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On the Dimerization of Carboxylic Acids: An Equation of State Approach

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Abstract

The association term of the Non-Random Hydrogen-Bonding theory, which is an equation of state model, is extended to describe the dimerization of carboxylic acids in binary mixtures with inert solvents and in systems of two different acids. Subsequently, the model is applied to describe the excess enthalpies and the vapor-liquid equilibrium of relevant binary mixtures containing low molecular weight organic acids. The model sheds light on the interplay of intermolecular interactions through the calculation of the various contributions to the mixing enthalpies, namely from hydrogen bonding and non-hydrogen bonding (dipolar, induced polar or dispersive) interactions. According to model predictions, the acid molecules are so strongly associated that the addition of inert solvents to carboxylic acids with small carbon numbers at ambient temperature does not dramatically alter their degree of association. Consequently, the observed endothermic dissolution process is mainly attributed to the hindering of polar interactions. Furthermore, upon mixing of two carboxylic acids, the rearrangement of hydrogen bonds due to the formation of cross associating species results in an insignificant contribution to the heats of mixing due to the rather constant dimerization enthalpy that is revealed by the available experimental data for low molecular weight compounds.

1. Introduction

The rational design of modern processes in chemical and pharmaceutical industries, as well as the great potential of new bioengineering applications, strengthened the need for accurate modeling of complex mixtures that often exhibit highly non-ideal solution behavior, such as aqueous systems, biological mixtures of aminoacids, proteins and other biomolecules, complex pharmaceutical systems, dyes, extractives and binders, gels, polymer solutions and blends. Hydrogen bonding dictates the phase behavior of most systems of such kind.

Carboxylic acids are among the groups of fluids with peculiar hydrogen bonding behavior and the accurate modeling of such fluid mixtures is important for many processes that include biological systems, but also traditional chemical applications, e.g the production of terephthalic acid.^{1,2} Such peculiar hydrogen bonding behavior arises from the formation of two hydrogen bonds between two acid molecules. Since the first bond is established, the formation of the second becomes more feasible (hydrogen bond cooperativity). The cooperativity in the establishment of the second bond results in the formation of stable dimers and, thus, the formation of linear oligomers is not favored.^{3,4,5}

Accounting for hydrogen bonding through an equation of state approach is usually performed using thermodynamic models of two broad families, i.e. models that are based on the lattice fluid theory⁶⁻¹², and all the variants of SAFT (Statistical Associating Fluid Theory) equation of state¹³⁻¹⁵, which are based on the perturbation theory of Wertheim.¹⁶⁻¹⁹

Such models were successfully applied in describing mixtures of hydrogen bonding fluids, such as aqueous solutions and systems with alcohols, amines or glycols, in many cases showing similar performance and limitations.²⁰⁻²² In order to describe thermodynamic properties of organic acids, two association schemes are mainly used in the framework of the aforementioned thermodynamic models: the so called “1A” and “2B” association schemes.²³⁻²⁶ According to the first one, every acid molecule has one association site, positive or negative, which can be bonded with the relevant site of another acid molecule. The latter one allows the modelling of linear hydrogen bonded oligomers and is, thus, a simplified way of describing carboxylic acid systems. In the “2B” scheme, every acid molecule has two sites: one proton donor and one proton acceptor. Such

association schemes, often result in successful description of the vapor-liquid equilibrium of carboxylic acid mixtures^{2,23-25}, however, present serious limitations in aqueous solutions, the description of liquid – liquid equilibrium and more demanding calculations, such as the description of thermal properties.^{1,2} Only recently, the association term of both types of models was extended in order to describe the dimerization of organic acids in a more realistic way.²⁷⁻³⁰

Most often, in order to test the validity of a model, its predictions are compared solely to phase equilibrium data.^{3,20-26} Such kind of predictions are very useful in designing applications, where models are applied to predict the phase behavior of multicomponent mixtures. However, in some cases, the accurate prediction of thermal properties, such as the mixing enthalpies, is also important for a successful prediction of the energy demands. Nevertheless, the description of calorimetric properties of complex hydrogen bonding systems by thermodynamic models is a challenging task, even though such models may satisfactorily describe their phase behavior and/or their volumetric properties. Furthermore, the accurate prediction of thermal properties is the recommended way in order to check if the various intermolecular interactions are properly accounted for. In some cases, such type of calculations revealed interesting phenomena not easily shown with experimental techniques. For example, when the NRHB model was applied to predict the mixing enthalpies in mixtures of hydrocarbons with alkoxy-alcohols, which are typical fluids interacting via, both, inter- and intra-molecular hydrogen bonding, allowed the calculation of separate contributions (from various types of hydrogen bonding and from non-hydrogen bonding intermolecular interactions) to the total value of the property.³¹ It was revealed that the value of the total and experimental measurable enthalpy of mixing was the sum of very different contributions, i.e. the endothermic contribution due to the decrease of the inter-molecular association and the exothermic contribution due to the simultaneous considerable increase of the intra-molecular association that occurs upon the addition of the inert solvent.

In this study, we present the formalism for describing the dimerization of organic acids in the framework of the Non Random Hydrogen Bonding theory, which is a lattice fluid thermodynamic model.^{11,12} The presented approach is based on the work of Panayiotou and coworkers²⁷ for pure fluids and here is extended to binary mixtures containing a carboxylic

acid with an inert solvent or another organic acid. The Non Random Hydrogen Bonding Theory^{11,12} is a recent development of previous lattice models and so far has been applied to the description of phase equilibria of various types of mixtures with low or high molecular weight compounds²⁰⁻²² including pharmaceuticals^{32,33}, hydrogen bonding polymer systems³⁴ and ionic liquids.³⁵

2. Theory

2.1 The basics of the Non Random Hydrogen Bonding theory

The Non-Random Hydrogen Bonding Theory (NRHB) is an equation of state model.^{11,12} It is an extension of previous successful compressible lattice models⁸⁻¹⁰, where holes are used to account for density variation as a result of temperature and pressure changes. It accounts explicitly for hydrogen bonding interactions and for the non-random distribution of empty and molecular sites in the quasi lattice.

Following the approach of Panayiotou and Sanchez⁹, the partition function of a system is factored into a “physical” term, Q_P , which accounts for all non-hydrogen bonding (dispersive and polar) interactions and a hydrogen-bonding (association) term, Q_H :

$$Q = Q_P Q_H \quad (1)$$

Consequently, thermodynamic properties, such as the enthalpy or the free energy of a system can be divided into a physical and a hydrogen bonding (or association) contribution. For example the Gibbs free energy of a system is given by the following relation [9]:

$$G = G_P + G_H \quad (2)$$

In this study, we extend the formalism for describing the dimerization of organic acids. The development of the association term of the partition function, Q_H , and the resulting contributions to the equation of state and the chemical potentials due to the dimerization are presented in section 2.2. The former contribution in equation (1), due to physical interactions, is calculated using a combinatorial term based on Staverman approximation^{11,12} and a correction for non-randomness based on the quasi chemical theory of Guggenheim⁸. Such approach and the resulting equations of the model are adequately presented in literature^{11,12,36}. Consequently, only some basic equations are briefly presented in section 2.3.

2.2 Association term

In mixtures of carboxylic acids and inert solvents, dimers are the overwhelming majority of the association species at least at the vapor phase. In the following approach, we neglect any side reactions that may result in linear oligomers and we consider only dimerization, since this is the dominant hydrogen bonding behavior in the studied systems^{3,4,5}. The presented approach is based on the formalism presented by Panayiotou and coworkers²⁷ for pure fluids and here is extended to binary mixtures containing a carboxylic acid with an inert solvent or another organic acid.

2.2.1 Mixtures of acids with inert solvents

In a mixture of N total molecules, which contains N_1 acid molecules and N_2 inert solvent molecules, let N_{dm} be the number of acid dimers. The number of ways of selecting the N_{dm} dimers is as follows:

$$\Omega = \frac{N_1!}{(2N_{dm})!(N_1 - 2N_{dm})!} (2N_{dm} - 1)(2N_{dm} - 3) \dots 1 = \frac{N_1!}{(N_1 - 2N_{dm})! N_{dm}! 2^{N_{dm}}} \quad (3)$$

The free energy change upon dimer (dm) formation is^{27,37}:

$$G^{dm} = E^{dm} + PV^{dm} - TS^{dm} \quad (4)$$

Consequently, the hydrogen-bonding term of the partition function is^{27,37}:

$$Q_H = \frac{N_1!}{(N_1 - 2N_{dm})! N_{dm}! 2^{N_{dm}}} \left(\frac{\tilde{\rho}}{rN} \right)^{N_{dm}} \exp\left(-\frac{N_{dm} G^{dm}}{RT} \right) \quad (5)$$

where $\tilde{\rho}$ is the reduced density of the system and r is the number of segments per molecule. The contribution to the free energy of the system due to dimerization is:

$$G_H = -RT \ln Q_H \quad (6)$$

The equilibrium number of dimers per mol of segments, v_{dm} , is obtained from the above equation through the free energy minimization condition:

$$\left(\frac{\partial G_H}{\partial N_{dm}} \right)_{T,P,N_i} = 0 \quad (7)$$

which results in the following relation:

$$v_{dm} = \frac{N_{dm}}{rN} = \frac{2x_1 + \frac{1}{K_{dm}} - \sqrt{\frac{1}{K_{dm}^2} + \frac{4x_1}{K_{dm}}}}{4r} \quad (8)$$

where x_1 is the mole fraction of the acid in its mixture with the inert solvent and:

$$K_{dm} = \frac{\tilde{P}}{r} \exp\left(\frac{-G^{dm}}{RT}\right) \quad (9)$$

The hydrogen bonding contribution to the chemical potential of the acid is (for a binary system with an inert solvent):

$$\frac{\mu_1^H}{RT} = \frac{1}{RT} \left(\frac{\partial G_H}{\partial N_1} \right) = r_1 v_{dm} - \ln \frac{x_1}{x_1 - 2r v_{dm}} \quad (10)$$

The relevant contribution to the chemical potential of the inert compound is:

$$\frac{\mu_2^H}{RT} = \frac{1}{RT} \left(\frac{\partial G_H}{\partial N_2} \right) = r_2 v_{dm} \quad (11)$$

2.2.3 Mixtures of two acids

In a mixture containing two acids of N total molecules, the N_1 and N_2 of which are molecules of the first and the second compound, respectively, let N_{dm} be the total number of dimers in the system, which include the N_{11} and N_{22} dimers consisting of molecules of the same kind (of type 1 and 2, respectively) and N_{12} dimers consisting of molecules of different kind.

One can select the dimerized molecules of type 1 out of the N_1 acid molecules in

$$\omega_1 = \frac{N_1!}{(2N_{11})!N_{12}!(N_1 - 2N_{11} - N_{12})!} \quad (12)$$

ways and the dimerized molecules of type 2 out of the N_2 acid molecules in

$$\omega_2 = \frac{N_2!}{(2N_{22})!N_{12}!(N_2 - 2N_{22} - N_{12})!} \quad (13)$$

ways. Between the $2N_{11}$ molecules of type 1, dimers can be formed in

$$\omega_3 = (2N_{11} - 1) \cdot (2N_{11} - 3) \cdot (2N_{11} - 5) \dots \cdot (1) \quad (14)$$

ways. Similarly, between the $2N_{22}$ molecules of type 2, dimers can be formed in

$$\omega_4 = (2N_{22} - 1) \cdot (2N_{22} - 3) \cdot (2N_{22} - 5) \dots \cdot (1) \quad (15)$$

ways, while between the N_{12} molecules of type 1 and the N_{12} molecules of type 2, dimers can be formed in $\omega_5 = N_{12}!$ ways. Consequently, the number of ways of selecting the N_{dm} dimers is:

$$\Omega = \omega_1 \omega_2 \omega_3 \omega_4 \omega_5 = \frac{N_1}{N_{11}!(N_1 - 2N_{11} - N_{12})!N_{12}!} \cdot \frac{N_2}{N_{22}!(N_2 - 2N_{22} - N_{12})!} \cdot 2^{N_{12}} \quad (16)$$

The free energy change upon formation of an ij dimer is:

$$G_{ij}^{dm} = E_{ij}^{dm} + PV_{ij}^{dm} - TS_{ij}^{dm} \quad (17)$$

Consequently, the hydrogen-bonding factor in the partition function becomes³⁷:

$$Q_H = \Omega \left(\frac{\tilde{\rho}}{rN} \right)^{N_{dm}} \exp \left(- \frac{N_{11}^{dm} G_{11}^{dm} + N_{22}^{dm} G_{22}^{dm} + N_{12}^{dm} G_{12}^{dm}}{RT} \right) \quad (18)$$

The contribution to the free energy of the system due to dimerization is given from equation (2), while the equilibrium number of dimers per mol of segments, v_{11} , v_{22} , v_{12} , is obtained from equations similar to equation (7), which result in the following relations:

$$\frac{2v_{11}}{v_{10}^2} = \tilde{\rho} \exp\left(-\frac{G_{11}^{dm}}{RT}\right) \quad (19)$$

$$\frac{2v_{22}}{v_{20}^2} = \tilde{\rho} \exp\left(-\frac{G_{22}^{dm}}{RT}\right) \quad (20)$$

$$\frac{v_{12}}{v_{10}v_{20}} = \tilde{\rho} \exp\left(-\frac{G_{12}^{dm}}{RT}\right) \quad (21)$$

where $v_{11}=N_{11}/rN$, $v_{22}=N_{22}/rN$, $v_{12}=N_{12}/rN$ and

$$v_{10} = \frac{x_1}{r} - 2v_{11} - v_{12} \quad (22)$$

and

$$v_{20} = \frac{x_2}{r} - 2v_{22} - v_{12} \quad (23)$$

where x_1 and x_2 are the mole fractions of the two compounds. The contribution to the chemical potential is:

$$\frac{\mu_i^H}{RT} = \frac{1}{RT} \left(\frac{\partial G_H}{\partial N_i} \right)_{T,P,N_j,\tilde{v},\{N_{ij}\}} = r_i v_{dm} - \ln \frac{x_i}{x_i - 2rv_{ii} - rv_{12}} \quad (24)$$

where \tilde{v} is the reduced molar volume. The total number of dimers per mol of segments in the system is:

$$v_{dm} = v_{11} + v_{22} + v_{12} \quad (25)$$

2.3 The NRHB model

According to the Non Random Hydrogen Bonding theory^{11,12}, the molecules are distributed in a three-dimensional quasi lattice, with a lattice coordination number, z , which contains N_r sites, N_0 of which are empty. Each molecule of type i occupies r_i sites and it is characterized by three scaling constants (pure fluid parameters) and one geometric, or surface-to-volume-ratio factor, s . The first two scaling constants, ε_h^* and ε_s^* , are used for the estimation of the mean interaction energy per molecular segment, ε^* , according to the following equation:

$$\varepsilon^* = \varepsilon_h^* + (T - 298.15) \varepsilon_s^* \quad (26)$$

while the third scaling constant, $v_{sp,0}^*$, is used for the estimation of the close packed density, $\rho^* = 1/v_{sp}^*$, through the following equation:

$$v_{sp}^* = v_{sp,0}^* + (T - 298.15)v_{sp,1}^* \quad (27)$$

The hard-core volume per segment, v^* , is constant and equal to $9.75 \text{ cm}^3 \text{ mol}^{-1}$ for all fluids. Parameter $v_{sp,1}^*$ in equation (27) is treated as a constant for a given homologous series. Finally, the shape factor, which is defined as the ratio of molecular surface to molecular volume, $s = q/r$, is calculated from the UNIFAC group contribution method.¹¹ The equation of state of the model is given by^{11,12}:

$$\tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) - \tilde{\rho} \left(\sum_i \phi_i \frac{l_i}{r_i} - v_{dm} \right) - \frac{z}{2} \ln \left(1 - \tilde{\rho} + \frac{q}{r} \tilde{\rho} \right) + \frac{z}{2} \ln \Gamma_{00} \right] = 0 \quad (28)$$

while the chemical potential for component i is calculated by the following equation¹²:

$$\begin{aligned} \frac{\mu_i}{RT} = & \ln \frac{\phi_i}{\omega_i r_i} - r_i \sum_j \frac{\phi_j l_j}{r_j} + \ln \tilde{\rho} + r_i (\tilde{v} - 1) \ln(1 - \tilde{\rho}) - \frac{z}{2} r_i \left[\tilde{v} - 1 + \frac{q_i}{r_i} \right] \\ & \ln \left[1 - \tilde{\rho} + \frac{q}{r} \tilde{\rho} \right] + \frac{z q_i}{2} \left[\ln \Gamma_{ii} + \frac{r_i}{q_i} (\tilde{v} - 1) \ln \Gamma_{00} \right] + r_i \frac{\tilde{P} \tilde{v}}{\tilde{T}} - \frac{q_i}{\tilde{T}_i} + \frac{\mu_i^H}{RT} \end{aligned} \quad (29)$$

where, l_i and ω_i are characteristic quantities for each pure fluid, while ϕ_i and θ_i are the site and the surface fraction of component i , respectively. Parameters Γ_{00} and Γ_{ii} are non-random factors, which characterize the distribution of empty and molecular sites, respectively. Finally, the parameters $\tilde{T} = T/T^*$, $\tilde{P} = P/P^*$ and $\tilde{v} (= 1/\tilde{\rho} = \rho^*/\rho)$ are the reduced temperature, pressure, and specific volume, respectively. The characteristic temperature, T^* , and pressure, P^* , are related to the mean intersegmental energy by:

$$\varepsilon^* = RT^* = P^* v^* \quad (30)$$

Detailed expressions for the calculation of such parameters can be found in previous studies.^{11,12,36}

For dimerizing molecules, NRHB has three more parameters that are the energy, E_{ij}^{dm} , the volume, V_{ij}^{dm} , and the entropy change, S_{ij}^{dm} , for the formation of a dimer. However, usually the volume change is set equal to zero, so the number of the association parameters are reduced to two without compromising the performance of the model.^{11,12}

3. Results and Discussion

3.1. Pure Fluids

One of the most important steps in applying equation of state models is the estimation of pure fluid parameters. Usually, this task is performed by adjusting model predictions to pure fluid experimental data, such as vapor pressures of liquids and saturated liquid densities. However, as already mentioned^{38,39}, such procedure may result in more than one parameter sets that similarly describe the pure fluid properties, but not all of them can be successfully used for describing properties of binary and multicomponent mixtures. Regarding organic acids, such difficulty may be partially attributed to the dimerization of acids in the vapor phase, which strongly affects properties such as the vapor density or the heat of vaporization. For this reason, the use of experimental data for other properties, such as enthalpies of vaporization and vapor phase compressibility factors has been suggested.^{3,24,29} However, for all hydrogen bonding fluids, such difficulty mainly arises from the fact that the parameters that characterize the strength of the various intermolecular interactions (physical or hydrogen bonding), are highly correlated to each other.^{38,39} Consequently, the estimation of the association (dimerization) parameters (E^{dm} and S^{dm}) for carboxylic acids is probably the most important step towards the parametrization of such fluids. Hopefully, such parameters can be adopted from experimental spectroscopic, calorimetric and volumetric data or ab initio theoretical studies, due to the sound physical base of the model. However, in such an approach the most common problem is the diverse values for the association enthalpy that can be found in literature.^{4,40,41}

Clague and Bernstein⁴⁰, using IR spectroscopy, determined the enthalpy of dimerization of several low molecular aliphatic acids (with one up to five carbon atoms). They found that the dimerization enthalpy remains rather constant, independently of the alkyl group connected to the carboxylic group, since the electron releasing capacity of the alkyl-group increases the proton accepting ability of the carbonyl group, but simultaneously decreases the proton donating ability of the hydroxyl group. The two phenomena tend to cancel each other and, consequently, the (negative of the) enthalpy of dimerization in the vapor phase remains rather constant, around 60 – 65 kJ/mol. Pimentel and McClellan⁴, who collected data from several literature experimental studies, report that hydrogen bonding enthalpies around 30 kJ per mole of hydrogen bonds (consequently a dimerization enthalpy around 60 kJ per mole of dimers is a reasonable approximation) for vapor phase associated acid molecules. In aliphatic acids these values are almost constant regardless of the branching or the length (up to heptanoic acid) of the carbon chain. On the other hand, according to the authors, the most reliable data for liquid stearic acid gives 28 kJ per mole of hydrogen bonds, which is somewhat lower than the reported values for the association in the vapor phase. Murthy and Rao⁴¹ collected data from IR experimental studies and report values between 35-62 kJ mol⁻¹ for acetic acid.

Since the hydrogen parameters are of great importance, the NRHB association parameters for carboxylic acids were estimated first. In accordance with the aforementioned literature studies, the association (dimerization) parameters (E^{dm} and S^{dm}) of the NRHB theory were kept constant for low molecular weight carboxylic acids, while the association enthalpy was allowed to vary between 50 and 65 kJ per mole of dimers. According to a preliminary investigation, the optimum values of such model parameters were 52.5 kJ mol⁻¹ and 46.2 J mol⁻¹ K⁻¹, for the association enthalpy and entropy, respectively. Subsequently, the rest three pure fluid parameters (scaling constants), \mathcal{E}_h^* , \mathcal{E}_s^* , $v_{sp,0}^*$, were estimated, by fitting the predictions of the NRHB theory to the experimental data and keeping the association parameters equal to the aforementioned values. As mentioned above, the $v_{sp,1}^*$ parameter (see equation (27)) is treated as a constant for a given homologous series and it was set equal to $-0.170 \cdot 10^{-3} \text{ cm}^3 \text{ g}^{-1} \text{ K}^{-1}$ for carboxylic acids.

Initially, the pure fluid scaling constants for acetic acid were estimated using data for saturated liquid densities and vapor pressures (DIPPR correlations⁴²) as well as data for enthalpies of vaporization (experimental data included in DIPPR database⁴²) and vapor phase compressibility factors^{43,44}. For all other acids, saturated liquid densities, vapor pressures and enthalpies of vaporization were used (DIPPR correlations⁴²). The estimated pure fluid parameters for the investigated acids are shown in Table 1 and some characteristic calculations are illustrated in Figures 1-4.

Table 1. NRHB pure fluid scaling constants for carboxylic acids and percentage average absolute deviations¹ (% AAD) from experimental data for vapor pressures, liquid densities and enthalpies of vaporization ($E^{dm} = 52.5 \text{ kJ mol}^{-1}$ and $S^{dm} = 46.2 \text{ J mol}^{-1} \text{ K}^{-1}$ for all acids).

Fluid	Temperature range (K)	\mathcal{E}_h^* (Jmol ⁻¹)	\mathcal{E}_s^* (Jmol ⁻¹ K ⁻¹)	$v_{sp,0}^*$ (cm ³ g ⁻¹)	s	% AAD in P^{sat}	% AAD in ρ^{liq}	% AAD in H^{vap}
Acetic acid	290-538	4527.5	1.5654	0.8494	0.941	1.5	0.5	1.2
Propanoic acid	287-542	4431.7	1.3577	0.8919	0.908	0.4	1.0	2.4
Butanoic acid	286-536	4394.2	1.6826	0.9075	0.888	1.6	1.5	2.0

¹ % AAD = $(100/n) \sum_i \left| (X_i^{cal} - X_i^{exp}) / X_i^{exp} \right|$, where X stands for the property of interest (vapor pressure, P^{sat} , saturated liquid density, ρ^{liq} , and enthalpy of vaporization, H^{vap}) and n is the number of experimental data.

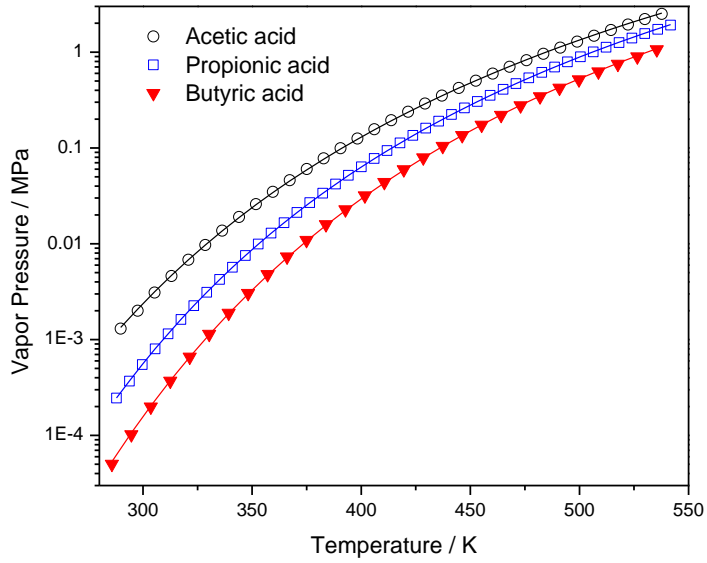


Figure 1. Vapor pressures of acetic, propionic and butyric acid. DIPPR⁴² correlations (symbols) and NRHB calculations (lines).

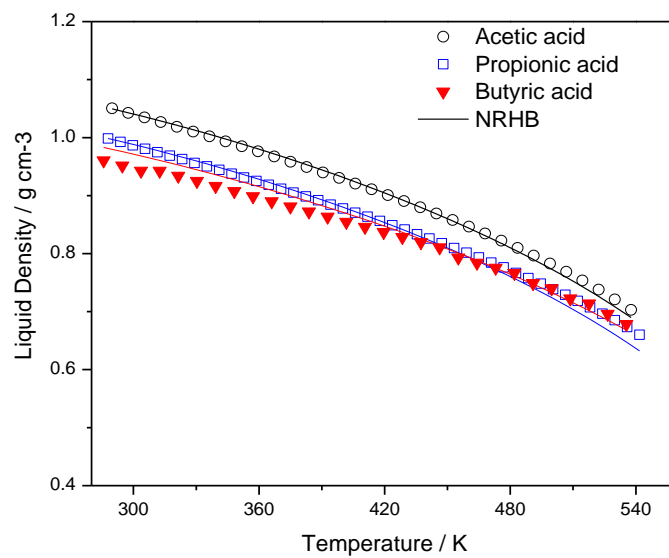


Figure 2. Saturated liquid densities of acetic, propionic and butyric acid. DIPPR⁴² correlations (symbols) and NRHB calculations (lines).

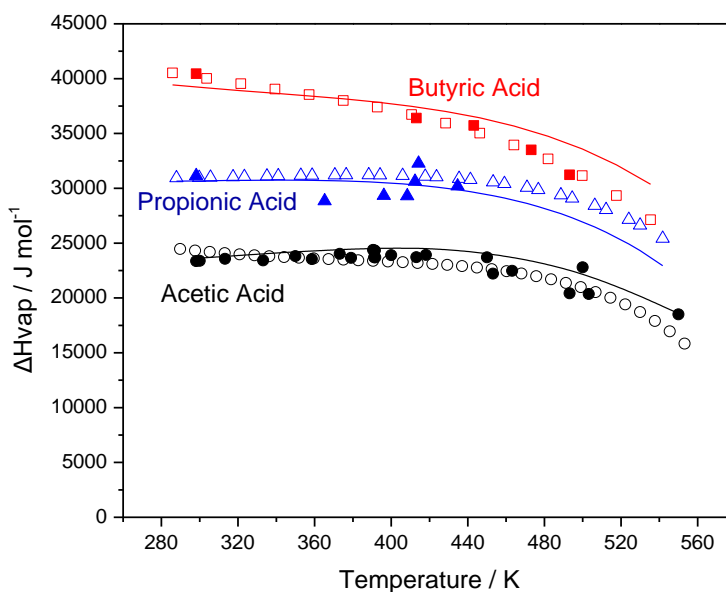


Figure 3. Enthalpies of vaporization for acetic, propionic and butyric acid. DIPPR⁴² correlations (open symbols), experimental data⁴² (solid symbols) and NRHB calculations (lines).

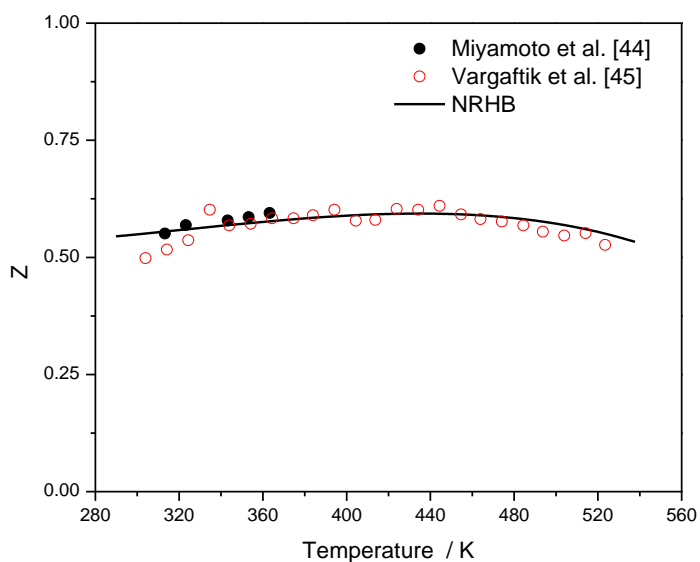


Figure 4. Acetic acid compressibility factors for saturated vapor. Experimental data (symbols)^{44,45} and NRHB calculations (line).

As presented in Figures 1 and 2, the NRHB model satisfactorily describes the vapor pressure and saturated liquid densities. However, as already mentioned, the dimerization in the vapor phase strongly affects properties such as the vapor densities (or equivalently the vapor phase compressibility factors) and the heats of vaporization, which are satisfactorily described by the NRHB model, as shown in Figures 3 and 4. The model presents a maximum in the compressibility factors curve (Figure 4), which is also shown by the experimental data. Here it is worth mentioning that such low molecular weight acids present a large deviation from ideal gas behavior (Z significantly deviates from unity) due to strong dimerization even at low pressures and even below 1 atm.³

It is worth mentioning that the heat of vaporization and the compressibility factors are not satisfactorily described if the formation of dimers is not accounted for, in accordance with previous literature studies.^{3,29} This is clearly shown in Figure 5, where the NRHB calculations are compared with the literature data for two cases: modeling acetic acid assuming a hydrogen bonding behavior similar to that of alcohols (one proton donor and one proton acceptor on every molecule that are able to cross associate and form oligomers), which is a frequently used approach²⁵, and restricting the formation of hydrogen bonds to the formation of cyclic dimers. When the formation of linear oligomers is assumed, the model cannot satisfactorily describe the enthalpies of vaporization, in agreement with a previous study²⁹. In that case, the model predictions are closer to the enthalpies of vaporization of 2-propanol, which can be considered as an associating homomorph of acetic acid, which does not form cyclic dimers. Consequently, the difference in the calculated heat of vaporization between the two modeling approaches is mainly attributed to the existence of dimerized molecules in the vapor phase.

As shown in Figure 6, the dimerization is significant even at low pressures or high temperatures. From this figure it is clear that the model predicts a non-negligible fraction of dimerized molecules in the vapor phase in agreement with the trend shown by the literature data⁴⁶ and other models, such as the association scheme proposed by Janecek and Paricaud²⁹, who mention that the part of molecules in non-bonded state and the fraction of molecules bonded in cyclic dimers is higher in the vapor phase. It is worth mentioning here that the used literature data⁴⁶ were obtained assuming only monomers and dimers in the vapor phase, which, seems to be a reasonable approximation⁶¹⁻⁶³.

At the same time, as also shown in Figure 6, the model predicts a liquid phase (the part of the curve at low temperatures in Figure 6) that mostly contains associated molecules. According to the model of Janecek and Paricaud²⁹, chain oligomers dominate in the liquid state of acetic acid. Kamath et al.⁵ have conducted molecular simulation studies and suggest that hydrogen bonding between hydroxyl groups is possible, but it occurs with much less frequency than between hydroxyl and carbonyl groups. Also, neutron scattering experimental data obtained from the same group show that there are exactly four atoms within a radius of 2.12 Å from the hydroxyl hydrogen, which suggests a planar dimer structure⁵. Nevertheless, at this point more detailed experimental data are needed in order to achieve a more physically correct representation of the liquid-phase structure.

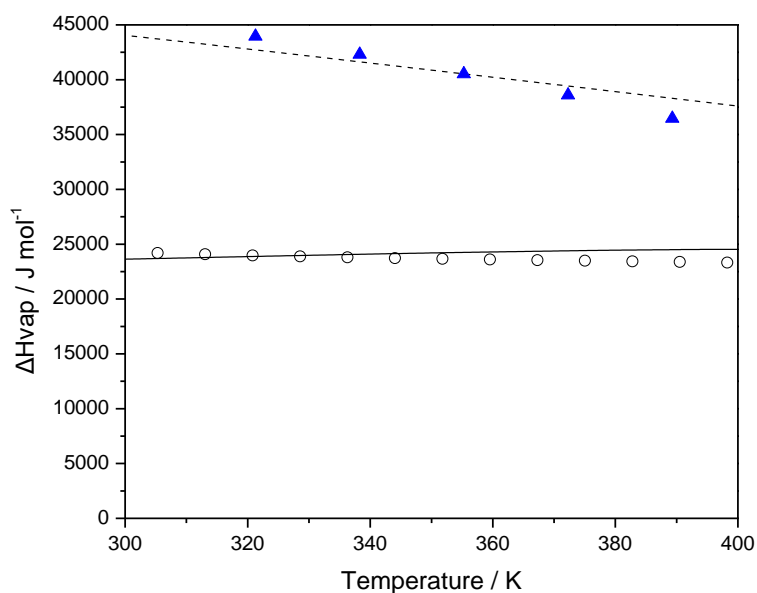


Figure 5. Enthalpy of vaporization for acetic acid. DIPPR⁴² correlations (open symbols) and NRHB calculations (lines) using two modeling approaches: assuming the formation of cyclic dimers (solid line) and the formation of linear oligomers (dash line). The DIPPR⁴² correlations for the enthalpy of vaporization of 2-propanol is also shown (solid symbols).

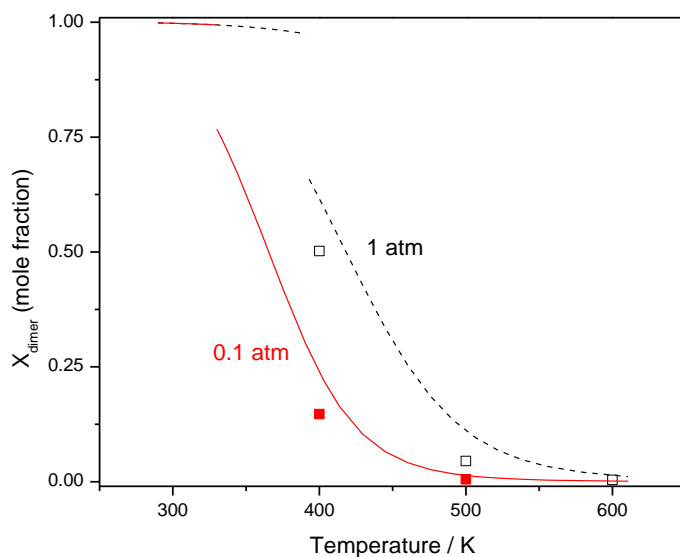


Figure 6. Fraction of dimers for acetic acid at low pressures. Literature data⁴⁶ (points) and NRHB calculations (lines).

3.2. Binary Mixtures

Having the NRHB parameters for pure fluids, the model can be used to predict thermodynamic properties of mixtures, including phase equilibria and thermal properties. As already mentioned, the accurate prediction of thermal properties, which are usually not investigated when testing thermodynamic models, is the recommended way in order to check if the various intermolecular interactions are properly accounted for and, as it will be revealed next in this section, allows the drawing of interesting conclusions for the interplay between various types of molecular interactions, which are not easily revealed by experimental measurements. The latter is feasible since the NRHB model permits the calculation of separate contributions to the enthalpies of mixing, namely, from hydrogen bonding and physical (non-hydrogen bonding: dispersion and polar) interactions.

Next, the NRHB model will be used to describe the enthalpies of mixing for binary systems of organic acids and inert solvents and in mixtures of two carboxylic acids using the acids' parameters obtained in this study and parameters for the rest of the fluids from literature.^{21,22,32,33} All correlations shown in Figures 7-14 were performed using one temperature independent binary interaction parameter, k_{ij} , which is presented in Table 2. However, as presented in Figures 7-9, most often such experimental data are in fair

agreement with each other and sometimes the temperature dependence of the reported excess enthalpies is not easily revealed.

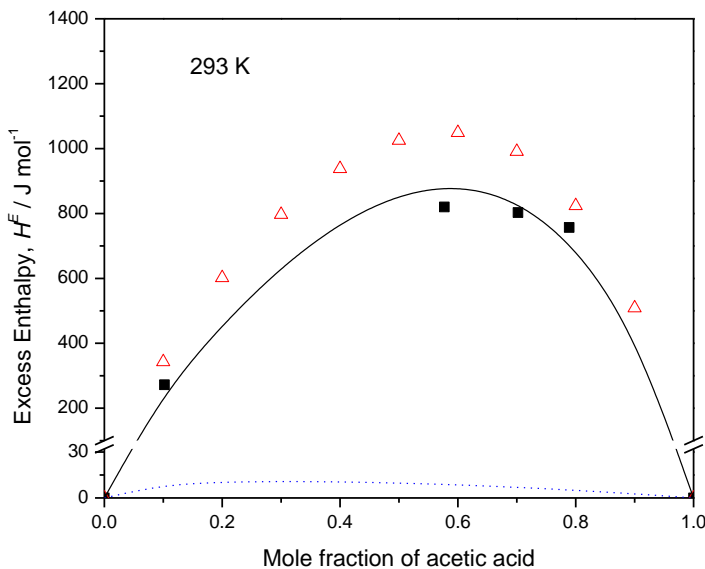


Figure 7. Excess enthalpies for the acetic – *n*-heptane mixture. Experimental data^{47,48} (points) and NRHB calculations (lines). The solid lines correspond to the total property, while the dotted lines to the hydrogen bonding contribution.

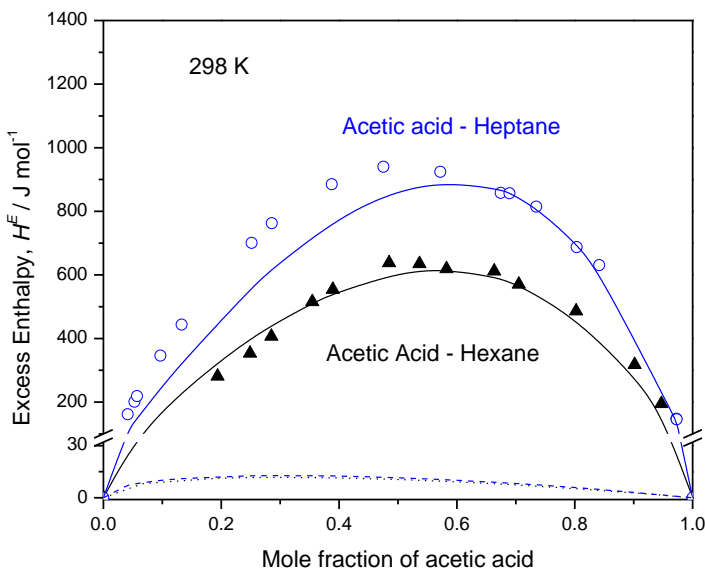


Figure 8. Excess enthalpies for acetic acid – *n*-hexane and acetic acid – *n*-heptane mixtures. Experimental data⁴⁹ (points) and NRHB calculations (lines). The solid lines correspond to the total property, while the dotted lines to the hydrogen bonding contribution.

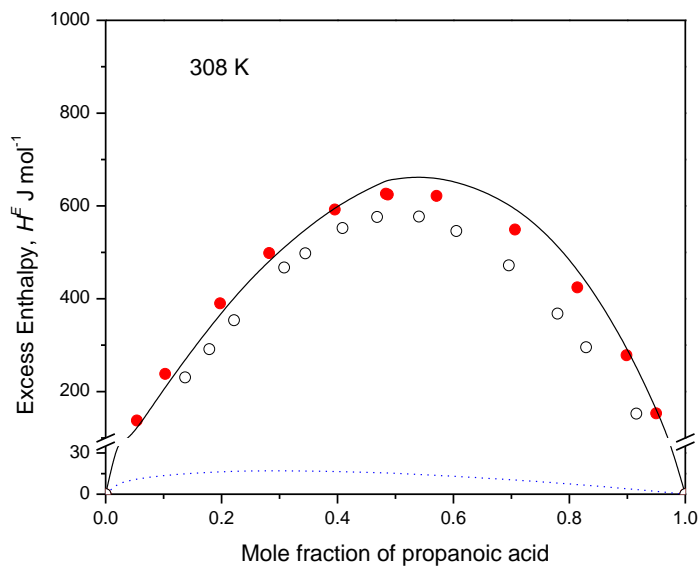
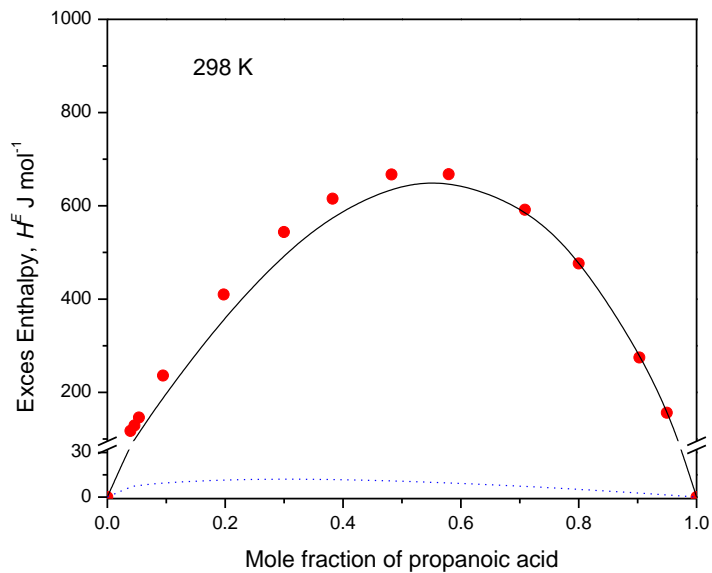


Figure 9. Excess enthalpies for the propanoic acid – *n*-heptane system. Experimental data^{50,51} (points) and NRHB calculations (lines). The solid lines correspond to the total property, while the dotted lines to the hydrogen bonding contribution.

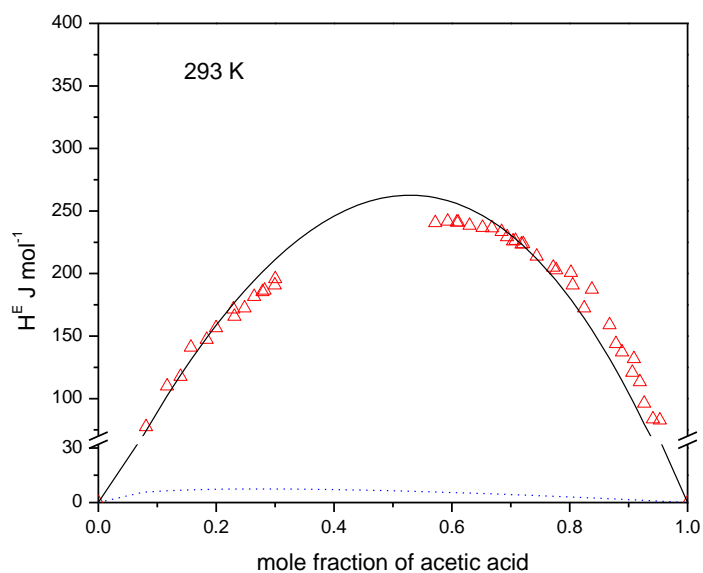


Figure 10. Excess enthalpies for the acetic acid – carbon tetrachloride system. Experimental data^{52,53} (points) and NRHB calculations (lines). The solid lines correspond to the total property, while the dotted lines to the hydrogen bonding contribution.

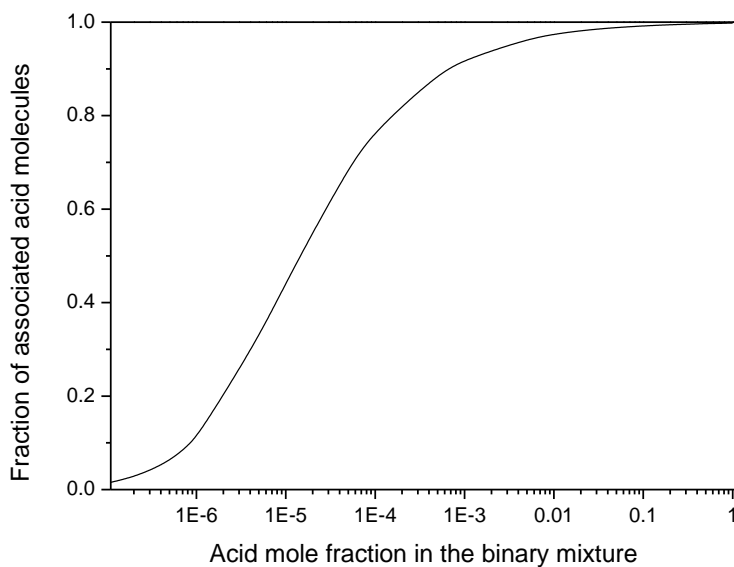


Figure 11. Fraction of associated acid molecules in the propanoic acid – *n*-heptane binary mixture at 313 K.

Nevertheless, the available experimental data for the heats of mixing of low molecular weight carboxylic acids with hydrocarbons show that the mixing is an endothermic process. Such behavior is rather expected and is usually attributed to the hindering of hydrogen bonding and the weakening of dipole – dipole interactions between acid molecules as more hydrocarbon molecules are added to the system. However, one cannot easily tell to which extent the various contributions from intermolecular forces affect the measurable property (heat of mixing). To answer such question, the NRHB model was applied to predict the separate contributions, from hydrogen bonding and from physical (polar and dispersive) intermolecular interactions, to the total values of mixing enthalpies. As shown in Figures 7-10, the model predicts that the hydrogen bonding contribution is positive (endothermic), which means that some hydrogen bonds break upon mixing with inert hydrocarbon molecules, but such contribution is very small compared to the contribution from physical interactions. In other words, the acid molecules are strongly associated in the liquid state and the number of the hydrogen bonded molecules is not significantly altered by the addition of an inert solvent. This is clearly shown in Figure 11, where the predictions of the model for the fraction of associated acid molecules versus the mole fraction of the acid in the binary mixture is presented for propanoic acid – *n*-heptane system. Furthermore, as shown in Figure 12, where the hydrogen bonding contribution to the total excess enthalpy ratio for propanoic acid – *n*-heptane mixture is presented, the contribution of hydrogen bonding becomes significant only in very dilute mixtures.

As shown in Figure 8, where the excess enthalpies of the acetic acid – *n*-hexane and acetic acid – *n*-heptane systems are compared, higher values are observed for the mixture with *n*-heptane. As the size of the hydrocarbon molecule increases, the hindering of the physical interactions (dispersive and polar) between acid molecules becomes more pronounced. This behavior is well described by the NRHB model.

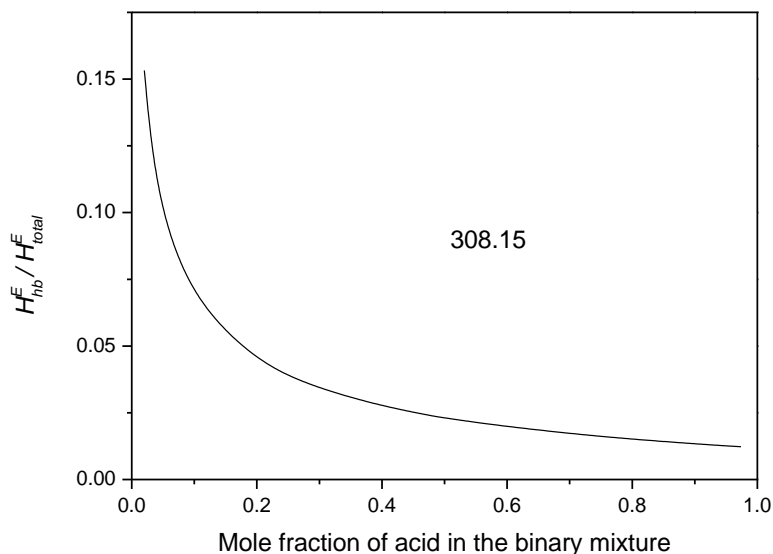


Figure 12. The ratio of the hydrogen bonding component to the total excess enthalpy for propanoic acid – *n*-heptane mixture at 308.15 K.

Next, the model was applied to describe the excess enthalpies of binary mixtures that contain two carboxylic acids. In all cases the hydrogen bonding parameters for the cross association interactions were considered equal to those for self association interactions. The results, which are compared with the limited experimental data that are available in the literature, are shown in Figures 13 and 14. From such figures it can be seen that in systems of two organic acids, the heats of mixing are positive, which means that the mixing is an endothermic process. According to the NRHB model, in mixtures of two acids, the hydrogen bonding contribution to the total excess enthalpy is very small (dotted lines in Figure 13). This behavior is rather expected, since, as already mentioned above, the dimerization enthalpy is rather constant for low molecular weight organic acids. Consequently, the addition of another acid results in a decrease of the self-association interactions, but, at the same time, more cross-association interactions occur in the system. In other words, upon addition of another acid, dimers of molecules of the same kind break but dimers consisting of molecules of different kind appear in the system. As shown by the calculations, the net effect of such rearrangement of hydrogen bonds is an insignificant contribution to the total enthalpies of mixing. This conclusion is further supported by the

vapor-liquid equilibrium (VLE) behavior of such binary mixtures, which present relatively strong hydrogen bonding behavior, but, at the same time, present a VLE phase diagram that resembles the behavior of ideal systems (Figure 15). As already known, the appearance of such VLE phase diagram, alone, indicates that the cross- intermolecular interactions are almost as strong as the interactions between molecules of the same kind.

However, the comparison of Figures 13 and 8 reveals another interesting phenomenon. The enthalpies of mixing in systems with two acids are almost one order of magnitude lower than the corresponding ones for mixtures of acids with hydrocarbons (*n*-hexane can be considered as a non-associating and non-polar homomorph of butanoic acid). Having in mind the small contribution of dimerization to the heats of mixing, the lower values that are observed can be attributed to the acid dipole-dipole interactions. Such intermolecular forces are significantly hindered in mixtures of acids with hydrocarbons, as the molecules of the non-polar inert solvent are placed between acid species (monomers and dimers).

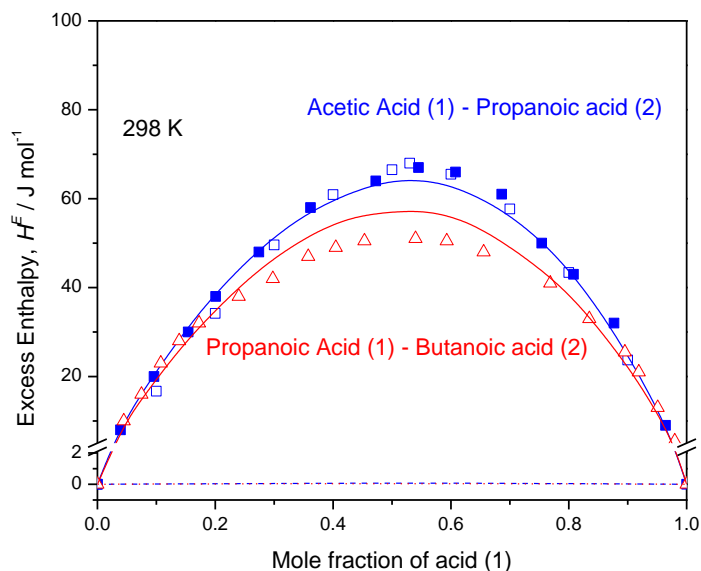


Figure 13. Excess enthalpies for the mixtures of acetic acid – propanoic acid and for propanoic acid – butanoic acid systems. Experimental data⁵⁴ (points) and NRHB calculations (lines). The solid lines correspond to the total property, while the dotted lines to the hydrogen bonding contribution.

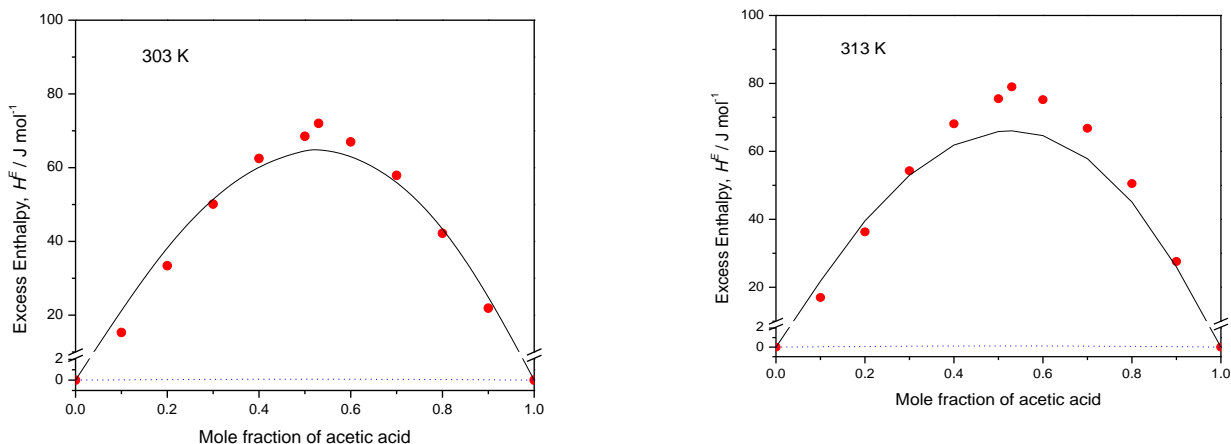


Figure 14. Excess enthalpies for the acetic acid – propanoic acid mixture. Experimental data (points)⁵⁵ and NRHB calculations (lines). The solid lines correspond to the total property, while the dotted lines to the hydrogen bonding contribution.

As mentioned above, all calculations of the excess enthalpies were performed using one temperature independent binary interaction parameter, k_{ij} (Table 2), which was optimized by the available H^E experimental data. It was observed that the calculated values of the excess enthalpy were very sensitive to small changes of such binary parameter. Usually, when testing thermodynamic models, the binary parameters are adjusted solely to phase equilibrium data, neglecting the thermal properties. It is then often observed that the model fail to satisfactorily describe the enthalpies of mixing, although the phase behavior, and especially the VLE, is accurately correlated. Such binary model parameter reflects a correction for the strength of cross- intermolecular physical (non-hydrogen bonding) interactions and, consequently, the calorimetric data are, probably, the most appropriate data for its optimization. Optimization of the binary parameters solely to phase equilibrium and especially VLE data may result in accurate correlations for this property, but may effectively hide limitations of the model.

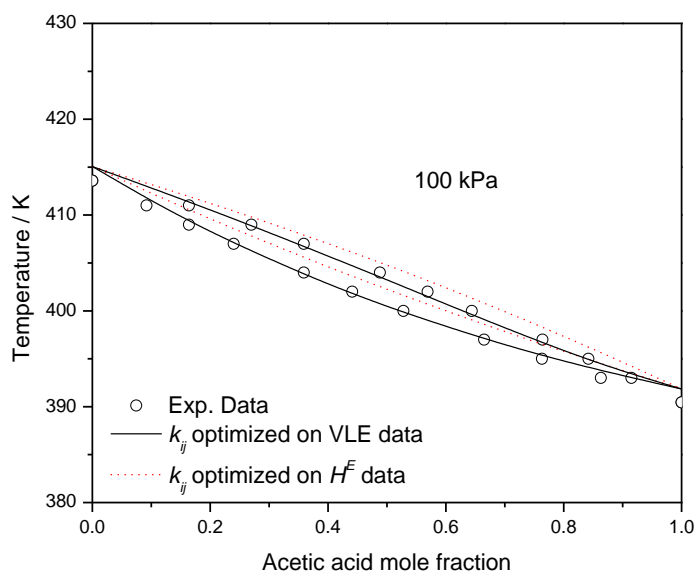
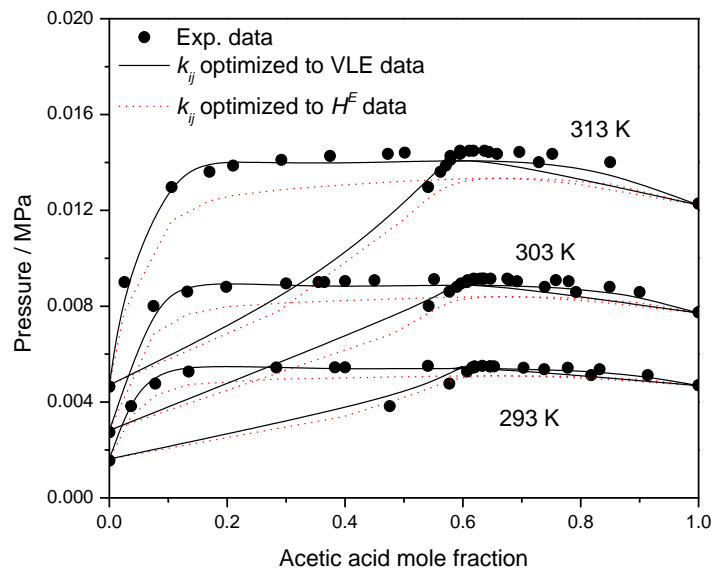


Figure 15. VLE for acetic acid – propanoic acid. Experimental data⁵⁶ (points) and NRHB calculations (lines).

Consequently, in order to evaluate if the calculated binary parameters, which were optimized to H^E data, are appropriate also for VLE calculations, the vapor liquid equilibrium was estimated for systems for which data are available. All the estimated binary parameters are shown in Table 2 and representative results are presented in Figures 15 and 16. It was observed that the values of the binary interaction parameters obtained from VLE data are close to the values that were estimated using only excess enthalpy data. As shown in Figures 15 and 16, the binary interaction parameters that were optimized using solely excess enthalpy data give a rather satisfactory description of the vapor – liquid equilibrium, although such calculations do not describe the experimental data as accurately as the parameters optimized by the VLE data.

Table 2. Binary interaction parameters used for the calculations in acid mixtures

System	$1-k_{ij}$ (optimized using H^E data)	$1-k_{ij}$ (optimized using VLE data)
Acetic acid – <i>n</i> -hexane	0.967	0.990
Acetic acid – <i>n</i> -heptane	0.954	0.939
Acetic Acid – carbon tetrachloride	0.986	0.967
Acetic acid – propanoic acid	0.995	0.985
Propanoic acid – <i>n</i> -heptane	0.970	0.965
Propanoic acid – butanoic acid	0.997	0.982



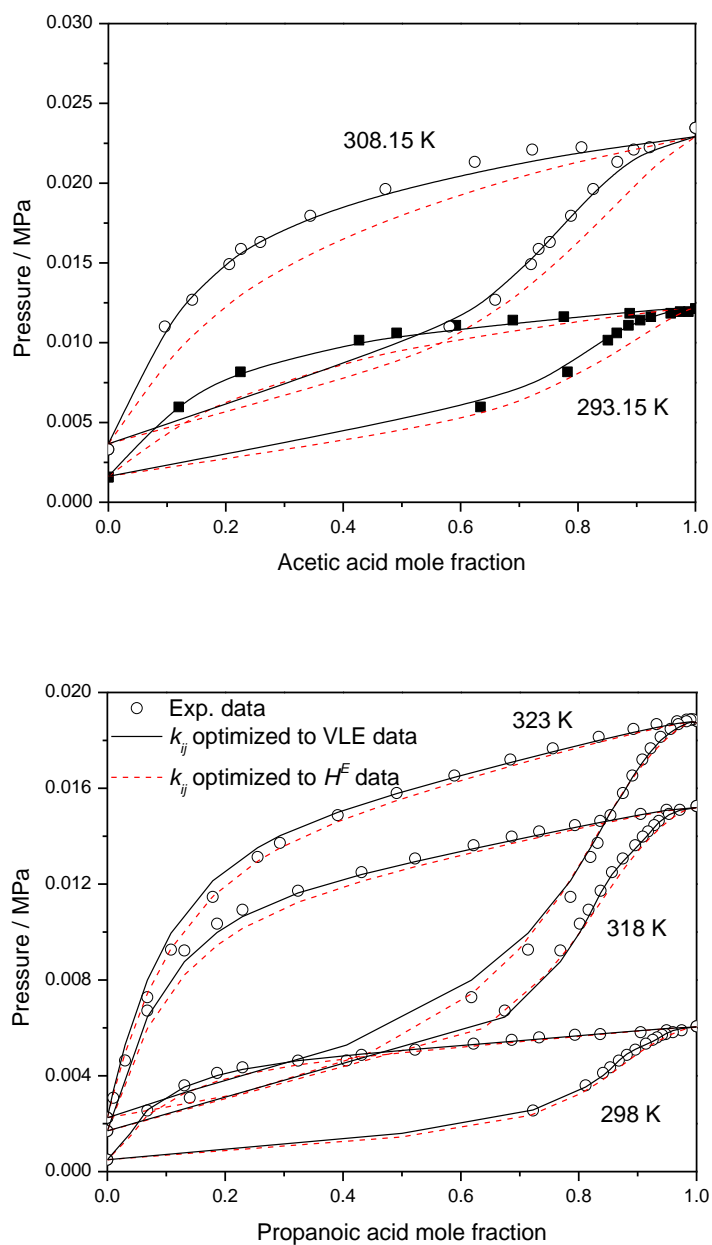


Figure 16. VLE for acetic acid – *n*-heptane (a) and acetic acid – carbon tetrachloride (b), propionic acid – *n*-heptane. Experimental data^{51, 57-60} (points) and NRHB calculations (lines).

4. Conclusions

The association term of the Non-Random Hydrogen-Bonding theory was extended to describe systems with dimerized acid molecules and the model was applied to calculate the thermal

properties, which are usually not considered when evaluating thermodynamic models and the vapor-liquid equilibrium of relevant fluid mixtures. The model permits the calculation of the separate contributions to the mixing enthalpies, namely, from hydrogen bonding and physical (non hydrogen bonding) interactions, while such “deconvolution” of the total property values permits the drawing of interesting conclusions. According to the NRHB model, in mixtures of organic acids with hydrocarbons (inert solvents), the contribution of hydrogen bonding is not significant, since the acid molecules are very strongly associated. Consequently, the endothermic mixing is mainly attributed to the hindering of dispersive and polar interactions between acid molecules upon the addition of inert solvent molecules. Furthermore, in systems with two carboxylic acids the rearrangement of hydrogen bonds due to the formation of cross associating dimers results in an insignificant contribution to the heats of mixing, since the dimerization enthalpy remains rather constant for low molecular weight carboxylic acids, as shown by the relevant experimental data.

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TOC graphic

