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**Tsivintzelis, Ioannis; Kontogeorgis, Georgios**

*Published in:*  
Industrial & Engineering Chemistry Research

*Link to article, DOI:*  
[10.1021/ie301388d](https://doi.org/10.1021/ie301388d)

*Publication date:*  
2012

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Tsivintzelis, I., & Kontogeorgis, G. (2012). Capabilities and Limitations of an Association Theory for Chemicals in Liquid or Supercritical Solvents. *Industrial & Engineering Chemistry Research*, 51(41), 13496-13517. DOI: 10.1021/ie301388d

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# Capabilities and Limitations of an Association Theory for Chemicals in Liquid or Supercritical Solvents

Ioannis Tsivintzelis\* and Georgios M. Kontogeorgis

Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

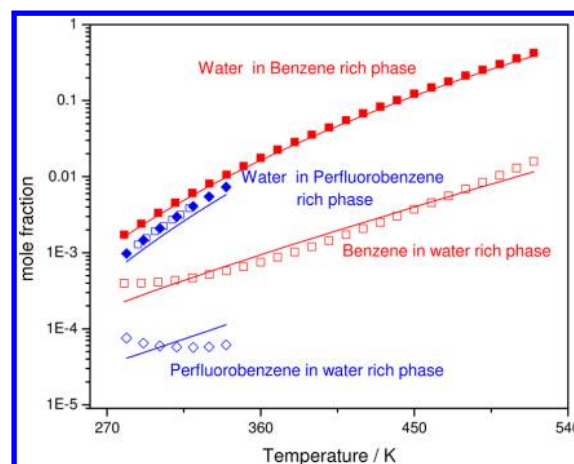
## Supporting Information

**ABSTRACT:** The cubic-plus-association (CPA) model is an equation of state (EoS) that combines the Soave–Redlich–Kwong (SRK) equation with the association term from Wertheim’s theory as used in statistical associating fluid theory (SAFT). In the form used here, the CPA EoS does not include separate terms for the polar and quadrupolar contributions. The capabilities and limitations of the CPA model when it is applied to mixtures with nonpolar and polar chemicals, as well as associating (hydrogen-bonding) compounds are illustrated. Three case studies are considered, all of which are of industrial relevance. The capabilities of the model are illustrated in the first two case studies: the phase behavior of mixtures used in the oxidation of 2-octanol in supercritical CO<sub>2</sub> and the investigation of systems containing acetone, methanol, water, chloroform, and methyl acetate. In each case, both correlations of vapor–liquid and liquid–liquid equilibria for binary systems and predictions for multicomponent mixtures are presented. Finally, the limitations of the CPA model are illustrated in the last case study, which focuses on the modeling of mixtures containing aromatic acids, such as benzoic and terephthalic acid. We also include a detailed discussion of the capabilities and limitations of the model in context and related to previous investigations. Finally, results are compared to observations from studies with other association models.

## 1. INTRODUCTION

The capabilities of association models such as those originating from statistical associating fluid theory (SAFT) in describing and predicting phase behavior for complex mixtures is well-established.<sup>1–3</sup> Several publications<sup>4,5</sup> outline many successful applications of such models.<sup>1–3</sup> In this work, we focus on a simplified version of SAFT, the so-called cubic-plus-association (CPA) equation of state (EoS) proposed by Kontogeorgis et al.<sup>6</sup> In this model, the physical and chain terms of SAFT have been replaced by the Soave–Redlich–Kwong (SRK) EoS.<sup>7</sup> The model has been extensively presented in the literature, and the reader is referred to the original publication<sup>6</sup> and recent reviews<sup>4,8,9</sup> for the equations and details on model development.

The capabilities of the CPA EoS for systems relevant to the petroleum industry are well-established.<sup>4</sup> For example, the CPA model can predict satisfactorily multicomponent, multiphase equilibria for mixtures containing water, hydrocarbons, and alcohols or glycols<sup>4,8–10</sup> as well as reservoir fluids.<sup>11,12</sup> The CPA model has recently been applied with success to systems containing acid gases (CO<sub>2</sub>, H<sub>2</sub>S).<sup>13,14</sup> A typical example is shown in Figure S1 of the Supporting Information using the experimental vapor–liquid and vapor–liquid–liquid equilibrium data of ref 15. Moreover, when the strong cross-association (solvation) between aromatic hydrocarbons or aromatic fluorocarbons and water is explicitly taken into account, the CPA EoS can describe satisfactorily liquid–liquid equilibria for these immiscible systems, as shown in Figure 1. In the CPA model, solvation for such systems (containing one non-self-associating compound) is taken into account using the modified CR-1 combining rule.<sup>4</sup> In this case, two interaction parameters are optimized using the experimental data: an interaction



**Figure 1.** Water–perfluorobenzene and water–benzene liquid–liquid equilibria: experimental data,<sup>16–18</sup> points; CPA correlations, lines. The solvation is explicitly taken into account in the CPA calculations using parameters from ref 23.

parameter in the physical term ( $k_{ij}$ ) and the cross-association volume parameter ( $\beta_{\text{cross}}$ ).

The solvation is important in other cases as well. That was evident, for example, in our study of vapor–liquid (VLE), vapor–liquid–liquid (VLLE), and liquid–liquid (LLE) equilibria in methanol–ethane and methanol–ethylene systems. One

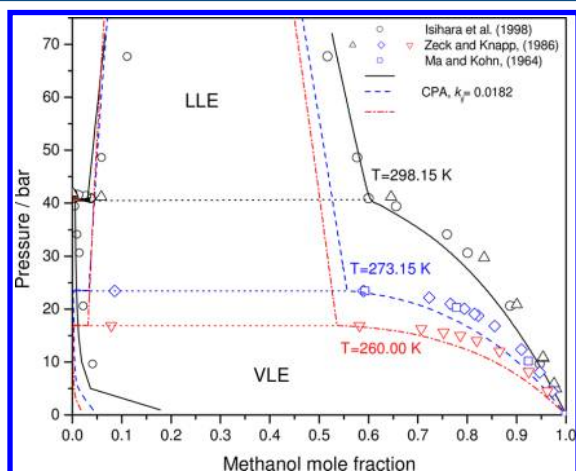
**Received:** May 28, 2012

**Revised:** September 10, 2012

**Accepted:** September 11, 2012

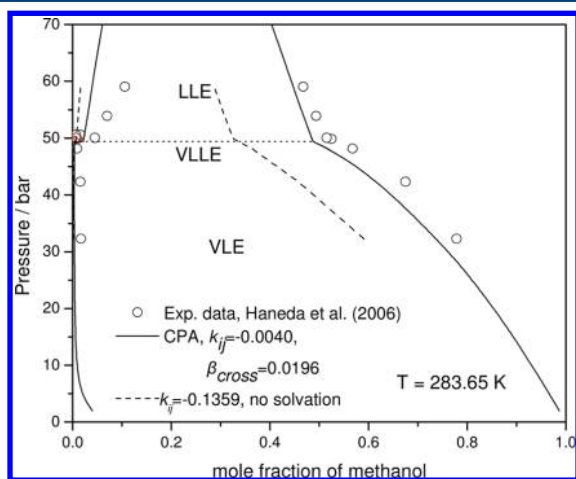
**Published:** September 11, 2012

temperature-independent binary interaction parameter was used for methanol–ethane, as shown in Figure 2, and satisfactory



**Figure 2.** Methanol–ethane phase equilibria: experimental data,<sup>19–21</sup> points; CPA calculations, lines. CPA pure-fluid parameters were adopted from ref 14.

results were obtained. However, to obtain good agreement to experimental data for methanol–ethylene, solvation was assumed, and thus two adjustable parameters were used. The results are shown in Figure 3, and it can be seen that the CPA model can describe this complex phase behavior (including the three-phase equilibrium) quite well.



**Figure 3.** Methanol–ethylene phase equilibria: experimental data,<sup>22</sup> points; CPA calculations with and without explicitly accounting for solvation, lines. The CPA methanol parameters were adopted from ref 14, and the ethylene CPA parameters are  $a_0 = 4.5453 \text{ L}^2 \text{ bar mol}^{-2}$ ,  $b = 0.0383 \text{ L mol}^{-1}$ , and  $c_1 = 0.5715$ .

More specifically, the results are satisfactory for the vapor–liquid equilibrium (VLE) and vapor–liquid–liquid equilibrium (VLLE) data, whereas somewhat higher deviations from the experimental data were obtained for the liquid–liquid equilibrium (LLE). The use of solvation is justified by the experimental observation of increased interactions of both aromatic and olefinic hydrocarbons with polar molecules such as methanol and water.

In conclusion, for systems of relevance to the petroleum industry, very satisfactory (and sometimes excellent) results can

be obtained with the CPA EoS. This is the case even though the model has a simple (cubic EoS) physical term and does not explicitly take polarity into account. For such systems, hydrogen bonding is the dominant factor, and the explicit account for association phenomena in the CPA model gives satisfactory results for VLE, LLE, and VLLE, for both binary and multicomponent systems.<sup>4</sup> As mentioned, for solvating systems such as water or glycols with BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds, solvation has to be taken into account. This introduces two adjustable parameters, but sometimes, one of them can be eliminated using the so-called homomorph approach, as shown by Breil et al.<sup>23</sup>

However, many more complex chemicals are of interest to the chemical industry, many of which have varying degrees of polarity and hydrogen bonding and exhibit complex interactions. The CPA model has previously been applied to a variety of chemicals, including amines,<sup>24</sup> aliphatic acids,<sup>25,26</sup> acetone–water,<sup>4,27</sup> heavy alcohols,<sup>27,4</sup> ethers and esters,<sup>4,26,27</sup> sulfolane,<sup>4</sup> glycol ethers,<sup>28</sup> and alkanolamines.<sup>29,30</sup>

In general, satisfactory results are obtained for mixtures of associating chemicals with hydrocarbons (and other inert compounds), but when water is present, a large interaction parameter is needed, and there is some uncertainty about which combining rule is best for cross-associating mixtures. The problem for aqueous mixtures is particularly pronounced for those containing acetic (or formic) acid with water, for which satisfactory results over extensive temperature ranges can be obtained only if the Huron–Vidal mixing rules are used instead of the van der Waals one-fluid mixing rules in the SRK part of the model.<sup>26,31</sup> Mixtures of ethers or esters with water again require that solvation be taken into account, especially for LLE.

Polar nonassociating compounds such as sulfolane and acetone can exhibit significant deviations from ideality (such systems present LLE with some alkanes at low temperatures), and these effects are not predicted satisfactorily with the CPA EoS, which reduces to the SRK EoS in these cases. Treating these polar compounds as pseudoassociating often improves the predictive and correlative capabilities of the model, especially for liquid–liquid equilibria,<sup>4</sup> although this is a physically incorrect approach.

Finally, advanced association schemes have been investigated for alkanolamines,<sup>30</sup> but the results are not much improved compared to a more conventional four-site scheme used for most alkanolamines.

Although the aforementioned studies give a good picture of the performance of the CPA EoS for mixtures with polar chemicals, the picture is far from complete. In most cases, low-pressure systems have been considered; many important families of compounds, such as heavy ketones and aromatic acids, have not been modeled; and most studies have involved one type of phase behavior, that is only VLE, LLE, or SLE (solid–liquid equilibrium) but not both or all of them. Finally, most studies involving complex chemicals are limited to binary systems, whereas in many practical applications, multicomponent systems are of importance.

These omissions become evident when one attempts to address a number of systems of industrial relevance. In this work, we illustrate the capabilities and the limitations of the CPA EoS for three case studies of industrial relevance, all involving complex chemicals, namely

- (1) the phase behavior of mixtures used in the oxidation of 2-octanol in supercritical  $\text{CO}_2$ ;

Table 1. CPA Parameters for Pure Fluids<sup>a</sup>

$T_c$ (K)	$a_o$ (L <sup>2</sup> bar mol <sup>-2</sup> )	$b$ (L mol <sup>-1</sup> )	$c_1$	$\varepsilon$ (bar L mol <sup>-1</sup> )	$\beta$	AAD <sup>b</sup> (%)	
						$P^{\text{sat}}$	$V^{\text{liq}}$
629.8	38.4586	0.1458	2-Octanol <sup>c</sup> (0.4–0.9 $T_c$ ) 1.1689	206.27	0.00107	0.4	0.9
535.5	18.1612	0.0774	2-Butanone (0.5–0.9 $T_c$ ) 0.8476	–	–	0.3	1.1
561.08	22.5775	0.0930	2-Pentanone (0.5–0.9 $T_c$ ) 0.9127	–	–	0.4	0.6
587.61	27.9298	0.1097	2-Hexanone (0.45–0.9 $T_c$ ) 0.9650	–	–	1.4	0.8
611.4	33.6294	0.1271	2-Heptanone (0.4–0.9 $T_c$ ) 1.0210	–	–	1.7	1.2
632.7	39.8656	0.1440	2-Octanone (0.4–0.9 $T_c$ ) 1.0432	–	–	1.6	1.9

<sup>a</sup>Temperature range of each regression shown in parentheses. <sup>b</sup>AAD (%) =  $1/n \sum_i |(X_i^{\text{cal}} - X_i^{\text{exp}})/X_i^{\text{exp}}| \times 100$ , where  $X$  represents  $P^{\text{sat}}$  or  $V^{\text{liq}}$  and  $n$  is the number of experimental data points. <sup>c</sup>The 2B association scheme was used for 2-Octanol.

- (2) the phase equilibrium of multicomponent systems containing acetone, methanol, water, chloroform, and/or methyl acetate; and
- (3) the phase equilibrium of mixtures containing aromatic acids such as benzoic acid and terephthalic acid.

Then, the Discussion section provides a unified assessment of all three cases and attempts to present the results in some perspective also in relation to other association models.

## 2. PHASE BEHAVIOR OF MIXTURES USED IN THE OXIDATION OF 2-OCTANOL IN SUPERCRITICAL CO<sub>2</sub>

A number of homogeneous and heterogeneous catalytic reactions have been performed successfully in supercritical fluids (SCFs),<sup>32,33</sup> particularly supercritical CO<sub>2</sub>. Compared to liquid organic solvents, supercritical CO<sub>2</sub> is environmentally friendly, safer in combination with oxygen, and chemically stable with respect to oxidation. Indeed, higher reaction rates were observed in alcohol oxidation.<sup>32,33</sup> To optimize catalytic processes involving CO<sub>2</sub> as a solvent, knowledge about the phase behavior is important, and depending on the substrate, it can be advantageous to work in the single- or two-phase region.<sup>32</sup>

In this case study, the phase behavior of mixtures that are used in the oxidation of 2-octanol to 2-octanone in supercritical CO<sub>2</sub> is modeled using the CPA equation of state. The modeling follows the standard approach: First, the pure-fluid parameters are estimated for the compounds involved. Next, the binary interaction parameters are estimated based on literature data. Finally, the phase behavior of the ternary systems CO<sub>2</sub>–2-octanol–O<sub>2</sub> (mixture of reactants) and CO<sub>2</sub>–2-octanone–water (mixture of products), as well as multicomponent mixtures containing CO<sub>2</sub>, reactants, and products, is predicted.

The CPA pure-compound parameters not available in the literature were estimated using saturated liquid density and vapor pressure data from the DIPPR correlation.<sup>34</sup> The parameters are listed in Table 1. The parameters for CO<sub>2</sub>, O<sub>2</sub>, and water were taken from literature.<sup>8,14,33</sup> The CPA model was found to correlate both properties satisfactorily, and as shown in previous studies,<sup>4</sup> the covolume parameter ( $b$ ) assumed a smoothed trend with the van der Waals volume (as presented in Figure S2 of the Supporting Information).

**2.1. Binary Mixtures.** To predict the phase behavior of multicomponent mixtures, the CPA binary parameters were obtained for the corresponding binary subsystems. In this

direction, calculations for binary systems containing 2-octanol, 2-octanone, CO<sub>2</sub>, O<sub>2</sub>, and/or water (the compounds included in the mixtures of reactants and products for the oxidation reaction) were performed to estimate the corresponding binary parameters. Because it was not possible to find experimental data for all of the corresponding binary systems, in some cases, calculations were performed for similar binary mixtures (which, for example, might contain 1-octanol instead of 2-octanol or other 2-ketones instead of 2-octanone). Binary parameters for CO<sub>2</sub>–water and CO<sub>2</sub>–oxygen were adopted from previous studies.<sup>14,33</sup> First, the 1-octanol–water system was investigated (because of a lack of data for 2-octanol–water). A satisfactory LLE correlation was obtained using one interaction parameter ( $k_{ij} = -0.059$ ) and the CR-1 combining rule. The average absolute deviation (AAD) between experimental<sup>35</sup> and correlated mole fractions (in the range of 293–333 K) is 38% for octanol in water and 23% for water in octanol. (The results are illustrated in Figure S3 of the Supporting Information.)

Next, various water–2-ketone systems were studied, as it was not possible to find experimental data for the phase behavior of the water–2-octanone mixture. We investigated whether a dependency of the binary parameter could be established so that the parameter for the missing system could be estimated. In this direction, the phase behavior of binary aqueous systems containing various 2-ketones of different molecular weight was modeled.

The water–ketone systems were modeled as solvating, assuming one negative association site in each ketone molecule that is able to cross-associate with only the positive sites of water. As is typically done with the CPA model, the modified-CR1 combining rule<sup>27</sup> was used. Very satisfactory results were obtained, using a constant cross-association volume parameter ( $\beta_{\text{cross}} = 0.400$ ). In this way, a linear correlation was established between the  $k_{ij}$  values and the molecular weight of ketones, as shown in Figure 4. Using this correlation, the binary interaction parameter for water–2-octanone was estimated to be  $k_{ij} = -0.112$ . The detailed results for all of the examined water–2-ketone systems are presented in Table S1 of the Supporting Information, and results for a typical mixture are presented in Figure 5.

Next, the vapor–liquid equilibrium of CO<sub>2</sub>–2-octanol was successfully modeled using a temperature-dependent binary interaction parameter:  $k_{ij} = -5.26 \times 10^{-4}T(\text{K}) + 0.16615$  regressed in the 303.15–323.15 K temperature range using the



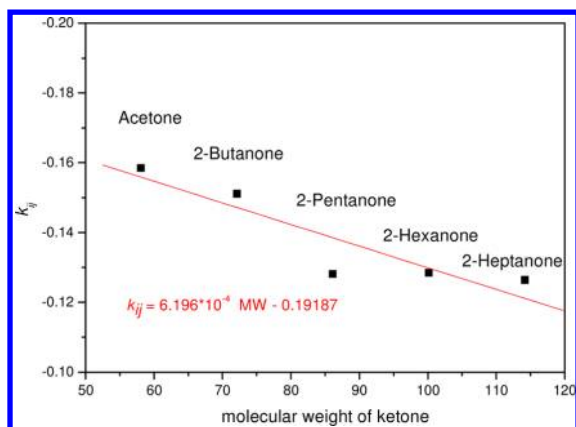


Figure 4. Binary interaction parameters versus molecular weight for 2-ketone–water VLE and LLE.

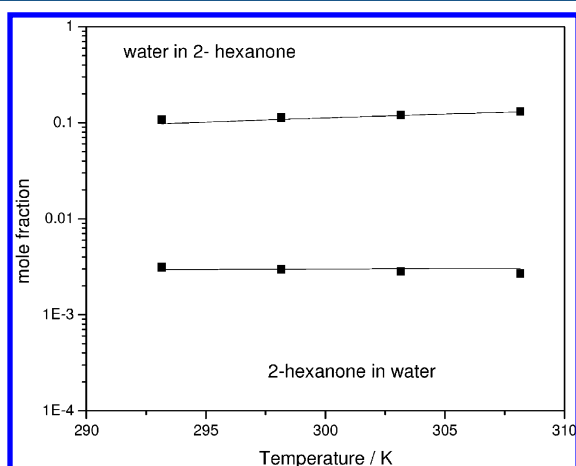


Figure 5. LLE for 2-hexanone–water: experimental data,<sup>35</sup> points; CPA calculations using  $k_{ij} = -0.1284$  and  $\beta_{\text{cross}} = 0.400$ , lines.

experimental data of Gamse and Marr<sup>36</sup>). No cross-association was assumed between  $\text{CO}_2$  and octanol molecules. In this way, satisfactory results were obtained (as presented in Figure S4 of the Supporting Information). Furthermore, very satisfactory results were obtained for  $\text{CO}_2$ –2-octanone, using  $k_{ij} = 0.0451$  as estimated from the solubility of  $\text{CO}_2$  in the liquid solvent at 298 K based on the data of Anitescu et al.<sup>37</sup>

Finally, it was not possible to find experimental data for the solubility of  $\text{O}_2$  in 2-octanol. For this reason, the binary interaction parameter for the similar  $\text{N}_2$ –1-octanol mixture was used. For the latter system, very satisfactory results were obtained over the 333.15–453.15 K temperature range using a temperature-independent binary interaction parameter ( $k_{ij} = 0.1474$ ) adjusted to the experimental data Weng and Lee.<sup>38</sup> (The results are presented in Figure S5 of the Supporting Information.)

**2.2. Multicomponent Mixtures.** Using the parameters for the binary systems for which experimental data were available, the CPA EoS was used to predict the phase behavior of multicomponent systems, which was the initial aim of this case study. Results for the phase behavior of the  $\text{CO}_2$ – $\text{O}_2$ –2-octanol and  $\text{CO}_2$ –water–2-octanone ternary mixtures, with characteristic compositions, are presented in Figures 6 and 7, respectively. According to the model predictions, the former system (mixture of reactants) exhibits vapor–liquid equilibrium or exists in a single phase under all of the investigated pressure and temperature conditions. The latter system (mixture of products)

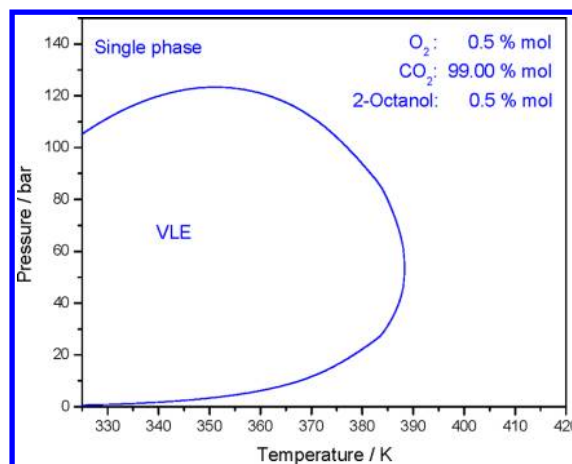


Figure 6. CPA predictions for the phase behavior of a mixture of reactants with a characteristic composition.

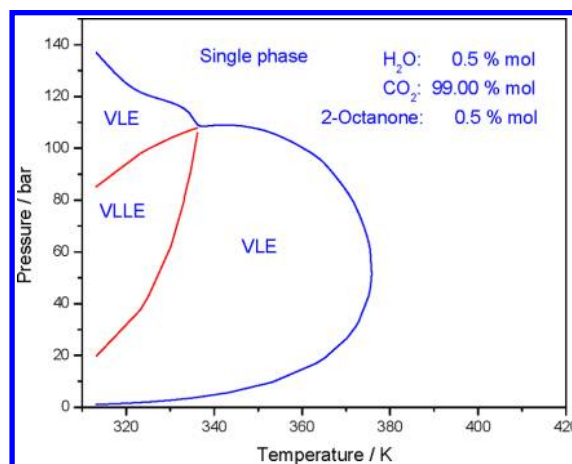


Figure 7. CPA predictions for the phase behavior of a mixture of products with a characteristic composition.

can exhibit three-phase (VLLE) or two-phase (VLE) equilibrium.

Finally, the phase behavior of multicomponent mixtures containing water, 2-octanol,  $\text{CO}_2$ , 2-octanone, and  $\text{O}_2$  was predicted. Results are presented in Figure 8a–c for three mixtures with different compositions. In the first mixture, only vapor–liquid equilibrium appears in the inhomogeneous region. As the reaction evolves in time and the concentrations of water and 2-octanone increase, a three-phase region (vapor–liquid–liquid equilibrium) might also appear. However, according to model predictions, all of the investigated mixtures are in a single phase at temperatures higher than 389 K.

In conclusion, the CPA equation of state was used for predicting the phase behavior of mixtures containing water, 2-octanol,  $\text{CO}_2$ , 2-octanone, and  $\text{O}_2$ , which are of interest in the catalytic oxidation of 2-octanol in supercritical  $\text{CO}_2$ . For this reason, pure-fluid parameters were estimated for all components of interest, and the CPA binary interaction parameters were calculated from the corresponding binary systems. It was found that the CPA EoS is a versatile model that can capture the complicated phase behavior of such systems. According to the predictions of this model, all of the investigated ternary and multicomponent systems are in a single phase at temperatures higher than 389 K.

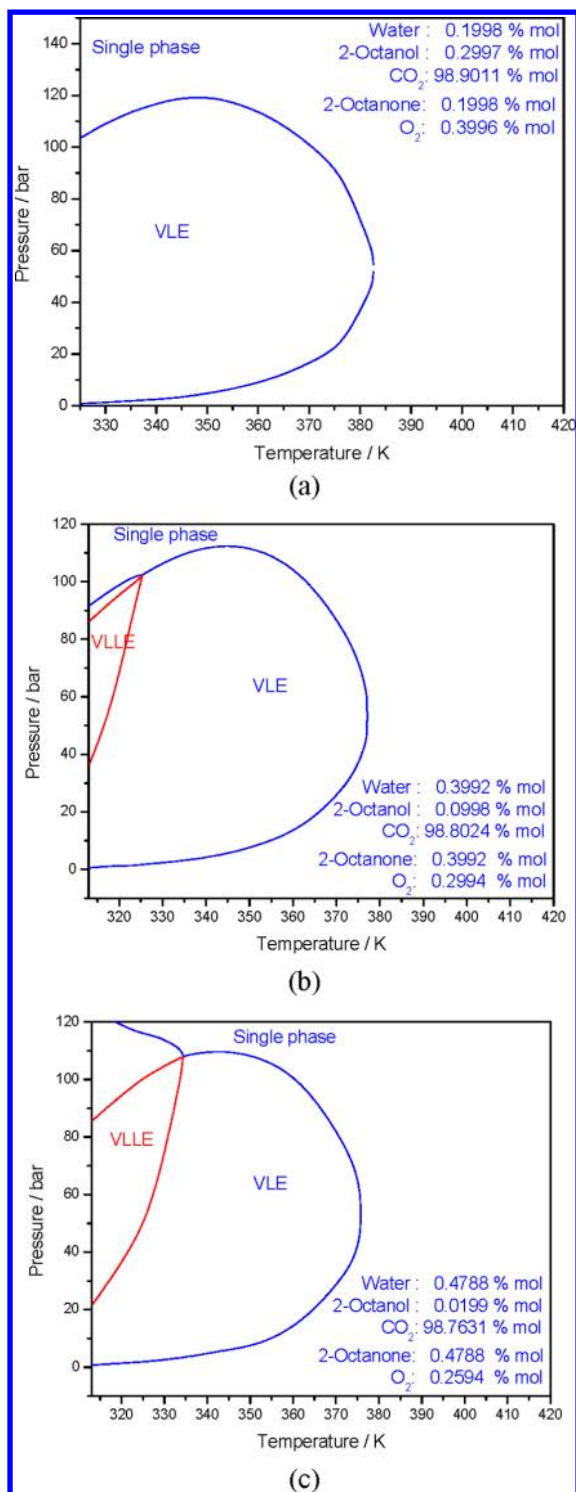


Figure 8. CPA predictions for the phase behavior of three multicomponent mixtures.

### 3. PHASE EQUILIBRIUM OF MULTICOMPONENT SYSTEMS CONTAINING ACETONE, METHANOL, WATER, CHLOROFORM, AND/OR METHYL ACETATE

The purpose of the second case study is to investigate the performance of the CPA EoS for mixtures of industrial relevance containing polar, nonpolar, and associating compounds. Of special interest is the study of the predictive performance of the CPA model for multicomponent systems. Pure-compound

parameters for water, methanol, acetone, and methyl acetate were obtained from the literature.<sup>26,27</sup> Pure-compound parameters for chloroform were estimated in this study using data from the DIPPR correlation<sup>34</sup> ( $a_0 = 15.0464 \text{ L}^2 \text{ bar mol}^{-2}$ ,  $b = 0.0663 \text{ L mol}^{-1}$ , and  $c_1 = 0.7568$ ). First, emphasis was placed on correlating the binary mixtures using either temperature-independent or temperature-dependent interaction parameters. The effect of considering some of the polar compounds as pseudoassociating was also investigated. The final test was to predict VLE for the methyl acetate–methanol–water, acetone–methanol–water, and chloroform–methanol–methyl acetate ternary systems.

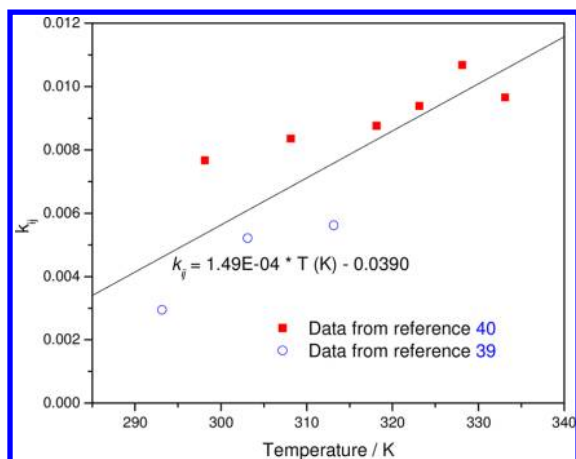
**3.1. Binary Mixtures.** **3.1.1. Acetone–Methyl Acetate.** Acetone–methyl acetate VLE was modeled assuming that both fluids are nonassociating. The use of a single temperature-independent binary interaction parameter ( $k_{ij}$ ) was found to result in satisfactory correlations of the VLE with an absolute average deviation in vapor pressures around 1%. The use of a temperature-dependent  $k_{ij}$  resulted in some improvement for the vapor pressure. The results are presented in Table 2.

Table 2. Binary Interaction Parameters and Deviations from Experimental Data for Acetone (1)–Methyl Acetate (2) VLE

temperature (K)	$k_{ij}$	AAD (%)		ref for experimental data
		$P$	$y_2$	
Temperature-Independent $k_{ij}$				
293.15	0.0069	1.4	0.8	39
303.15		0.8	1.9	39
313.15		0.5	1.0	39
323.15		1.1	–	40
333.15		1.1	–	40
overall		1.0	1.2	
Temperature-Dependent $k_{ij}$				
293.15	0.00295	0.7	1.7	39
298.15	0.00767	0.5	–	40
303.15	0.00521	0.6	1.8	39
308.15	0.00835	0.5	–	40
313.15	0.00561	0.5	1.2	39
318.15	0.00875	0.5	–	40
323.15	0.00939	0.5	–	40
328.15	0.01068	0.5	–	40
333.15	0.00965	0.5	–	40
overall		0.5	1.3	

As shown in Figure 9,  $k_{ij}$  values obtained based on data from the same group (for example, Olson et al.<sup>40</sup>) follow a linear trend. However, the linear trend is not as pronounced if data from all sources are included, indicating differences between the experimental data sets. However, a rough linear correlation of  $k_{ij}$  was obtained, including all data sources.

**3.1.2. Methanol–Acetone.** Methanol–acetone VLE was modeled using two approaches: First, acetone was assumed to be non-self-associating (and solvation in methanol was taken into account), whereas in a second approach, acetone was modeled as self-associating fluid using the 2B association scheme. As reported in section 1, treating these polar compounds as pseudoassociating often improves the predictive and correlative capabilities of the CPA model,<sup>4,27,41</sup> although this is a physically incorrect approach. Using the first approach, acetone was modeled assuming that each molecule has one proton-acceptor site that is able to cross-associate only with methanol's proton-donor site. The modified CR-1 rule<sup>27</sup> was used to estimate the



**Figure 9.** CPA binary interaction parameters as a function of temperature for acetone–methyl acetate.

cross-association parameters. In the second approach, in which acetone was modeled as self-associating fluid using the 2B association scheme, the cross-association with methanol was taken into account, and the corresponding parameters were estimated using the CR-1 combining rule.<sup>27</sup> Results using both temperature-dependent and temperature-independent  $k_{ij}$  values are presented in Table 3. In Figure 10,  $k_{ij}$  values are plotted against temperature, and a linear trend can be assumed. However, as was also observed for acetone–methyl acetate, the values obtained from different sources of experimental data are slightly scattered. It can be seen that somewhat better results were obtained when acetone was treated as self-associating fluid, even though only one adjustable parameter was used.

**3.1.3. Methanol–Methyl Acetate.** The methanol–methyl acetate system was modeled assuming solvation. Methyl acetate was modeled assuming that each molecule has one proton-acceptor site that is able to cross-associate only with methanol's

proton-donor site. The modified CR-1 combining rule<sup>27</sup> was used to estimate the cross-association parameters. The results are presented in Figure 11 for both temperature-dependent and temperature-independent  $k_{ij}$  values. In the latter case, when the  $k_{ij}$  values were plotted against temperature, a linear dependency was observed [ $k_{ij} = 7.77 \times 10^{-4} T(\text{K}) - 0.1730$ ].

**3.1.4. Methyl Acetate–Water.** Methyl acetate–water was modeled similarly to methanol–methyl acetate mixture, namely, by assuming solvation with one proton-acceptor site in the ester that can cross-associate with water. The corresponding cross-association parameters were estimated using the modified CR-1 rule.<sup>27</sup> Excellent correlation of the LLE was obtained, as shown in Figure 12. The estimated binary parameters were used to predict the VLE and VLLE occurring at lower pressures. The results, presented in Figure 13, demonstrate that the model predicts this complex phase behavior very accurately.

**3.1.5. Water–Acetone VLE.** Water–acetone is a very complex system. The compounds are miscible at all temperatures, and vapor–liquid equilibrium data are available over an extensive temperature range (298–523 K). There is evidence for very strong cross-interactions between these two compounds.<sup>51</sup> For this reason, modeling the phase behavior over the whole temperature range with thermodynamic models has been notoriously difficult. In this study, an extensive investigation of water–acetone mixture using either temperature-independent or temperature-dependent interaction parameters was performed. Moreover, acetone was considered either as an inert compound capable of solvating with water or as a self-associating molecule (with two sites, using the so-called 2B association scheme).

**3.1.5.1. Temperature-Independent Binary Parameters.** Using temperature-independent binary parameters, this system was modeled with four approaches. Initially, acetone was treated as non-self-associating and capable of solvating with water. Acetone was assumed to have one proton-acceptor site that can cross-associate with water. In the first approach, the modified CR-1 rule<sup>27</sup> was used to estimate the cross-association

**Table 3.** Binary Parameters and Deviations from Experimental Data for Methanol (1)–Acetone (2) VLE

temperature (K)	temperature-independent $k_{ij}$		temperature-dependent $k_{ij}$		ref for experimental data		
	$k_{ij}/\beta_{\text{cross}}$	AAD (%)	$k_{ij}/\beta_{\text{cross}}$	AAD (%)			
		P	$y_2$	P	$y_2$		
Acetone as a Non-Self-Associating Fluid but Accounting for Solvation							
298.15	0.0285/0.2301	7.8	3.5	−0.0009/0.2301	3.8	6.6	42
308.15		7.9	6.6	−0.0108/0.2301	3.9	4.8	43
318.15		7.2	5.4	−0.0092/0.2301	3.0	4.3	
328.15		4.9	4.4	0.0000/0.2301	2.3	3.2	
372.80		1.9	3.1	0.0180/0.2301	1.5	3.8	44
397.70		0.9	4.3	0.0316/0.2301	3.0	5.7	
422.60		0.9	2.8	0.0358/0.2301	0.6	1.7	
473.15		5.5	7.7	0.0959/0.2301	0.8	3.9	45
overall		4.7	4.3		2.4	4.2	
Acetone as a Self-Associating Fluid (2B)							
298.15	0.0695/CR-1	1.9	5.0	0.0736/CR-1	2.0	4.3	42
308.15		1.8	1.6	0.0699/CR-1	1.8	1.6	43
318.15		1.1	2.0	0.0671/CR-1	1.1	1.9	
328.15		1.1	2.6	0.0721/CR-1	1.0	2.6	
372.80		1.4	2.4	0.0611/CR-1	1.0	2.1	44
397.70		1.3	3.1	0.0586/CR-1	0.8	3.7	
422.60		2.0	2.8	0.0488/CR-1	0.9	1.5	
473.15		2.5	6.1	0.0600/CR-1	2.2	5.5	45
overall		1.6	3.1		1.3	2.9	

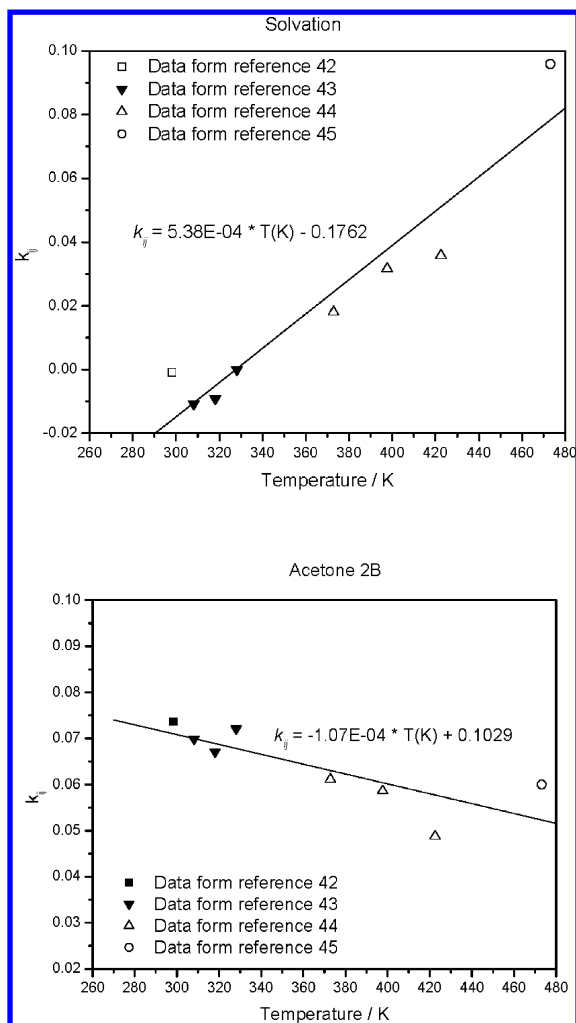


Figure 10. Binary interaction parameters as a function of temperature for methanol–acetone VLE.

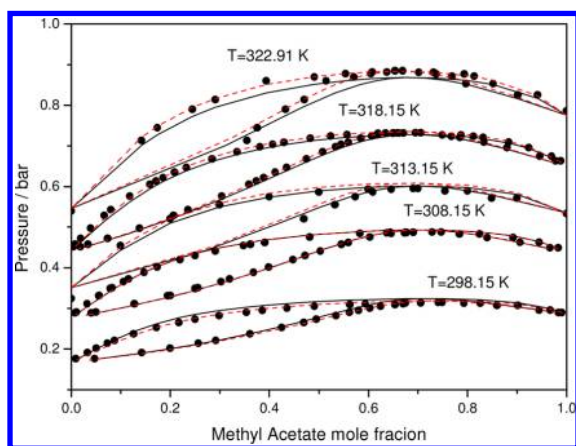


Figure 11. Methanol–methyl acetate VLE: experimental data<sup>46–48</sup> and CPA correlations using (a) a temperature-independent  $k_{ij}$  (equal to 0.0670), solid lines, and (b) a temperature-dependent  $k_{ij}$  (equal to 0.0574 at 298.15 K, 0.0667 at 308.15 K, 0.0736 at 313.15 K, 0.0725 at 318.15 K, and 0.0770 at 322.91 K), dashed lines. In all correlations,  $\beta_{\text{cross}} = 0.3492$ .

parameters, whereas in the second approach, a value for the association energy based on experimental calorimetric data was used.<sup>51</sup> In the third and fourth approaches, acetone was modeled

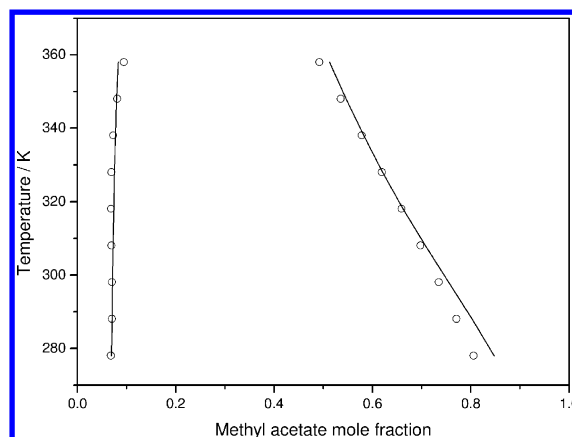


Figure 12. Methyl acetate–water LLE: experimental data,<sup>35</sup> points; CPA calculations, lines. The values of the  $k_{ij}$  and  $\beta_{\text{cross}}$  parameters were  $-0.0844$  and  $0.5453$ , respectively.

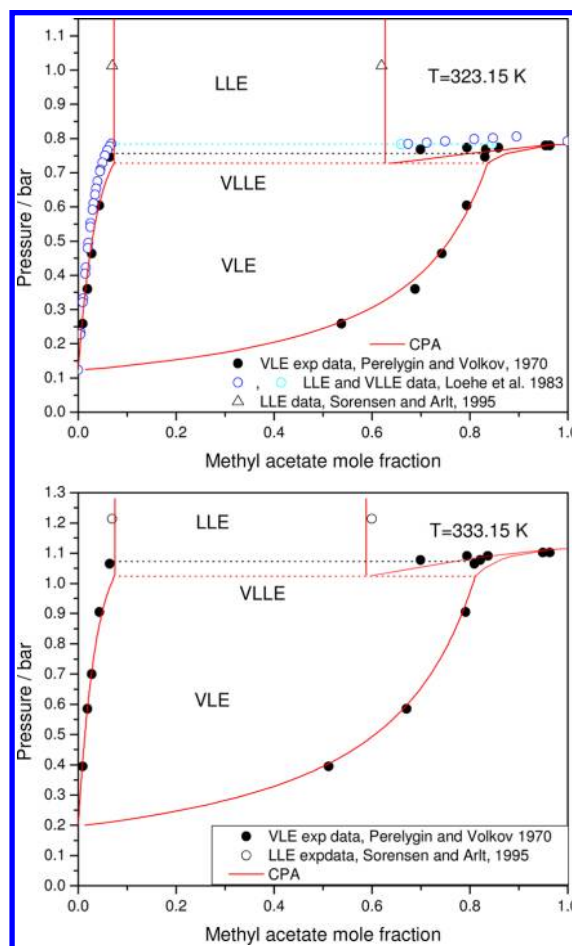


Figure 13. Methyl acetate–water VLE, VLE, and LLE: experimental data,<sup>35,49,50</sup> points; CPA calculations, lines.

as self-associating using the 2B association scheme. In the third approach, the cross-association parameters were estimated using the CR-1 combining rule,<sup>27</sup> whereas in the fourth approach, a value for the association energy based on experimental calorimetric data was used.<sup>51</sup> Except for the third approach, where only one  $k_{ij}$  value was adjusted to the experimental data, two parameters were optimized ( $k_{ij}$  and  $\beta_{\text{cross}}$ ) using the experimental data.



All of the results are presented in Table 4, from which it is clear that using the experimental value for the cross-association energy

**Table 4. Binary Parameters (Temperature-Independent) and Deviations from Experimental Data for Water (1)–Acetone (2) VLE**

temperature (K)	AAD (%)		reference for experimental data
	P	y <sub>2</sub>	
Binary Parameters (solvation): $k_{ij} = -0.1460$ , $\epsilon_{\text{cross}} = \text{mCR-1 (8.3 kJ mol}^{-1}\text{)}$ , $\beta_{\text{cross}} = 0.4626$			
298.15	5.5	0.7	52
323.15	3.4	0.8	53
373.15	3.0	4.1	45
423.15	4.6	3.9	
473.15	5.4	5.7	
523.15	7.7	9.7	
overall	5.0	4.5	
Binary Parameters (solvation): $k_{ij} = -0.0884$ , $\epsilon_{\text{cross}} = 20.2 \text{ kJ mol}^{-1} \text{ (exp)}$ , $\beta_{\text{cross}} = 0.0107$			
298.15	15.3	4.3	52
323.15	8.3	2.6	53
373.15	4.3	10.0	45
423.15	7.7	10.7	
473.15	11.8	19.5	
523.15	14.7	25.9	
overall	10.2	13.4	
Binary Parameters (Acetone 2B): $k_{ij} = -0.1201$ , $\epsilon_{\text{cross}} = \text{CR-1 (13.9 kJ mol}^{-1}\text{)}$ , $\beta_{\text{cross}} = \text{CR-1 (0.1414)}$			
298.15	14.3	5.6	52
323.15	11.2	3.8	53
373.15	10.3	6.3	45
423.15	9.2	6.9	
473.15	7.8	7.8	
523.15	7.9	11.2	
overall	9.8	7.1	
Binary Parameters (Acetone 2B): $k_{ij} = -0.1345$ , $\epsilon_{\text{cross}} = 20.2 \text{ kJ mol}^{-1} \text{ (exp)}$ , $\beta_{\text{cross}} = 0.0129$			
298.15	21.7	6.8	52
323.15	10.6	3.5	53
373.15	6.4	12.3	45
423.15	12.4	14.1	
473.15	17.6	25.6	
523.15	15.8	35.9	
overall	14.1	17.9	

(second and fourth approaches) resulted in higher deviations from the experimental data. It is worth mentioning that the experimental value for the cross-association energy is relatively high and higher than the water self-association energy. A comparison of the second (solvation) and fourth (acetone 2B) approaches, in which the same number (two) of adjustable parameters was used, reveals that the more physically correct approach (i.e., accounting for solvation and treating acetone as a non-self-associating fluid) resulted in better correlations.

**3.1.5.2. Temperature-Dependent Binary Interaction Parameter ( $k_{ij}$ ).** The water–acetone system was also modeled using a temperature-dependent binary interaction parameter ( $k_{ij}$ ). Bearing in mind that, as shown in Table 4, deviations from the experimental data are higher using the experimental value for the cross-association energy, the cross-association parameters were obtained only using combining rules. In a first approach, acetone was modeled assuming that it has only one proton-acceptor site that is able to cross-associate with water (solvation). In this case,

the modified CR-1 rule<sup>27</sup> with a constant temperature-independent cross-association volume ( $\beta_{\text{cross}}$ ) was used. In a second approach, acetone was treated as a 2B self-associating molecule, and the cross-association parameters were estimated using the CR-1 rule.<sup>27</sup> The results are presented in Table 5. In

**Table 5. Binary Parameters (Temperature-Dependent) and Deviations from Experimental Data for Water (1)–Acetone (2) VLE**

temperature (K)	$k_{ij}$	AAD (%)		reference for experimental data
		P	y <sub>2</sub>	
(Solvation) $\epsilon_{\text{cross}} = \text{mCR-1 (8.3 kJ mol}^{-1}\text{)}$ , $\beta_{\text{cross}} = 0.4626$				
298.15	-0.1510	5.3	1.4	52
323.15	-0.1442	3.3	0.7	53
373.15	-0.1289	1.8	1.2	45
423.15	-0.1100	1.8	1.4	
473.15	-0.1032	3.3	2.9	
523.15	-0.0724	3.7	8.4	
overall		3.2	2.7	
(Acetone 2B) $\epsilon_{\text{cross}} = \text{CR-1 (13.9 kJ mol}^{-1}\text{)}$ , $\beta_{\text{cross}} = \text{CR-1 (0.1414)}$				
298.15	-0.1298	13.4	4.6	52
323.15	-0.0991	10.2	3.2	53
373.15	-0.0772	7.5	12.0	45
423.15	-0.0477	6.1	6.4	
473.15	-0.0431	5.2	6.9	
523.15	-0.0075	3.6	12.7	
overall		7.7	7.6	

Figure 14, the binary interaction parameters are plotted versus temperature, revealing a linear dependence on temperature. Assuming solvation and using temperature-dependent interaction parameters, the percentage deviations in both pressure and vapor-phase mole fraction were reduced by about 35% compared to the values obtained using temperature-independent interaction parameters.

**3.1.6. Systems with Chloroform. 3.1.6.1. Methanol–Chloroform VLE.** In this work, chloroform was modeled as a non-self-associating fluid. However, it was assumed that each molecule has one proton-donor site that is able to cross-associate with hydrogen-bonding fluids, such as alcohols. Thus, solvation was assumed in the methanol–chloroform system, and the parameters for the cross-interactions were estimated using the modified CR-1 combining rule.<sup>27</sup> The results are presented in Figure 15. A very small improvement was obtained by including a temperature dependency in the interaction parameter over the narrow temperature range used. However, when the binary interaction parameters were plotted as a function of temperature, a linear dependency was assumed [ $k_{ij} = 5.12 \times 10^{-4} T(\text{K}) - 0.18547$ ].

**3.1.6.2. Acetone–Chloroform VLE.** Acetone–chloroform VLE was modeled using three approaches. First, assuming both fluids to be inert compounds, model predictions were carried out using no adjustable binary parameter. In the second approach, one temperature-independent  $k_{ij}$  value was optimized using experimental data. In a third approach, one proton-acceptor site was assumed on each acetone molecule, and one proton-donor site was assumed on each chloroform molecule. In this way, both acetone and chloroform could not self-associate, but cross-association interactions between molecules of different kind were possible. Using the third approach, the  $k_{ij}$  value was set equal to zero, and the cross-association energy was adopted from the

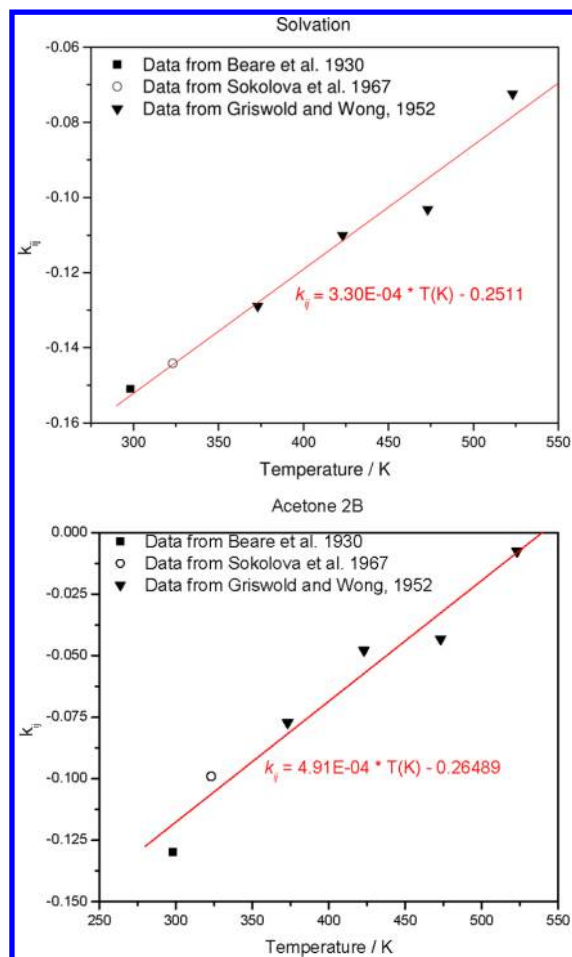


Figure 14. Binary interaction parameters as a function of temperature for water–acetone VLE.

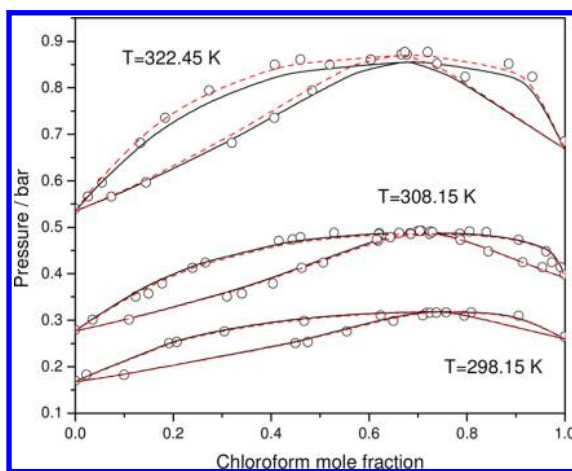


Figure 15. Methanol–chloroform VLE: experimental data<sup>42,54</sup> and CPA correlations using (a) a temperature-independent  $k_{ij}$  (equal to  $-0.0283$ ), solid lines, and (b) a temperature-dependent  $k_{ij}$  (equal to  $-0.0307$  at 298.15 K,  $-0.0312$  at 308.15 K, and  $-0.0190$  at 322.15 K), dashed lines. In both correlations,  $\beta_{\text{cross}} = 0.0254$ .

literature (experimental value),<sup>55</sup> whereas the cross-association volume was fitted to the experimental data for the binary system. Consequently, in both the second and third approaches, one adjustable binary parameter was used. The results are presented

in Table 6, and it can be concluded that accounting for cross-association improved the model correlations.

Table 6. Binary Parameters and Average Absolute Deviations from Experimental Data<sup>56–59</sup> for Acetone (1)–Chloroform (2) VLE

association scheme	$k_{ij}$	$\epsilon_{\text{cross}}$ (kJ mol <sup>-1</sup> )	$\beta_{\text{cross}}$	AAD (%)	
				$P$	$y_1$
no association	0	–	–	15.7	14.5
no association	$-0.0612$	–	–	1.35	1.71
cross-association	0	$11.367^a$	$0.0125^b$	1.11	1.70

<sup>a</sup>experimental, <sup>55</sup> <sup>b</sup>fitted.

3.1.6.3. Methyl Acetate–Chloroform VLE. The methyl acetate–chloroform system was modeled using two approaches. First, both fluids were modeled as inert compounds, and one temperature-independent binary interaction parameter was used. In a second approach, one proton-donor site was assumed on each chloroform molecule, and one proton-acceptor site was assumed on each acetate molecule. In this way, cross-association interactions could occur between molecules of different kind. Using the second approach, because of a lack of experimental data, the cross-association energy for the chloroform–acetone system was used,<sup>55</sup> which is a rather arbitrary approach. The  $k_{ij}$  value was set equal to zero, and only the  $\beta_{\text{cross}}$  parameter was fitted to the experimental data. With the first approach (no solvation), the system was also modeled using a temperature-dependent  $k_{ij}$  value. The results are presented in Table 7. It can

Table 7. Binary Parameters and Deviations from Experimental Data for the Methyl Acetate (1)–Chloroform (2) System

temperature (K)	$k_{ij}$	AAD (%)		reference for experimental data
		$P$	$y_2$	
		No Solvation		
313.15	$-0.057$	1.47	4.04	60
323.15		1.42	3.12	61
overall		1.44	3.58	
		$\beta_{\text{cross}} = 0.0109, \epsilon_{\text{cross}} = 11.367^a$		
313.15	0.0	1.45	3.89	60
323.15		1.44	2.98	61
overall		1.44	3.42	
		No Solvation <sup>b</sup>		
313.15	$-0.0533$	1.46	4.05	60
323.15	$-0.0521$	1.42	3.10	61
overall		1.44	3.57	

<sup>a</sup>Cross-association energy adopted from the chloroform–acetone system (experimental value<sup>55</sup>) in kJ mol<sup>-1</sup>. <sup>b</sup> $k_{ij} = 1.2 \times 10^{-4} \times T(\text{K}) - 0.09088$ .

be concluded that the use of a temperature-dependent binary interaction parameter did not substantially improve the results over the rather narrow temperature range of the experimental data. As also shown in Table 7, the results were improved only marginally by assuming cross-association interactions.

3.2. Ternary Mixtures. Experimental data for three ternary systems containing methyl acetate, water, methanol, acetone, and/or chloroform are available in refs 45 and 62–64. The CPA model was applied to these systems by calculating the vapor

pressures and vapor compositions and keeping the experimental liquid compositions and the temperature constant.

The binary interaction parameter for the water–methanol system ( $k_{ij} = -0.075$ , temperature-independent) was adopted from calculations presented in the literature,<sup>65</sup> using the CR-1 combining rule, whereas all other binary parameters were adopted from the corresponding binary systems presented in section 3.1. Acetone was modeled as non-self-associating fluid with one proton-acceptor site on every molecule, which is only able to cross-associate with water or methanol.

The results are summarized in Table 8. (Some characteristic results are also presented in Figure S6 of the Supporting

**Table 8. Average Absolute Deviations (AAD, %) between CPA and Experimental Data**<sup>45,62–64</sup>

$k_{ij}$	$P$	$y_1$	$y_2$	$y_3$
System 1: Methyl Acetate (1)–Methanol (2)–Water (3) VLE <sup>62</sup>				
temperature-independent	6.4	6.5	6.0	20.4
temperature-dependent	3.8	5.4	8.1	17.3
System 2: Acetone (1)–Methanol (2)–Water (3) Low-Pressure VLE <sup>63</sup>				
temperature-independent	3.8	10.9	13.6	10.2
temperature-dependent	3.8	7.7	12.0	10.1
System 2: Acetone (1)–Methanol (2)–Water (3) High-Pressure VLE <sup>45</sup> (373.15 and 523.15 K)				
temperature-independent	5.0	9.0	13.3	4.6
temperature-dependent	2.0	8.1	11.8	4.0
System 3: Chloroform (1)–Methanol (2)–Methyl Acetate (3) VLE <sup>64</sup>				
temperature-independent	5.9	8.3	6.4	10.4
temperature-dependent	3.5	8.9	4.8	8.2

Information.) It can be seen that use of temperature-dependent binary parameters resulted in somewhat better predictions.

### 3.3. Concluding Remarks for the Second Case Study.

The vapor–liquid and liquid–liquid equilibria of systems containing acetone, methanol, water, chloroform, and/or methyl acetate were modeled using the CPA equation of state. First, the binary parameters were estimated using experimental VLE data from the corresponding binary systems. Then, the model was applied to predict the VLE of three ternary systems (methyl acetate–methanol–water, acetone–methanol–water, and chloroform–methanol–methyl acetate).

In all cases, methyl acetate was modeled as a non-self-associating fluid with one proton-acceptor site that is able to cross-associate with other hydrogen-bonding fluids, such as water or alcohols (solvation). Results for all of the investigated binary mixtures containing methyl acetate were found to be in very satisfactory agreement with the experimental data. In particular, the model accurately predicted the complicated phase behavior of methyl acetate–water, which includes a three-phase vapor–liquid–liquid equilibrium.

Acetone was modeled using two approaches: as a non-self-associating fluid with one proton-acceptor site that is able to cross-associate with other hydrogen-bonding fluids, such as water or alcohols (solvation), and as a self-associating fluid using the 2B association scheme. The first approach seems to be more realistic and resulted in better calculations for mixtures with water (and slightly worse calculations for mixtures with methanol).

Chloroform was modeled as a non-self-associating fluid with one proton-donor site that is able to cross-associate with other hydrogen-bonding fluids, such as alcohols (solvation). Using this approach, the results for methanol–chloroform and chloro-

form–acetone were in very good agreement with the experimental data. For simplicity, the methyl acetate–chloroform mixture can be modeled without considering any possible cross-association, as satisfactory results were obtained with a single  $k_{ij}$  value.

Using the binary parameters obtained in this study from the corresponding binary systems, the model satisfactorily predicted the vapor–liquid equilibria of the investigated ternary mixtures. The use of temperature-dependent binary interaction parameters improved the correlations for the binary systems and the predictions for the ternary systems.

## 4. PHASE EQUILIBRIA OF MIXTURES RELEVANT TO THE PTA PROCESS

Purified terephthalic acid (PTA) is an important compound in the production of polyester, plastics, and fibers, being the monomer needed for the polymerization reactions that provide the desired products. The production of purified terephthalic acid involves compounds such as benzoic acid (BA), *p*-toluic acid, 4-carboxybenzaldehyde, and *p*-tolualdehyde. Most of these compounds (benzoic acid, *p*-toluic acid, and terephthalic acid) contain at least one carboxylic group in their molecule, and all of them have one aromatic ring.

The purpose of this study was to develop and evaluate the performance of the CPA equation of state in correlating/predicting the phase behavior of the five aforementioned phenolic compounds (benzoic acid, *p*-toluic acid, terephthalic acid, 4-carboxybenzaldehyde, and *p*-tolualdehyde) in various solvents, such as water, methanol, benzene, acetic acid, and hexane. It is of importance to assess the performance of the CPA model for these systems over extensive conditions, including the liquid–liquid, vapor–liquid, and solid–liquid equilibria present over an extended temperature range.

A significant drawback in this study was the lack of experimental data, even for some of the pure compounds. We modeled all five compounds, but we limit this presentation to those aromatic acids (benzoic acid, hereafter abbreviated BA, and terephthalic acid, hereafter abbreviated PTA) for which the modeling of the phase behavior was more challenging. It will become clear that the modeling of these compounds is a great challenge for the CPA model, and both standard and advanced association schemes were investigated. The results are presented in sections 4.2 and 4.3. The challenging nature of the association of organic acids is discussed first.

**4.1. Associating Nature of Organic Acids.** Carboxylic acids present a peculiar association behavior. Depending on their molecular structure and pressure–temperature conditions, the formation of hydrogen bonds can lead to the formation of dimers or linear oligomers. For example, formic acid forms dimers in the vapor phase. Thus, equilibrium exists between monomers and dimers. In the solid phase, crystalline formic and acetic acid form chains, whereas heavier acids tend to form dimers.<sup>66</sup>

Most of the experimental and theoretical studies in the literature consider the association behavior of aliphatic acids, rather than aromatic acids. Clague and Bernstein<sup>67</sup> determined the enthalpy and entropy of dimerization of several low-molecular-weight aliphatic acids using IR spectroscopy. They concluded that the dimerization enthalpy and entropy remain rather constant, independent of the length the alkyl group connected to the carboxylic group. They reported that this happens because, when the electron-releasing capacity of the alkyl group increases, the proton-accepting ability of the carbonyl group also increases, but, at the same time, the ability of the

Table 9. Pure-Fluid Parameters for Benzoic Acid and Terephthalic Acid

association scheme	$T_c$ (K) <sup>34</sup>	$a_0$ (L <sup>2</sup> bar/mol <sup>2</sup> )	$b$ (L/mol)	$c_1$	$\epsilon$ (bar L/mol)	$\beta$	AAD (%)	
							$p^{\text{sat}}$	$\rho^{\text{liq}}$
Benzoic Acid								
1A	751.0	30.8880	0.10178	1.1874	286.00	0.0033	0.6	1.0
2B	751.0	31.8220	0.10165	1.3670	170.44	0.0012	0.9	0.8
Terephthalic Acid								
2x(1A)	883.60	50.8415	0.13501	1.32691	286.00	0.0033	1.9	17.0
2x(2B)	883.60	54.5564	0.13501	1.48450	170.44	0.0012	2.2	18.0

hydroxyl group to act as a proton donor decreases. The two phenomena tend to cancel each other, and consequently, the enthalpy of dimerization remains almost constant.

Pimentel and McClellan<sup>68</sup> collected experimental data from several studies. They reported that, for carboxylic acids in the gas phase, the hydrogen-bonding enthalpy ( $-\Delta H$ ) is essentially constant at  $7 \pm 0.5$  kcal per mole of hydrogen bonds. In nonaromatic carboxylic acids, these values are almost constant regardless of the length or branching of the carbon chain or substitution of electronegative groups. On the other hand, Pimentel and McClellan reported that there are not enough experimental studies on liquid acids to suggest general conclusions but that the most reliable data for liquid stearic acid give  $-\Delta H = 6.7$  kcal per mole of hydrogen bonds, which is very close to the value reported for acids in the gas phase. They also reported<sup>68</sup> that solvent disturbances of the acid dimerization can be clearly detected. In benzene or in  $\text{CHCl}_3$ , the equilibrium constant can have a value that is only 10% of its value in  $\text{CCl}_4$ . The difference in the reported values shows that the solvent influences the equilibrium constant, by influencing the monomer concentration or the dimer formation (through cross-association). Considering that benzene can have proton-acceptor sites (the  $\pi$ -electrons of the aromatic ring) and that  $\text{CHCl}_3$  has one proton-donor site (the hydrogen atom), the most representative value for the enthalpy of dimerization should be the value obtained in  $\text{CCl}_4$ .

As can be concluded from the aforementioned discussion, it is not immediately evident which association scheme should be used for organic acids, and the aromatic rings in BA and PTA can cause additional challenges. Initially, we modeled the two acids using the conventional 1A and 2B schemes, previously used with success for aliphatic acids and alcohols, respectively. These results are presented next.

**4.2. Modeling Aromatic Acids Using the 1A and 2B Association Schemes.** In a first approach, aromatic acids were modeled using simple association schemes. For benzoic acid (BA), pure-fluid parameters were estimated using the 1A and 2B association schemes (see the notation of Huang and Radosz<sup>69</sup>), whereas for terephthalic acid (PTA), because each molecule contains two carboxylic groups, the so-called  $2 \times 1A$  and  $2 \times 2B$  association schemes were used. CPA parameters are typically estimated from vapor pressure and liquid densities, but such experimental data are available only for BA from the DIPPR database,<sup>34</sup> and they were used in the parameter estimation. For PTA, no experimental data are available for liquid densities and vapor pressures. Consequently, the association parameters (for each  $-\text{COOH}$  group) were adopted from benzoic acid, whereas the covolume parameter was calculated using its correlation with the van der Waals volume (see Kontogeorgis and Folas<sup>4</sup> or Figure S2 of the Supporting Information). The remaining CPA parameters ( $a_0$  and  $c_1$ ) were estimated by fitting the predictions of the model to DIPPR's correlations. The CPA parameters

obtained for the two acids using the 1A and 2B schemes are shown in Table 9. For the SLE calculations, the following values were used for the fusion properties of solutes:<sup>34</sup> For benzoic acid,  $T_m = 395.52$  K,  $\Delta H_m = 18.07$  kJ mol<sup>-1</sup>,  $\Delta C_p = 58.8$  J mol<sup>-1</sup> K<sup>-1</sup>. For terephthalic acid,  $T_m = 700.15$  K,  $\Delta H_m = 63.428$  kJ mol<sup>-1</sup>.

Using the parameters in Table 9, vapor–liquid, liquid–liquid, and solid–liquid equilibria of binary systems containing the investigated compounds and liquid solvents were determined. For all cross-associating systems, the CR-1 combining rule<sup>27</sup> was used. Moreover, in all cases, a temperature-independent binary interaction parameter ( $k_{ij}$ ) was used.

**4.2.1. Nonaqueous Systems.** Initially, the vapor–liquid equilibrium (VLE) of benzoic acid–methanol and benzoic acid–benzene was investigated. For benzoic acid–benzene, no cross-association interactions were considered, because the results obtained were rather satisfactory using a single binary interaction parameter ( $k_{ij}$ ). Such VLE results are presented in Table 10 from which it can be observed that, at least for the

Table 10. Binary Interaction Parameters and Average Deviations from Experimental VLE<sup>70,71</sup> and SLE<sup>72–74</sup> Data of Benzoic Acid Systems

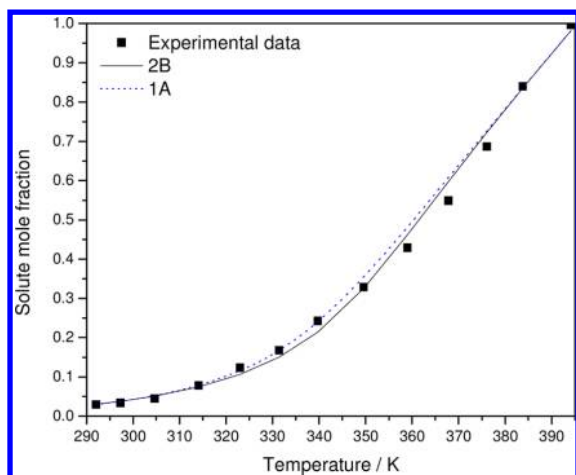
association scheme for acids	$k_{ij}$	AAD (%) in $x_1$
Benzoic Acid (1)–Methanol (2) (VLE)		
1A	-0.0409	9.0
2B	-0.0511	7.8
Benzoic Acid (1)–Benzene (2) (VLE)		
1A	0.0008	8.2
2B	0.0179	16.7
Benzoic Acid (1)–Benzene (2) (SLE)		
1A	0.0127 <sup>a</sup>	6.0
2B	0.0059 <sup>a</sup>	7.4
1A	0.0008 <sup>b</sup>	40.2
2B	0.0179 <sup>b</sup>	21.1
Benzoic Acid (1)–Hexane (2) (SLE)		
1A	-0.0258 <sup>a</sup>	2.5
2B	-0.0293 <sup>a</sup>	9.4
Benzoic Acid (1)–Acetic Acid (2) (SLE)		
1A	0.0380 <sup>a</sup>	44.1
2B	0.0428 <sup>a</sup>	48.0

<sup>a</sup>Optimum for SLE. <sup>b</sup>Optimum for VLE.

benzoic acid–benzene system, the 1A association scheme resulted in much smaller deviations from the experimental data than the 2B scheme. (Some characteristic results for benzoic acid–methanol are presented in Figure S7 of the Supporting Information.)

For some BA systems, including BA–benzene, solid–liquid equilibrium (SLE) data are also available. The SLE calculations performed for three systems are summarized in Table 10, and results from one typical example are shown in Figure 16. In all

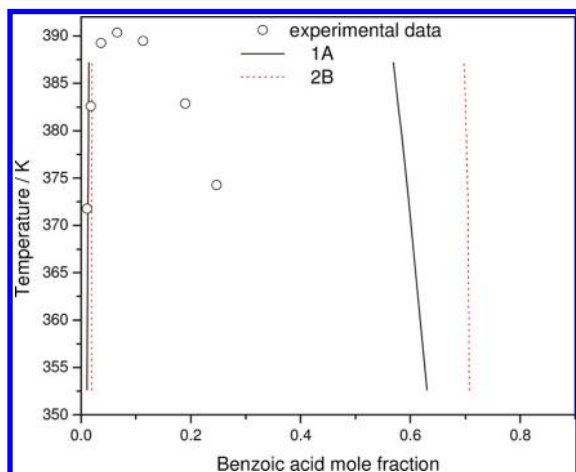




**Figure 16.** Benzoic acid–benzene SLE: experimental data,<sup>72</sup> points; CPA calculations using a  $k_{ij}$  optimized by SLE data, lines.

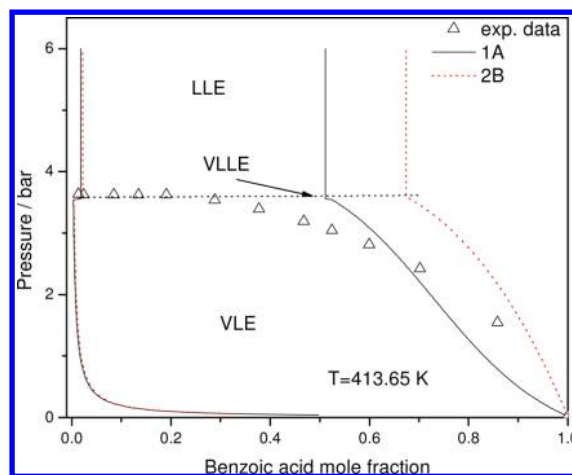
cases, a single binary interaction parameter ( $k_{ij}$ ) was optimized using the experimental data. As observed for VLE, the 1A association scheme resulted in smaller deviations from the experimental data. Moreover, it is evident that, for benzoic acid–benzene, different interaction parameters are needed in the VLE and SLE regions. The results for the mixtures of two acids are not very satisfactory either.

**4.2.2. Aqueous Systems.** BA–water is a very interesting system, and VLE, LLE, and SLE experimental data over an extensive temperature range are available for it. For PTA–water, only SLE data are available. The results for BA–water LLE and VLE are shown in Figures 17 and 18, respectively. From Figure



**Figure 17.** Benzoic acid (1)–water (2) LLE: experimental data,<sup>75</sup> points; CPA calculations using the CR-1 rule and  $k_{ij} = -0.077$  for the 1A association scheme and  $k_{ij} = -0.073$  for the 2B association scheme, lines.

17 it can be seen that, in aqueous systems of BA, the CPA EoS overestimates the mixture's critical point and presents high deviations from experimental data at least for the organic-phase composition (and similar trends are seen for other aromatic acids). Because of the overestimation of the critical point, the CPA model fails to satisfactorily describe the VLE of BA–water. This is illustrated in Figure 18, where it can be seen that the model predicts VLE at low pressures, but also predicts LLE at higher pressures, where experimental evidence for a single phase exists.



**Figure 18.** Benzoic acid–water VLE: experimental data,<sup>76</sup> points; CPA calculations using binary interaction parameters obtained from LLE data, lines.

Next, the model was applied to describe the SLE of binary aqueous systems. One binary interaction parameter ( $k_{ij}$ ) was used, which was obtained from the experimental data or, where possible, adopted from LLE calculations. As shown in Table 11,

**Table 11. Binary Interaction Parameters and Deviations from Experimental Data<sup>77–82</sup> for the SLE of Aqueous Systems**

association scheme	$k_{ij}$	AAD (%) in $x_1$
Benzoic Acid (1)–Water (2)		
1A	$-0.0280^a$	8.6
2B	$-0.0108^a$	16.3
1A	$-0.077^b$	>100
2B	$-0.073^b$	>100
Terephthalic Acid (1)–Water (2)		
$2 \times 1A$	$-0.1611^a$	62.8
$2 \times 2B$	$-0.1384^a$	57.2

<sup>a</sup>Optimum for SLE. <sup>b</sup>Optimum for LLE.

by adopting the binary interaction parameter from LLE calculations, the model failed to predict the SLE of BA–water. On the other hand, the SLE results obtained were satisfactory when the binary interaction parameter was optimized using the experimental SLE data. As was also observed in nonaqueous systems, the 1A association scheme results in smaller deviations from the experimental data (than 2B), at least for benzoic acid, for which more accurate experimental data exist. Some characteristic calculations are shown in Figure 19.

In conclusion, the use of simple association schemes (1A or 2B) for aromatic acids (benzoic acid and terephthalic acid) in the CPA model results in satisfactory or at least acceptable calculations for nonaqueous systems, but the performance of the CPA model is not satisfactory for LLE and VLE of aqueous systems (for BA–water). Moreover, in all cases, SLE and VLE/LLE require different interaction parameters.

In an attempt to improve the model performance, different approaches have been investigated:

- (1) use of advanced association schemes for the aromatic acids,
- (2) use of more adjustable interaction parameters either by adding a temperature dependency in  $k_{ij}$  or by optimizing both  $k_{ij}$  and the cross-association volume,

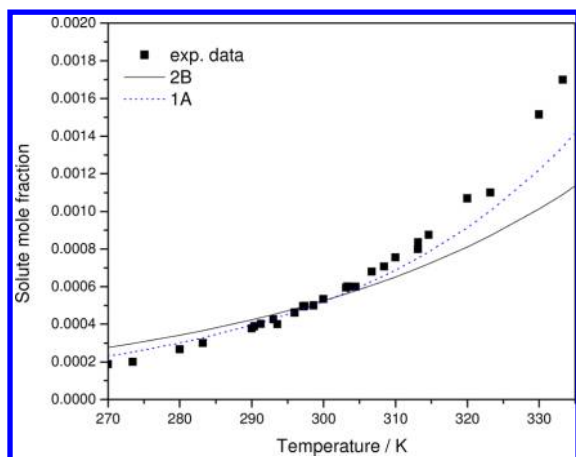


Figure 19. Solubility of benzoic acid in water: experimental data,<sup>77–79</sup> points; CPA correlations, lines (using the optimum  $k_{ij}$  value for SLE).

The results are presented in the next section, and especially for BA, for which many data are available, an extensive investigation is carried out.

**4.3. Revising the Parameter Estimation for Aromatic Acids.** 4.3.1. *Aromatic Acids Using Various Association Schemes.* We carried out a systematic analysis of the parametrization of BA using diverse association schemes (1A, 2B, 3B, 4C), as well as the advanced schemes listed in Table 12.

Table 12. Advanced Association Schemes for Benzoic Acid and Terephthalic Acid<sup>a–c</sup>

association scheme	–COOH	–Ar
1A+	one site (positive or negative, 1A)	one negative site
2B+	two sites (one positive and one negative, 2B)	one negative site

<sup>a</sup>Physical term parameters and association parameters for –COOH··Ar– were fitted to vapor pressures and liquid densities. <sup>b</sup>Association parameters for –COOH··HOOC– were taken from hexanoic acid. <sup>c</sup>Combining rule<sup>27</sup> CR-1 was used to estimate the association strength for every possible self-associating interaction (i.e., –COOH··HOOC–, –COOH··Ar–).

To estimate these parameter sets, the association strength,  $\epsilon$ , was set constant, and the remaining pure-fluid parameters were optimized by experimental vapor pressures and liquid densities. In the advanced schemes 1A+ and 2B+, positive and negative sites were assumed in the –COOH group, whereas one negative

site was assumed in the aromatic ring (–Ar). Many parameter sets were tested on systems containing BA with water, methanol, and benzene, and the sets that provided the best results are presented in Table 13.

Using the new pure-fluid parameters, the model was first applied to describe aqueous aromatic acid systems. The CR-1 combining rule<sup>27</sup> was used for all associating interactions between the various associating sites. Figures 20 and 21 present

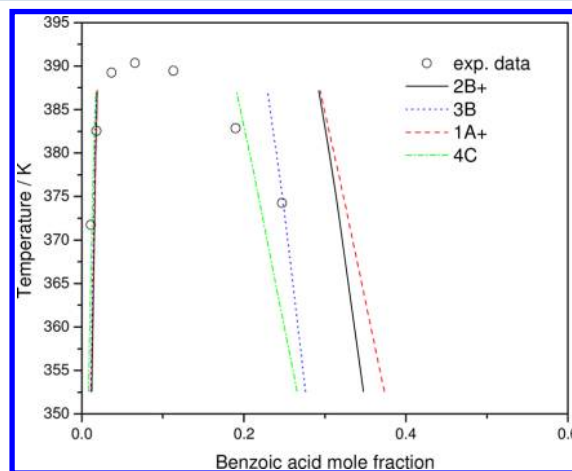


Figure 20. Benzoic acid–water LLE: experimental data,<sup>75</sup> points; CPA calculations using the CR1 rule and the binary interaction parameters of Table 14, lines ( $k_{ij}$  values obtained using LLE data).

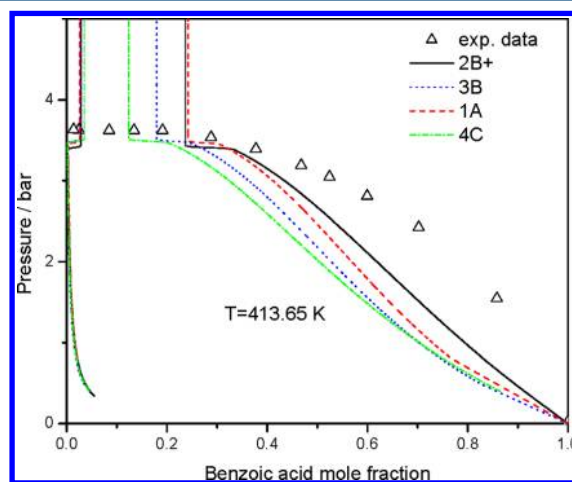


Figure 21. Benzoic acid–water VLE: experimental data,<sup>76</sup> points; CPA predictions (using  $k_{ij}$  from LLE), lines.

Table 13. Pure-Fluid Parameters for Aromatic Acids Using Various Association Schemes

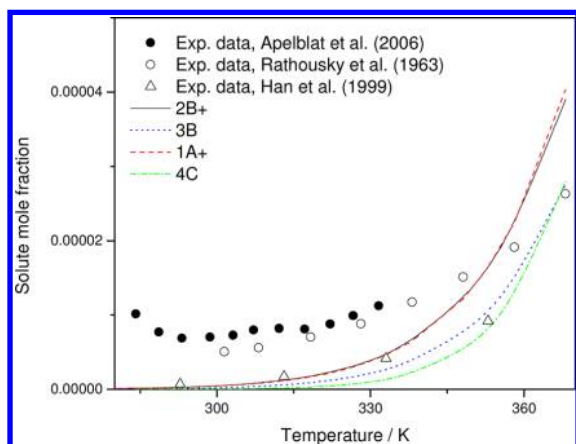
association scheme	$a_0$ (bar L <sup>2</sup> /mol <sup>2</sup> )	$b$ (L/mol)	$c_1$	–COOH		Ar–		AAD (%) in $P^{\text{sat}}/\rho^{\text{liq}}$
				$\epsilon$ (bar L/mol)	$\beta$	$\epsilon$ (bar L/mol)	$\beta$	
Benzoic Acid ( $T_c = 751.0$ K)								
4C	19.7750	0.09820	0.7338	240.0	0.0093	–	–	0.4/1.1
3B	27.6710	0.09970	0.9063	263.3	0.0039	–	–	0.2/1.0
1A+	27.2454	0.09825	0.7026	379.09	0.00013	306.05	0.0467	0.2/0.9
2B+	28.8330	0.10302	1.2658	180.83	0.01068	120.82	0.0375	0.7/1.9
Terephthalic Acid ( $T_c = 883.6$ K)								
2 × 4C	13.2362	0.13501	1.3363	240.00	0.00930	–	–	1.3/14.2
2 × 3B	40.2391	0.13501	1.0653	263.33	0.00391	–	–	1.3/14.5
2 × 1A+	52.1490	0.13501	1.0201	379.09	0.00013	306.05	0.04670	1.6/15.8
2 × 2B+	48.0074	0.13501	1.5054	180.83	0.01068	120.82	0.03747	1.7/16.2

the LLE and VLE results, respectively, for the aqueous BA systems. In Figure 20 it can be seen that the model overestimates the mixture's critical point. The CPA EoS also fails to satisfactorily predict the VLE of the benzoic acid–water mixture using the binary interaction parameter optimized by the LLE data. This is a consequence of the overestimation of the mixture's critical point in the LLE.

Next, the model was applied to describe the SLE of binary aqueous systems. One binary interaction parameter ( $k_{ij}$ ) was used, which was optimized using the experimental data or, where possible, adopted from the LLE calculations. Results are presented in Table 14, and some characteristic calculations are

**Table 14. Binary Interaction Parameters and Deviations from Experimental Data for the SLE of Aqueous Systems**

association scheme	$k_{ij}$ (optimum SLE)	AAD (%) in $x_1$	$k_{ij}$ (from LLE)	AAD (%) in $x_1$
Benzoic Acid (1)–Water (2)				
4C	0.0650	20.9	0.0127	>100
3B	0.1020	2.1	0.0182	>100
1A+	0.0225	8.8	−0.0272	>100
2B+	0.0545	1.9	0.0009	>100
Terephthalic Acid (1)–Water (2)				
4C	−0.1393	83.7		
3B	0.0423	75.6		
1A+	−0.1283	69.8		
2B+	−0.0685	68.8		



**Figure 22.** Solubility of terephthalic acid in water: experimental data,<sup>80–82</sup> points; CPA calculations, lines.

illustrated in Figure 22. It can be seen that, when the binary interaction parameter from LLE calculations was used, the model failed to predict the SLE of the corresponding systems. On the other hand, the results were satisfactory when the binary interaction parameter was optimized using experimental SLE data, at least for benzoic acid, for which reliable experimental data exist.

Next, the CPA EoS using the new parameters was tested for nonaqueous systems. We present the results only in tabular form (Table 15). The CR-1 combining rule<sup>27</sup> was used for cross-associating interactions unless otherwise indicated. Using the new parameters, the results for benzoic acid–methanol VLE (Table 15) are rather similar to the results obtained using the 1A and 2B association schemes (see Table 10). For benzoic acid–

**Table 15. Binary Interaction Parameters and Average Deviations from Experimental VLE and SLE Data for Benzoic Acid Nonaqueous Mixtures**

association scheme for BA	$k_{ij}$	$\beta_{\text{cross}}$	AAD (%) in $x_1$
Vapor–Liquid Equilibrium (VLE)			
Benzoic Acid (1)–Benzene (2) (Benzene As Inert Compound)			
4C	−0.2412	–	46.5
3B	−0.0892	–	8.5
1A+	–	–	–
2B+	–	–	–
Benzoic Acid (1)–Benzene (2) (Benzene with One Negative Site, Solvation)			
4C	−0.0578 <sup>a</sup>	0.0899	6.6
3B	0.0034 <sup>a</sup>	0.0160	6.0
1A+	0.1430	CR-1	14.7
2B+	0.0275	CR-1	15.7
Benzoic Acid (1)–Methanol (2)			
4C	0.0397	CR-1	7.9
3B	0.0906	CR-1	9.7
1A+	0.0450	CR-1	11.8
2B+	0.0245	CR-1	10.1
Solid–Liquid Equilibrium (SLE)			
Benzoic Acid (1)–Benzene (2) (Benzene with One Negative Site, Solvation)			
4C	−0.0174 <sup>a</sup>	0.0899 <sup>a</sup>	43.3
3B	0.0692 <sup>a</sup>	0.0160 <sup>a</sup>	22.3
1A+	0.1370	CR-1	12.3
2B+	0.0322	CR-1	13.0
4C	−0.0578 <sup>a,b</sup>	0.0899 <sup>a,b</sup>	80.0
3B	0.0034 <sup>a,b</sup>	0.0160 <sup>a,b</sup>	>100
1A+	0.1430 <sup>b</sup>	CR-1	16.4
2B+	0.0275 <sup>b</sup>	CR-1	15.3
Benzoic Acid (1)–Hexane (2)			
4C	−0.0815	–	99.4
3B	−0.0467	–	71.9
1A+	−0.0275	–	64.2
2B+	−0.0625	–	18.2

<sup>a</sup>mCR-1 rule<sup>27</sup> used for cross-association. <sup>b</sup>Adopted from VLE.

benzene VLE, it was necessary to take solvation into account (using the modified CR-1 combining rule) and to use two adjustable parameters to obtain the correct phase behavior for the 1A+ and 2B+ association schemes.

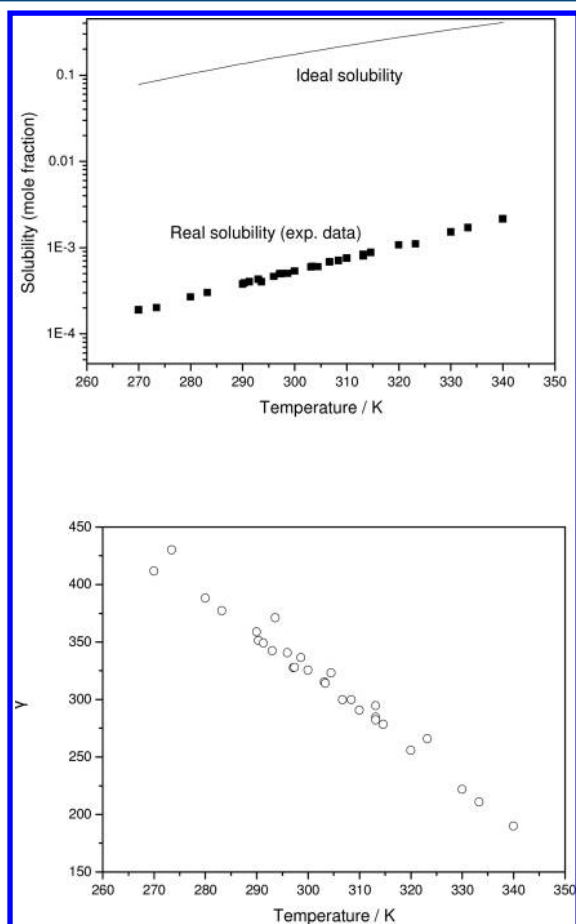
The results for SLE are also presented in Table 15. For the benzoic acid–benzene system, calculations were also performed using the binary parameters obtained from VLE data. Tables 10 and 15 reveal that the performance of all new schemes (3B, 4C, 1A+, and 2B+) for SLE was very poor and clearly worse compared to that of the previous schemes, especially 1A (see section 4.2).

#### 4.3.2. Aromatic Acids Using More Adjustable Parameters.

The effect of using more interaction parameters in the CPA model (and in combination with various pure-compound parameter sets) was investigated by Rørstrøm.<sup>83</sup> A short discussion is given here of the two approaches that were studied:

- (1) Using linearly temperature-dependent interaction parameters for BA–water, the description of LLE was greatly improved, but the representation of SLE and VLE using these LLE-based interaction parameters was actually worse (compared to that obtained using temperature-independent  $k_{ij}$ ). Thus, the simultaneous modeling of LLE, VLE, and SLE of BA–water remains a difficult task, even with temperature-dependent parameters. The problems can be partially attributed to the high degree

of nonideality of the system, as exemplified by the activity coefficient values shown in Figure 23.



**Figure 23.** Benzoic acid–water SLE: comparison of ideal and real solubilities (left) and calculation of experimental activity coefficients based on SLE data (right).

- (2) The second approach studied by Rørstrøm<sup>83</sup> was the use of two adjustable parameters in the modeling of aromatic acid–water systems. The two parameters were the  $k_{ij}$  value and either the cross-association energy or the cross-association volume; scheme 3B+ was used for all acids. It was concluded that, when the  $k_{ij}$  value and the cross-association energy are fitted (and the cross-association volume is obtained from the CR-1 rule), rather satisfactory results are obtained for all three aromatic acid–water systems and all types of phase equilibria (LLE, VLE, and SLE for BA–water and TA–water; only SLE for PTA–water). There is significant improvement over using a single adjustable parameter per system. However, there are problems. The  $k_{ij}$  values are still dependent on the type of phase behavior; that is, different values are used for SLE, VLE, and LLE, although the  $k_{ij}$  from LLE for BA–water can approximately be used for VLE as well. However, for all systems, the SLE description requires a much higher interaction parameter.

**4.4. Concluding Remarks for the Third Case Study.** The phase behavior of two aromatic acids (benzoic acid and terephthalic acid) has been investigated using the CPA equation of state. In a first attempt, the pure-fluid parameters were estimated using two simple association schemes (1A and 2B) for

acids, by fitting the predictions of the theory to experimental (or predicted) data for liquid densities and vapor pressures. It can be concluded that satisfactory, or at least acceptable, results were obtained for nonaqueous systems especially with the 1A scheme, but the performance of the model for the LLE and VLE of aqueous systems was not satisfactory. Moreover, different interaction parameters were needed for the different types of phase behavior.

In a second attempt, many parameter sets were estimated for benzoic acid using simple (3B and 4C) and complex (1A+ and 2B+) association schemes. These parameter sets were tested for benzoic acid–water LLE, as well as for benzoic acid–methanol and benzoic acid–benzene VLE. By adopting the association constants from benzoic acid, the corresponding parameter sets for terephthalic acid were estimated. Somewhat better results (compared to the 1A scheme) were obtained for aqueous systems using the 3B, 4C, and advanced association schemes. However, the results are still not satisfactory. For benzoic acid–water, the CPA EoS overestimates the mixture’s critical point (for LLE) and, consequently, fails to satisfactorily describe the mixture’s VLE. Moreover, the performance of the CPA EoS using the 3B, 4C, and advanced association schemes for the nonaqueous systems is less satisfactory compared to that obtained using the 1A scheme.

## 5. DISCUSSION

The three case studies presented in this work illustrated some of the capabilities (cases 1 and 2) and limitations (case 3) of the CPA EoS in describing phase behavior of mixtures containing various polar/associating chemicals. In the first two cases, it was shown that the CPA EoS can correlate binary VLE and LLE and predict multicomponent phase equilibria satisfactorily. Typically, one interaction parameter is needed (two for solvating systems). The predictions for multicomponent systems of case 2 are good, and they appear to be reasonably good in the first case as well, for which no direct data exist for comparing the calculated values. For systems similar to the investigated systems of the first case, previous investigations<sup>33,84</sup> showed that CPA calculations and multicomponent experimental data are in good agreement and moreover illustrated the importance of knowing the phase behavior in oxidation reactions in supercritical CO<sub>2</sub> systems. The conversion of the reaction can depend greatly on thermodynamics, especially on whether the reacting mixture is in the one- or two-phase region.

On the other hand, in the third case (aromatic acids), there is no point in pursuing multicomponent calculations for evaluating the model. Serious limitations are observed for binary systems, especially in the presence of water. The CPA model cannot describe VLE or LLE for aromatic acid–water mixtures, and the interaction parameter fitted to SLE data (which provides a satisfactory correlation) is not suitable for VLE or LLE calculations and vice versa.

The above represent a brief account of the results seen in this work. We believe that a thorough assessment of the model requires a more detailed discussion of several aspects and, moreover, is of interest to put the results of this work in a general perspective and compare them with those obtained using other association equations of state. We address several of these issues in the remainder of this section.

**5.1. Trends of CPA Parameters.** Both some pure-compound parameters and the interaction parameters of the model follow certain trends, which are useful and can be conveniently used when data are not available or when the goal is



to improve the model performance. The well-known covolume/van der Waals volume linear trend (Kontogeorgis and Folas<sup>4</sup> or see Figure S2 of the Supporting Information) was used in the third case. Moreover, we saw (in cases 1 and 2) linear trends of the interaction parameter ( $k_{ij}$ ) with temperature for the same mixture and with the carbon chain for a certain family of compounds (e.g., water–ketones). The  $k_{ij}$  value increases with temperature in most cases and decreases with chain length.

Similar trends of  $k_{ij}$  with chain length (always decreasing with increasing chain length or molecular weight) have been reported for the CPA model for numerous systems by Coutinho and co-workers<sup>85–91</sup> (water with alkanes, fatty acids, and esters or esters with alcohols) and by Mourah et al. and co-workers<sup>92</sup> for methanol–alkanes. Moreover, increasing  $k_{ij}/T$  trend has been reported for two SAFT variants by Yarrison and Chapman<sup>93</sup> for methanol–alkanes.

Whereas the trend in chain length with  $k_{ij}$  might appear to be physically reasonable, the increased  $k_{ij}$  values at higher temperatures (where polar and associating effects diminish) could be considered surprising. This trend might be related to limitations of the physical (especially dispersion) term, which might become apparent at higher temperatures (where the stronger forces that are taken into account explicitly are less important) or to a wrong temperature dependence in accounting for specific cross-associating interactions.

**5.2. How Important Is It To Consider Polarity for Phase Behavior Calculations?** The version of the CPA EoS used in this work does not include an explicit term accounting for the effect of polar interactions. Thus, such effects are taken into account implicitly through the interaction parameters or by considering the polar compounds as pseudoassociating. Solvation (induced association) effects (i.e., interactions between polar and associating compounds) can be taken into account through the association term. Even though the CPA model does not account explicitly for polar effects, as shown in cases 1 and 2, it describes the phase behavior (VLE, LLE, and multicomponent behavior) very well for many mixtures containing polar, nonpolar, and associating compounds (esters, ketones, water, hydrocarbons, and CO<sub>2</sub>). Accounting for solvation effects yields, for the systems studied, better results compared to considering polar compounds such as acetone as pseudoassociating. The fact that an explicit consideration of polar effects was not necessary for these systems does not indicate that such effects can be neglected in all cases.

Explicitly accounting for polarity can be important for correct representation of more sensitive properties such as heats of mixing.<sup>94–97</sup> Another case in which polarity effects are crucial is that of highly polar systems such as nitriles, with dipole moments higher than 3 D. In these cases,<sup>4,98</sup> polar versions of association models are expected to perform better. There are also cases where highly polar compounds can exhibit both VLE and LLE (at lower temperatures) when water or hydrocarbons are present. Examples are acetone with hexane, sulfolane with hydrocarbons and methyl ethyl ketone with water. Satisfactory representation of both VLE and LLE with association models might also be difficult in these cases without accounting explicitly for polarity, as shown in the literature.<sup>4,99</sup>

Multicomponent multiphase equilibria with the CPA model for complex mixtures of polar and associating compounds such as dimethyl ether, water, CO<sub>2</sub> or N<sub>2</sub>, and methanol is not entirely satisfactory.<sup>27</sup> Inclusion of polar effects might help, but this remains to be seen. The “trick” of considering polar compounds as pseudoassociating might work well in some cases,<sup>4,100</sup> but as

shown by the results of this work, it does not represent the optimum approach in all cases. Nevertheless, we do not consider that the existing implementations of polarity in association models are fully satisfactory, especially for mixtures containing both polar and associating compounds. As an example, the results presented for water–acetone by Kleiner and Sadowski<sup>101</sup> with a polar version of PC-SAFT are satisfactory only when the polar term of water is “turned off” and the polar term is considered only for acetone. Even in this way, the results with this polar PC-SAFT model are similar to those shown for water–acetone in this work considering solvation only.

**5.3. Problems of Aromatic Acids.** Whereas the parameter trends discussed in section 5.1 and overall the results in the first and second cases are positive, the performance of the CPA model in the third case is clearly disappointing. Isolated SLE correlations are successful for mixtures with aromatic acids. However, different interaction parameters are needed for the different types of phase behavior (VLE, LLE, SLE) and what is worse the steep LLE curve of benzoic acid–water (e.g., Figure 17) cannot be correlated well and this affects also negatively the model performance for VLE at higher temperatures. What can be considered as a further limitation is that the results are not really improved by more advanced association schemes or more interaction parameters e.g. by using temperature-dependent interaction parameters. In addition, the aforementioned problems cannot be attributed, in the case of benzoic acid, to uncertainties related to pure compound parameters. For other heavier aromatic acids (such as terephthalic acid) vapor pressure and liquid density data do not exist and thus their parameter estimation is difficult. This is not the case for benzoic acid, where many data for pure compound properties are available. For these reasons, we decided to investigate the possible origin of these problems in various ways as follows:

- (1) by comparison to literature studies for benzoic acid and similar systems;
- (2) by comparison of the obtained results to those obtained previously with the CPA EoS for other aromatic polar or associating compounds, such as aromatic aldehydes, aromatic amines, and aromatic alcohols; and
- (3) through a general account of the problems of the Wertheim approach, which are inherent in the CPA model, and of course the limitations of the physical term (SRK term).

General point 3 will be discussed separately (section 5.4), whereas points 1 and 2 are discussed now.

**5.3.1. Literature Studies.** Naturally, if successful literature modeling results had been presented for benzoic acid systems, especially aqueous ones, these could point to possible improvements in our approach. We have not been able to identify many modeling literature studies for benzoic acid systems and essentially none that consider benzoic acid–water VLE, LLE, and SLE. Queimada and co-workers<sup>102–105</sup> applied the CPA model to many multifunctional aromatic acid and related systems, many of which are relevant to pharmaceutical applications. The results were generally in good agreement with the experimental data, but only SLE studies were shown. Among the systems studied is benzoic acid–water, but again, only SLE calculations were shown. As mentioned, we also find that SLE alone can be described well.

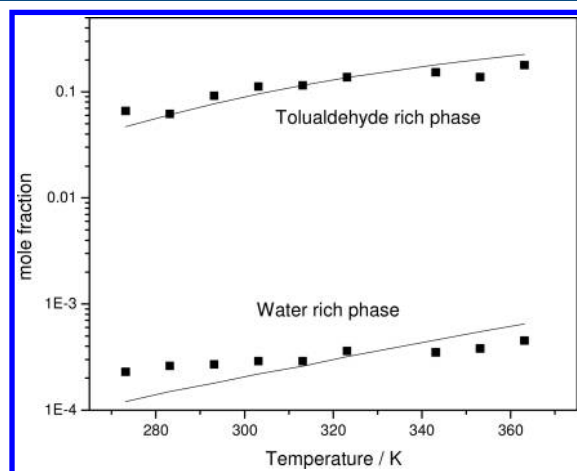
**5.3.2. CPA EoS for Other Aromatic Polar or Associating Compounds.** The CPA model has previously been applied to a number of compounds that contain both an aromatic ring and a

polar or associating group. The CPA model was applied to aqueous and CO<sub>2</sub> systems with aromatic aldehydes and benzylalcohols by Tsvintzelis et al.<sup>33</sup> and in this work, to aniline (an aromatic amine)–water by Kontogeorgis and Folas,<sup>4</sup> and to mixtures containing phenol and cresols with water and alkanes.<sup>4,106</sup> We present here a discussion of these results and compare them to those obtained in this work for aromatic acids–water.

Aniline and water exhibit a broad LLE in the region 300–420 K. The CPA model using either two or three association sites for aniline and one interaction parameter correlates LLE quite well and similarly to PC-SAFT and the SRK EoS with Huron–Vidal parameters. Equally good predictions are obtained, using solely binary parameters from binary data, for the ternary LLE of aniline–water–toluene.

In the study of Tsvintzelis et al.<sup>33</sup> various benzaldehyde systems were studied, including the one with water. Solvation was taken into account through the modified CR-1 rule. It can be seen that the results are not as satisfactory as for water–hydrocarbons, especially for the aqueous phase. (Calculations are presented in Figure S8 of the Supporting Information.) The temperature dependency is captured, however.

Interestingly enough, the CPA correlation for (the even more immiscible) water–*p*-tolualdehyde system is more successful, as shown in Figure 24. Again, solvation is taken into account in the



**Figure 24.** Water–*p*-tolualdehyde LLE: experimental data,<sup>107</sup> points; CPA calculations, lines.

usual way, using the modified CR-1 rule (and thus two adjustable parameters). Thus, it can be concluded that, despite some difficulties, the correlation performance of the model for water/aromatic aldehydes is much better than for water/benzoic acid.

As mentioned, Kontogeorgis and co-workers<sup>4,106</sup> provided a preliminary study of *m*-cresol with water and alkanes. Various parameter sets for *m*-cresol were obtained based on different considerations and tested against VLE data for *m*-cresol–alkanes and LLE data for *m*-cresol–water. Using the selected set of *m*-cresol parameters, the AAD in pressure for all *m*-cresol–alkane systems was less than 3%. Moreover, using the CR-1 rule, good results were obtained for *m*-cresol–water LLE. The AAD of cresol in water is 22%, and the corresponding percentage deviation of water in cresol is 19%. These deviations are much lower (less than half) than those of benzoic acid–water (compare to Figure 17).

Comparing Figure 17 to Figure 8 of ref 106, it can be seen that the phase diagrams are quite similar, with one phase (aqueous)

consisting mostly of water and the organic phase having 20–40% benzoic acid and 20–60% cresol. The LLE region for water–*m*-cresol is in the range of 300–410 K, whereas it is at somewhat lower temperatures (350–385 K) for water–benzoic acid. Equally satisfactory results are seen for *n*-decane–phenol and water–*o*-cresol LLE. (Results, obtained using literature experimental data,<sup>108,109</sup> are illustrated in Figures S9 and S10 of the Supporting Information.) The latter is similar to water–*m*-cresol LLE.

#### 5.4. Problems of the Association and Physical Terms.

The analysis presented in section 5.3 indicates that the problems that we experienced for water–benzoic acid (and the other aromatic acids) are not necessarily explained by the simultaneous presence of an aromatic ring and a polar or associating group, as we did not encounter problems at the same level for aromatic aldehydes, amines, and alcohols. For this reason, we decided to examine the model a bit deeper to see whether the problems can be understood by the limitations inherent in the Wertheim theory (association term) or the physical term of the model (SRK EoS).

The Wertheim theory, as it is incorporated in the CPA EoS or most SAFT-type models, does have a number of limitations. The most important are the following:

- (1) When two molecules are close enough to associate, the repulsive cores of the molecules will prevent a third molecule from coming close to associate.
- (2) No site on one molecule can bond simultaneously to two sites on another molecule.
- (3) No double bonding between two molecules is allowed.

Furthermore, cooperativity (present, for example, in the dimerization of organic acids), ring-like structures, intramolecular association present in many mixtures (e.g., in heavy glycols and glycolethers), and steric hindrance cannot be considered. Cross-association effects are of course included, but there is a difficulty in estimating the correct values of the cross-association parameters without the use of experimental data, because the existing combining rules (for example, the CR-1 and modified CR-1 rules used in this study) have no physical meaning. Furthermore, water's many special effects (such as the hydrophobic phenomenon) are not explicitly taken into account, except for its three-dimensional network structure, which is taken into account by the four-site (4C) association scheme. Finally, multifunctional chemicals such as alkanolamines and glycolethers can associate in manners different from those assumed and tested for monofunctional chemicals such as amines and alcohols.

Although these limitations are serious, for practical applications, they should also be seen in relation to the importance of parametrization (parameter estimation), which is crucial for multiparameter models such as the CPA EoS and SAFT. In many cases, serious limitations of the models are masked by using many carefully estimated and effective parameters.

Several researchers have attempted to develop theories and other ways to address some of the limitations of the Wertheim association term. For example, Avlund et al.<sup>122</sup> developed (and applied in PC-SAFT) a theory that accounts for the intramolecular association present in molecules such as glycolethers. The theory was applied to three glycolethers.<sup>111,123</sup> For demanding systems, it is necessary to include LLE data in the parameter estimation, whereas the 2-butoxyethanol–water closed-loop behavior is very difficult to correlate with one adjustable parameter. Partially successful results can be obtained,

but the difference between inter-PC-SAFT and intra-PC-SAFT is marginal, and the differences can be masked by the way parameters are estimated. Maybe more demanding properties should be considered (such as enthalpies or heat capacities) to identify the true value of including intramolecular association. Moreover, advanced association schemes have been tried for both alkanolamines<sup>123,22</sup> and glycols.<sup>124</sup> The improvement is minimal for alkanolamines, whereas for glycols, the improvement is seen for properties such as infinite-dilution activity coefficients and excess enthalpies, as well as for obtaining good descriptions of triethylene glycol (TEG)–methane and TEG–heptanes mixtures simultaneously over an extensive temperature range. Recently, a new 2C association scheme was presented for alcohols<sup>125</sup> that (compared to the 2B and 3B schemes) results in better calculations for water–alcohols VLE (but somewhat worse for alcohol–alkane and multicomponent systems).

Finally, the effect of the physical term in the CPA EoS can be partially evaluated by comparing the CPA EoS with PC-SAFT or other SAFT variants, because SAFT models have a theoretically more correct term for the physical interactions. Many studies have been published that can be used for comparing the performance of the CPA EoS and SAFT variants, especially PC-SAFT, such as those by Tybjerg et al.<sup>110</sup> for water–methanol–hydrocarbons, Avlund et al.<sup>29,30,111</sup> and Garrido et al.<sup>28</sup> for alkanolamines and glycol ethers, Voutsas et al.<sup>112</sup> for water–hydrocarbons, Voutsas and co-workers<sup>113,114</sup> for diverse mixtures (CO<sub>2</sub>, ethers, ketones, acetic acid), and Li and Englezos<sup>115</sup> and Grenner et al.<sup>116,117</sup> for various alcohol and glycol mixtures. A general conclusion from all of these studies is that, for these types of associating mixtures, the CPA model and PC-SAFT (and even other SAFT variants) perform similarly, with the possible exception of binary water–alkane systems, where the CPA model performs overall better than PC-SAFT and “original” SAFT versions. Moreover, both the CPA EoS and PC-SAFT (as well as other SAFT variants) have problems in correlating water–small acid (formic acid, acetic acid) VLE.<sup>4,26</sup> Finally, other systematic comparisons between different association models have revealed that, when the parameter estimation is carried out in the same way, the performance of the models is overall similar.<sup>118</sup> A recent study carried out by Grenner et al.<sup>119</sup> and Tsvintzelis et al.<sup>120</sup> showed that PC-SAFT and nonrandom hydrogen bonding (NRHB) theory overall perform similarly when tested against the standard database by Danner,<sup>121</sup> as well as for a number of systems exhibiting LLE.

Here, it worth mentioning that, in many cases, deviations of model predictions from experimental data can be partially attributed to inadequacies of the EoS mixing and combining rules used in the physical term. The binary interaction parameters, which are estimated using experimental equilibrium data for binary systems, are not completely empirical parameters. Haslam et al.<sup>126</sup> extended the Hudson–McCoubrey combining rules to intermolecular potentials that are not of Lennard-Jones form. They showed that care should be taken in transferring the binary interaction parameter,  $k_{ij}$ , of systems with polar fluids to conditions other than the conditions under which it was obtained. Furthermore, they showed that different values of the binary interaction parameter might be needed for different phases (liquid or vapor), which is a conclusion that arises from the density dependencies of both the dielectric and dipole moments.

Based on these considerations, it is difficult to identify the explanation for the poor performance of the CPA model for water–aromatic acids or to predict whether improvements can

be expected by incorporating polar or more advanced physical terms instead of the SRK term used in the CPA model. It appears that fundamental modifications in the association term are needed to improve the performance of the CPA model for aromatic acid–water mixtures, exactly as is the case for water–aliphatic acids.<sup>31</sup> In this direction, possible approaches to model improvement are to develop association schemes that allow the simultaneous existence of acid dimers and linear oligomers in mixtures of acids with other hydrogen-bonding fluids and to account for acid dissociation in aqueous media.

## 6. CONCLUSIONS

Following a short review on the performance of the CPA EoS to mixtures of relevance to the oil and gas industry (mixtures with water, hydrocarbons, and acid gases), where the role of solvation is also discussed, the CPA model was applied to three case studies of relevance to the chemical industry. All three case studies are linked to specific practical applications and involve mixtures containing nonpolar, polar, and hydrogen-bonding compounds. In most of the cases, diverse types of phase behavior (vapor–liquid, liquid–liquid, and solid–liquid equilibria) occur. The three case studies cover a range of applications and are suitable for illustrating several capabilities and limitations of the association model used in this study.

It is shown that the CPA model correlates well the mixtures involved in the oxidation of 2-octanol in supercritical CO<sub>2</sub>, specifically water–octanol LLE, water–2-ketones LLE, and VLE for CO<sub>2</sub> or nitrogen with octanols. It is shown that missing parameters can be obtained from trends that were established between the interaction parameter of the model and the molecular weight for water–ketones.

Good results were also obtained for multicomponent vapor–liquid equilibria for mixtures containing acetone, methanol, water, chloroform, and methyl acetate. Overall, the best results were obtained by considering acetone as a non-self-associating molecule that can cross-associate with water. For all binary systems, it is seen that linear trends of the interaction parameter with temperature were obtained. The CPA model describes very well both VLE and LLE and with the same interaction parameters for mixtures such as water–methyl acetate, which exhibit both types of phase behavior.

Finally, in the third case study, the phase behavior of mixtures containing aromatic acids was studied. Overall (i.e., considering both aqueous and nonaqueous mixtures), the best results were obtained using the 1A scheme for aromatic acids. However, the results were not satisfactory. The CPA EoS cannot correlate well the VLE and LLE of the benzoic acid–water system. The CPA EoS can correlate the SLE of benzoic acid–water and terephthalic acid–water mixtures with a temperature-independent interaction parameter. However, the same interaction parameter cannot be used for all types of phase behavior exhibited by benzoic acid–water. Use of advanced association schemes and more adjustable parameters did not improve the performance of the model to an acceptable degree.

A discussion of the results revealed that the poor performance for water–aromatic acids does not occur to the same degree for mixtures containing other complex aromatic compounds containing polar and/or associating groups such as aromatic aldehydes and phenols. Fundamental modifications in the association term of the CPA EoS might be needed to improve the model performance of the CPA model for aromatic acid–water mixtures, exactly as is the case for water–aliphatic acids.



## ■ ASSOCIATED CONTENT

### ● Supporting Information

Characteristic results of this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Tel.: +45 45252866. Fax: +45 45882258. E-mail: [it@kt.dtu.dk](mailto:it@kt.dtu.dk) or [gtsivint@eng.auth.gr](mailto:gtsivint@eng.auth.gr).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank Statoil and Gassco (Norway), BP International Limited (U.K., U.S.), TOTAL (France), and DONG Energy and Mærsk Oil and Gas (Denmark) for supporting this work as part of the CHIGP (Chemicals in Gas Processing) Project. Especially, the authors thank BP International Limited (U.K., U.S.) for the fruitful collaboration and discussions and Tim Rørstrøm, who contributed to this study.

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