}}{a_{ac}} + x_{a_1}^3 \Theta_{a3} \frac{a_{a_3}^{\frac{1}{2}}}{a_{ac}})^2 = (x_{a_1} A_1 + x_{a_1}^3 \Theta_{a3} A_3)^2 \tag{72}$$

$$G(x) = (x_{a_1} \frac{b_{a_1}}{b_{a_c}} + x_{a_1}^3 \Theta_{a3} \frac{b_{a_3}}{b_{ac}}) = (x_{a_1} B_1 + x_{a_1}^3 \Theta_{a3} B_3) \quad (73)$$

Using the same procedure [24] as used in driving Equation (55) the acceptable root for Equation (71) will be obtained as:

$$x_{a1} = L_1 + L_2 \quad (74)$$

where L_1 and L_2 are given by Equations (58) and (59). By substituting Equations (72) and (73) respectively in Equations (72) and (73) and then by substituting for x_{a_1} from Equations (74) in the resulting equation, two equations for parameters a_a and b_a are derived. The equations for parameters a_a and b_a are used in Equation (64) and then by utilizing Equation (21), the following equations for γ_a and γ_s are obtained:

$$RT \ln \gamma_a = \frac{M_2}{x_a M_1} + \frac{a_s x_s}{b_s} - \frac{N}{M_1 x_a + b_s x_s}$$
$$- 2x_a \frac{N((B_1 + 3(L_1 + L_2)^2 B_3 \Theta_{a3})x_a + M_1}{(M_1 x_a + b_s x_s)^2} \quad (75)$$

$$RT \ln \gamma_s = \frac{M_2}{M} + \frac{a_s x_s}{b_s} - \frac{N}{M x_a + b_s x_s}$$
$$- x_s [\frac{a_s}{b_s} - \frac{2a_s x_s + 2x_a M_1}{M x_a + b_s x_s} + \frac{N b_s}{(M x_a + b_s x_s)^2}] \quad (76)$$

where,

$$N = M_2 x_a + a_s x_s^2 + 2x_a x_s M \quad (77)$$

$$M = (((L_1 + L_2)A_1 + (L_1 + L_2)^3 \Theta_{a3} A_3)^2 a_s)^{0.5} \quad (78)$$

$$M_1 = (L_1 + L_2)B_1 + (L_1 + L_2)^3 B_3 \Theta_{a3} \quad (79)$$

$$M_2 = ((L_1 + L_2)A_1 + (L_1 + L_2)^3 A_3 \Theta_{a3})^2 x_a \quad (80)$$

In the above equations $L_1, L_2, A_1, A_3, B_1, B_3$ and Θ_{a_3} are given respectively by Equations (56), (57), (72), (73) and (68).

Results and Discussion

In the present work the NMR chemical shifts for methanol/solvents (CCl$_4$, C$_6$H$_{12}$) ethanol/solvents (CCl$_4$, C$_6$H$_{12}$), propanol/CCl$_4$ obtained from previous references [13,20,22] were treated by all the available models, Equations (36)-(37). These results were obtained by minimizing the calculated error (Absolute Average Error, *AAE*) according to the following equation:

$$AAE = \frac{1}{N} \sum_{j=1}^{N} \left| \frac{\Delta_o - \Delta_{calc}}{\Delta_o} \right|_j^2 \quad (81)$$

where, Δ_o is the observed chemical shift, Δ_{calc} is the chemical shift calculated by the model and N is the number of data points.

From the results presented, it was evident that the minimum *AAE* and the maximum equilibrium constant were obtained for the tetramer as the dominant species for the mixtures of methanol/solvent and ethanol/solvent. These results are in concordance with the VLE results that will be dealt with later in this section. Also the results of examining the measured NMR chemical shifts for the propanol/CCl$_4$ [20] by various models showed that the trimer model expressed by Equation (10) gave the best fit and was in agreement with our VLE calculations.

The association models presented by Equations (22) and (23) were used to calculate the chemical part of the activity coefficients for binary mixtures of methanol/solvent (CCl$_4$, C$_6$H$_{12}$), ethanol/solvent (CCl$_4$, C$_6$H$_{12}$), propanol/CCl$_4$ at different temperatures. For calculating the physical part of the activity coefficient the Scatchard Hildebrand model Equations (29) and (30), van Laar model Equations (31) and (32) were used. The experimental Raoult's law activity coefficients were calculated from VLE results obtained from reference [26]. The fitting of the models with experimental data was done by calculating the absolute average error *AAE* defined as:

$$AAE = \frac{1}{N} \sum_{j=1}^{N} \left| \frac{\gamma_{exp} - \gamma_{calc}}{\gamma_{exp}} \right|_j^2 \quad (82)$$

where, *N* is the number of data points used in the fitting. The Raoult's law experimental activity coefficient can be evaluated from VLE measurements by using the following equation:

$$(\gamma_{exp})_i = \frac{y_i P}{x_i P_i^0} \quad (83)$$

where, y_i and x_i are the measured mole fractions of component i (alcohol or solvent) respectively, in vapor and liquid phases, P_i^0 is the pure i saturation vapor pressure and P is the total pressure at given temperatures.

The calculated results for the model parameters of physical part of activity coefficient were in agreement with NMR results and the minimum *AAE* and the maximum equilibrium constant were obtained for

methanol and ethanol as the tetramer species and for propanol as the trimer species.

The distribution of association species in an associating mixture is a decisive criteria to judge which species is really the dominant one. Figures (1) and (2) as examples represent the distribution function for methanol/solvent. This distribution function is defined as:
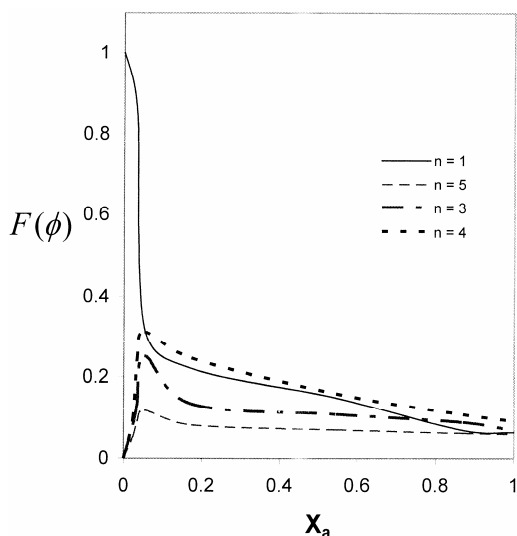

Figure 1. Distribution function $F(\phi)$ *vs.* mole fraction of alcohol X_a for (methanol/CCl$_4$) mixture at 328.15 K calculated by NMR data.
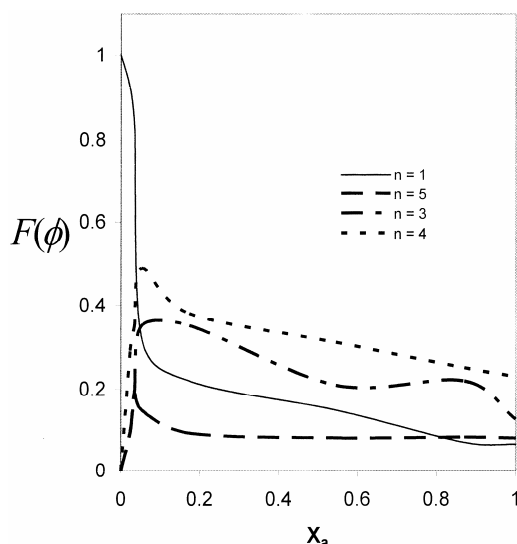

Figure 2. Distribution function $F(\phi)$ *vs.* mole fraction of alcohol X_a for (methanol/CCl$_4$) mixture at 328.15 K calculated by VLE data.

$$F(\phi) = \frac{\phi_n}{\phi_a} = \frac{n(\prod\limits_{n=3}^{n} K)\phi_1^n}{[\phi_1 + \sum\limits_{n=3}^{n}\phi_n]} \tag{84}$$

where ϕ_n is the volume fraction of *n*-mer and ϕ_a is the volume fraction of alcohol. As Figures (1) and (2) show, the tetramer has the maximum distribution for methanol. The same results can be presented for ethanol/solvent mixtures. The distribution function for propanol/solvent mixture indicates that the trimer is the dominant species. It is interesting that the same conclusion is derived by considering Figures (2) where the distribution function $F(\phi)$ is calculated by Equation (84) using the VLE data. The same results can be presented for ethanol and propanol on the basis of distribution function calculated from VLE data.

Without considering the molecular associations and the presences of various species in the alcohol/solvent mixtures the usual procedure has been used to fit the experimental VLE results with the activity coefficient models and to evaluate the parameters of the models. We did the same fitting and calculated the parameters of activity coefficients models on this basis. As expected, the results indicated that the parameters of each model were different in the case where the activity coefficient were not separated into chemical and physical parts, and fitted directly to the experimental data, compared with the case where the physical and chemical contributions were used separately. Therefore to account for the differences a residual activity coefficient must be involved and will be represented by the following equation for the van Laar model, as an example:

$$\ln \gamma_{(A'^o, B'^o)} = \ln \gamma^C + \ln \gamma^P_{(A'^P, B'^P)} + \ln \gamma^p_{(A'^{Pr}, B'^{Pr})} \tag{85}$$

In the above equation $\gamma_{(A'^o, B'^o)}$ is the activity coefficient as a whole and is evaluated from VLE experimental results directly using the Margules model. In this case A'^o, B'^o are parameters of the model. The activity coefficients γ^c and $\gamma^P_{(A'^P, B'^P)}$ are respectively the chemical and the physical parts and A'^P, B'^P are the van Laar parameters for physical part of the activity coefficient. From Equation (85) the residual activity coefficient $\gamma^R_{(A'^r, B'^r)}$ can also be presented as:

$$\gamma^R_{(A'^r, B'^r)} = \frac{\gamma_{(A'^o, B'^o)}}{\gamma^c \gamma^P_{(A'^P, B'^P)}} \tag{86}$$

where A'^{rP} and B'^{rP} are the Margules model residual

parameters and are calculated by fitting the above ratio Equation (86) to the experimental data. It is useless that for the case where the activity coefficient were not separated into physical and chemical parts the VLE experimental data [26] were fitted to the following equation:

$$\ln \gamma_a^P = \frac{A'^P}{(1 + \frac{A'^P}{B'^P} \frac{x_a}{x_s})^2} \tag{87}$$

where, γ_a is the activity of alcohol based on van Laar model for alcohol/solvent mixture and A'^0 and B'^0 are the model parameters. The same VLE experimental data [26] were used to calculate the product of chemical and physical activity coefficients ($\gamma^c \gamma_{(A'^P, B'^P)}^p$). The calculated residual parameters, according to Equation (86) were calculated by minimizing the error function as defined by Equation (82).

More evidences are available to support our conclusion about the presence of dominant species in alcohol/solvent mixtures. The Mont Carlo simulation for methanol, proved that on average three methanol molecules are at least involved in the process of hydrogen bonding with a single methanol molecule [27] which is in agreement with the result obtained in this work that tetramer is the dominant species in the methanol/solvent mixture.

The computation of inter nuclear oxygen-oxygen distance on the basis of energetic considerations for the mixture of methanol/CCl$_4$ indicated that the most favorable configuration for methanol is as the tetramer [28]. These results are also in agreement with the viscosity measurements where the lower viscosity has been measured for propanol, which is explained by the presence of species with lower n-mer (trimer) and lower relaxation time compared with higher viscosity of methanol and ethanol which is explained by the presence of higher n-mer (tetramer) and higher relaxation time [28].

Considering the calculated values of equilibrium constant (K) it was concluded that K_4 the equilibrium constants for the tetramer formation in the case of methanol and ethanol were higher than the other K_n, whereas for propanol, K_3, the equilibrium constant of trimer was higher. Therefore the species that have higher equilibrium constant can be considered as the more stable and favorable species in the process of association.

Also for the n-hexane as the solvent, the equilibrium constant is higher than CCl$_4$. This point has been investigated by other researchers using various techniques [28]. Their conclusion which is consistent with the results obtained in this work is that; n-hexane as the solvent, in alcohol mixtures is more inert compared with CCl$_4$.

The results obtained in this work indicate that upon increasing the temperatures the equilibrium constant (K) decreases. This can be related to the obvious fact that at higher temperatures lower n-mer are more stable and therefore the higher n-mers decompose to the lower ones.

The interesting result is observed by considering the values of the corrected parameters for van Laar model, as expressed by Equations (65), (66), (75) and (76). These parameters (a_{a_n} and b_{a_n}) are reported in Tables (1) and (2). Plotting the calculated values of a_{a_n} and b_{a_n} vs. respectively a_{a_1} and b_{a_1} give good linear variation, therefore the following expression can be proposed:

$$a_{a_n} = n^2 a_{a_1} \tag{88}$$

$$b_{a_n} = n b_{a_1} \tag{89}$$

These linear plots are shown in Figures (3)-(4) as examples for methanol/solvent mixtures. The values of n for methanol and ethanol are 3.899 and 4 respectively, which confirms that the associated species for these alcohols are the tetramer, whereas for propanol n is 3.29 and confirms that the associated species for this alcohol is the trimer.

Conclusion

NMR, FTIR and VLE data were used to examine the association of methanol, ethanol and propanol in binary mixtures with solvents CCl$_4$ and n-hexane. The calculated values of equilibrium constant for association reactions and the calculated absolute average errors (*AAE*) indicated that for methanol and ethanol the tetramer is the dominant associated species whereas for propanol the trimer is the dominant species.

The physical and chemical contributions in activity coefficient models were considered and the parameters of the models were evaluated.

The parameters of van Laar model were corrected on the basis of the presence of the dominant association species in the alcohol/solvent binary mixtures and the effectiveness of the correction was examined by a simple linear relation between the parameters of the dominant species in terms of the parameters of the monomer species.

Table 1. The parameters of Equations 88, 89 and AAE for (methanol and ethanol/solvent) mixtures

Mixture	T/K	a_a		b_a		AAE
		a_{a_1}	a_{a_4}	b_{a_1}	b_{a_4}	
Methanol/CCl$_4$	293.15	0.1510	2.5673	0.0934	0.3739	0.0063
	303.15	01361	2.2174	0.0164	0.0656	0.0152
	328.15	0103	0.1650	0.0134	0.0536	0.0049
Methanol/C$_6$H$_{12}$	318.15	0.1915	3.1025	0.0902	0.3608	0.0345
	323.15	0.1515	2.5036	0.0134	0.0536	0.1002
	328.15	0.0992	1.5825	0.0029	0.0380	0.0025
Ethanol/CCl$_4$	293.15	0.3903	6.2488	0.1225	0.4900	0.0201
	323.15	0.2789	4.4644	0.0913	0.3652	0.0723
	338.15	0.1993	3.1890	0.0734	0.2936	0.0342
Ethanol/C$_6$H$_{12}$	278.15	0.5983	9.5879	0.2148	0.8592	0.0072
	298.15	0.3882	6.2890	0.1912	0.7648	0.0566

Table 2. The parameters of Equations 88, 89 and the *AAE* for (propanol/solvent) mixture

Mixture	T/K	a_a		b_b		AAE
		a_{a_1}	a_{a_3}	b_{a_1}	b_{a_3}	
Propanol/CCl$_4$	293.15	1.1951	10.7557	0.4512	1.3985	0.0856
	313.15	1.0765	9.6732	0.2495	0.7485	0.0025
	343.15	0.8873	7.8021	0.5121	1.5362	0.1235

Figure 3. The tetramer parameter (a_{a_4}) *vs.* monomer parameter (a_{a_1}) for (methanol/CCl$_4$) mixture (*) and for (ethanol/CCl$_4$) mixture (Δ) at 298.15 K. From slope of the line in this Figure and Equation (88) *n* = 3.899.
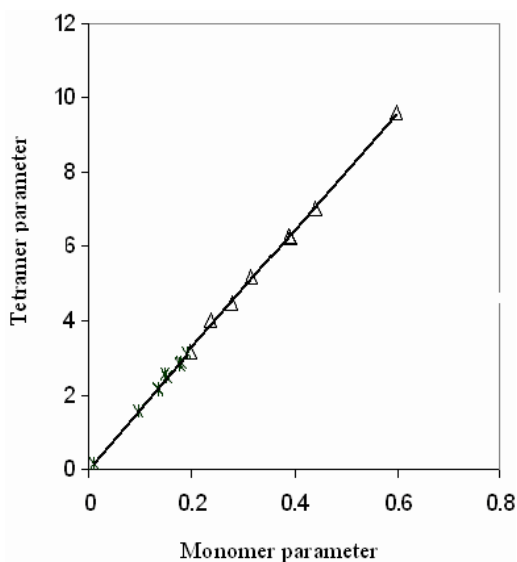

Figure 4. The tetramer parameter (b_{a_4}) *vs.* monomer parameter (b_{a_1}) for (methanol/CCl$_4$) mixture (*) and for (ethanol/CCl$_4$) mixture (Δ) at 298.15 K. From slope of the line in this Figure and Equation (89) *n* = 3.899.
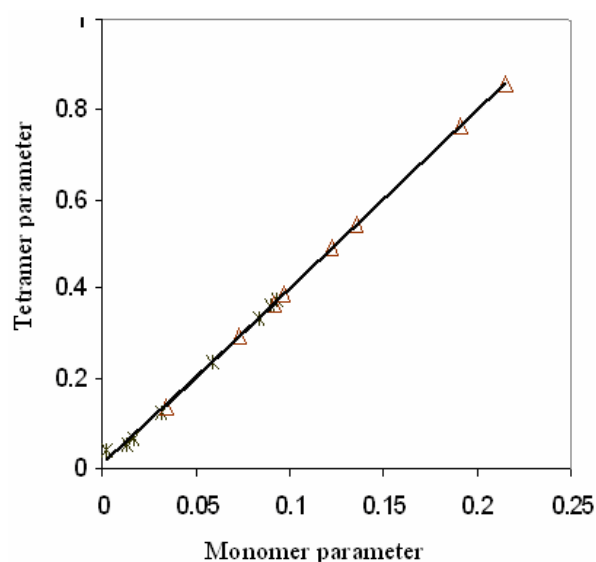
List of Symbols

A', B'	Parameters of Margules and van Laar models
D, L	Functions of corrected van Laar model, Equations (45)- (49)
G, g	Energy parameters in NRTL model
g^E	Excess Gibbs energy
$F(x),$ $G(x)$	Functions of corrected van Laar model, Equations (62)- (63)
$F(\phi)$	Distribution function
K	Equilibrium constant for association reaction
N	Number of experimental data points
N, M	Functions of corrected van Laar model, Equations (77)- (78)
M_1, M_2	Functions of corrected van Laar model, Equations (79)- (80)
R	Universal gas constant
T	Temperature
X	Mole fraction
x	Mole fraction in liquid phase
y	Mole fraction in gas phase
$\overline{X_n^*}$	Average number of segments per n-mer in pure alcohol
$\overline{X_n}$	Average number of segments per n-mer in mixture
Γ	Activity coefficient ratio, Equation (46)

Greek letters

β	Physical interaction parameter in Scatchard Hildebrand model
γ	Activity coefficient
δ	Chemical shift
η	Mole fraction ratio, Equation (47)
σ	Hildebrand solubility parameter in Scatchard Hildebrand model
ϕ	Volume fraction

Subscript and superscripts

1	Monomer species
nl	Linear n- mer
nc	Cyclic n- me
a	Alcohol
s	Solvent
c	Chemical contribution
p	Physical contribution
n	n-mer species
sa, as	Alcohol and solvent interaction
C_i	Critical point of pure compound i
i	Component
j	Data point

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