

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/249313915>

# Thermodynamic Modeling of Mixtures Containing Carboxylic Acids Using the PC-SAFT Equation of State

ARTICLE in INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · OCTOBER 2012

Impact Factor: 2.59 · DOI: 10.1021/ie301930q

CITATIONS

5

READS

284

## 5 AUTHORS, INCLUDING:



Yushu Chen

Atomic Energy and Alternative Energies Com...

6 PUBLICATIONS 41 CITATIONS

SEE PROFILE



Fabrice Mutelet

Ecole Nationale Supérieure Des Industries Chi...

89 PUBLICATIONS 1,996 CITATIONS

SEE PROFILE



Roland Solimando

Ecole Nationale Supérieure Des Industries Chi...

32 PUBLICATIONS 399 CITATIONS

SEE PROFILE

# Thermodynamic Modeling of Mixtures Containing Carboxylic Acids Using the PC-SAFT Equation of State

Chen Yushu,<sup>†</sup> Attia Afef,<sup>†,‡</sup> Mutelet Fabrice,<sup>\*,†</sup> Solimando Roland,<sup>†</sup> and Mohamed Razzak Jeday<sup>‡</sup>

<sup>†</sup>Laboratoire de Réactions et Génie des Procédés (UPR CNRS 3349), Université de Lorraine, 1 rue Grandville, BP 20451 54001 Nancy, France

<sup>‡</sup>National Engineering School, Research unit of Energetic and Environment UR/99, University of Gabes, Street of Omar El Khattab, 6029, Gabes, Tunisia

**ABSTRACT:** The aim of this work is to investigate whether the PC-SAFT (perturbed chain-statistical associating fluid theory) equation of state can describe the vapor–liquid equilibria for carboxylic acid-containing systems. Carboxylic acids, unlike many other associating compounds, have a strong tendency to dimerize in the vapor phase at normal conditions resulting in strong nonideal behavior at low pressures. In this work, we will focus on five binary systems {water + acetic acid}, {water + propionic acid}, {water + acrylic acid}, {acetic acid + propionic acid}, and {acetic acid + acrylic acid} due to their importance for chemical industries. The study was performed in a systematic method: first, the PC-SAFT equation has been applied to the pure carboxylic acid in order to determine the pure molecular parameters and then to the binary system. In this case, the interaction parameter  $k_{ij}$  was determined using liquid–vapor equilibria data. This work shows that the PC-SAFT equation of state is able to represent the pure carboxylic acid as well as mixtures containing carboxylic acid.

## ■ INTRODUCTION

Carboxylic acids have an important role in chemical industries. For instance, acrylic acid is an important constituent to produce copolymers which have applications in superabsorbents, detergent cobuilders, dispersants, flocculants, and thickeners.<sup>1</sup> The step of purification and separation of impurities such as water and acetic and propionic acids remains an indispensable step for production of acrylic acid.

Use of carboxylic acids requires knowledge of the phase behavior of their mixtures. However, the phase behavior of carboxylic acids is complex, because of its strong hydrogen-bonding character.<sup>2–4</sup> The particular feature of association of carboxylic acids is that two hydrogen bonds usually form simultaneously, resulting in a stable ring with a hydroxyl site bond to carbonyl oxygen. Therefore, carboxylic acid is characterized by a dimerization in the vapor phase. This may lead to nonideal behavior at low pressures. If these complex interactions due to hydrogen bonding are not taken into account, the phase diagrams of carboxylic acid cannot be represented with high accuracy. This is especially important for predicting a variety of thermodynamic properties (phase equilibria, densities, enthalpies, etc.) over wide ranges of temperature and pressure.

Considerable progress has been made over the last two decades in the modeling of hydrogen-bonding solutions. Usually two approaches are used. The first approach was through the use of Gibbs free energy models and subsequently through activity models coefficients,<sup>5</sup> and hydrogen bonding has been modeled as being an analogue to chemical reaction equilibria.<sup>6</sup> The second one is based on the  $\varphi$ - $\varphi$  method,<sup>7,8</sup> such as cubic association<sup>9</sup> and statistical fluid theory SAFT.<sup>10,11</sup>

Cubic plus associated equation (CPA) is widely applied to systems containing associating compounds.<sup>12</sup> Derawi<sup>13,14</sup> proposed an extension of the equation of state (CPA) to

modeling of pure carboxylic acids. In order to present the system containing carboxylic acids by CPA, knowledge of association sites of acids is required. Among the three tested association schemes (one site, two site, and four site), it was found that only the one-site association scheme describes satisfactorily the association in both the gas and the liquid phases. Besides, Kontogeorgis<sup>15–17</sup> developed the CPA equation of state in order to take into account various types of associated systems such as {acetic acid–water}, {formic acid + water}, {propionic acid + water}, {formic acid + alcohols}, and {propionic acid + alcohols}. Finally, Breil<sup>18</sup> proposed a new variant of CPA for representation of the behavior of pure acetic acid and acetic acid mixtures.

A molecular equation of state based on Wertheim's thermodynamic perturbation theory of first order has been proposed by Chapman.<sup>10,11</sup> The essence of their approach, referred to as the statistical associating fluid theory (SAFT), is to use a reference fluid that incorporates both the chain length (molecular size and shape) and molecular association in place of the much simpler hard-sphere reference fluid used in most equations of state. The advantage of these equations of state not only provides a useful thermodynamic basis for deriving chemical potentials or fugacities that are needed for phase equilibrium simulations but also allows for separating and quantifying the effects of molecular structure and interactions on bulk properties and phase behavior. In the late 1990s, many studies and efforts were involved to ameliorate the equation, especially to enhance the accuracy of the term used for the reference fluid, in spite of the more complex mathematical

**Received:** July 20, 2012

**Revised:** September 14, 2012

**Accepted:** September 20, 2012

**Published:** September 20, 2012

Table 1. Pure-Component Parameters of the Perturbed-Chain SAFT Equation of State for Carboxylic Acid

compounds	$\sigma$	$\epsilon$	$\mu$	$\kappa^{AB}$	$\epsilon^{AB}/\kappa$	AAD%	refs
acetic acid	3.8582	211.59	1.3403	0.075550	3044.4	2.21	39, 40 <sup>a</sup>
propionic acid	3.3900	204.70	2.5200	0.075550	3044.4	0.72	<i>a</i>
acrylic acid	3.8500	180.20	2.8900	0.075550	3044.4	2.41	<i>a</i>
water	3.0007	366.51	1.0656	0.034868	2500.7		39

<sup>a</sup>This work.

form. This led to a different version of the equation with different acronyms, such as SAFT-VR, Soft-SAFT, and later PC-SAFT.

Some researchers have treated carboxylic acids by the SAFT version equation reported in the literature; first, Chapman<sup>7,8</sup> investigated the original SAFT to determine pure-component parameters of acetic acid. Then, Huang and Radosz,<sup>19</sup> Wolbach,<sup>20–23</sup> and Fu<sup>24</sup> presented an extension of the equation (CK-SAFT) based on molar mass and chemical structure characterized specific interactions, such as hydrogen bonding by two association parameters, association energy, and volume. Kouskoumvekaki et al.<sup>25</sup> focused their work on the phase diagram of the binary system {water–acetic acid}. Indeed, Gross et al.<sup>26,27</sup> obtained good results with this particular equation to determine interaction parameters  $k_{ij}$  of liquid–liquid and liquid–vapor equilibrium of mixtures containing water and acetic acid. The work of Gupta<sup>28</sup> has shown that the PC-SAFT equation gives interesting results on the binary system {water–formic acid} compared to the cubic equation of states.

Grenner et al.<sup>29</sup> compared the PC-SAFT equation of state with nonrandom hydrogen-bonding (NRHB) theory. They obtained satisfactory results for mixtures containing water, alcohols, acetic acids, and amines with both models. Kleiner et al.<sup>30</sup> represented correctly the heat capacity of acetic acid and excess enthalpy of mixtures containing acetic acid. The performance of CPA and SAFT is not satisfactory for design purposes of mixtures containing water with small organic acids (formic and acetic). In general, large negative  $k_{ij}$  values are required for presentation of these mixtures, and the relative volatilities are not represented accurately.<sup>19</sup>

In this work, we choose the PC-SAFT (perturbed-chain SAFT) version, modeling the pure components, carboxylic acids, and the behavior of the binary system {water + carboxylic acid} and two carboxylic acids. A theory like PC-SAFT that is a molecularly based equation of state offers several advantages. The first advantage is that each of the approximations made in the development of SAFT, such as the chain, association term, and polar term, has been verified against molecular simulation results. In this way, the range of applicability and the shortcomings of each term in the equation of state have been assessed. A second advantage is that the SAFT parameters have physical meaning which can help us check the accuracy and correctness of the parameters of PC-SAFT during modeling of the pure components. A third advantage is that like all molecularly based equations of state, PC-SAFT is a useful tool in which the effects of molecular structure on the thermodynamic properties can be separated and quantified.

## ■ PC-SAFT MODELING

When using the PC-SAFT model with organic acids, the number and type of association sites have to be known. In our approach, the acetic acid and water parameters of PC-SAFT equation of state were taken from the work of Radosz and

Hung.<sup>19</sup> It is considered that acetic acid and water have two association sites (often referred to as the 2B model). Therefore, all carboxylic acids are assumed to have two association sites.

The perturbed chain-statistical associating fluid theory (PC-SAFT) EoS was derived and described in detail by Gross and Sadowski.<sup>26,27</sup> Applying a perturbation theory for chain molecules inspired from two papers of Barker and Henderson,<sup>31,32</sup> Gross and Sadowski<sup>26,27</sup> derived a dispersion expression for chain molecules and used a hard-chain reference fluid compared with other classical SAFT EoS use a hard-sphere reference meaning that the dispersion term accounts for attraction between spherical segments, not for attraction between hard chains.

The PC-SAFT equation is usually written in terms of residual Helmholtz free energy. Each term in the equation represents different microscopic contributions to the total free energy of the fluid. The equation is written as

$$\tilde{a}^{\text{res}} = \tilde{a}^{\text{hc}} + \tilde{a}^{\text{disp}} + \tilde{a}^{\text{assoc}} \quad (1)$$

The superscripts hc, disp, and assoc refer to a reference hard-sphere chain contribution, a dispersion contribution, and an associating contribution.

The hard-sphere chain contribution was provided and defined by

$$\tilde{a}^{\text{hc}} = \tilde{m}\tilde{a}^{\text{hs}} - \sum_{i=1}^{nc} x_i(m_i - 1) \ln g_i^{\text{hs}} \quad (2)$$

The dispersion contribution to the Helmholtz free energy  $\tilde{a}^{\text{disp}}$  accounts for van der Waals forces

$$\tilde{a}^{\text{disp}} = -2\pi\tilde{\rho}\tilde{I}_1\tilde{m}^2\epsilon\sigma^3 - \pi\tilde{\rho}\tilde{m}\tilde{C}_1\tilde{I}_2\tilde{m}^2\epsilon^2\sigma^3 \quad (3)$$

The Helmholtz free energy due to association  $\tilde{a}^{\text{assoc}}$  is defined by

$$\tilde{a}^{\text{assoc}} = \sum_{i=1}^{nc} x_i \left[ \sum_{A_i} \left( \ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{1}{2} M_i \right] \quad (4)$$

For representing thermodynamic properties of pure carboxylic acid such as densities, vapor pressure, etc., five parameters of PC-SAFT, the segment number ( $m$ ), the segment energy parameter ( $\epsilon/k$ ), the segment diameter ( $\sigma$ ), the association energy ( $\epsilon^{A,B_i}$ ), and the association volume ( $\kappa^{A,B_i}$ ), are required to characterize. Generally, the parameters of the PC-SAFT equation are estimated from vapor pressures and/or liquid densities.

Conventional combining rules for  $\epsilon_{ij}$  and  $\sigma_{ij}$  were employed

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (5)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} (1 - k_{ij}) \quad (6)$$

where  $k_{ij}$  is the binary interaction parameter. The combining rules suggested by Wolbach<sup>20,21</sup> and Sandler are expressed by

$$\varepsilon^{A_i B_j} = \frac{1}{2}(\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}) \quad (7)$$

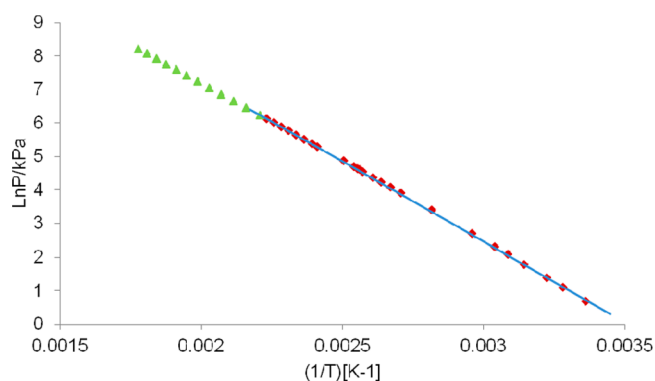
$$k^{A_i B_j} = \sqrt{k^{A_i B_i} k^{A_j B_j}} \left( \frac{\sqrt{\sigma_{ii} \sigma_{jj}}}{0.5(\sigma_{ii} + \sigma_{jj})} \right)^3 \quad (8)$$

## RESULTS AND DISCUSSION

**1. Pure Components.** The performance of the PC-SAFT equation was evaluated for representation of the thermodynamic properties of pure carboxylic acids such as critical points, boiling temperature, and vapor pressure. The set of PC-SAFT parameters for water and acetic acid was taken from the literature and is listed in Table 1. The parameters of the PC-SAFT equation for propionic acid and acrylic acid were obtained by fitting to selected experimental vapor pressure data from the literature. For the reason of keeping a minimum number of fitting parameters and a good estimation of the vapor pressure of propionic acid and acrylic acid, the associating parameters were kept constant (association energy  $\varepsilon^{A_i B_j}$  and association volumes  $k^{A_i B_j}$  were transferred from acetic acid,  $\varepsilon^{A_i B_j} = 3044.4$  [K] and  $k^{A_i B_j} = 0.075550$  [ $\text{\AA}^3$ ]) and the last three nonassociating parameters,  $m$ ,  $\varepsilon/k$ , and  $\sigma$ , were obtained fitting pure-component data. The PC-SAFT parameters of these two acids are those which minimize the following objective function (OF)

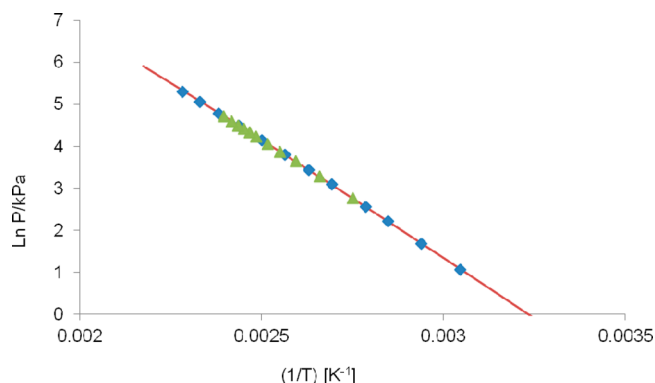
$$OF = \sum_{i=1}^{npts} \left( \frac{P_i^{\text{sat,exp}} - P_i^{\text{sat,cal}}}{P_i^{\text{sat,exp}}} \right) \quad (9)$$

Parameters obtained after optimization for propionic and acrylic acid but also the absolute average deviation (AAD%) between the calculated vapor pressure and experimental data are provided in Table 1. Furthermore, pressure–temperature diagrams and experimental data taken from the literature are presented in Figures 1–3. Good agreement between the vapor pressure calculated by PC-SAFT EOS and experimental data is observed.

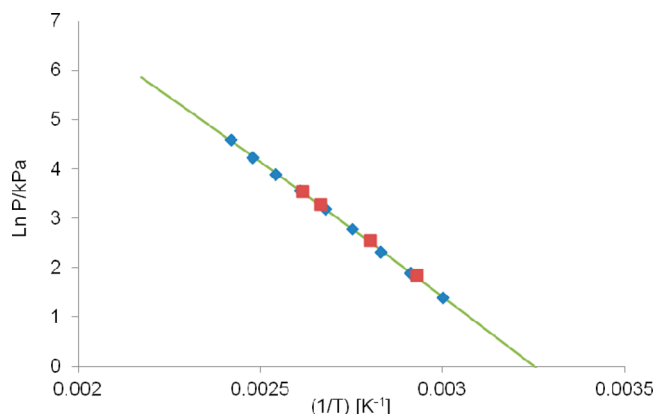


**Figure 1.** Experimental  $\ln P = f(1/T)$  diagram for acetic acid using molecular parameters from the literature. Comparison of PC-SAFT (solid line) to experimental data (♦ from ref 33 and ▲ from ref 34).

Critical properties and normal boiling temperature were estimated using the parameters obtained after optimization. Results for critical pressure and boiling temperature are presented in Table 2. It was found that estimates of the normal boiling temperature of pure carboxylic acid using PC-SAFT EoS is in good agreement with experimental data.<sup>33–44</sup>



**Figure 2.** Experimental  $\ln P = f(1/T)$  diagram for the propionic acid used in the molecular parameters estimation. Solid lines are the PC-SAFT calculation ▲ from ref 35 and ♦ from ref 36.



**Figure 3.** Experimental  $\ln P = f(1/T)$  diagram for the acrylic acid used in the molecular parameters estimation. Solid lines are the PC-SAFT calculation Comparison of PC-SAFT (solid line) to experimental data (■ from ref 37 and ♦ from ref 38).

**Table 2.** Binary Interaction Parameters  $k_{ij}$

binary system	$k_{ij}$		$k_{ij}$	
	isobaric	AAD%	isotherm	AAD%
water–acetic acid	−0.111	3.79	−0.152	7.13
water–propionic acid	−0.042	13.20		
water–acrylic acid	−0.163	16.32		
acetic acid–propionic acid	0.021	4.76	−0.018	0.74
acetic acid–acrylic acid	0.011	4.21		

However, a larger deviation between calculated critical properties and experimental data of pure carboxylic acid was observed. The deviation is mainly due to the fact that only experimental data below  $1.2T_b$  is used to determine the PC-SAFT parameters of pure carboxylic acids.

**2. Mixture.** The PC-SAFT model has been applied to binary systems: {water + acid} and {acid + acid}. Use of the PC-SAFT equation of state for mixtures requires knowledge of the binary interaction parameter  $k_{ij}$ . In a general manner, the  $k_{ij}$  parameter is determined using liquid–vapor equilibria data. In this work,  $k_{ij}$  have been determined in order to minimize the deviations between that calculated by the PC-SAFT model and experimental VLE data. A flash algorithm has been used to perform VLE calculations (for a selected binary system at  $T$  and  $P$ , we found the composition of liquid phase ( $x$ ) and vapor

Table 3. Critical Parameters and Boiling Point Using PC-SAFT Models

compounds	PC-SAFT calculation			literature		
	$T_c$ /K	$P_c$ /atm	$T_b$ /K	$T_c$ /K	$P_c$ /atm	$T_b$ /K
acetic acid	618.83	75.1838	392.04	594.786 <sup>41</sup>	57.862 <sup>[41]</sup>	391.05 <sup>42</sup>
propionic acid	619.69	62.9558	414.19	603.96 <sup>43</sup>	41.000 <sup>[44]</sup>	414.32 <sup>42</sup>
acrylic acid	578.83	32.0849	414.43	615.00 <sup>42</sup>	55.8599 <sup>42</sup>	414.15 <sup>42</sup>
water	675.38	293.2643	373.27	647.13 <sup>42</sup>	217.666 <sup>42</sup>	373.15 <sup>42</sup>

phase (y) in equilibrium). Values of interaction parameters  $k_{ij}$  are given in Table 3.

Then, experimental data for the systems (water + carboxylic acid) and two carboxylic acids were compared with data calculated using the PC-SAFT model.

**Mixture {Water + Carboxylic Acid}.** In this work, the binary mixtures {water + acetic acid}, {water + propionic acid}, and {water + acrylic acid} were studied. The phase behavior of water and carboxylic acid at  $P = 1.013$  bar is given in Figures 4–6 in a  $T$ – $x$ – $y$  diagram. A globally good agreement between

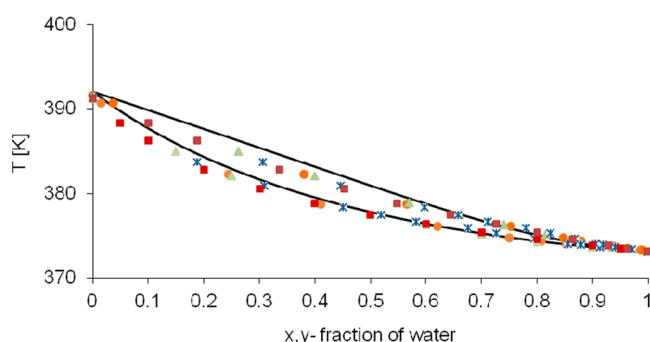


Figure 4. Vapor–liquid equilibria of water–acetic acid at  $P = 1.013$  (solid line). Comparison of experimental data (● from ref 45, ■ from ref 46, ▲ from ref 47 and \* from ref 48) to calculation results of PC-SAFT,  $k_{ij} = -0.111$ .

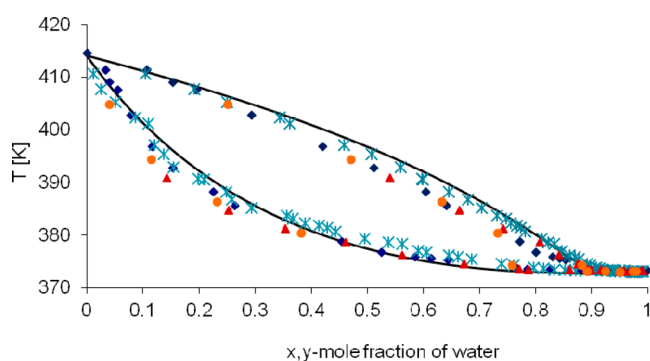


Figure 5. Vapor–liquid equilibria of water–propionic acid at  $P = 1.013$  bar. Comparison of experimental data (● from ref 49, ◆ from ref 50, ▲ from ref 51, and \* from ref 52) to calculation results of PC-SAFT,  $k_{ij} = -0.042$ .

experimental vapor–liquid equilibrium data and the calculated values using the PC-SAFT model is observed. The mixture {water + acetic acid} is particularly well represented with an average absolute deviation (AAD) between the calculated composition and the experimental data of about 3.79%. In the case of the binary mixtures {water + propionic acid} and {water + acrylic acid}, the AAD on the calculated liquid and vapor molar fractions is higher than 10%, Table 4. This deviation may be explained by the fact that the interaction parameter  $k_{ij}$  was

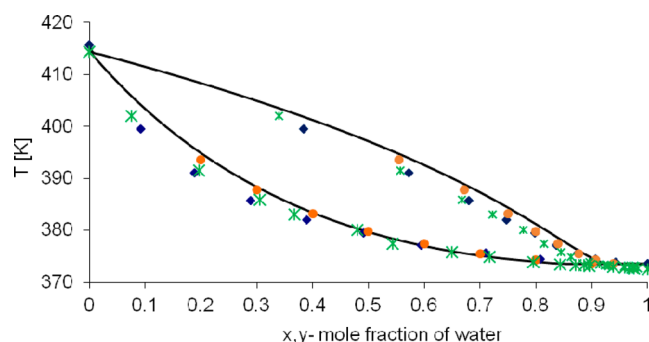


Figure 6. Vapor–liquid equilibria of water–acrylic acid at  $P = 1.013$  bar. Comparison of experimental data (◆ from ref 53, ● from ref 54, and \* from ref 55) to calculation results of PC-SAFT,  $k_{ij} = -0.163$ .

Table 4. Binary Interaction Parameters  $k_{ij}$  of {Water–Acid + Acetic} System at Constant Temperature and Deviation with Experimental Data

$T$ /K	$k_{ij}$	AAD%
293.15	−0.155	16.35
372.8	−0.105	26.5
412.6	−0.096	6.75
502.9	−0.086	3.13

kept constant for calculation of isobaric phase diagrams of both binary mixtures. It is well known that use of a temperature-dependent interaction parameter leads to better results. Another explanation is the experimental data dispersion. Indeed, the binary mixture {water + acrylic acid} is particularly difficult to measure while acrylic acid tends to polymerize in the vapor phase. The phase behavior of a mixture of water and acetic acid at  $T = 303.15$  K is displayed in Figure 7 in a  $P$ – $x$ – $y$  diagram. We notice low deviation between these calculations by PC-SAFT and experimental VLE data at high mole fraction.

Figure 8 represents relative volatility diagrams for {water–acetic acid}, {water–propionic acid}, and {water–acrylic acid}

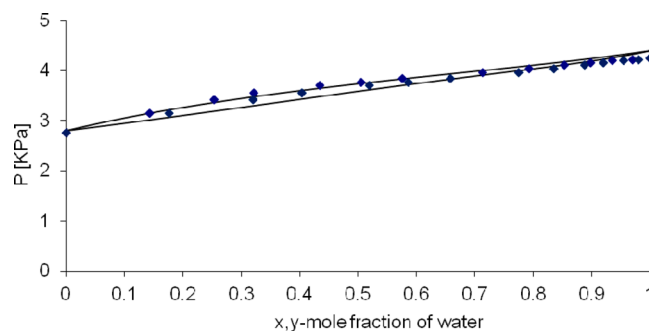
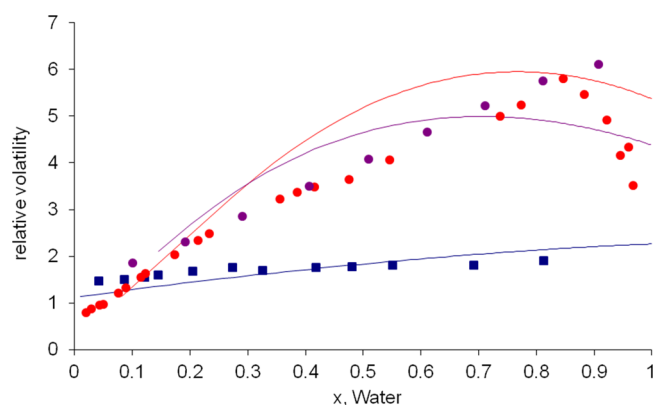


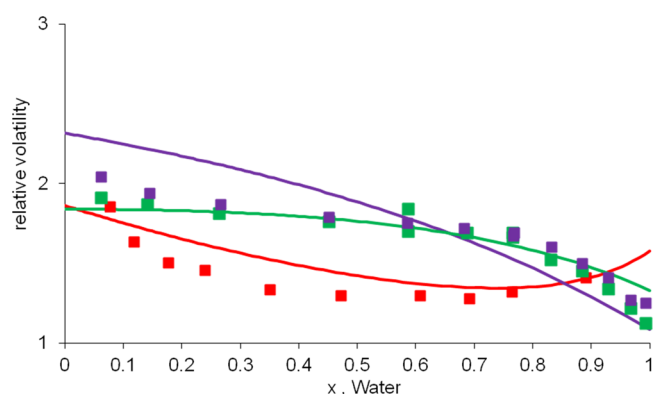
Figure 7. Vapor–liquid equilibria of water–acetic acid at  $T = 303.15$  K. Comparison of experimental data (◆ from ref 56) to calculation results of PC-SAFT,  $k_{ij} = -0.152$ .





**Figure 8.** Experimental and predicted by PC-SAFT relative volatilities for {water–acetic acid},<sup>48</sup> {water–propionic acid},<sup>50</sup> and {water–acrylic acid}<sup>53</sup> at atmospheric pressure.

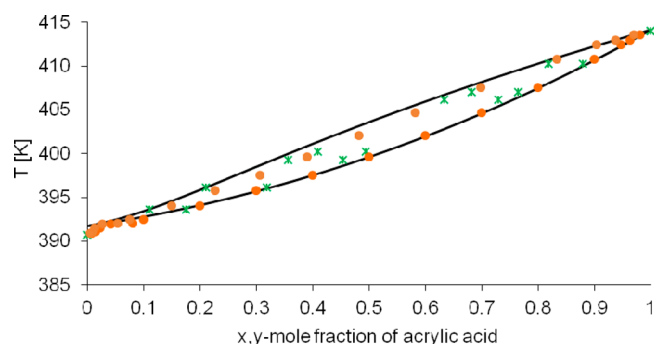
systems at atmospheric pressure. Figure 9 illustrates the trends of the relative volatility for the binary system {water–acetic



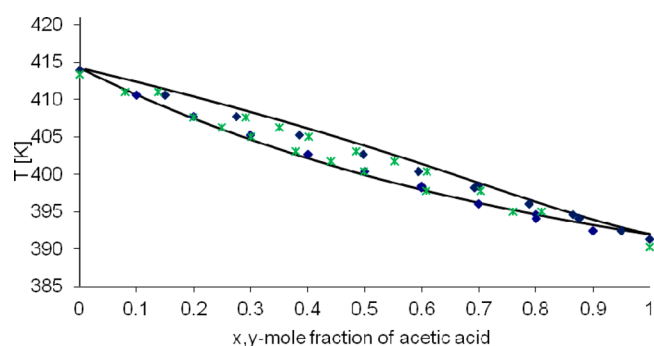
**Figure 9.** Experimental (square) and calculated (solid line) by PC-SAFT relative volatilities for water–acetic acid at different temperatures  $T = 293.15$ ,<sup>57</sup>  $412.6$ ,<sup>58</sup> and  $502.9$  K<sup>58</sup>.

acid} at different temperatures. It was found that the PC-SAFT model is able to represent the relative volatility with reasonable accuracy (from 3% to 16%). These calculations have been also made using the CPA equation.<sup>18</sup> Breil et al. found a deviation between experimental and calculated relative volatilities between 3% and 6%. In this case, better results are obtained using the CPA equation than PC-SAFT. Nevertheless, it must be noted that CPA parameters have been fitted to experimental vapor compressibility factor data and experimental relative volatility data at different temperatures.

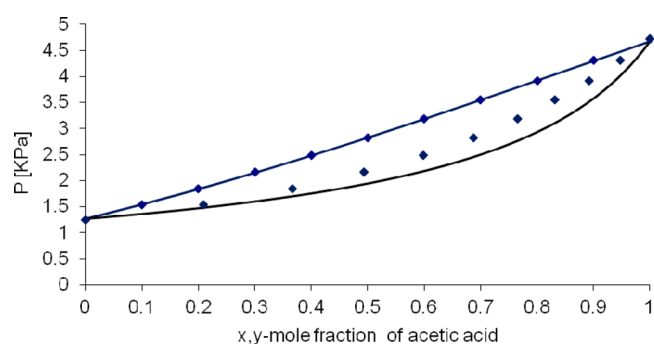
**Mixture of Two Carboxylic Acids.** The same approach was applied to binary systems {acetic acid–acrylic acid} and {acetic acid–propionic acid}. Experimental data for the isothermal vapor–liquid equilibrium of {acetic acid–acrylic acid} are very scarce in the literature. These very complex systems containing acids carboxylic have a tendency to dimerize in the vapor phase even at moderate pressures. Isobaric phase diagrams are presented in Figures 10 and 11. It is striking to see the accuracy of these calculations by the PC-SAFT model as compared to the experimental VLE data. Figure 12 depicts the phase behavior of acetic acid and propionic acid at  $T = 313.15$  K in a  $P$ – $x$ – $y$  diagram. Good agreement between experimental data and calculated values is observed.



**Figure 10.** Vapor–liquid equilibria of acrylic acid–acetic acid at  $P = 1.0044$  bar. Comparison of experimental data (● from ref 54 and \* from ref 55) to calculation results of PC-SAFT,  $k_{ij} = 0.011$ .



**Figure 11.** Vapor–liquid equilibria of acetic acid–propionic acid at  $P = 1.0133$  bar. Comparison of experimental data (◆ from ref 59 and \* from 55) to calculation results of PC-SAFT,  $k_{ij} = 0.021$ .



**Figure 12.** Vapor–liquid equilibria of acetic acid–propionic acid at  $T = 313.15$  K. Comparison of experimental data (◆ from ref 60) to calculation results of PC-SAFT,  $k_{ij} = -0.018$ .

The correlation is satisfactory for mixtures with two associating substances such as {acetic acid–propionic acid} and {acetic acid–acrylic acid}. In these cases, the average absolute deviations between the calculated composition and the experimental data are lower than 5%. This deviation is mainly due to the use of a constant  $k_{ij}$  parameter in the case of isobaric vapor–liquid equilibria. Indeed, the binary interaction parameter for binary system {acetic acid + propionic acid} is equal to  $k_{ij} = -0.018$  at  $T = 313.15$  K and is completely different from the interaction parameter used for calculation of the isobaric phase diagram at atmospheric pressure ( $k_{ij} = 0.021$ ).

Generally, from a physical point of view, the 2B model describes the monomer–dimer ‘chemical’ reaction and is suitable for description of the vapor-phase dimerization process.

## CONCLUSIONS

The perturbed-chain SAFT equation of state was used to model the phase equilibrium of a mixture of associating components such as carboxylic acids. Physically meaningful parameters of PC-SAFT for carboxylic acid were estimated on the basis of pure-component vapor pressure data. Deviations of 0.72% and 2.41% on vapor pressure after optimization were observed for propionic acid and acrylic acid, respectively. The capability of PC-SAFT to describe the binary systems {acid + acid} and {water + acid} using one constant interaction parameter  $k_{ij}$  is shown in this work. The accuracy of calculations by the PC-SAFT equation of state as compared to experimental VLE data is observed. In summary, the PC-SAFT model is able to model the phase behavior of carboxylic acid families.

## AUTHOR INFORMATION

### Corresponding Author

\*Phone: +33 3 83 17 51 31. Fax: +33 3 83 17 53 95. E-mail: fabrice.mutelet@ensic.inpl-nancy.fr.

### Notes

The authors declare no competing financial interest.

## REFERENCES

- (1) Asci, Y. S.; Inci, I. Extraction Equilibria of Acrylic Acid from Aqueous Solutions by Amberlite LA-2 in Various Diluents. *J. Chem. Eng. Data* **2010**, *55*, 2385.
- (2) Elliott, J. R.; Lira, C. T. Introductory Chemical Engineering Thermodynamics. *Series in the Physical and Chemical Engineering Sciences*; Prentice-Hall International: Upper Saddle River, NJ, 1999.
- (3) Elliott, J. R.; Vahid, A. Transferable intermolecular potentials for carboxylic acids and their phase behavior. *AIChE J.* **2010**, *56*, 485.
- (4) Jaspersen, L. V.; Wilson, L. C.; Brady, C. J.; Wilding, W. V.; Wilson, G. M. Vapor association of monocarboxylic acids from heat of vaporization and PVT measurements. *AIChE Symp. Ser.* **1989**, *85*, 102.
- (5) Kretschmer, C. B.; Wiebe, R. Thermodynamics of alcohol-hydrocarbon mixtures. *J. Chem. Phys.* **1954**, *22*, 1697.
- (6) Dolezalek, F. Theory of Binary Mixtures and Concentrated Solutions. *Z. Phys. Chem.* **1909**, *64*, 727.
- (7) Wertheim, M. Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations. *J. Stat. Phys.* **1984**, *35*, 35.
- (8) Wertheim, M. Fluids with highly directional attractive forces. III. Multiple attraction sites. *J. Stat. Phys.* **1986**, *42*, 459.
- (9) Kontogeorgis, G. M.; Voutsas, E.; Yakoumis, I.; Tassios, D. P. «An equation of state for associating fluids. *Ind. Eng. Chem. Res.* **1996**, *35*, 4310.
- (10) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New reference equation of state for associating liquids. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709.
- (11) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. SAFT: Equation-of-state solution model for associating fluids. *Fluid Phase Equilib.* **1989**, *52*, 31.
- (12) Perakis, C. A.; Voutsas, E. C.; Magoulas, K. G.; Tassios, D. P. Thermodynamic modeling of the water plus acetic acid + CO<sub>2</sub> system: The importance of the number of association sites of water and of the non association contribution for the CPA and SAFT-type models. *Ind. Eng. Chem. Res.* **2007**, *46*, 932.
- (13) Derawi, S. O.; Zeuthen, J.; Michelsen, M. L.; Stenby, E. H.; Kontogeorgis, G. M. Extension of the CPA equation of state to organic acids. *Fluid Phase Equilib.* **2004**, *225*, 107.
- (14) Folas, G. K.; Derawi, S. O.; Michelsen, M. L.; Stenby, E. H.; Kontogeorgis, G. M. Recent applications of the Cubic-Plus-Association (CPA) equation of state to industrially important systems. *Fluid Phase Equilib.* **2005**, *121*, 228.
- (15) Kontogeorgis, G. M.; Folas, G. K.; Muro-Sune, N.; Von Solms, N.; Michelsen, M. L.; Stenby, E. H. Modelling of Associating Mixtures for applications in the oil & gas and chemical industries. *Fluid Phase Equilib.* **2007**, *261*, 205.
- (16) Kontogeorgis, G. M.; Folas, G. K.; Muro-Sune, N.; Leon, F. R.; Michelsen, M. L. Solvation Phenomena in Association Theories with applications to oil & gas and chemical industries. *OGST Revue d'IFP.* **2008**, *63*, 305.
- (17) Muro-Sune, N.; Kontogeorgis, G.; Von Solms, N.; Michelsen, M. L. Phase equilibria modelling for mixtures with acetic acid using an association equation of state. *Ind. Eng. Chem. Res.* **2008**, *47*, 5660.
- (18) Breil, M. P.; Kontogeorgis, G. M.; Behrens, P. K.; Michelsen, M. L. Modeling of the Thermodynamics of the Acetic Acid-Water Mixture Using the Cubic-Plus-Association Equation of State. *Ind. Eng. Chem. Res.* **2011**, *50*, 5795.
- (19) Huang, S. H.; Radosz, M. Equation of state for small, large, polydisperse, and associating molecules—extension to fluid mixtures. *Ind. Eng. Chem. Res.* **1991**, *30*, 1994.
- (20) Wolbach, J. P.; Sandler, S. I. Using molecular orbital calculations to describe the phase behavior of hydrogen-bonding fluids. *Ind. Eng. Chem. Res.* **1997**, *36*, 4041.
- (21) Wolbach, J. P.; Sandler, S. I. Thermodynamics of hydrogen bonding from molecular orbital theory: 1. Water. *AIChE J.* **1997**, *43*, 1589.
- (22) Sandler, S. I.; Wolbach, J. P.; Castier, M.; Escobedo-Alvarado, G. Modeling of thermodynamically difficult systems. *Fluid Phase Equilib.* **1997**, *136*, 15.
- (23) Wolbach, J. P.; Sandler, S. I. Using molecular orbital calculations to describe the phase behavior of cross-associating mixtures. *Ind. Eng. Chem. Res.* **1998**, *37*, 2917.
- (24) Fu, Y. H.; Sandler, S. I. A simplified SAFT equation of state for associating compounds and mixtures. *Ind. Eng. Chem. Res.* **1995**, *34*, 1897.
- (25) Kouskoumvekaki, I. A.; Krooshof, G.; Michelsen, M. L.; Kontogeorgis, G. M. Application of the simplified PC-SAFT equation of state to the vapor\_liquid equilibria of binary and ternary mixtures of polyamide 6 with several solvents. *Ind. Eng. Chem. Res.* **2004**, *43*, 826.
- (26) Gross, J.; Sadowski, G. Application of the perturbed-chain SAFT equation of state to associating systems. *Ind. Eng. Chem. Res.* **2002**, *5510*, 41.
- (27) Gross, J.; Sadowski, G.; Perturbed-Chain, SAFT An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244.
- (28) Gupta, S.; Olson, J. D. Industrial needs in physical properties. *Ind. Eng. Chem. Res.* **2003**, *42*, 6359.
- (29) Grenner, A.; Tsivintzelis, I.; Kontogeorgis, G. M.; Economou, I. G.; Panayiotou, C. Evaluating the non-random hydrogen bonding (NRHB) and the simplified perturbedchain chain-statistical associating fluid theory (PC-SAFT). 1. Vapor\_liquid equilibria. *Ind. Eng. Chem. Res.* **2008**, *47*, 5636.
- (30) Kleiner, M. Thermodynamic modeling of complex systems: Polar and Associating fluids and mixtures. Ph.D. Thesis, Technical University of Dortmund, Dortmund, Germany, 2008.
- (31) Baker, J. A.; Henderson, D. Perturbation theory and equation of state for fluids: The square-well potential. *J. Chem. Phys.* **1967**, *47*, 2856.
- (32) Baker, J. A.; Henderson, D. Perturbation theory and equation of state for fluids. II. A successful theory of liquids. *J. Chem. Phys.* **1967**, *47*, 4714.
- (33) *Selected Values of Properties of Chemical Compounds, Data Project*; Thermodynamics Research Center, Texas A&M University, College Station, TX, 1984.
- (34) Young, S. The Vapour-Pressure, Specific Volumes, Heats of Vaporization, and Critical Constants of Thirty Pure Substances. *Proc. Roy. Soc. A* **1910**, *12*, 374.
- (35) Child, W. Ph.D. Thesis, University of Wisconsin, 1955.
- (36) Ambrose, D.; Ellender, J. H.; Gundry, H. A.; Lee, D. Thermodynamic Properties of Organic Oxygen Compounds. II. The Vapour Pressures of Some Esters and Fatty Acids. *J. Chem. Thermodyn.* **1981**, *13*, 795.

- (37) Linek, J.; Wichterle, I. Liquid-Vapor Equilibrium LX. The System Acetic Acid - Acrylic Acid at 200 Torr. *Collect. Czech. Commun.* **1973**, *38*, 1853.
- (38) Kirk-Othmer, *Encyclopedia of Chemistry*; Interscience: New York, 1978.
- (39) VDI-Warmeatlas; VDI-Gesellschaft Verfahrenstechnik und Chemieingenieurwesen (GVC): Dusseldorf, Germany, 1994.
- (40) Daubert, T. E.; Danner, R. P.; Sibul, H. M.; Stebbins, C. C. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Taylor & Francis, Washington, DC, 1989.
- (41) Young, S. The Internal Heat of Vaporization constants of thirty pure substances. *Sci. Proc. R. Dublin Soc.* **1910**, *12*, 374.
- (42) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The properties of gas and liquids*, 5th ed.; McGraw Hill: New York, 2001.
- (43) Pryanikova, R. O.; Plenkina, R. M.; Kuzyakina, N. V. Phase equilibriums and volume correlations in the propionic acid-isobutylene system. *Himi. promy.* **1987**, *1*, 13.
- (44) Ambrose, D.; Ghassee, N. B. Vapor Pressures and Critical Temperatures and Critical Pressures of Some Alkanoic Acids: C1 to C10. *J. Chem. Thermodyn.* **1987**, *19*, 505.
- (45) Gillmont, R.; Othmer, D. Composition of vapors from boiling binary solutions; H<sub>2</sub>O-AcOH system at atmospheric and subatmospheric pressures. *J. Ind. Eng. Chem.* **1944**, *36*, 1061.
- (46) Othmer, D. F.; Silvis, S. J.; Spiel, A. Composition of vapors from boiling binary solutions. Pressure equilibrium still for studying water-acetic acid system. *J. Ind. Eng. Chem.* **1952**, *44*, 1864.
- (47) Brusset, H.; Kaiser, L.; Hocquel, J. New cyclic ebulliometer. *Chim. Ind., Gen. Chim.* **1968**, *99*, 220.
- (48) Shanghai, S. C. C. E.; , INST. **1976**, *Petrochem. Acta Chimica Sinica* *34*, 79.
- (49) Rivenq, F. Vapor-liquid data for the system water-propionic acid. *Bull. Soc. Chim. Fr.* **1961**, 1392.
- (50) Amer Amezaga, S. Vapor-liquid equilibrium at 760 mm of binary systems formed by propionic acid with water and n-amyl, isoamyl, sec-amyl, tert-amyl, and n-hexyl alcohols. *Anal. Quim.* (1968–1979). **1975**, *71*, 127.
- (51) Kushner, T. M.; Tatsievskaya, G. I.; Serafimov, L. A. Liquid-vapor phase equilibrium in the water-formic acid-propionic acid system under atmospheric pressure,». *Zh. Fiz. Khim.* **1967**, *41*, 237.
- (52) Ito, T.; Yoshida, F. Vapor-liquid equilibria of water-lower fatty acid systems: Water-formic acid, water acetic acid and water-propionic acid. *J. Chem. Eng. Data* **1963**, *8*, 315, 1963.
- (53) Olson, J. D.; Morrison, R. E.; Wilson, L. C. Thermodynamics of Hydrogen-Bonding Mixtures. S.GE. HE. and TSE and Zeotropy of Water + Acrylic acid. *Ind. Eng. Chem. Res.* **2008**, *47*, 5127.
- (54) Chubarov, G. A.; Danov, S. M.; Brovkina, G. V. Liquid-vapor equilibrium in butyl alcohol-acrylic acid, propyl alcohol-acrylic acid, water-acrylic acid, and acetic acid-acrylic acid systems. *J. Appl. Chem. USSR* **1976**, *49*, 1447.
- (55) Attia, A.; Mutelet, F.; Moise, J. C.; Solimando, R.; Jeday, M. R.; Tretjak, S.; Baba-ahmed, A. Thermodynamic modeling of acrylic acid purification process. *Abstracts of Papers, 243rd ACS National Meeting & Exposition*, San Diego, CA, United States, Mar. 25–29, 2012; American Chemical Society: Washington, DC, 2012; IEC-217.
- (56) Marek, J. Vapor-liquid equilibria in mixtures containing an associating substance. III. Binary and ternary systems of water, acetic acid, and acetic anhydride at 400 mm. Hg. *Collect. Czech. Chem. Commun.* **1956**, *21*, 269.
- (57) Lazeeva, M.; Markuzin, N. Experimental Data on Phase Equilibrium and on Chemical Equilibrium in the Vapor in the System Acetic Acid-Water at 20 deg. *Zh. Prikl. Khim. (Leningrad)* **1973**, *46*, 360.
- (58) Freeman, J. R.; Wilson, G. M. High Temperature Vapor-Liquid Equilibrium Measurements on Acetic Acid/Water Mixtures. *AIChE Symp. Ser.* **1985**, *81*, 14.
- (59) Serafimov, L. A.; Kushner, T. M.; L'vov, S. V. Liquid-vapor equilibrium in the system acetic acid-propionic acid at atmospheric pressure. *Zh. Fiz. Khim.* **1962**, *36*, 1830.
- (60) Mikhailova, O.; Markuzin, N. Study of liquid-associated vapor equilibrium in the formic acid–acetic acid–propionic acid system at 40 °C. *Zh. Obshch. Khim.* **1983**, *53*, 713.