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An extensive study of the capabilities and limitations of the CPA and sPC-SAFT equations of state in modeling a wide range of acetic acid properties

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ABSTRACT

The accurate description of many thermodynamic properties of acetic acid and its mixtures can be a challenge to model with standard thermodynamic models like local-composition activity coefficient models and cubic equations of state. A possible solution is offered by association equations of state, e.g. those belonging to the Statistical Associating Fluid Theory (SAFT) family. While several researchers have studied the use of SAFT variants to model acetic acid properties (pure compound and mixtures), with few exceptions, those studies focused exclusively on phase equilibria including vapor pressure and density. Other important properties, such as the speed of sound, second virial coefficient, compressibility factor, enthalpy of vaporization, and the isobaric heat capacity have not been considered yet. Few studies investigate which is the appropriate association scheme to be used for acetic acid. In this work, we compare the capability of two association models, Cubic Plus Association (CPA) and simplified Perturbed-Chain SAFT (sPC-SAFT), to predict a wide range of properties of acetic acid (mixtures) including derivative properties. We evaluate the influence of including one or more of those properties in the parameter estimation procedure for sPC-SAFT, we compare the results obtained with various choices of the association schemes (one or two sites) and finally we evaluate the efficiency of CPA and sPC-SAFT in correlating the phase equilibria of the binary mixtures of acetic acid with water, hexane or ethanol. It is concluded that both equations of state perform overall similarly, with the one-site scheme performing better overall, especially for some properties. The results of the evaluation also show that some properties are inter-correlated in the parameter estimation process making it essentially impossible to obtain sets that can accurately describe all the properties of acetic acid.

INTRODUCTION

Acetic acid plays a very important role in the chemical industry. Despite the simplicity of its chemical formula, the interactions with other molecules make its study complex. The reason for this complexity is that this molecule can exhibit strong hydrogen bonds, forming dimers or higher oligomers in both vapor phase[1,2] and liquid phase.[3]

The thermodynamic properties of acetic acid containing systems can be a challenge to model using standard thermodynamic models and it is hoped that better results may be obtained with association models, such as the SAFT variant models based on the perturbation theory proposed by Wertheim.[4–7] Following the definition of Huang and Radosz,[8] the acetic acid can be modelled using either one site (1A) or two-site (2B) associating scheme. The 1A scheme considers that the molecule has only one "glue-type" association site, allowing the formation of dimers between acetic acid molecules. In the 2B scheme, the molecule has two association sites, allowing the formation of linear oligomer chains.

Many researchers have conducted studies with SAFT variants for modeling acetic acid properties and its mixtures,[8–20] especially using the PC-SAFT and CPA equations of state (EOS).

Huang and Radosz[8] expanded the SAFT framework to describe the vapor pressure and the density of acetic acid, Fu and Sandler[9] correlated the phase equilibria of binary mixtures containing acetic acid. Gross and Sadoski[10] developed the perturbed-chain SAFT (PC-SAFT), and together with other authors[11,15,18,20] obtained excellent results describing the vapor pressure and the density of acetic acid and in correlating phase equilibria. Derawi et al.[12] applied the CPA EOS to carboxylic acids obtaining excellent results predicting the vapor pressure and the density of acetic acid and successfully correlating the phase equilibria of binary mixtures containing acetic acid but the model was only able to represent qualitatively the second virial coefficient. Breil et al.[17] included data of the compressibility factor and the enthalpy of vaporization during the parameter estimation procedure of the CPA pure component parameters to obtain parameters that offered an excellent representation of the vapor pressure, the density, the compressibility factor and the enthalpy of vaporization of the acetic acid and successfully correlated its phase equilibria of binary mixtures.

Table 1 summarizes several relevant studies from recent literature.

Table 1. Application of association models for acetic acid

Ref	Model	Scheme	Application *
Huang and Radosz[8]	SAFT	1A	P_s, ρ
Fu and Sandler[9]	sSAFT, CK-SAFT	1A	P_s, ρ, acetic acid - alcohol/ carboxylic acid/ water VLE
Gross and Sadoski[10]	PC-SAFT	2B	P_s, ρ
Kouskoumvekaki et al.[11]	PC-SAFT	2B	P_s, ρ, acetic acid - water VLE
Derawi et al.[12]	CPA	1A, 2B	P_s, ρ, B, K_2, acetic acid - alkanes VLE
Folas et al. [13]	CPA	1A	acetic acid – water – hexane VLE
Kontogeorgis et al.[14]	CPA	1A, 2B	acetic acid - water/ alcohols VLE
Grenner et al.[15]	sPC-SAFT, NRHB	1A	P_s, ρ, acetic acid - choloroalkanes VLE
Muro-Suné et al.[16]	CPA	1A	P_s, ρ, acetic acid - water/ alkane VLE/LLE, acetic acid - water - hydrocarbons LLE
Breil et al.[17]	CPA-HV	1A	P_s, ρ, B, Z, $Hvap$, acetic acid - water VLE and Relative volatility
Soo[18]	PC-SAFT	1A	P_s, ρ, acetic acid - water/ cycloalkanes/ alcohol/ ketones /alkanes VLE/LLE
Tsivintzelis and Kontogeorgis[19]	CPA	1A	acetic acid - benzoic acid VLE/SLE
Yushu et al.[20]	PC-SAFT	2B	acetic acid - water/ carboxylic acid VLE
Tsivintzelis and Kontogeorgis[21]	CPA-HV	1A	acetic acid – water VLE
Janeček and Paricaud[22,23]	PC-SAFT, PC-SAFTDBD	1A	P_s, ρ, H_{vap}, acetic acid – water VLE
Sum and Sandler[24]	UNIQUAC		acetic acid – water VLE

* P_s is the vapor pressure, ρ is the density, B is the second virial coefficient, K_2 is the dimerization constant, Z is the compressibility factor, H_{vap} is the enthalpy of vaporization, VLE is vapor-liquid equilibrium, LLE is liquid-liquid equilibrium, SLE is solid-liquid equilibrium.

It is clear that, with few exceptions,[12,17] these studies summarized above and in Table 1 only focused on phase equilibria, vapor pressure (P_s) and density (ρ), thus not evaluating the use of SAFT models in predicting other properties, such as the speed of sound (u), second virial coefficient (B), vapor phase compressibility factor (Z), enthalpy of vaporization (H_{vap}), the isobaric heat capacity (C_p) and the influence that the chosen association scheme may have in the representation of the various properties.

In this study, we aim to expand this knowledge by comparing the capability of CPA and the simplified PC-SAFT (sPC-SAFT) to predict or correlate such properties. We also compare the use of both of these equations of state in correlating phase equilibria of acetic acid and its mixtures, and propose new parameter sets for sPC-SAFT, evaluating the influence of including one or more of those properties in the parameter estimation procedure, and finally comparing the model performance with parameter sets that were previously proposed in the literature.

MODELS

PC-SAFT. The PC-SAFT equation of state was proposed by Gross and Sadowski[10,25] and it is based on the theory of Wertheim [4–7] for associating fluids. In this work, the sPC-SAFT proposed by von Solms et al.[26] is used. It is a simplified version only in terms of mixing rules of the original model, which means the pure component parameters are the same. More information of the model can be found in the work of von Solms et al.[26] The sPC-SAFT model is usually presented as the sum of contributions of the Helmholtz free energy expressed as:

$$a^r = a^{hs} + a^{chain} + a^{disp} + a^{assoc} \qquad \text{Equation 1}$$

where a^r is the reduced sum of contribution of the Helmholtz free energy, a^{hs} is the contribution of the hard sphere, a^{chain} is the contribution of the chain formation, a^{disp} is the contribution of the dispersion forces, and a^{assoc} is the association contribution expressed as:

$$a^{assoc} = \sum_i x_i \left[\sum_{A_i} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{M_i}{2} \right]$$ Equation 2

where x_i is the molar fraction of the component i, M_i is the number of association sites of molecule i, and X^{A_i} is the fraction of molecules i at site A not bonded to other active sites, given by Equation 3:

$$X^{A_i} = \frac{1}{1 + \sum_j \sum_{B_j} \rho_j X^{B_j} \Delta^{A_i B_j}}$$ Equation 3

where ρ is the molar density and $\Delta^{A_i B_j}$ is the association strength between site A on molecule i, and site B on molecule j, given by Equation 4:

$$\Delta^{A_i B_j} = \sigma_{ij}^3 g_{ij}^{hs} \kappa^{A_i B_j} \left[\exp\left(\frac{\epsilon^{A_i B_j}}{kT} \right) - 1 \right]$$ Equation 4

where $\epsilon^{A_i B_j}$ and $\kappa^{A_i B_j}$ are the cross-association energy and volume respectively, and g_{ij}^{hs} is the radial distribution function, expressed as:

$$g^{hs} = \frac{1 - \eta/2}{(1 - \eta)^3}$$ Equation 5

where η is calculated by Equation 6, and d is the segment diameter, defined by Equation 7:

$$\eta = \frac{\pi \rho}{6} \sum_i x_i m_i d_i^3$$ Equation 6

$$d_i = \sigma_i \left[1 - 0.12\, exp\left(-\frac{3\epsilon_i}{kT} \right) \right]$$ Equation 7

The parameters for the pair of unlike segments are calculated using the Berthelot-Lorentz combining rule:[25]

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \qquad \text{Equation 8}$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}\left(1 - k_{ij}\right) \qquad \text{Equation 9}$$

where k_{ij} is the binary interaction parameter.

To calculate the cross section energy and area, we have used the near Elliott[27] combining rule given as:

$$\epsilon^{A_i B_j} = \frac{\epsilon^{A_i B_i} + \epsilon^{A_j B_j}}{2} \qquad \text{Equation 10}$$

$$\sigma_{ij}^3 \kappa^{A_i B_j} = \sqrt{\kappa^{A_i B_i} \sigma_{ii}^3 \kappa^{A_j B_j} \sigma_{jj}^3} \qquad \text{Equation 11}$$

CPA. The CPA EOS proposed by Kontogeorgis et al.[28] combines a cubic equation of state for the physical part (e.g. SRK) with the association term from SAFT theory.[28] The CPA EOS for mixtures can be expressed in terms of pressure (P) as:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \rho \frac{\partial \ln g}{\partial \rho}\right) \sum_i x_i \sum_{A_i} (1 - X^{A_i}) \qquad \text{Equation 12}$$

where ρ is the molar density, a is the energy parameter, and b is the co-volume.

The X^{A_i} term is calculated almost in the same way as in PC-SAFT, with the difference that $\Delta^{A_iB_j}$ is now expressed as:

$$\Delta^{A_iB_j} = b_{ij} g_{ij} \beta^{A_iB_j} \left[\exp\left(\frac{\epsilon^{A_iB_j}}{kT} \right) - 1 \right] \quad \text{Equation 13}$$

where $\beta^{A_iB_j}$ is the association volume and g_{ij} is defined by

$$g_{ij} = \frac{1}{1 - 1.9\left(b_{ij}/4V_m\right)} \quad \text{Equation 14}$$

The cross parameters for CPA are calculated by

$$b_{ij} = \frac{b_i + b_j}{2} \quad \text{Equation 15}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right) \quad \text{Equation 16}$$

where k_{ij} is the binary interaction parameter.

To calculate the cross-association energy ($\epsilon^{A_iB_j}$) and the cross-association volume ($\beta^{A_iB_j}$) we have used the near Elliott combining rule[27], which for CPA is given by the following equations:

$$\epsilon^{A_iB_j} = \frac{\epsilon^{A_iB_i} + \epsilon^{A_jB_j}}{2} \quad \text{Equation 17}$$

$$\beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}} \frac{\sqrt{b_i b_j}}{b_{ij}} \quad \text{Equation 18}$$

PROPERTIES EVALUATED

We have in this work evaluated the performance of sPC-SAFT and CPA in predicting the vapor pressure (P_s), density (ρ), speed of sound (u), second virial coefficient (B), compressibility factor (Z), enthalpy of vaporization (H_{vap}) and the isobaric heat capacity (C_p), for the acetic acid considering both the one-site (1A) and two-site (2B) association schemes. The terminology of Huang and Radosz[8] is used for the association schemes.

All sets were evaluated under the same conditions. The saturated pressure (P_s), the density (ρ) and the enthalpy of vaporization (H_{vap}) were evaluated in the temperature range of 293 – 543 K against the data from DIPPR.[29] The speed of sound (u) was evaluated at atmospheric pressure in the temperature range 293 – 353 K against the data from Goodman and Whittenburg[30] that was available at the Dortmund Data Bank.[31] The second virial coefficient was evaluated in the temperature range 410 – 574 K using the data of Bich et al.[32] to fit the virial equation (B_1) and the methodology proposed by Tsonopoulos and Prausnitz[1] (B_2) to obtain its experimental value. The compressibility factor (Z) was evaluated in the temperature range 373 – 503 K, against the data from Freeman and Wilson.[33] The isobaric heat capacity (C_p) was evaluated at the temperature ranges 290 – 380 K. In order to calculate the speed of sound and the isobaric heat capacity is necessary to know the ideal gas heat capacity (C_p^{id}).[34,35] This was taken from the DIPPR[29] correlation that presented a deviation lower than 1% from the experimental points. The relative equations can be found in the literature. [34,35] The number of data points used in the evaluation of each property is respectively, 59, 30, 31, 12, 21, 49 and 11.

Because of its associative nature, the acetic acid has low values for the compressibility factor[33] and quite low negative values for the second virial coefficient.[1,12,36,37] We compared the use of sPC-SAFT and CPA to see if the association theory models can consider these trends.

The values for the compressibility factor were taken from Freeman and Wilson.[33] There is no clear consensus in the literature on how we can determine the experimental value of the second virial coefficient for the acetic acid.[1,2,32,36,37] We have, thus, chosen two approaches for representing the second virial coefficient data.

The first one (B_1) is by fitting the $P\rho T$ data with the "classical" virial equation truncated in the third term. [38,39] In this method we used the data from Bich et al.[32]

$$\frac{P}{RT} = \rho + B(T)\rho + C(T)\rho^2 \qquad \text{Equation 19}$$

The second approach (B_2) considers the relation of the second virial coefficient with the dimerization constant.[1,32,36,37] This approach is better explained elsewhere.[1,32,36,37] A simplified explanation is that at low temperatures, the negative values of the dimerization constant (K_2) can be used to calculate the second virial coefficient through the relation:

$$K_2 = \frac{-B_{exp}}{RT} \qquad \text{Equation 20}$$

Tsonopoulos and Prausnitz[1] proposed a correlation for the dimerization constant for temperatures above 353.15 K:

$$-log_{10}\, K_2(mmHg^{-1}) = 10.1 - \frac{3040}{T} \qquad \text{Equation 21}$$

Combining Equation 20 and 21 it is possible to obtain the pseudo experimental values of the second virial coefficient

The calculated values of the second virial coefficient were obtained numerically by using the $\lim_{P\to 0} \frac{Z-1}{\rho} = B$ and with the $P\rho T$ data of Bich et al.[32]

The deviations of the various properties were calculated using the percentage average absolute deviation, AAD (%):

$$AAD\ (\%) = \frac{1}{N}\sum_{i=1}^{N} \frac{\left|\theta_i^{calc} - \theta_i^{exp}\right|}{\theta_i^{exp}} * 100 \qquad \text{Equation 22}$$

where θ represents the evaluated property (i.e. P_s, u, etc.) and i is the data index.

PARAMETERIZATION

sPC-SAFT has five adjustable parameters: the segment number, m, the segment diameter, σ, the segment energy, ϵ/k, the effective association volume, κ^{AB}, and the association energy, ϵ^{AB}/k. These parameters are often obtained by fitting the data of vapor pressure and density,[10,11,15,25] but this could lead to parameters that may not satisfactorily represent other properties, e.g. sound velocity, second virial coefficient, compressibility factor, enthalpy of vaporization and heat capacity. In this work we evaluated the influence that these properties may have if included in the parameter estimation procedure. This was done by including one or more of those properties in the objective function during the parameter estimation procedure, considering both association schemes (1A and 2B) and both ways of calculating the second virial coefficient as mentioned in the properties evaluated section, this approach has led to many parameter sets. The sets that presented an AAD higher than 10 % in vapor pressure or density where immediately discarded. The remaining sets were evaluated by plotting the AAD of vapor pressure, density, speed of sound, compressibility factor, enthalpy of vaporization, heat capacity and the average between these properties as a pair in a two-dimensional scatterplot matrix.

The scatterplot matrix is created by plotting of the variables on a single page in a matrix format, each row and column defines a single scatterplot. For example, given a set of variables, $A_1, A_2, \dots A_j$, where $A_j \in \{P_s, \rho, u, B, Z, H_{vap}, C_P, their\ average\}$ with A being the AAD of the property and j is the number of variables, the scatterplot matrix will have $j-1$ rows and $j-1$ columns, and the ith row and jth column of this matrix is a plot of deviations in A_i versus deviations in A_j. More details are referred to the reference. [40] The same methodology was applied to the parameters obtained. This was done in order to try to identify a correlation between them and/or the average of the properties.

Objective function and minimization procedure. The objective function used to fit the data was the sum of the AAD (%) of the evaluated properties:

$$Fobj = \frac{\varphi^{P_s}}{N_{P_s}}\sum_{i}^{N_{P_s}}\left|\frac{P_{s_i}^{calc} - P_{s_i}^{exp}}{P_{s_i}^{exp}}\right| + \frac{\varphi^{\rho}}{N_{\rho}}\sum_{i}^{N\rho}\left|\frac{\rho_i^{calc} - \rho_i^{exp}}{\rho_i^{exp}}\right| + \frac{\varphi^{u}}{N_{u}}\sum_{i}^{N_u}\left|\frac{u_i^{calc} - u_i^{exp}}{u_i^{exp}}\right| + \frac{\varphi^{B}}{N_{B}}\sum_{i}^{N_B}\left|\frac{B_i^{calc} - B_i^{exp}}{B_i^{exp}}\right| + \frac{\varphi^{Z}}{N_{Z}}\sum_{i}^{N_Z}\left|\frac{Z_i^{calc} - Z_i^{exp}}{Z_i^{exp}}\right| + \frac{\varphi^{Hvap}}{N_{H_{vap}}}\sum_{i}^{N_{H_{vap}}}\left|\frac{Hvap_i^{calc} - Hvap_i^{exp}}{Hvap_i^{exp}}\right| + \frac{\varphi^{Cp}}{N_{Cp}}\sum_{i}^{N_{Cp}}\left|\frac{Cp_i^{calc} - Cp_i^{exp}}{Cp_i^{exp}}\right|. \quad \text{Equation 23}$$

where $\varphi^j, j \in \{P_s, \rho, u, B, Z, H_{vap}, C_P\}$ represents a binary variable, which can assume 0 or 100, depending on the response variable considered in the minimization of the objective function. For P_s and ρ, φ^j is always 100. $N_{P_s}, N_\rho, N_u, N_B, N_Z, N_{H_{vap}}$ and N_{C_P} are the number of experimental points for vapor pressure, density, speed of sound, second virial coefficient, compressibility factor, enthalpy of vaporization and isobaric heat capacity, respectively. And i is the evaluated experimental data point.

The minimization procedure used was the particle swarm optimization (PSO) [41] which is very simple to implement and is commonly used in the optimization of nonlinear problems. This algorithm is described elsewhere.[42–44]

The upper and lower limits of parameters considered in PSO are presented in Table 2. This range was chosen based on the literature cited on Table 1 as well as our preliminary results estimating parameters with the PSO for the acetic acid pure component parameters sets, where we increased the search range for the optimum parameters when the estimation led to multiple values very close or at one of the imposed parameter search limits.

Table 2. Upper and lower limits used in the particle swarm settings during the estimation for the pure component parameters.

	m	σ	ϵ/k	κ^{AB}	ϵ^{AB}/k	N_p[a]	N_i[a]
Upper Limit	4	4	400	1	9000	80	60
Lower Limit	2	2	100	1e-6	1000	40	20

[a] N_p and N_i, are the number of particles and number of interactions, respectively. Its upper limit represents the values used during the parameter estimation of the model and the lower limit represents the values used during the estimation of the binary interaction parameter

Binary interaction parameter. To fit the binary interaction parameter (k_{ij}) for vapor-liquid equilibrium calculations, we used as the objective function the percentage average absolute deviation in the temperature or in the pressure plus the deviation in the relative volatility between water and acetic acid (α), as shown below:

$$ObjF_T = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|T_i^{calc} - T_i^{exp}\right|}{T_i^{exp}} * 100 + \frac{1}{N}\sum_{i=1}^{N}\frac{\left|\alpha_i^{calc} - \alpha_i^{exp}\right|}{\alpha_i^{exp}} * 100 \qquad \text{Equation 24}$$

$$ObjF_P = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|P_i^{calc} - P_i^{exp}\right|}{P_i^{exp}} * 100 + \frac{1}{N}\sum_{i=1}^{N}\frac{\left|\alpha_i^{calc} - \alpha_i^{exp}\right|}{\alpha_i^{exp}} * 100 \qquad \text{Equation 25}$$

RESULTS

New sets. Various parameter sets were obtained for the pure acetic acid using sPC-SAFT. The results of the AAD (%) for all the evaluated properties with the different sets were plotted as a pair in a two-dimensional scatter plot matrix. A similar representation was done for the obtained parameter sets and the average of the cited properties. This is presented in Figures 1 and 2.

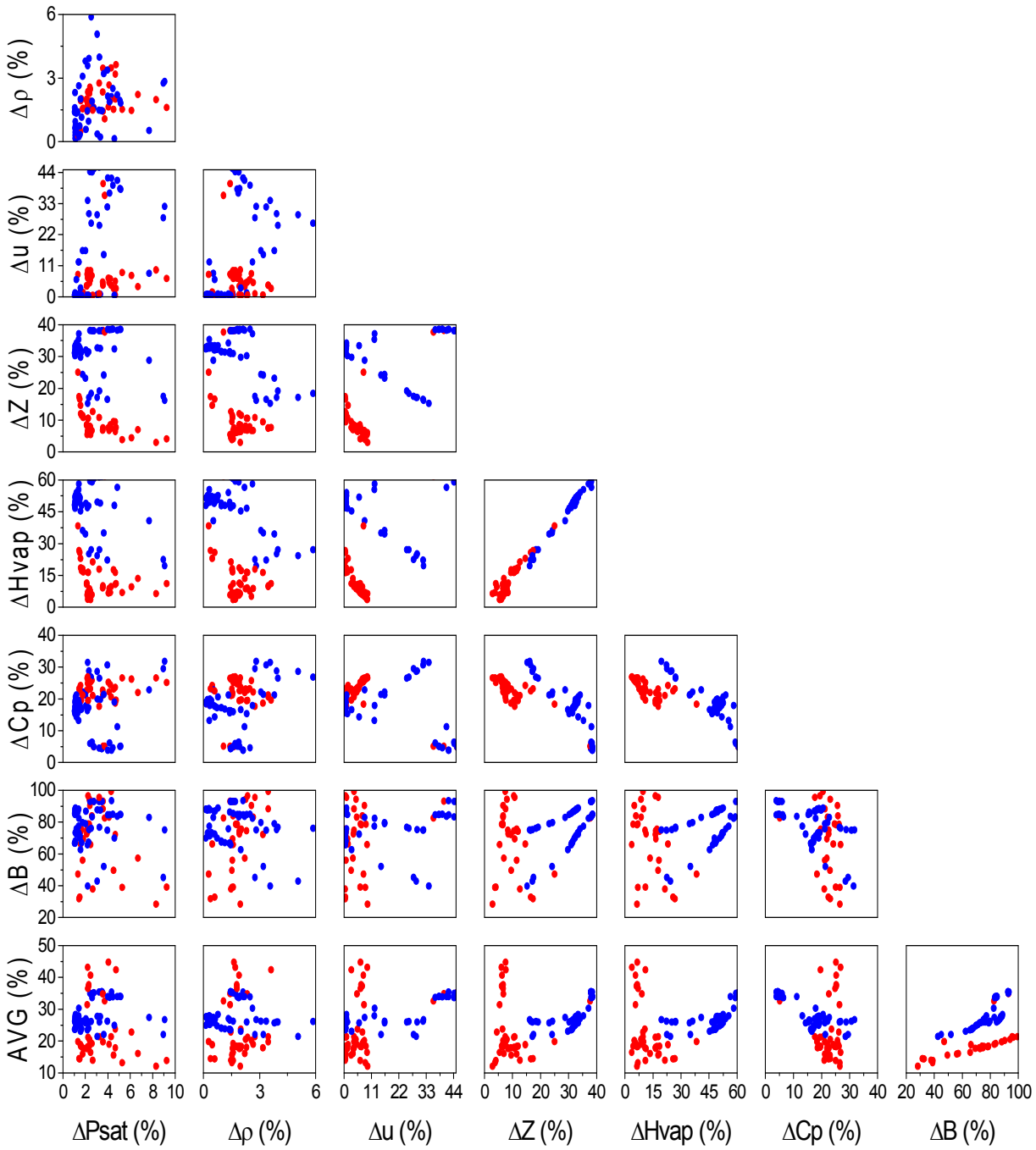

Figure 1. Two-dimensional scatter plot matrix of the AAD (%) for vapor pressure (P_s), density (ρ), speed of sound (u), compressibility factor (Z), enthalpy of vaporization (H_{vap}), heat capacity (C_p), second virial coefficient (B) and their average (AVG), plotted as a pair. Results are for the sets obtained for sPC-SAFT. X,Y-axis units are in %. ●Results for the 1A scheme; ●Results for the 2B scheme

From the analysis of Figure 1 it is possible to see that some properties are inter-correlated.

The deviations of the enthalpy of vaporization and of the compressibility factor have the same behavior. This means that it is not necessary to use both of these properties in the parameter estimation procedure and that if a set is able to predict one of these properties, it will also predict the other. This result may be expected since we excluded parameter sets with high deviations in vapor pressure or liquid density, and the model correlates well the ratio enthalpy of vaporization over variation in volume in the vaporization.

The speed of sound seems to have an inverse relation with the enthalpy of vaporization making it impossible for the model to describe both properties with the same pure component parameters. Besides, the model will not be able to predict the isobaric heat capacity together with the other properties.

The analysis of the scatter pattern of the deviations for P_s and ρ also shows that both association schemes can lead to sets that have a good prediction for these two properties, with the 2B scheme having the lowest deviation for the two properties. The lower average deviations are obtained with the use of the 1A scheme and this scheme is the recommended if a single parameter set will be used to correlate several properties simultaneously.

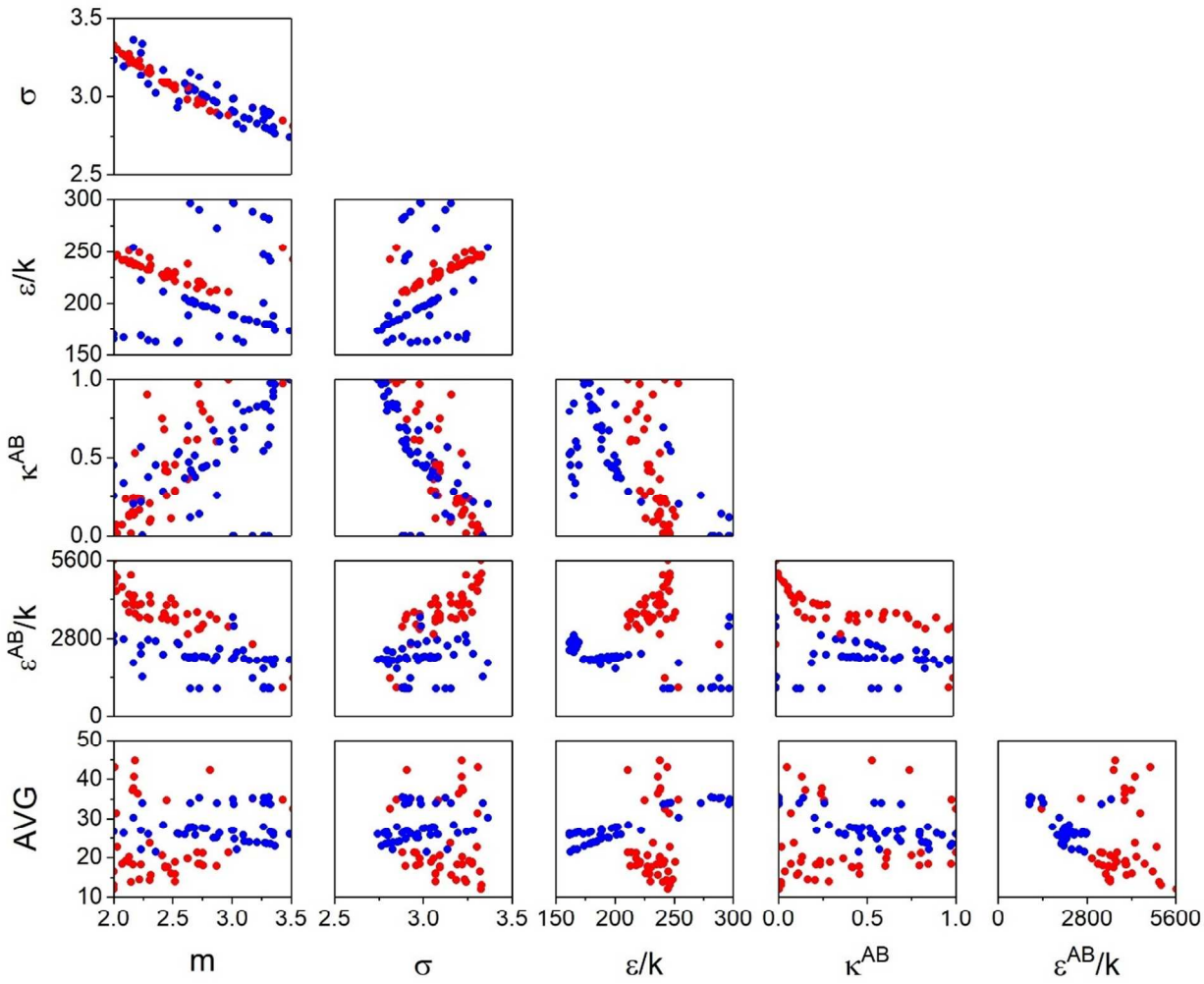

Figure 2. Scatter plot of each pair of parameters and average of the evaluated properties with the different sets obtained for sPC-SAFT. ●Results for the 1A scheme; ●Results for the 2B scheme

The analysis of Figure 2 shows that the parameters that can lead to better results with the 1A scheme are in the 5000 – 5600 K range of the association energy, getting closer to the experimental values reported for the association energy of the acetic acid[17] meaning that the 1A scheme used in the evaluated models is theoretically more correct compared to the 2B scheme, at least for pure acetic acid, but this does not necessarily mean that all the properties will be accurately represented. The better results were obtained with scheme 1A and m about 2, σ about 3.3 Å, ε/k about 240 K and low κ^{AB}. It was possible to identify some clear correlations between

the parameters (i.e. σ x m or σ x κ^{AB}) this are expected results as the van der Walls volume is proportional to $m\sigma^3$ and should be constant in the optimal parameters. Because of these reasons, we conclude that it is impossible to obtain a single pure compound parameter set to represent all the properties of acetic acid. This is especially the case because a lower AAD for the compressibility factor, enthalpy of vaporization and heat capacity can lead to parameters that cannot describe the vapor pressure or/and the density satisfactorily.

In the absence of a clear set to use, the sets presented in this work were chosen among those showing the lowest deviation average between vapor pressure, density, speed of sound, compressibility factor, enthalpy of vaporization and heat capacity, and presented deviations lower than 2% in vapor pressure and density. With these conditions, the most successful sets, for both schemes, were the ones fitted using the data from DIPPR[29] for vapor pressure and density, in the temperature range of 0.5-0.97 T_r, and the data for the speed of sound from the Dortmund Data Bank.[31]

In the next section, these new sets are presented together with sets that were available in the literature for both sPC-SAFT and CPA. All sets used are shown in Table 3 and 4.

Pure properties evaluation. In this work, several sets of parameters for the acetic acid were evaluated using PC-SAFT and CPA. They are presented in Table 3 and 4 and were named as follows (TW = this work = new parameter sets estimated in this work):

- For the acetic acid using the 2B scheme – PC-SAFT 2B1,[10] PC-SAFT 2B2,[11] PC-SAFT TW 2B(new), CPA 2B;[12]
- For the acetic acid using the 1A scheme – PC-SAFT 1A1,[18] PC-SAFT 1A2,[15] PC-SAFT TW 1A(new), CPA 1A1,[12] CPA 1A2,[17] CPA 1A3,[17]

Table 3. Pure component parameters set for sPC-SAFT

Sets	m (-)	σ (Å)	ϵ/k (K)	κ^{AB} (-)	ϵ^{AB}/k (K)	Scheme	Ps / ρ T_r range	ref
PC-SAFT 2B1	1.340	3.858	211.6	0.075	3044	2B	0.51-0.99	10
PC-SAFT 2B2	2.342	3.185	199.9	0.260	2456	2B	0.51-0.96	11
PC-SAFT 1A1	1.983	3.309	238.8	0.001	7133	1A	0.50-0.98	18
PC-SAFT 1A2	1.503	3.701	286.1	0.007	5248	1A	0.51-0.91	15
PC-SAFT TW 2B	2.689	3.041	201.5	0.376	2187	2B	0.50-0.97	TW
PC-SAFT TW 1A	2.220	3.233	248.7	0.165	3543	1A	0.50-0.97	TW

Table 4. Pure component parameters set for CPA

Sets	a_0 bar L^2 mol^{-2}	b L mol^{-1}	c_1 (-)	ϵ^{AB}/k (K)	β^{AB} ($\times 10^3$) (-)	Ps / ρ T_r range	ref
CPA 1A1	9.119	0.0468	0.464	4850	4.5	0.50-0.91	12
CPA 1A2	8.296	0.0455	0.494	5789	1.6		17
CPA 1A3	8.199	0.0453	0.506	5867	1.5		17
CPA 2B	7.059	0.0478	0.880	2263	140		12

All sets were evaluated under the same conditions. The saturated pressure (P_s), the density (ρ) and the enthalpy of vaporization (H_{vap}) were evaluated in the temperature range of 293 – 543 K against the data from DIPPR.[29] The speed of sound (u) was evaluated at atmospheric pressure in the temperature range 293 – 353 K against the data from the Dortmund Data Bank.[31] The second virial coefficient was evaluated in the temperature range 410 – 574 K using the data of Bich et al.[32] to fit the virial equation (B_1) and the methodology proposed by Tsonopoulos and Prausnitz[1] (B_2) to obtain its experimental value. The compressibility factor (Z) was evaluated in the temperature range 373 – 503 K, against the data from Freeman and Wilson.[33] The isobaric heat capacity (C_p) were evaluated using the DIPPR correlations[29] at the temperature ranges 290 – 380 K.

The performance of the two models was compared by calculating the AAD (%) for the above mentioned properties with each set. These results are presented in Table 5.

Table 5. Average absolute deviation (%) for the pure component properties.

Sets	P_s[1]	ρ[1]	u[2]	Z[3]	H_{vap}[1]	C_p[1]	AVG[4]	B_1[5]	B_2[6]
PC-SAFT 2B1	2.16	0.64	28.0	22.8	34.8	34.4	20.5	78.4	49.7
PC-SAFT 2B2	1.24	1.20	9.1	30.5	47.6	23.2	18.8	85.8	66.7
PC-SAFT TW 2B	1.45	0.23	0.70	33.3	52.7	18.7	17.8	88.6	73.1
PC-SAFT TW 1A	1.44	0.38	0.53	17.3	26.7	23.1	11.6	69.0	31.7
PC-SAFT 1A1	0.86	2.49	13.1	17.8	12.0	27.9	12.4	385	949
PC-SAFT 1A2	0.97	0.16	10.5	4.18	7.91	31.3	9.17	36.3	83.7
CPA 2B	1.15	0.26	4.58	31.4	49.0	19.6	17.7	86.4	68.1
CPA 1A1	1.11	0.17	12.2	14.2	21.3	33.2	13.7	60.5	14.2
CPA 1A2	1.45	1.15	17.3	2.73	4.99	34.0	10.3	21.2	110
CPA 1A3	1.49	1.31	17.6	3.07	3.64	33.9	10.2	25.0	136

1 Data from DIPPR,[29] 2 Data from Dortmund Data Bank,[31] 3 Data from Freeman and Wilson;[33] 4 average calculated without the values of B; 5 Data from Tsonopoulos and Prausnitz[1]; 6 Data from Bich et al.;[32] The properties inside the rectangle were used in the parameter estimation procedure

All sets can represent well the vapor pressure and the density data of pure acetic acid. In pipe flows is important to know the speed of sound, in this aspect the inclusion of the speed of sound in the parameter estimation procedure lead to parameters that could simulate this property with low deviations, namely sPC-SAFT parameter sets PC-SAFT TW 1A, PC-SAFT TW 2B.

The sPC-SAFT parameter set PC-SAFT 1A2 had the best overall performance and was the only set of PC-SAFT that was able to represent the compressibility factor and the enthalpy of vaporization with low deviations.

The sets PC-SAFT 1A2, CPA 1A2 and CPA 1A3 have similar values for the parameter of the association energy, in the region of 5000 – 6000 K. These parameters had a better performance in describing the compressibility factor and the enthalpy of vaporization. This region is still a bit far from the experimental region reported in the literature (7000 – 8000 K),[17] and the set that had the association value in this range (PC-SAFT 1A1), didn't perform as well as the aforementioned three sets.

The sets PC-SAFT TW 2B and CPA 2B were able to describe qualitatively the results of the isobaric heat capacity, but no set was able to perform quantitatively well.

The results obtained from the AAD of the properties for the different sets confirm the tendency that when a parameter set had a rather good representation of a property, this comes at the cost of reducing the accuracy for the speed of sound. This tendency is clearly seen from the results of the sets CPA 2B, CPA 1A3 and PC-SAFT 1A2.

Overall, the best correlation of properties of liquid phase and vapor pressure were obtained with the parameter sets presented in this work, with deviations below 1.45% for vapor pressure, liquid density and liquid speed of sound. Also, the lower deviations for liquid heat capacity were also obtained with the parameters presented here. Some results are plotted in Figures 3 – 10.

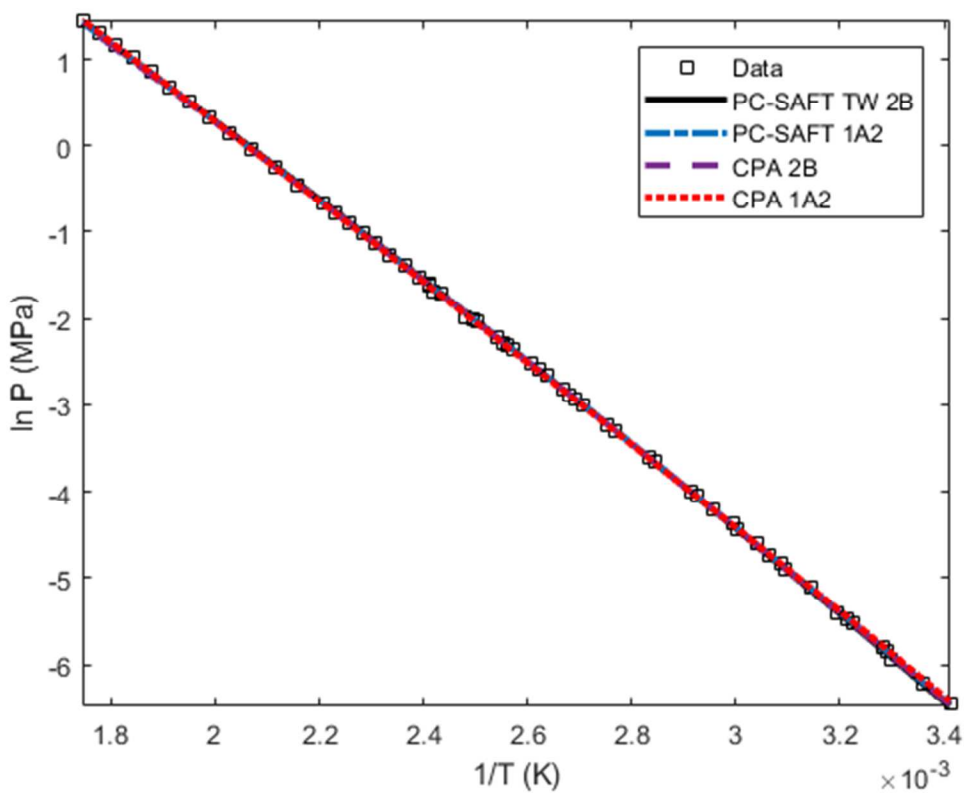

Figure 3. Experimental and calculated vapor pressure of acetic acid with sPC-SAFT and CPA using different parameters sets. Data are taken from DIPPR[29],

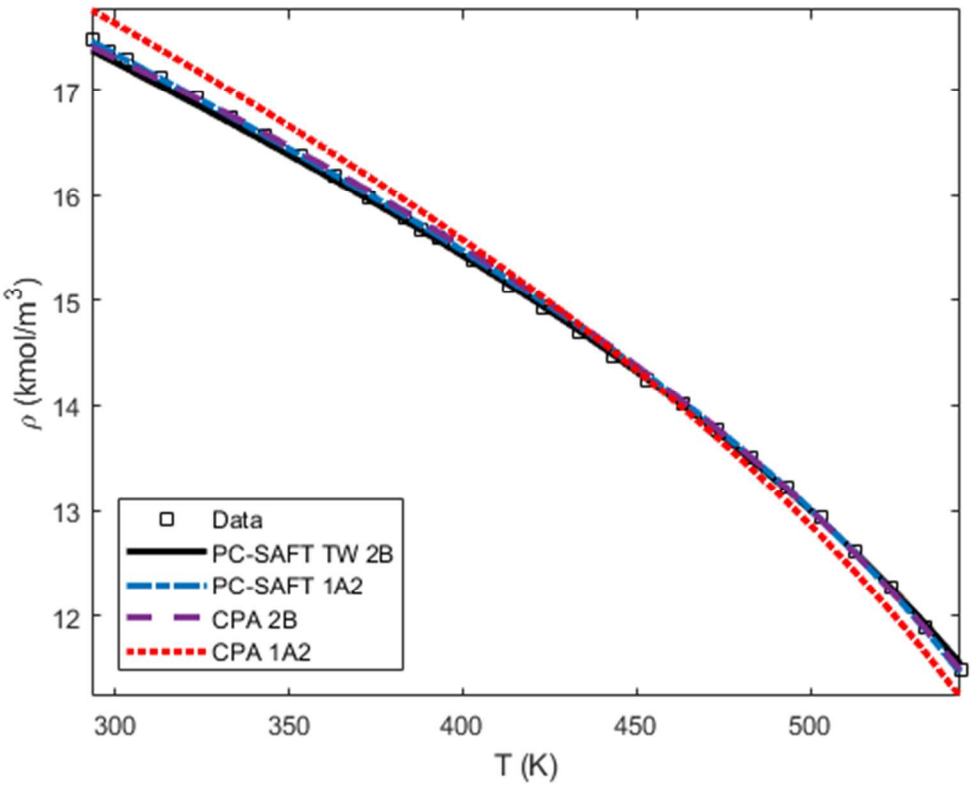

Figure 4. Experimental and calculated density of acetic acid with sPC-SAFT and CPA using different parameters sets. Data are taken from DIPPR[29]

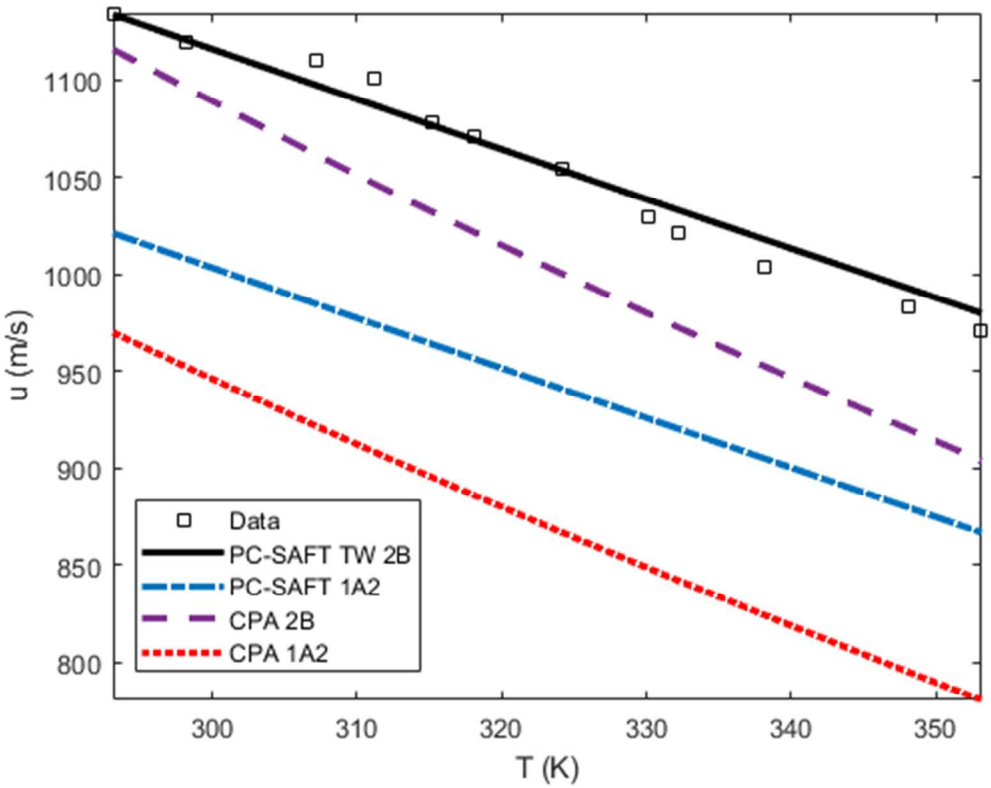

Figure 5. Experimental and calculated speed of sound of acetic acid with sPC-SAFT and CPA using different parameters sets. Data are taken from Dortmund Data Bank[31]

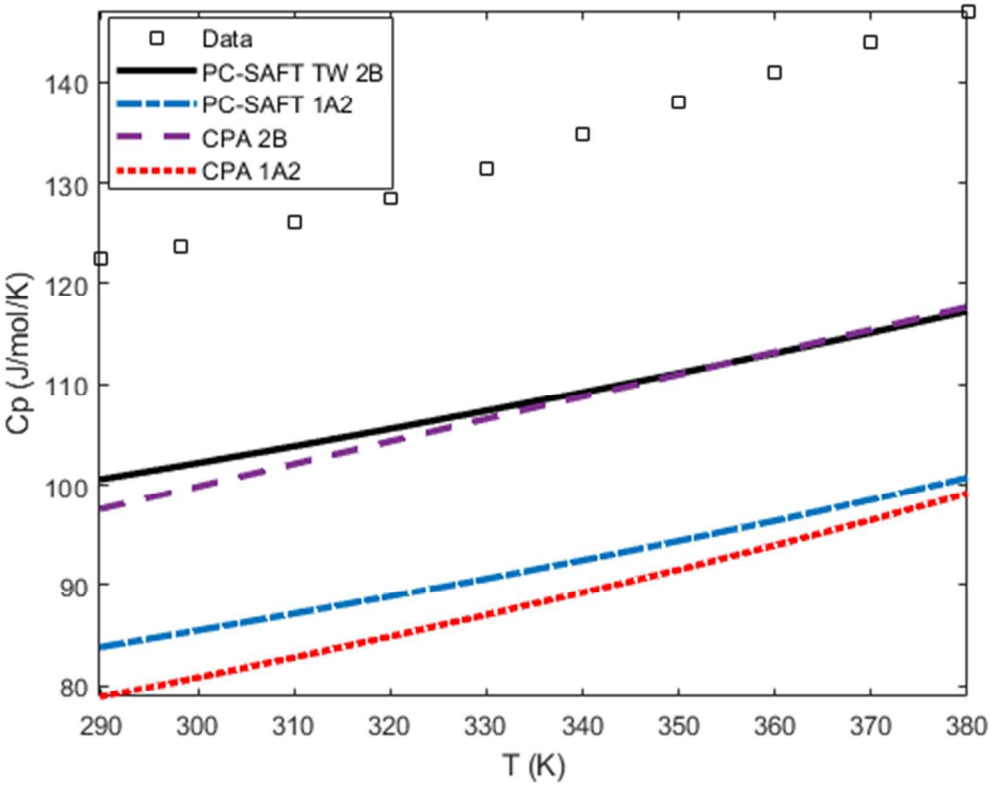

Figure 6. Experimental and calculated C_p of acetic acid with sPC-SAFT and CPA using different parameters sets. (□) Data from DIPPR[29]

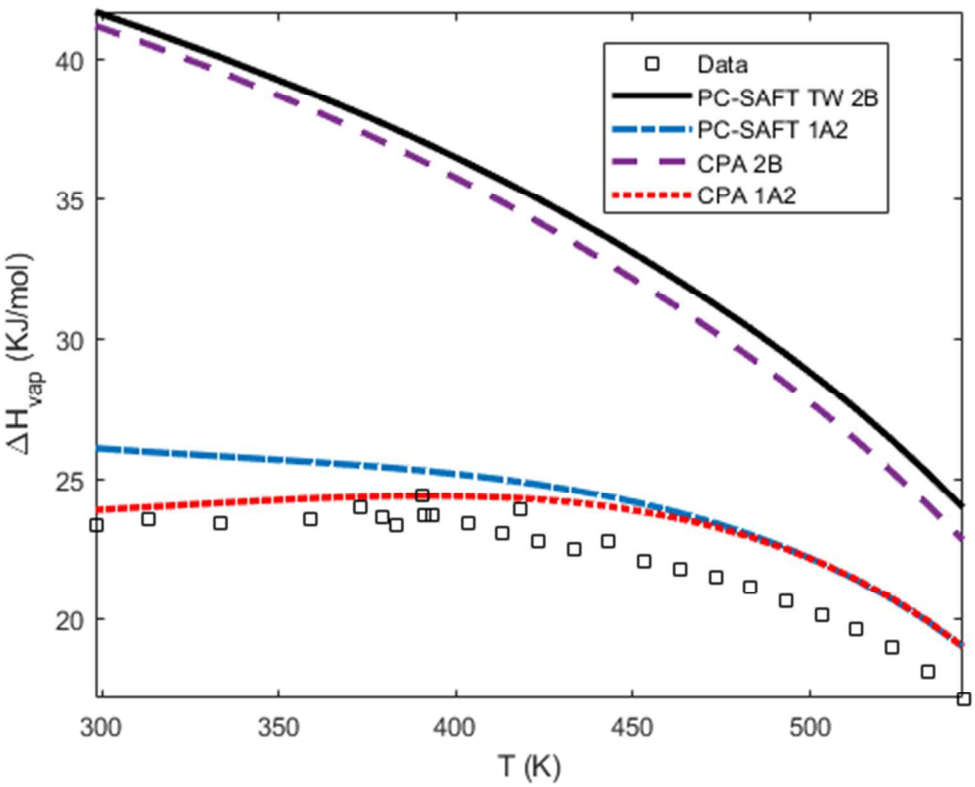

Figure 7. Experimental and calculated enthalpy of vaporization of acetic acid with sPC-SAFT and CPA using different parameters sets. Data are taken from DIPPR[29]

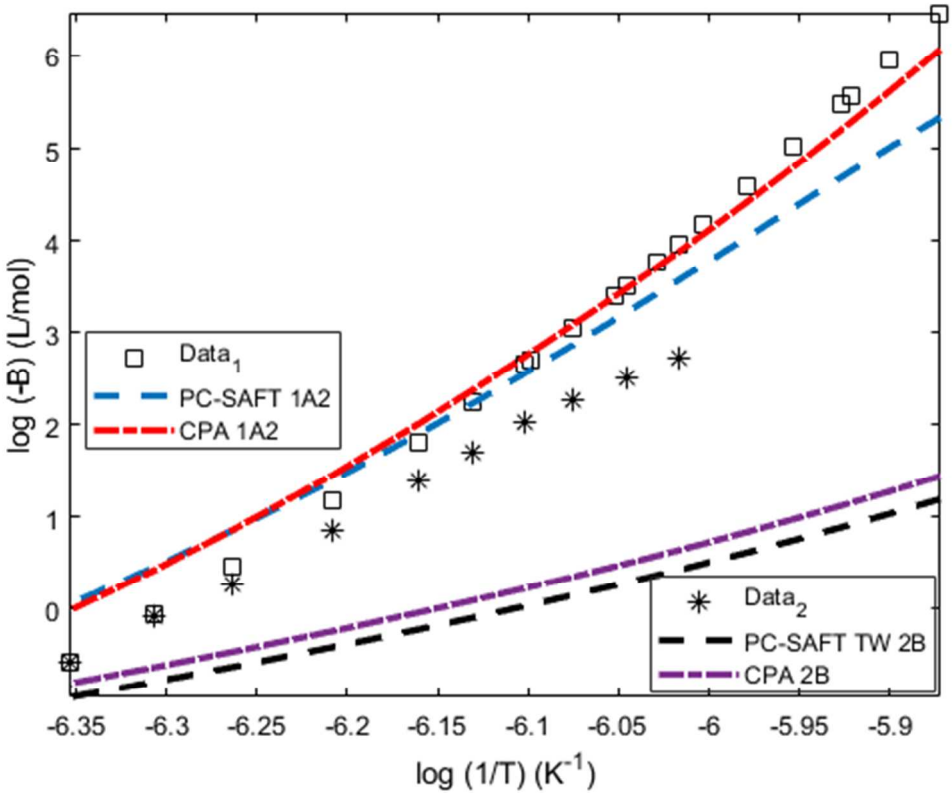

Figure 8. Experimental and calculated second virial coefficient of acetic acid with sPC-SAFT and CPA using different parameters sets. Data$_1$ taken from (□) Tsonopoulos and Prausnitz[1], (*) Data$_2$ taken from Bich et al.[32]

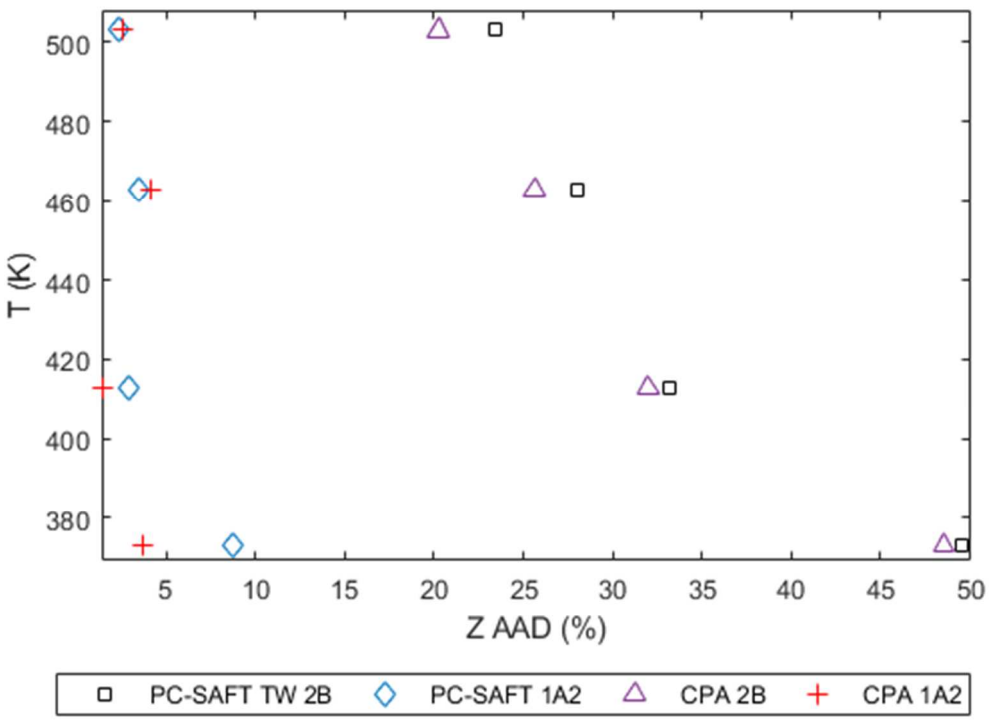

Figure 9. Results of the Average Absolute Deviation (AAD %) in different temperatures of the compressibility factor of acetic acid with sPC-SAFT and CPA using different parameters sets.

Binary mixtures. It is important to evaluate the capabilities of a model for phase equilibria. This was done in this work by fitting the phase equilibria data of three binary mixtures (Water – Acetic Acid, Hexane – Acetic Acid and Ethanol – Acetic Acid) and using both associating schemes of the acetic acid.

For the mixture with water, three schemes of association that are used for water (2B, 3B, 4C) were tested. This was done in order to see if the chosen scheme could influence the optimal results. The results are presented in Figure 10-14 and in Table 6-8.

Water - Acetic Acid. The water parameters were taken from the literature and were named as follows:

- For water using the 2B scheme – PC-SAFT W 2B.[45]
- For water using the 3B scheme – PC-SAFT W 3B.[45]
- For water using the 4C scheme – PC-SAFT W 4C,[46] CPA W 4C;[47]

The sets of the acetic acid and water where fitted using the data of Freeman and Wilson[33] and Nass, available at the Dortmund Data Bank[31] for the binary mixture phase equilibria. The results are presented in Figure 10-12 and in Table 6.

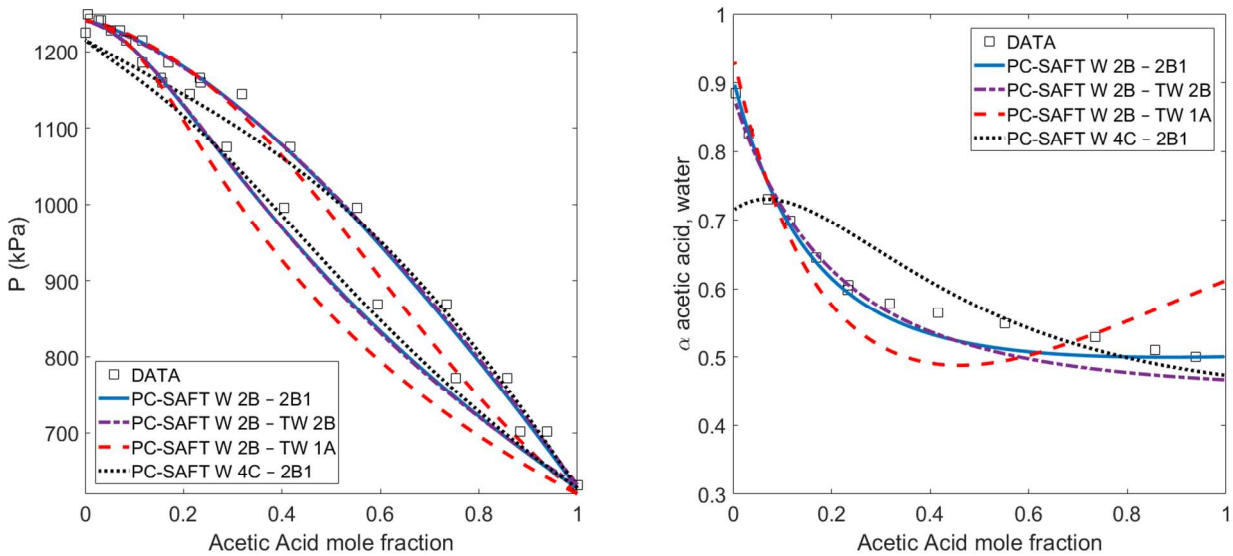

Figure 10. Correlated and experimental results of vapor-liquid equilibria (Left) and acetic acid relative volatility (Right) between acetic acid and water at 462.05 K using sPC-SAFT. Data are taken from Freeman and Wilson[33], The k_{ij} values can be found in Table 6.

Table 6. Values of the ΔP (%), Δy (%), $\Delta\alpha$ (%) for fitted k_{ij}, for water - acetic Acid with sPC-SAFT and CPA

Sets	k_{ij}	ΔP (%)	Δy (%)	$\Delta\alpha$ (%)	k_{ij}	ΔP (%)	Δy (%)	$\Delta\alpha$ (%)	k_{ij}	ΔP (%)	Δy (%)	$\Delta\alpha$ (%)
	462.05K				372.75K				318.15K			
sPC-SAFT												
PC-SAFT 2B1												
PC-SAFT W 2B	-0.1713	1.17	0.78	2.48	-0.2092	3.76	2.63	6.05	-0.2355	4.59	3.72	8.61
PC-SAFT W 3B	-0.2178	2.04	2.17	6.64	-0.2548	4.33	2.98	8.77	-0.2802	5.20	3.99	10.4
PC-SAFT W 4C	-0.1669	2.32	1.40	7.89	-0.1721	3.37	5.12	12.1	-0.1838	0.72	7.57	12.9
PC-SAFT 2B2												
PC-SAFT W 2B	-0.0929	1.01	1.54	3.76	-0.1188	3.15	2.72	4.97	-0.1362	4.70	4.18	8.77
PC-SAFT W 3B	-0.1128	1.53	1.28	3.87	-0.1407	3.67	2.18	4.95	-0.1569	4.94	4.35	9.56
PC-SAFT W 4C	-0.1054	2.12	2.42	9.92	-0.1100	3.10	5.80	14.7	-0.1168	0.62	8.41	14.4
PC-SAFT TW 2B												
PC-SAFT W 2B	-0.0729	1.03	1.64	3.62	-0.0965	3.21	2.34	4.32	-0.1091	4.88	4.65	9.58
PC-SAFT W 3B	-0.0875	1.52	1.29	3.87	-0.1119	3.65	2.16	4.86	-0.1248	5.36	4.84	10.7
PC-SAFT W 4C	-0.0942	2.05	2.79	10.5	-0.0983	3.10	5.97	15.2	-0.1016	0.55	9.34	14.9
PC-SAFT TW 1A												
PC-SAFT W 2B	-0.0558	2.57	2.69	7.90	-0.0795	3.81	3.51	9.36	-0.0751	6.09	3.41	10.8
PC-SAFT W 3B	-0.0607	3.05	3.80	12.2	-0.0789	4.26	4.51	13.4	-0.0846	6.23	3.93	13.9
PC-SAFT W 4C	-0.1065	2.31	2.67	11.4	-0.1128	3.56	3.62	13.9	-0.1098	1.17	8.08	15.0
PC-SAFT 1A1												
PC-SAFT W 2B	-0.0581	2.23	3.45	8.33	-0.0743	3.17	3.97	9.60	-0.0830	3.84	3.48	9.50
PC-SAFT W 3B	-0.0637	2.73	4.61	13.3	-0.0721	3.12	4.91	13.5	-0.0772	4.16	4.38	13.9
PC-SAFT W 4C	-0.1115	2.41	3.95	14.8	-0.0997	3.50	4.31	16.9	-0.0935	1.25	4.95	15.7
PC-SAFT 1A2												
PC-SAFT W 2B	-0.0766	2.66	3.72	10.4	-0.0956	3.65	4.58	13.3	-0.1048	4.95	4.33	14.6
PC-SAFT W 3B	-0.0924	3.17	4.91	15.1	-0.1046	4.04	5.73	18.1	-0.1047	4.92	5.18	18.9
PC-SAFT W 4C	-0.1248	2.26	3.17	12.5	-0.1197	3.61	3.75	13.9	-0.1097	1.26	6.04	13.6
CPA (only 4C parameter set was used to represent water)												
CPA 2B	-0.2271	2.03	2.14	8.21	-0.2271	3.24	4.95	13.2	-0.2284	3.21	6.93	12.8
CPA 1A1	-0.2410	1.96	2.73	10.8	-0.2468	4.01	3.49	13.2	-0.2332	3.73	5.30	12.3
CPA 1A2	-0.2441	2.19	3.31	12.1	-0.2355	4.20	3.86	13.6	-0.2127	2.98	4.28	11.3
CPA 1A3	-0.2440	2.23	3.38	12.2	-0.2339	4.21	3.89	13.6	-0.2102	2.88	4.25	11.3

As one can see from Table 6, at 462.05 K the smallest total deviations were achieved with sPC-SAFT using the sets PC-SAFT W 2B - PC-SAFT 2B1, followed by PC-SAFT W 2B - PC-SAFT TW 2B. Scheme 1A for acetic acid performed poorer than 2B in almost all cases. Using scheme 2B for acetic acid, scheme 4C did not perform as well as scheme 2B for water. Analyzing Figure 10 (Right), the experimental data monotonically decreases with increase in acetic acid content, presenting a positive second-order derivative of α with respect to acetic acid mole fraction at low acid concentrations. This behavior was correctly correlated with sPC-SAFT sets PC-SAFT W 2B - PC-SAFT 2B1 and PC-SAFT W 2B - PC-SAFT TW 2B, but the second-order function derivative was not matched when using scheme 1A for acetic acid or 4C for water.

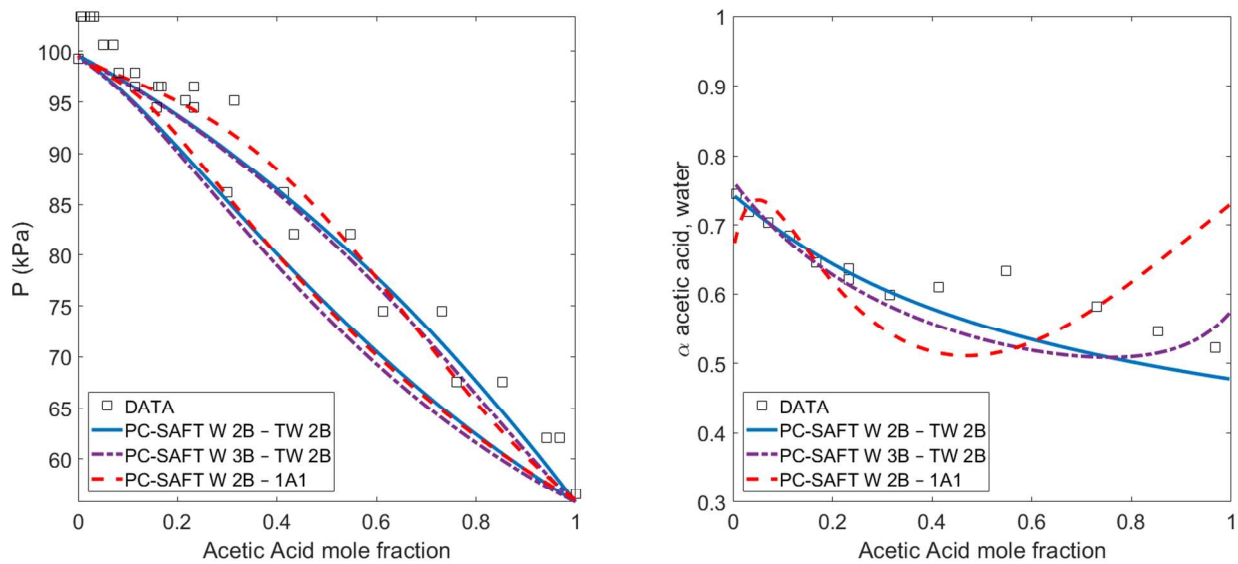

Figure 11. Correlated and experimental results of vapor-liquid equilibria (Left) and acetic acid relative volatility (Right) between acetic acid and water at 372.75 K, using sPC-SAFT. Data are taken from Freeman and Wilson.[33] The k_{ij} values can be found in Table 6.

At the temperature 372.75 K, the best results were achieved with the sPC-SAFT sets PC-SAFT W 2B - PC-SAFT TW 2B, PC-SAFT W 3B - PC-SAFT TW 2B and by PC-SAFT W 3B - PC-SAFT 2B2. Schemes 2B and 1A for acetic acid led to compatible results, with a little advantage to 2B. Using scheme 1A for acetic acid, scheme 4C performed poorer for water.

Analyzing Figure 11 (Right), the experimental data in general monotonically decreases with increase in acetic acid content, except at about 0.5 mole fraction, where data increases with acetic acid content. The general behavior is correctly correlated with PC-SAFT W 2B - TW 2B and PC-SAFT W 3B - PC-SAFT TW 2B, and also with the best parameter set for scheme 1A, PC-SAFT W 2B - PC-SAFT TW 1A, although in this case the derivative of α with respect to acetic acid mole fraction at low acid concentrations is lower than that of experimental data. In addition, when one compares the deviations at 462.05 K with those at 372.75 K, it is clear that the deviations are higher at the lowest temperature.

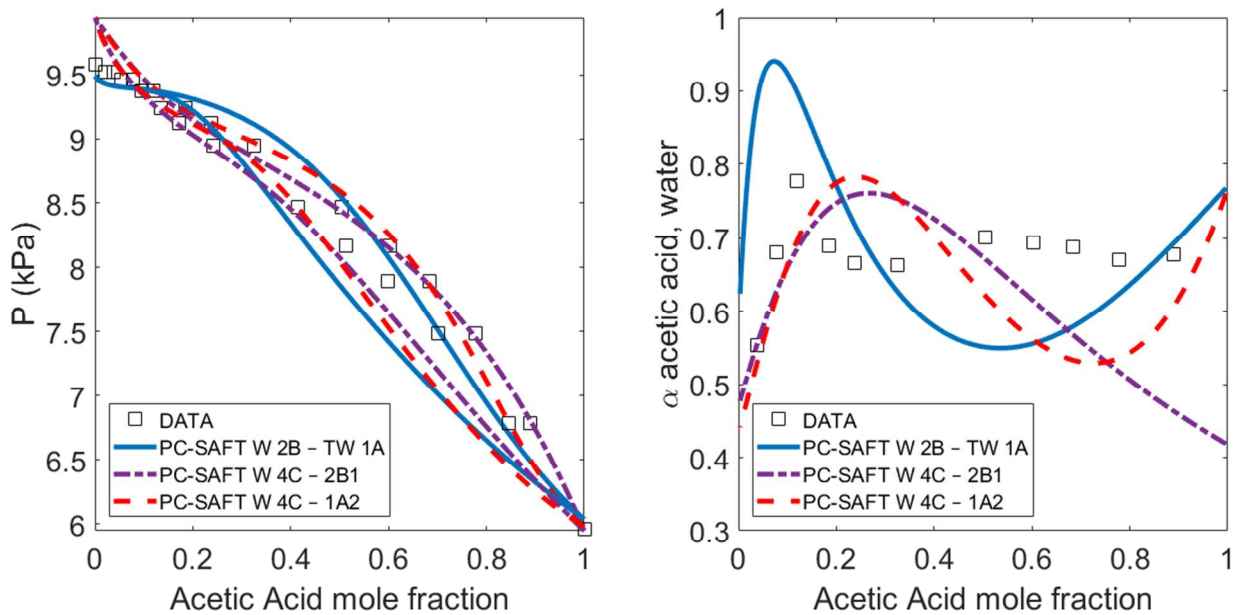

Figure 12. Correlated and experimental results of vapor-liquid equilibria (Left) and acetic acid relative volatility (Right) between acetic acid and water at 318.15 K, using sPC-SAFT. Data are taken from Nass, available at the Dortmund Data Bank.[31] The k_{ij} values can be found in Table 6.

At the temperature 318.15 K, the best results based on the total deviation were achieved with the schemes PC-SAFT W 2B - PC-SAFT 1A1, followed by PC-SAFT W 2B - PC-SAFT 2B1 and by PC-SAFT W 2B - PC-SAFT 2B2. Schemes 2B and 1A for acetic acid led to comparable

results, and results depend more on the parameter set used. Scheme 3B performed poorer for water. Analyzing Figure 12 (Right), the experimental data, in general, scatter a cross a constant, presenting both positive and negative first and second derivative. This behavior was not well correlated by the models, with PC-SAFT W 2B - PC-SAFT 1A1 closer to experimental data. Also, comparing deviations at 318.15 K with those at 372.75 and 462.05 K, it is clear that the deviations increase as the temperature decreases.

sPC-SAFT and CPA had similar performances in the three temperatures and with the evaluated schemes. From the highest to the lowest studied temperature, the deviations decreased and, while for the water the best association scheme remained the 2B, for the acetic acid, the chosen association scheme was he 2B scheme. The scheme PC-SAFT TW 2B was among the best performances at the highest temperatures, and PC-SAFT TW 1A performed equivalently to TW 2B at the lowest temperature.

Although it was possible to attain low deviations in pressure and composition, the use of the 2B scheme to represent water is not recommended as it is a simplification that does not take in account all the hydrogen bounds that the water can perform (4), furthermore the relative volatility also presented deviations higher than 10%. For this case, the studies presented by Breil et al.[17] and Tsivintzelis and Kontogeorgis[21] had better performance, but they used an equation that was specifically developed for the water – acetic acid system, the CPA-HV, and has a necessity of more parameters to correlated with the phase equilibria. The details of this equations can be found elsewhere.[16]

Hexane - Acetic Acid. The acetic acid and hexane system was fitted using the data from Miyamoto et al,[48] available at the Dortmund Data Bank[31] for the phase equilibria. The results are presented in Figure 13 and in Table 7.

Both models performed very similarly, with the 1A scheme leading to better correlations, but only CPA and the PC-SAFT 1A set could simulate the shape of the homogeneous azeotrope.

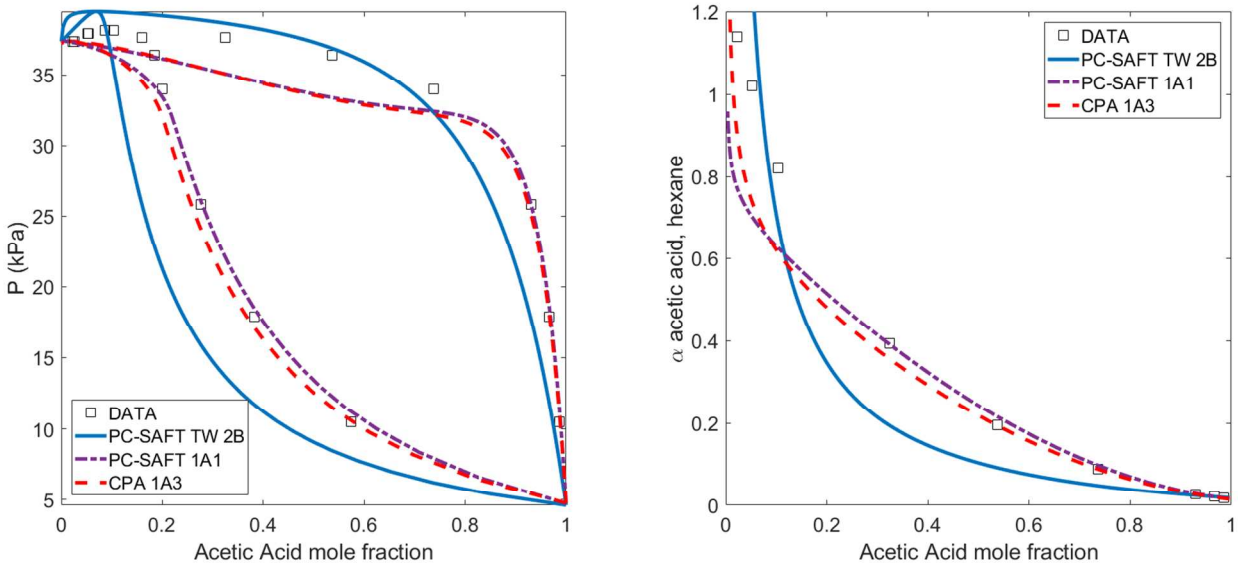

Figure 13. Correlated and experimental behavior of vapor-liquid equilibria (Left) and acetic acid relative volatility (Right) between hexane and acetic acid at 313.2 K with sPC-SAFT and CPA. Data are taken from Miyamoto et al,[48] available at the Dortmund Data Bank,[31] sPC-SAFT Hexane parameters from Liang et al.[34] CPA Hexane parameters from Kontogeorgis et al.[14] The k_{ij} can be found in Table 7.

Table 7. Values of the ΔP (%), Δy (%), $\Delta\alpha$ (%) for fitted k_{ij}, for hexane - acetic acid at 313.2K with sPC-SAFT and CPA

Sets	k_{ij}	ΔP (%)	Δy (%)	$\Delta\alpha$ (%)	Parameter set	k_{ij}	ΔP (%)	Δy (%)	$\Delta\alpha$ (%)
sPC-SAFT					CPA				
2B scheme for acetic-acid									
PC-SAFT 2B1	-0.0008	12.03	4.69	46.7	CPA 2B	-0.0188	11.7	4.36	35.3
PC-SAFT 2B2	0.0011	12.33	4.62	41.3					
PC-SAFT TW 2B	-0.0090	12.42	4.56	37.4					
1A scheme for acetic-acid									
PC-SAFT TW 1A	0.0328	5.11	7.40	27.1	CPA 1A1	0.0591	3.63	6.04	21.20
PC-SAFT 1A1	0.0540	4.51	1.50	13.0	CPA 1A2	0.0653	4.05	2.31	12.74
PC-SAFT 1A2	0.0514	4.05	3.73	17.1	CPA 1A3	0.0654	4.10	2.02	12.10

As one can see from Table 7, the best results were achieved with the schemes CPA 1A3, followed by CPA 1A2 and by AC 1A1. Scheme 2B for acetic acid performed poorer than 1A in all cases. Analyzing Figure 13 (Right), the experimental data monotonically decreases with increase in acetic acid content, presenting a positive second derivative and starting above 1 and then falling below 1 around 0.05 acetic acid mole fraction. This behavior is correctly correlated with the best parameter sets, and also with the best set for scheme 2B, PC-SAFT TW 2B.

Ethanol - Acetic Acid. For ethanol-acetic acid, we have used the data from from Rius et al.,[49] available at the Dortmund Data Bank.[31] The results are presented in Figure 14 and in Table 8. Once again, both models show similar behavior, with 1A scheme leading to better correlations.

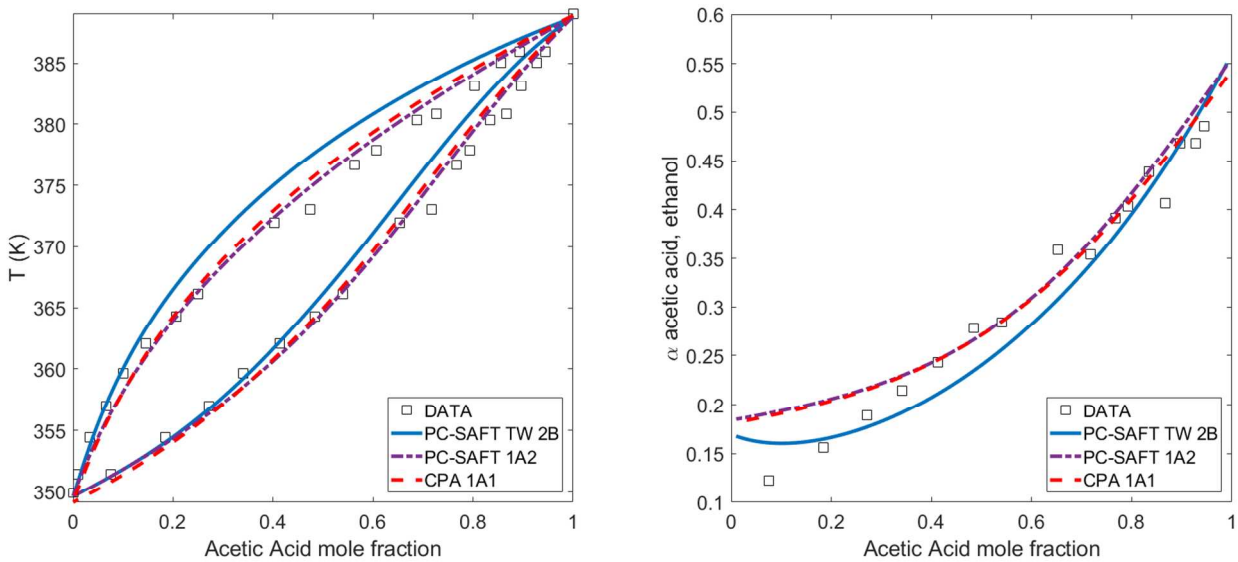

Figure 14. Correlated and experimental behavior of vapor-liquid equilibria (Left) and acetic acid relative volatility (Right) between ethanol and acetic acid at P = 94 kPa with sPC-SAFT and CPA. Data are taken from Rius et al.,[49] available at the Dortmund Data Bank.[31] sPC-SAFT ethanol parameters from Gross and Sadowski[10]. CPA ethanol parameters from Kontogeorgis et al.[14] The k_{ij} can be found in Table 8.

Table 8. Values of the ΔP (%), Δy (%), $\Delta \alpha$ (%) for fitted k_{ij}, for ethanol - acetic acid at 94 kPa with sPC-SAFT and CPA

Sets	k_{ij}	ΔP (%)	Δy (%)	$\Delta \alpha$ (%)	Parameter set	k_{ij}	ΔP (%)	Δy (%)	$\Delta \alpha$ (%)
sPC-SAFT					CPA				
2B scheme for acetic-acid									
PC-SAFT 2B1	-0.0860	0.55	1.47	4.63	CPA 2B	-0.0968	0.47	1.41	4.19
PC-SAFT 2B2	-0.0805	0.42	1.99	7.20					
PC-SAFT TW 2B	-0.0817	0.40	2.33	8.78					
1A scheme for acetic-acid									
PC-SAFT TW 1A	-0.0382	0.33	2.60	11.0	CPA 1A1	-0.0167	0.28	1.55	8.95
PC-SAFT 1A1	-0.0029	0.22	2.34	12.3	CPA 1A2	-0.0023	0.27	1.89	10.4
PC-SAFT 1A2	-0.0057	0.21	1.97	9.88	CPA 1A3	-0.0004	0.26	1.88	10.5

As one can see from Table 8, the best results were achieved with the schemes CPA 2B, followed by PC-SAFT 2B1and by CPA 1A1. Scheme 1A for acetic acid performed poorer than 2B in all cases. Analyzing Figure 14 (Right), the experimental data monotonically increases with increase in acetic acid content, linearly to a straight line. This behavior is correctly correlated with the best models for acetic acid mole fraction above 0.5. PC-SAFT TW 2B led to a minimum in this curve, misleading the experimental behavior.

Comparing the results for water, hexane and ethanol, one can see that acetic acid was better represented with scheme 1A for pure properties and in mixtures with hexane (at 313.2 K) and was satisfactorily well represent as scheme 1A with water (4C) at 318.15 K. Acetic acid was better represented with scheme 2B in mixture with water at 372.75 K and 462.05 K, but water had to be represented by schemes 3B and 2B. The need for changing the association scheme of water shows the complexity of this system, and it is the probable cause of change from 1A to 2B the best association scheme for acetic acid.

DISCUSSION

For the acetic acid, the best overall correlation of properties of liquid phase and vapor pressure were obtained with the parameter sets presented in this work, with deviations below 1.5% for vapor pressure, liquid density and liquid speed of sound. Also, the lowest deviations for liquid heat capacity were obtained with the parameters presented in this work.

As previously shown[8–20], the Wertheim theory[4–7] has been used with some success for predicting a few of the acetic acid pure component properties, especially vapor pressure and density, but it was not successful in predicting the various derivative properties where it has not been extensively used either. This is also supported by the findings of Kontogeorgis,[50] where the author summarizes some comparative studies focusing on association theories with different frameworks to predict the derivative properties (e.g. Cp, Cv, speed of sound).

At this stage, it is of interest and for comparison to the present work to summarize some related studies also for aqueous acetic acid mixtures. The Wertheim theory has been used in diverse frameworks for correlating phase equilibria data of acetic acid mixtures, especially with water.

Fu and Sandler[9] proposed a simplified SAFT (sSAFT) equation. The authors substitute the dispersion term implemented by Huang and Radosz in the SAFT equation[8] with a single attraction term for the square-well fluid. They show in their work that sSAFT and SAFT are not able to obtain good correlations for the acetic acid and water phase equilibria.

It is clear from these results (from literature and from this work) that the association theory has some limitations. For example, the Wertheim theory does not consider the possibility of differences between the hydrogen bonds, neither the formation of cyclic structures nor the presence of intramolecular association,[22,23,27,50–54] and because of these limitations some suggestions for changes have been proposed in the literature.

Muro-Suñé et al.[16] studied the water (4C) and acetic acid (1A) phase equilibria using CPA. After trying to improve the correlation using several methods without success, they modified the mixing rule of the energy parameter by using the Huron-Vidal mixing rule together with a modified non-random two-liquid (NRTL) equation instead of the van der Waals one-fluid mixing

rule and they were able to obtain a satisfactory correlation at the cost of more adjustable parameters.

This Huron-Vidal modification of CPA was later studied by Breil et al.,[17] Kontogeorgis and Folas[27] and Tsivintzelis and Kontogeorgis[21]. Breil et al.[17] and Kontogeorgis and Folas[27] applied the CPA EOS with the Huron-Vidal mixing rule[16] to correlate the water (4C) and acetic acid (1A) phase equilibria. They fitted the parameters for the Huron-Vidal mixing rule using the relative volatility data of acetic acid and water. The authors were able to obtain excellent correlation results, but they were not able to use only one set of parameters to describe the whole range of the temperatures studied, and they recommended the use of different sets, one for temperatures below 373 K, and one for higher temperatures.

Tsivintzelis and Kontogeorgis[21], using the same sets for pure acetic acid parameters as proposed by Breil et al.,[17] investigated if including infinite dilution and/or vapor compressibility data of the phase equilibria together with the relative volatility data of acetic acid and water during the estimation of the parameters for the Huron-Vidal mixing rule could lead to a better correlation of the phase equilibria. The findings of Tsivintzelis and Kontogeorgis[21] were in agreement to those by Breil et al.[17] and Kontogeorgis and Folas.[27] They obtained excellent correlation results for phase equilibria and they also noticed the need of more than one parameter sets to describe the phase equilibria over an extensive temperature range.

A different approach was followed by Janeček and Paricaud[22,23] and Sum and Sandler.[24] Sum and Sandler[24] proposed a modification of the UNIQUAC model to include the Wertheim theory using parameters obtained from ab initio quantum mechanics calculations, but the authors did not get good results when they tried to correlate the phase equilibria of water and acetic acid. Janeček and Paricaud[22,23] correlated the water (4C) and acetic acid (2B) phase equilibria with a modified PC-SAFT, named PC-SAFT-DBD.[22,23]. This modification is based on the work of Sear and Jackson[52], that extended the classical 2B association model[8] to take in account the formation of cyclic dimers, and includes one term and one more adjustable parameter to the expression for the association contribution used in PC-SAFT. They compared the results of the new implementation with the standard PC-SAFT model. In their work, they limit the formation of cyclic dimers to the acetic acid, not allowing that the water molecule nor the hydroxyl group form a cyclic association with the carboxyl group. Both models have similar performance

correlating the phase equilibria, presenting low deviations in pressure and in the vapor composition using large negative values (closer to -1) for the binary interaction parameter. Unfortunately, Janeček and Paricaud,[23] did not provide information about the relative volatility of the acetic acid-water systems they tested and, as can be observed from the results of Tables 6-8, the relative volatility is an important sensitive property in order to truly evaluate the model correlation performance for the water – acetic acid phase equilibria. We see the same problem in numerous other studies with SAFT models like the one mentioned before by Fu and Sandler[9] and also Kouskoumvekaki et al.[11] and Wolbach and Sandler;[3] i.e. VLE results are presented for water-acetic acid in *Pxy* or *Txy* plots. Such plots are very much deceiving for this mixture and without presenting detailed results in form of relative volatilities over extended temperature ranges it is difficult to appropriately assess the model performance.

We summarized some of the results previously presented in literature in Table 9.

Table 9. Summary of some literature correlation results for the acetic acid-water mixture compared also to selected results from this work

Model		k_{ij}	ΔP (%)	Δy (%)	$\Delta\alpha$ (%)
SAFT (2B-4C)[a]	T=372.75 K	0.2335	2.9	-	106
Or. PC–SAFT (2B-2B)[a]		-0.1221	3.7	-	5.9
PC–SAFT (2B-4C)[a]		-0.0228	4.4	-	24.6
PC–SAFT (2B-4C)[a]		-0.15	2.1	-	21.8
PC–SAFT (2B-2B)[a]		-0.08	2.9	-	16.5
CPA - HV (1A-4C)[a]		-	4	0.3	2.4
CPA - HV (1A-4C)[b]		-	-	-	3.8
CPA - HV (1A-4C)[c]		-	-	-	1.9
sPC–SAFT (2B-2B)[d]		-0.0965	3.2	2.7	4.9
sPC–SAFT (1A-2B)[d]		-0.0795	3.8	3.5	9.3
CPA (2B-4C)[d]		-0.2271	3.2	4.9	13.2
Or. PC–SAFT (2B-4C)[a]	T=462.05 K	-0.0896	1.4	-	3.3
PC–SAFT (2B-4C)[a]		0.0091	2.5	-	17.1
PC–SAFT (2B-4C)[a]		-0.15	1	-	9.8
PC–SAFT (2B-2B)[a]		-0.08	2.4	-	4
CPA - HV (1A-4C)[a]		-	1.5	0.4	4.3
CPA - HV (1A-4C)[b]		-	-	-	12.3
CPA - HV (1A-4C)[c]		-	-	-	12
sPC–SAFT (1A-2B)[d]		-0.0558	2.6	2.7	7.9
sPC–SAFT (2B-2B)[d]		-0.0729	1.0	1.6	3.6
CPA (2B-4C)[d]		-0.2271	2.0	2.1	8.11
PC-SAFT(DBD-4C)[e]	P=101.3 Kpa	-0.1178	1.3	0.9	-
Or. PC-SAFT(2B-4C)[e]		-0.1472	0.9	1.6	-
PC-SAFT(DBD-4C)[e]	P=26.67 Kpa	-0.1148	2.1	1.2	-
Or. PC-SAFT(2B-4C)[e]		-0.1404	2.2	2.4	-
PC-SAFT(DBD-4C)[e]	P=9.33 Kpa	-0.1154	1.9	1.4	-
Or. PC-SAFT(2B-4C)[e]		-0.1454	2	2.3	-

[a] Results from Kontogeorgis and Folas (2010)[27]; [b] Results from Breil. et al (2011)[17]; [c] Results from Tsivintzelis and Kontogeorgis(2014)[21]; [d] Results from this work; [e] Results from Janeček and Paricaud (2013);

Analyzing the results from Table 9 we conclude that the performance of sPC-SAFT and CPA is not satisfactory for correlating the acetic acid – water mixture. Different combination of association schemes were tried and both models needed large values for the binary interaction parameter and can not provide an accurate description of the relative volatility. In this scenario, sPC-SAFT had the best performance using the 2B scheme for both compounds. The performance

of CPA improves when the Huron-Vidal mixing rule is used for the correlation, but this came with a cost of more parameters and it was not possible to use only one set of parameters to describe the whole extension of temperatures studied. With only the results provided by Janeček and Paricaud[23], it is not possible to say that his modification can provide better correlations than sPC-SAFT as both model have comparable performance correlating the phase equilibria and it is still necessary to use a large negative binary interaction parameter.

In conclusion, it is possible to have a qualitative correlation for the pure component properties of acetic acid and phase equilibria of water and acetic acid. However, to achieve quantitative results and for both phase equilibria and a wide range of properties including derivatives ones, modifications on these models addressing some of the limitations of the Wertheim theory are required. The ultimate test of all approaches should be, on one hand, the accurate representation of various pure acetic acid properties over extensive conditions, binary mixtures with water (and other compounds) and last but not least the prediction of ternary and in general multicomponent VLE and LLE of acetic acid-containing mixtures (with water, alkanes, CO2, etc).

CONCLUSIONS

In this work, we have evaluated the capabilities of the sPC-SAFT and CPA EoS for representing an extensive range of properties for acetic acid and its mixtures.

Both equations of state can describe well the behavior of the vapor pressure and the density (293 - 543 K) of the acetic acid using the two association schemes considered, 1A and 2B, with the 2B scheme performing slightly better for these two properties. None of the models describes very well the isobaric heat capacity, with CPA presenting lower deviations when used with the 1A scheme.

sPC-SAFT was not able to describe accurately the compressibility factor of the vapor phase and the enthalpy of vaporization, especially at low temperatures. This behavior was also observed when using the 2B scheme in CPA.

The correlation of the phase equilibria using sPC-SAFT and CPA also presented a rather similar picture with the two models. Both equations of state cannot provide an accurate description of the relative volatility for water-acetic acid mixtures and, except for the phase equilibria with water, the 1A scheme performed better.

Overall, the 1A scheme had the best performance to correlate all the properties of the acetic acid, but more than one parameter set is required to describe all the pure properties or the phase equilibria in a wide temperature range.

Acetic acid can form dimers and even have an intramolecular association.[54] The results may indicate that the association theory proposed by Wertheim is not adequate for predicting all the pure properties of acetic acid and for accurately correlating its mixture with water, as the Wertheim theory does not consider the possibility of differences between the hydrogen bonds, neither the formation of cyclic structures nor the presence of intramolecular association.[22,23,27,50–53]

New developments focusing in having a better description of the interactions of associating compounds are needed, and although there is some development being done, it is still early to

say whether a single association scheme or thermodynamic model in general will be able to describe accurately all the properties of acetic acid.

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List of Symbols

a	contribution of the Helmholtz free energy	-
a_0	energy parameter	bar L^2 mol^{-2}
A_i	site A in molecule i	-
B	second virial coefficient	L mol^{-1}
b	co-volume	L mol^{-1}
B_j	site B in molecule j	-
Cp	isobaric heat capacity	-
CPA 1A1	CPA parameter set	J/mol/K
CPA 1A2	CPA parameter set	-
CPA 1A3	CPA parameter set	-
CPA 2B	CPA parameter set	-
d	segment diameter	-
g	radial distribution function	Å
$Hvap$	enthalpy of vaporization	-
K_2	dimerization constant	KJ/mol
k_{ij}	binary interaction parameter	$mmHg^{-1}$
m	segment number	-
M_i	number of association sites of molecule i	-
N	number of experimental points	-
Ni	number of interactions	-
Np	number of particles	-
P	pressure	-
P_s	saturated pressure	Pa
PC-SAFT 1A1	PC-SAFT parameter set	Pa
PC-SAFT 1A2	PC-SAFT parameter set	-
PC-SAFT 2B1	PC-SAFT parameter set	-
PC-SAFT 2B2	PC-SAFT parameter set	-
PC-SAFT TW 1A	PC-SAFT parameter set	-
PC-SAFT TW 2B	PC-SAFT parameter set	-
R	gas constant	-
T	temperature	
u	speed of sound	K
Vm	molar volume	m/s
X	monomer fraction	m^3/mol
x_i	liquid molar fraction	-
y	vapor molar fraction	-
Z	compressibility factor	-

List of abbreviations

AAD	average absolute deviation
AVG	average
CPA	cubic plus association
EOS	equation of state
LLE	liquid-liquid equilibria
ObjF	objective function
PC-SAFT	perturbed chain-statistical associating fluid theory
PSO	particle swarm optimization
SLE	solid-liquid equilibria
sPC-SAFT	simplified perturbed chain-statistical associating fluid theory
VLE	vapor-liquid equilibria

Greek letters

ρ	molar density	$kmol/m^3$
α	relative volatility	-
β^{AB}	association volume	-
Δ^{AB}	association strength	-
ϕ	binary variable	-
η	reduced density	-
κ^{AB}	association volume	-
θ	evaluated property	-
σ	segment energy	Å
ϵ/κ	association energy	K

Superscript/Subscripts

r	reduced
chain	chain formation
hs	hard sphere
disp	dispersion forces
assoc	association
exp	experimental
calc	calculated
id	ideal

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Table of Contents (TOC) Graphic