Evaluation of association schemes in the CPA and PC-SAFT equations of state in modeling VLE of organic acids + water systems

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Abstract

The performance of various association schemes was evaluated in modeling isothermal and isobaric vapor – liquid equilibria of mixtures of organic acids and water with the CPA and the PC-SAFT equations of state. The organic acids considered were formic, acetic, propanoic and butanoic acid. Combinations of the 1A and 2B association schemes for the acids and the 2B, 3B and 4C for water were tested. Polar contributions were also studied in PC-SAFT. The case in which no association contribution is included in the thermodynamic model was also assessed. It is concluded that the chosen association scheme greatly affects the performance of the equation of state. It was not possible to identify a single association scheme combination that would work well for all the systems and conditions studied. On average, PC-SAFT with the organic acid modeled as 1A and water as 4C showed the greatest accuracy. Interestingly, for some of the mixtures the non-association case gave considerably better representations than when the association term was used. When a binary interaction parameter is used the performance of the equations studied is comparable to the classic PR.

Introduction

While in the past traditional cubic EoS haven been used to compute phase equilibria properties, nowadays, these have been gradually replaced by modern thermodynamic models developed from statistical molecular thermodynamics, capable of modeling complex mixtures that exhibit hydrogen bonding and polar interactions.

In a previous communication (Román-Ramírez and Leeke 2020) a comparison was made between the PR EoS and CPA in modeling the phase equilibria of binary mixtures of carboxylic acids and water. In this paper, and in order to extend the investigation, a comparison is made of the performance between CPA and PC-SAFT, in modeling the VLE of these systems by testing different association schemes, a different combining rule in CPA and polar contributions in PC-SAFT.

In the Huang and Radosz (1990) association scheme classification, the organic acids are rigorously modeled by the 1A association type that allows for cyclic dimer formation, the prevalent form in the vapor phase, given by hydrogen bonding between two carboxylic groups of two acid molecules (Crupi et al. 1996). However, the chain-monomer formation, as may appear in the liquid phase (Heisler et al. 2011), can be captured by the 2B scheme. Water, on the other hand, can be modeled by the 4C scheme that corresponds to the two lone-pairs of electrons and two hydrogen atoms, but also by the 3B (one site for the two lone-pairs of electrons, and one site each hydrogen atom, or one site for the two hydrogen atoms and one for each of the pair of electrons), or the 2B schemes (the two pairs of electrons are one site and the two hydrogen atoms one site) (Figure 1). Experimental spectroscopy data supports the 4C rigorous type for water, but in practice there is no general agreement on the best association model (Román-Ramírez et al. 2015).

Kleiner (2008) compared pure component parameters of water as 2B, 3B and 4C obtaining slightly better representations of the saturated liquid densities with 3B, whereas the 4C type gave the best results for the vapor pressures; for mixtures with hydrocarbons, the mutual solubilities could only be described by the 4C scheme. It was also noted that, for other mixtures than hydrocarbons, the 2B is superior than the 4C if the other compound has a functional group (e.g. polar or associating), in agreement with previous observations of Perakis et al. (2007). Moreover, Kleiner also concluded that the phase behavior is very sensitive to the chosen parameters by comparing results employing three different sets of pure component parameters for water modeled as 4C. A similar conclusion was reached by von Solms et al. (2006) using other sets. On the other hand, Kontogeorgis et al. (2010) have shown that (for CPA and sPC-SAFT) the 4C model is superior in representing properties of pure water, in particular with CPA. In addition to vapor pressures and liquid densities, the authors also included experimental monomer fraction data in the fitting procedure. Liang et al. (2014) arrived at the same conclusion when comparing in addition to saturated properties, speed of sound and isochoric and isobaric heat capacities.

Kleiner (2008) has shown that the 1A scheme for organic acids represents better pure compound properties compared with the 2B in PC-SAFT. Derawi et al. (2004) concluded the same when testing types 1A, 2B and even 4C in predicting vapor pressures and equilibrium constants of formic, acetic and propanoic acids with CPA. Janecek and Paricaud (2012) compared the cases for water modeled as 2B and 4C, and acetic and propanoic acid modeled as 2B, 4C or the DBD scheme. Predictions with the 2B model where superior to the 4C, but the latter showed better correlations. The DBD scheme resulted in the highest deviations of saturated properties.

Kontogeorgis et al. (2006b) reported that representations are improved when acetic acid is modeled as 2B instead of 1A, in mixtures with water modeled as 4C, with CPA and the ECR. Muro-Suné et al. (2008) modified CPA by introducing the HV-NRTL model to improve the CPA capabilities in modeling the acetic acid + water mixture. The same system was satisfactorily modeled by Román-Ramírez and Leeke (2016) using the 2B (for acetic acid) and 4C (water) with PC-SAFT. Perakis et al. (2007) in their study of water + acetic acid + CO_2 with CPA (with PR instead of SRK) showed that better representations were obtained when water is modeled as 3B and acetic acid as 1A.

Propanoic acid + water was studied by Kontogeorgis et al. (2007) defining the acid as 1A and water as 4C with CPA and CR1. Satisfactory results were obtained but required a large value of the binary interaction parameter. In contrast, Román-Ramírez et al. (2015) compared the results in modeling propanoic acid + water with PC-SAFT, PCP-SAFT and CPA with CR1 setting both compounds as 2B. PCP-SAFT resulted the best model for this system. Kouskoumvekaki et al. (2004) and Chen et al. (2012) modeled carboxylic acids + water systems with PC-SAFT with both compounds as 2B. More recently, Ribeiro et al. (2018) have made a comparison of CPA and sPC-SAFT in modeling properties of pure acetic acid and in mixtures with water, hexane or ethanol. The authors concluded that the 1A scheme for acetic acid performed better overall.

There is therefore no general conclusion about the best combination of association scheme for modeling aqueous mixtures of organic acids. The discrepancies on the conclusions of the previous works can be explained by the fact in differences of the organic acids considered, temperature and pressure ranges studied, pure component parameters used, fitting procedure (including search algorithm, source of experimental data and temperature range for saturated properties) and whether additional pure component properties were used in the fitting (e.g. monomer fraction data). Pareto optimization technique have been recently applied to obtain a “best” set of parameters for water as either 2B or 4C with or without polar contributions in PC-SAFT (Forte et al. 2018) showing that there will always be a trade-off when choosing a specific model. It has also been shown that different values of the universal constants in PC-SAFT can result in improved representation of certain properties but in detriment of others (Liang and Kontogeorgis 2015; Pina-Martinez et al. 2019), Similarly, Ribeiro et al. (2018) arrived at the same conclusion when including saturated pressure, density, speed of sound, second virial coefficient, compressibility factor, enthalpy of vaporization and isobaric heat capacity of acetic acid. Consequently, it is not possible to obtain a single set capable of describing all properties satisfactorily.

The present work is therefore only focused in describing the VLE and not second-order thermodynamic derivative properties. The 1A and 2B schemes are tested for organic acids, whereas the 2B, 3B and 4C for water. In CPA, the ECR and CR1 are evaluated. PC-SAFT with polar contributions (PCP-SAFT) is also included in the study. Additionally, and in order to test the effect of the association term in PC-SAFT and PCP-SAFT, the modeling without association contributions is also examined.

Thermodynamic models

CPA

The CPA EoS in terms of A^{res} is (Kontogeorgis and Folas 2010):

$$\frac{A^{res}(T,V,n)}{RT}=\frac{A^{SRK}(T,V,n)}{RT}+\frac{A^{assoc}(T,V,n)}{RT} \quad (1)$$

The expressions for A^{SRK} and A^{assoc} can be found in the SI. In a previous publication (Román-Ramírez and Leeke 2020), the CR1 was employed for mixture calculations. In this work, the alternative ECR (Kontogeorgis et al. 2006a) is used and compared:

$$\varepsilon^{A_iB_j}=\frac{\varepsilon^{A_iB_i}+\varepsilon^{A_jB_j}}{2} \quad (2)$$

$$\beta^{A_iB_j}=\sqrt{\beta^{A_iB_i}\beta^{A_jB_j}}\frac{b_ib_j}{b_{ij}} \quad (3)$$

The equation is referred here as CPA-ECR. Five pure component parameters are required to define a compound: a_0, b, c_1, ε^{AB} and β^{AB}.

PC-SAFT and PCP-SAFT

PC-SAFT is expressed in terms of A^{res} as (Kleiner and Gross 2006):

$$\frac{A^{res}(T,V,n)}{RT}=\frac{A^{hc}(T,V,n)}{RT}+\frac{A^{disp}(T,V,n)}{RT}+\frac{A^{assoc}(T,V,n)}{RT}+\frac{A^{polar}(T,V,n)}{RT} \quad (4)$$

Details of the hc, $disp$, $assoc$ and $polar$ expressions can be found in the SI. When the $polar$ term is included, the equation is referred as PCP-SAFT. The following parameters are required to define a compound: m, σ, ε, ε^{AB}, and κ^{AB}. The dipole moment (μ) is additionally needed in PCP-SAFT.

Pure component and binary interaction parameters

Pure component parameters were obtained following the methodology described in (Román-Ramírez and Leeke 2020) or taken from the relevant literature.

The optimum binary interaction parameter was obtained by regressing experimental data of bubble-point pressures (P) and vapor compositions of the organic acid (y_1) simultaneously, according to the following objective function:

$$F_1 = \sum_{i=1}^{N} \left[\left(\frac{P_i^{exp} - P_i^{calc}}{P_i^{exp}} \right)^2 + \left(y_{1,i}^{exp} - y_{1,i}^{calc} \right)^2 \right] \tag{5}$$

Superscripts exp and $calc$ stand for an experimental and a calculated property, respectively. N is the number of experimental points used in the optimization.

The following objective function was used for the butanoic acid + water system (isobaric data) due to the limited availability of isothermal data:

$$F_2 = \sum_{i=1}^{N} \left[\left(T_i^{exp} - T_i^{calc} \right)^2 + \left(y_{1,i}^{exp} - y_{1,i}^{calc} \right)^2 \right] \tag{6}$$

Where T is the bubble temperature. The references for the experimental data employed can be found in Table S1.

Thermodynamic evaluation

The performance of the equations was evaluated by comparing the deviations in saturated properties (P_V and ρ_L) for pure components, and of P and y (and T and y, for the case of butanoic acid) for mixtures, according to Equations (7) and (8). The predictive ($k_{ij} = 0$), and correlative ($k_{ij} \neq 0$) capabilities of the models were assessed. The experimental data used in the evaluation can be found in Table S1.

$$\Delta\theta_1 = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{\theta_{1,i}^{exp} - \theta_{1,i}^{calc}}{\theta_{1,i}^{exp}} \right| \tag{7}$$

$$\Delta\theta_2 = \frac{1}{N} \sum_{i=1}^{N} \left| \theta_{2,i}^{exp} - \theta_{2,i}^{calc} \right| \tag{8}$$

where $\theta_1 = P_V$, ρ_L or P, and $\theta_2 = y_1$ or T.

Results and Discussion

The notation to be used in the rest of the text is as follows: the first position of the subscript next to the equation is the association scheme for the organic acid while the second position is the association scheme for water. For instance, PCP-SAFT$_{1A\text{-}2B}$, means that the PCP-SAFT equation of state is used with the organic acid modeled as 1A and water as 2B. The subscript *non-assoc* denotes that association interactions are not being considered.

Pure components

Fitted pure component parameters and the corresponding calculated deviations in saturated properties are shown in Table 1. There is no model resulting in the best fit for both properties. Considering the association scheme only, the 1A performed best for PC-SAFT and PCP-SAFT for all organic acids; whereas for CPA, formic acid and propanoic acid were better correlated by 1A, while acetic acid and butanoic acid by 2B. As a whole, however, formic acid was better represented by CPA_{1A}, acetic acid by $\mathrm{PC\text{-}SAFT}_{1A}$, propanoic acid by $\mathrm{PC\text{-}SAFT}_{1A}$, butanoic acid by CPA_{2B}, while water by CPA_{4C}. PCP-SAFT did not provide any clear advantage on correlating the properties; the deviations between PC-SAFT and PCP-SAFT are very similar among the same association schemes, including the non-association case. This may be as a result of the dipole moment being considered constant over the whole temperature range in the model. Only for the case of water modelled without association there is a real difference in introducing the polar term in PC-SAFT, where the deviations in P_V and ρ_L were reduced in more than 70% and 40%, respectively, with PCP-SAFT.

Compared with the PR versions studied before (Román-Ramírez and Leeke 2020), it is interesting to note that PR-f gives lower deviations in the saturated properties than PC-SAFT and PCP-SAFT without the association term, considering that the same parameterization method was used (i.e. from fitting vapor pressure and liquid density data). Clearly, this does not mean that the physical term in PR-f is more accurate than that in PC-SAFT and PCP-SAFT, but that the results will largely depend on the pure component parameters employed. As mentioned before, studies have shown that it is not possible to obtain a single set that will result in the best fitting for all properties (Liang and Kontogeorgis 2015; Forte et al. 2018; Ribeiro et al. 2018). The deviations when the association term is omitted are larger than those of the models that include them. Nevertheless, larger deviations in saturated properties will not necessarily lead to poor representations of mixture properties, as has been shown by Liang et al. (2014). The set of parameters obtained here are adequate for VLE but may not be able to represent accurately pure component properties. An improvement in saturation properties estimation with PC-SAFT can be achieved by applying a volume-translation technique as recently demonstrated by Moine et al. (2019), although it was only applied to non-associating compounds.

Regarding water, CPA_{4C} was overall the best model to correlate water saturation properties. Interestingly, $\mathrm{PCP\text{-}SAFT}_{\text{non-assoc}}$ was the second-best option to correlate its properties, closely followed by $\mathrm{PCP\text{-}SAFT}_{3B}$.

Binary mixtures

The calculated ΔP and Δy_1 for the predictions and correlations are presented in Tables S2 and S3. In order to visualize some trends, Figures 2 – 5 show interaction plots in which ΔP and Δy_1 are shown as a function of system, equation of state, association scheme and temperature.

Predictions

The best predictions ($k_{ij} = 0$) over the whole temperature range are given on average by PC-SAFT (Figures 2 and 3). PCP-SAFT performs slightly better than CPA. The highest deviations are observed for the butanoic acid system, but since the results comprise one single temperature its analysis is skewed, particularly as the available data is in the low temperature range and as appreciated by the temperature interaction plot there is a tendency for better predictions (for all models and association schemes) as the temperature increases.

Compared with the previous study (Román-Ramírez and Leeke 2020), the association term in CPA clearly improves the predictive capabilities of the cubic term. The ΔP with CPA are on average more than 60% lower than the best case given by PR-f.

It was not possible to identify a best association scheme combination for all systems. Results vary depending on equation of state used and temperature. On average, considering all four systems, PC-SAFT$_{\text{1A-4C}}$ gives the best predictions in P (ΔP = 9.98%), followed by PCP-SAFT$_{\text{1A-3B}}$ (11.37%). On average, the predictions with PC-SAFT are superior to those when the dipolar moment term is included, even for the instances without the association term.

Poor predictions would have been expected when the association interactions are not considered explicitly in the model, however, as shown in Figure 2 there are instances in which the non-association versions outperform the corresponding associating ones. As an example, Figure 6 shows that whereas PC-SAFT$_{\text{2B-4C}}$ (on average the best association combination for the propanoic acid system), fails to represent the azeotropic behavior of the mixture, PC-SAFT$_{\text{non-assoc}}$ at least represents it qualitatively and is also closer to the experimental compositions. The polar term does not provide any advantage in this case. This supports the idea that the appropriate association scheme combination must be chosen in order to obtain satisfactory results.

In some instances CPA outperforms PC-SAFT or PCP-SAFT, as is the case for CPA-CR1$_{\text{1A-3B}}$ with errors more than 50% lower compared with the 2B-2B, 2B-3B and the 2B-4C PCP-SAFT versions. Nevertheless, predictions with CPA are in general rather poor, especially for some combinations such as 1A-4C or 2B-2B, in agreement with previous results of Kontogeorgis et al. (2007). Although the 1A-3B provides the lowest overall deviations in CPA, the model is either unable to give a satisfactory representation or predicts experimentally unobserved azeotropic behavior for acetic acid. For instance, at 293.15 K (Figure 7), CPA-CR1$_{\text{1A-3B}}$ cannot handle the strong non-ideality overpredicting the phase diagram. Breil et al. (2011) coupled CPA with the Huron-Vidal mixing rule to obtain a reasonable representation. PC-SAFT$_{\text{2B-4C}}$ predicts erroneously an azeotrope at this temperature. In contrast, the 1A-3B, the overall best combination in PCP-SAFT, is closer to the experimental data. It is worth mentioning that PC-SAFT$_{\text{1A-3B}}$ results in an inverted phase diagram prediction. A similar behavior is observed for formic acid + water with the 2B-2B and 2B-4C schemes in PC-SAFT and PCP-SAFT, in agreement with previous observations using PC-SAFT by Kontogeorgis et al. (2007).

Within CPA, the predictions with CR1 are overall better than ECR, resulting on average in 17% lower ΔP. The 1A-3B combination provides the best predictions regardless of combining rule.

The results for the vapor phase composition follow a similar trend to the bubble pressures. Nevertheless, in this case, the Δy_1 tend to be higher on the extremes of the temperature range reaching a minimum around the 350 – 400 K region.

Correlations

The performance in correlative mode was studied using a linear temperature dependency of the binary interaction parameter ($k_{ij} = A_{ij} + B_{ij}T$). Values for parameters A and B are presented in Table 2, whereas the corresponding calculated deviations can be found in Table S4. The values of k_{ij} for each temperature and system can be found in Table S4, and the corresponding deviations in Table S5.

The lowest absolute magnitudes of the k_{ij} are observed for PC-SAFT but are mainly negative. In fact, the k_{ij} for all the EoS are negative except for PC-SAFT 1A-2B, 1A-3B and 1A-4C; and PCP-SAFT$_{1A\text{-}3B}$. This negative magnitude may indicate an underestimation of the cross-association (Kontogeorgis et al. 2007). The lowest obtained deviations with PC-SAFT$_{1A\text{-}4C}$ in predictive mode and the small positive value of the k_{ij} suggest that the best combination for PC-SAFT is the 1A-4C. The best combination in PCP-SAFT is 1A-3B.

The magnitudes of k_{ij} for CPA are larger than those of PC-SAFT and PCP-SAFT and are comparable to the ones of the PR versions studied before (Román-Ramírez and Leeke 2020). Magnitudes as large as -0.26 for the 1A-4C scheme with ECR were found, in agreement with previous publications (Kontogeorgis et al. 2007). However, good representations are obtained even when large values of the k_{ij} are required, in such a way that differences in the performance in correlative mode become narrower. CPA-ECR, PC-SAFT and PCP-SAFT give similar overall average ΔP and Δy_1 of 6% and 0.07, respectively. CPA-CR1 resulted in just slightly higher average ΔP (7%).

Like the predictive mode, it was not possible to identify a single association combination that will provide the best results for all systems. The best overall average correlations were given by CPA-ECR$_{1A\text{-}4C}$ with ΔP of 5.1%, followed by PC-SAFT$_{1A\text{-}2B}$ and PCP-SAFT$_{1A\text{-}2B}$ (5.4%). Nevertheless, the performance is different when looking at specific temperatures and systems. For instance, CPA-ECR$_{1A\text{-}2B}$ correlates the formic acid + water at 398.2 K better than PC-SAFT and PCP-SAFT with the same association scheme (Figure 8). Unexpectedly, the deviations when the dipolar term is included in PC-SAFT are higher in spite of the complexity of the term introduced in the model. Even more surprising, when no association term is used in PCP-SAFT the performance overcomes some of the association combinations, as also observed in the predictions. As an example, Figures 9 and 10 present the VLE diagram and the relative volatilities ($\alpha = \frac{y_i/x_i}{y_j/x_j}$), respectively, for the propanoic acid + water system at 303.2 K. α is used as a parameter to determine the feasibility of using distillation as the separation process (Sorensen 2014; Martín 2016). PCP-SAFT without association interactions is clearly closer to the experimental relative volatilities compared to PC-SAFT$_{1A\text{-}4C}$. PC-SAFT$_{\text{non-assoc}}$ wrongly estimates a poor separation by distillation ($\alpha < 1.05$) in the propanoic acid dilute region, in addition to show the worst correlations.

The different performance between the models can be mainly attributed to the pure component parameters employed, but it is interesting to note that it is possible to ignore the association term and yet still to obtain acceptable estimations. It is important to keep in mind that the association term in SAFT has been constructed based on different simplifications (Ramdin et al. 2018) and inaccuracies can therefore be expected in actual applications.

Comparing these results with the previous findings (Román-Ramírez and Leeke 2020) the PR correlations result in some instances in comparable or even better accuracy than some of the association equations depending on the system and temperature. This is exemplified in Figure 11a for the butanoic acid system at 303.2 K. The best correlations at this condition are given by CPA-ECR$_{2B\text{-}4C}$ and PC-SAFT$_{2B\text{-}2B}$ (Figure 11b). A similar situation was observed by Diamantonis et al. (2013) when testing SRK, PR, SAFT and PC-SAFT in modeling gas mixtures involving CO_2. This again supports the idea that the appropriate association term must be chosen to obtain satisfactory results. However, the lack of a clear trend in both predictive and correlative mode makes this task difficult if not impossible.

Similar to the predictions, all models tend to give better correlations with the increase in temperature. PC-SAFT and PCP-SAFT converged essentially to the same solution at the highest temperatures, which could be explained by the fact that the potential energy due to polar-polar interactions diminishes at high temperatures (Israelachvili 2011). Hydrogen bonding and dipolar moment are closely related (Smith 1955) and since no temperature dependency on the dipolar term is being considered (McCabe and Galindo 2010), jointly with the fact that the dipole moment values were taken from experimental data at vacuum, could potentially explain the inaccuracy of the PCP-SAFT model.

It is possible that a different set of pure component parameters will result in a different performance of the equations. However, as mentioned in the Introduction recent research has shown that even if other properties and/or methods are included in the fitting procedure for getting the best set, there is no guarantee that the obtained set will perform well for all the properties, either for pure component or mixture.

Conclusions

The phase equilibria modeling of organic acids + water systems were performed with 24 different equations of state, as a product of the combination of the main equations of state: CPA, PC-SAFT and PCP-SAFT; the ECR and CR1 in CPA; the association schemes 1A and 2B for the carboxylic acids and the 2B, 3B and 4C for water.

On average, PC-SAFT$_{1A\text{-}4C}$ showed the best predictive and correlative capabilities together with lowest magnitudes of the binary interaction parameter. However, a different EoS may be the best option for a particular system and temperature, and may include non-association contributions. CPA with CR1 provides better predictions whereas the ECR better correlations.

Explicitly accounting for the dipolar term in PC-SAFT did not necessary improve its modeling capabilities when comparing the same association scheme. One reason for this inaccuracy may be because the dipole moment is taken from experimental measurements at vacuum, but also that it is assumed constant over the entire temperature range.

Regarding the association interactions, the association scheme has to be chosen appropriately in order to obtain satisfactory predictions and/or correlations. It should also be contemplated the possible inaccuracy of the association term to capture the strong interactions of these systems, as illustrated by the results with the non-association scenario. However, the problem is obscured by the multiplicity of the parameters. More experimental data for these and other systems are necessary to arrive at a better conclusion on this aspect.

Testing of the performance of EoS in modeling such systems should be done at the low temperature range, where the association and dipolar interactions become more important.

Correlations with PR are comparable to the results obtained with CPA, PC-SAFT and PCP-SAFT therefore, the use of the traditional cubic equation is recommended when the binary interaction parameter is available. In the lack of binary interaction parameter, PC-SAFT with 1A-4C is recommended for VLE calculations.

Abbreviations

CPA	Cubic Plus Association
CR1	Combining Rule 1
DBD	Doubly Bonded Dimers
ECR	Elliot Combining Rule
EoS	Equation of State
HV-NRTL	Huron-Vidal Non-Random-Two-Liquid
PCP-SAFT	Perturbed-Chain Polar SAFT
PC-SAFT	Perturbed-Chain SAFT
PR	Peng-Robinson
PR-f	Peng-Robinson with fitted parameters
SAFT	Statistical Associating Fluid Theory
sPC-SAFT	simplified PC-SAFT
SRK	Soave-Redlich-Kwong
VLE	Vapor – Liquid equilibrium

Symbols

A	Helmholtz free energy	[J mol^{-1}]
A, B	Parameters A and B in $k_{ij} = A + BT$	
a_0	characteristic parameter in CPA	[bar L^2 mol^{-2}]
b	repulsive parameter	[L mol^{-1}]
c_1	characteristic parameter in CPA	
k_{ij}	binary interaction parameter	
m	number of segments	
N	number of data points	
n	number of moles	[mol]
P	bubble pressure	[bar]
P_v	vapor pressure	[bar]
R	universal gas constant	[J mol^{-1} K^{-1}]
T	temperature	[K]
x	liquid mole fraction	
y	vapor mole fraction	

Greek letters

α	relative volatility	
β^{AB}	association volume in CPA	
κ	association volume	
μ	dipole moment	[D]
σ	segment diameter	[Å]
Δ	average deviation	
ε	depth of pair potential	[J]
ε^{AB}	association energy	[K]
θ	property	
ρ	density	[kg L^{-1}]

Subscripts

i, j	i^{th}, j^{th} component

Superscripts

assoc	association
calc	calculated
disp	dispersion
exp	experimental
hc	hard-chain
polar	polar
res	residual

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Table 1. Pure component parameters for CPA, PC-SAFT and PCP-SAFT for the different association schemes and calculated deviations in vapor pressure (ΔP_V) and saturated liquid density ($\Delta \rho_L$).[a]

CPA

Compound	Association scheme	a_0 / bar L^2 mol^{-2}	b / L mol^{-1}	c_1	ε^{AB} / K	β^{AB}	ΔP_v / %	$\Delta \rho_L$ / %
formic acid	1A	5.0492	0.0294	0.4657	6642.6	0.0034	0.29	1.44
	2B[b]	3.6216	0.0304	1.1000	1704.8	1.0070	0.49	1.27
acetic acid	1A	8.4754	0.0459	0.4976	5453.7	0.0025	0.68	1.04
	2B[b]	6.5145	0.0473	1.0015	2209.0	0.1864	0.64	0.94
propanoic acid	1A	12.1348	0.0628	0.7544	4900.9	0.0035	0.57	0.54
	2B[c]	9.4034	0.0635	1.0730	2695.9	0.0588	0.47	0.66
butanoic acid	1A	17.2859	0.0820	1.2493	2843.9	0.0614	0.52	0.77
	2B[b]	13.1186	0.0810	1.3744	2372.3	0.0884	0.35	0.71
water	2B[c]	2.5108	0.0150	1.0049	1817.6	0.2882	0.81	1.66
	3B	2.2150	0.0151	1.2596	1525.7	0.2300	0.50	1.74
	4C	0.9036	0.0144	1.4898	1796.8	0.1188	0.44	1.68

PC-SAFT / PCP-SAFT

Compound	Association scheme	m	σ / K	ε/κ / K	κ^{AB}	ε^{AB}/κ / K	μ / D	ΔP_v / %	$\Delta \rho_L$ / %
formic acid	None	1.7842	3.1891	397.72	-	-	-	2.52	6.80
		1.7554	3.2087	394.35	-	-	1.415	2.45	6.64
	1A	1.4179	3.2581	275.24	0.000327	8367.4	-	0.61	0.87
		1.2536	3.4222	273.53	0.000485	8041.9	1.415	0.50	0.84
	2B	2.1501	2.8112	192.04	0.994510	2040.3	-	0.86	1.81
		2.0845	2.8348	171.56	0.999380	2140.8	1.415	0.40	1.43
acetic acid	None	3.2544	2.9205	283.20	-	-	-	2.88	3.59
	None	3.2001	2.9373	282.28	-	-	1.739	2.89	3.47
	1A	1.5286	3.6681	279.91	0.003102	5778.9	-	0.52	0.63
	1A	1.3869	3.8145	279.65	0.003294	5634.4	1.739	0.56	0.60
	2B[d]	2.5969	3.0474	190.22	0.368320	2379.0	-	0.83	0.96
	2B	2.3857	3.1464	188.31	0.309125	2413.2	1.739	0.87	0.94
propanoic acid	None	4.4934	2.8404	248.19	-	-	-	4.80	2.54
	None	4.4552	2.8490	247.92	-	-	1.751	4.86	2.50
	1A	2.8793	3.2416	233.37	0.030267	4261.1	-	0.46	0.32
	1A	2.8316	3.2633	232.62	0.029629	4229.5	1.751	0.46	0.34
	2B[c]	3.2579	3.1047	192.67	0.192751	2647.5	-	0.55	0.40
	2B[c]	3.1508	3.1436	192.01	0.179171	2664.4	1.751	0.52	0.40

Table 1. Continuation.

butanoic acid	None	5.3682	2.8484	236.84	-	-	-	2.78	1.17
	None	5.3487	2.8521	236.72	-	-	1.649	2.82	1.16
	1A	4.2711	3.0527	221.02	0.100925	3290.1	-	0.32	0.76
	1A	4.2211	3.0658	221.15	0.095679	3314.1	1.649	0.33	0.76
	2B	4.1831	3.0734	198.08	0.262227	2409.8	-	0.41	0.74
	2B	4.1292	3.0880	197.91	0.253155	2423.4	1.649	0.42	0.74
water	None	2.7528	2.0879	328.03	-	-	-	2.19	3.29
	None	2.7515	2.0737	288.15	-	-	1.850	0.49	1.95
	2B[c]	2.7028	2.0526	218.96	0.561417	2045.0	-	0.61	2.01
	2B[c]	2.6206	2.1120	211.82	0.635842	1394.5	1.850	0.58	1.74
	3B	3.5642	1.8609	198.07	0.675246	1546.0	-	0.48	2.19
	3B	3.1392	1.9769	194.36	0.721409	1073.6	1.850	0.67	1.92
	4C[d]	3.0639	1.9701	150.10	0.429973	1523.7	-	0.75	2.00
	4C	2.7801	2.0840	146.26	0.445384	1140.6	1.850	0.84	1.74

[a] Experimental P_V and ρ_L for the correlation, as well as dipolar moment (μ) taken from DIPPR (DIPPR 2012) database. Temperature range from the triple point up to 0.99Tc. See (Román-Ramírez and Leeke 2020) for details. [b] Parameters taken from (Román-Ramírez and Leeke 2020). [c] Parameters taken from (Román-Ramírez et al. 2015). [d] Parameters taken from (Román-Ramírez and Leeke 2016).

Table 2. Parameters A_{ij} and B_{ij} in $k_{ij} = A_{ij} + B_{ij}T$ for the organic acids + water systems for the EoS and association schemes studied.[a]

	1A-2B		1A-3B		1A-4C		2B-2B		2B-3B		2B-4C		Non-assoc.	
	A_{ij}	B_{ij} x 10^4	A_{ij}	B_{ij} x 10^4	A_{ij}	B_{ij} x 10^4	A_{ij}	B_{ij} x 10^4	A_{ij}	B_{ij} x 10^4	A_{ij}	B_{ij} x 10^4	A_{ij}	B_{ij} x 10^4
CPA-CR1														
formic acid	-0.25	3.86	-0.12	2.34	-0.14	-1.99	-0.37	3.43	-0.46	3.76	-0.37	1.77		
acetic acid	-0.27	3.76	-0.15	2.40	-0.09	-3.16	-0.35	5.09	-0.33	4.93	-0.24	2.14		
propanoic acid	-0.48	9.60	-0.36	7.64	-0.28	2.66	-0.54	10.77	-0.59	12.41	-0.41	8.55		
butanoic acid	-0.97	25.31	-3.39	88.54	-0.56	11.96	-0.98	25.00	-2.88	70.13	-0.77	20.67		
CPA-ECR														
formic acid	-0.26	3.78	-0.13	2.43	-0.13	-2.69	-0.36	2.90	-0.47	3.86	-0.36	0.60		
acetic acid	-0.28	3.70	-0.18	2.57	-0.17	-1.70	-0.36	4.35	-0.35	4.61	-0.26	1.05		
propanoic acid	-0.45	8.40	-0.35	7.14	-0.24	1.07	-0.49	8.45	-0.52	9.50	-0.37	5.46		
butanoic acid	-0.66	15.81	-2.13	51.01	-0.40	6.66	-0.68	14.98	-1.50	32.77	-0.26	3.15		
PC-SAFT														
formic acid	-0.06	1.62	0.06	0.50	0.00	-0.48	-0.24	4.00	-0.23	4.36	-0.21	2.87	-0.09	1.62
acetic acid	-0.03	2.08	0.07	1.18	0.00	1.03	-0.14	3.25	-0.14	3.66	-0.12	2.49	-0.10	2.24
propanoic acid	-0.11	4.11	-0.01	2.72	-0.04	1.76	-0.15	4.79	-0.13	4.61	-0.11	3.54	-0.15	3.81
butanoic acid	-0.23	8.18	-0.19	7.95	0.00	0.80	-0.22	7.59	0.04	0.79	0.00	1.11	-0.25	6.82
PCP-SAFT														
formic acid	-0.15	2.82	-0.13	3.81	-0.17	2.59	-0.30	3.67	-0.27	3.31	-0.32	3.60	-0.12	2.11
acetic acid	-0.16	4.08	-0.09	3.61	-0.17	3.69	-0.25	4.34	-0.22	4.33	-0.28	4.73	-0.12	2.25
propanoic acid	-0.18	4.43	-0.12	3.72	-0.23	4.44	-0.24	5.18	-0.22	5.04	-0.28	5.55	-0.16	3.66
butanoic acid	0.00	-0.58	0.00	0.34	-0.56	13.00	-0.23	5.52	-0.23	5.74	0.00	-1.88	-0.17	3.94

[a] Temperature range: formic acid: 303 - 398 K; acetic acid: 293 - 483 K; propanoic acid: 303 - 483 K and butanoic acid: 324 - 436 K.

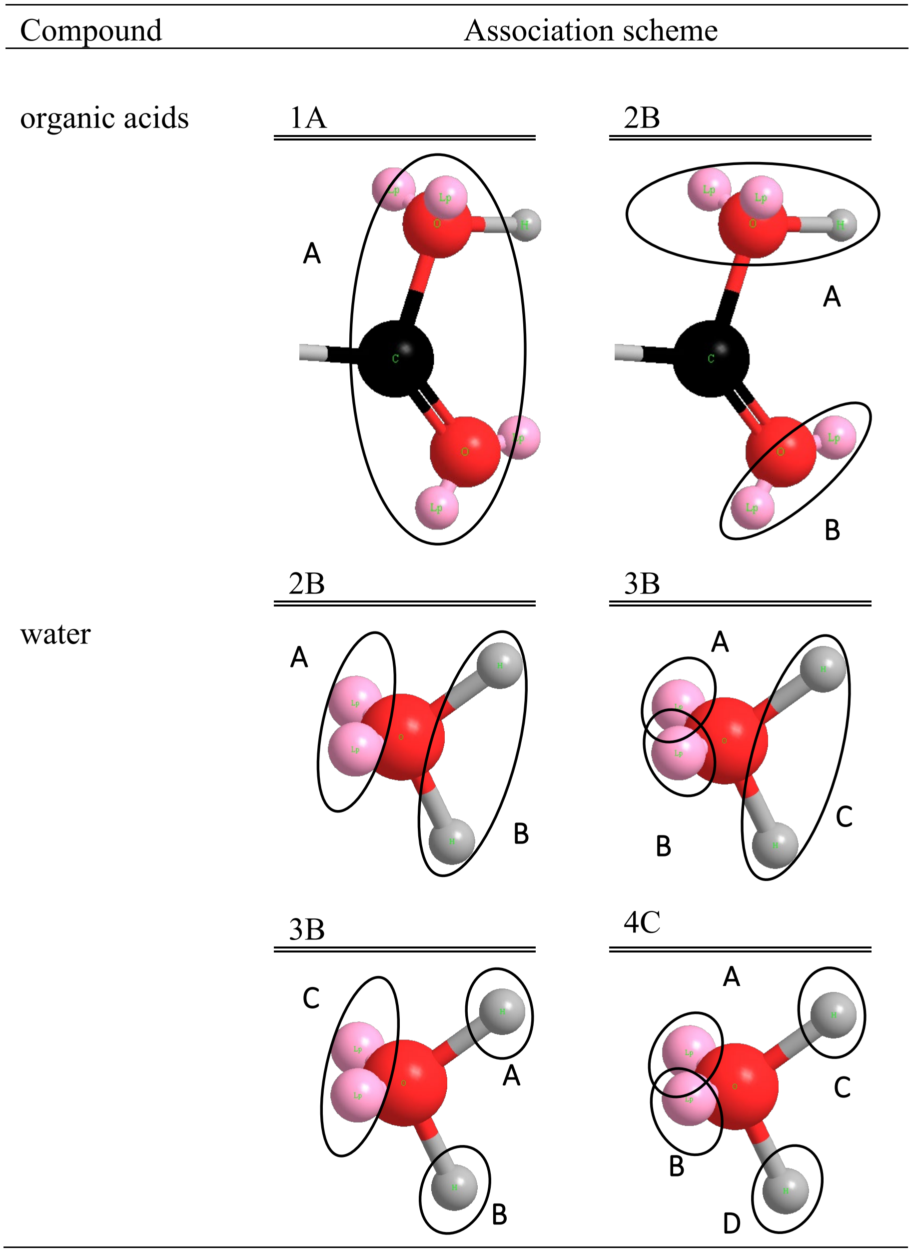

Figure 1. Possible association schemes for organic acids and water based on the classification of Huang and Radosz (1990).

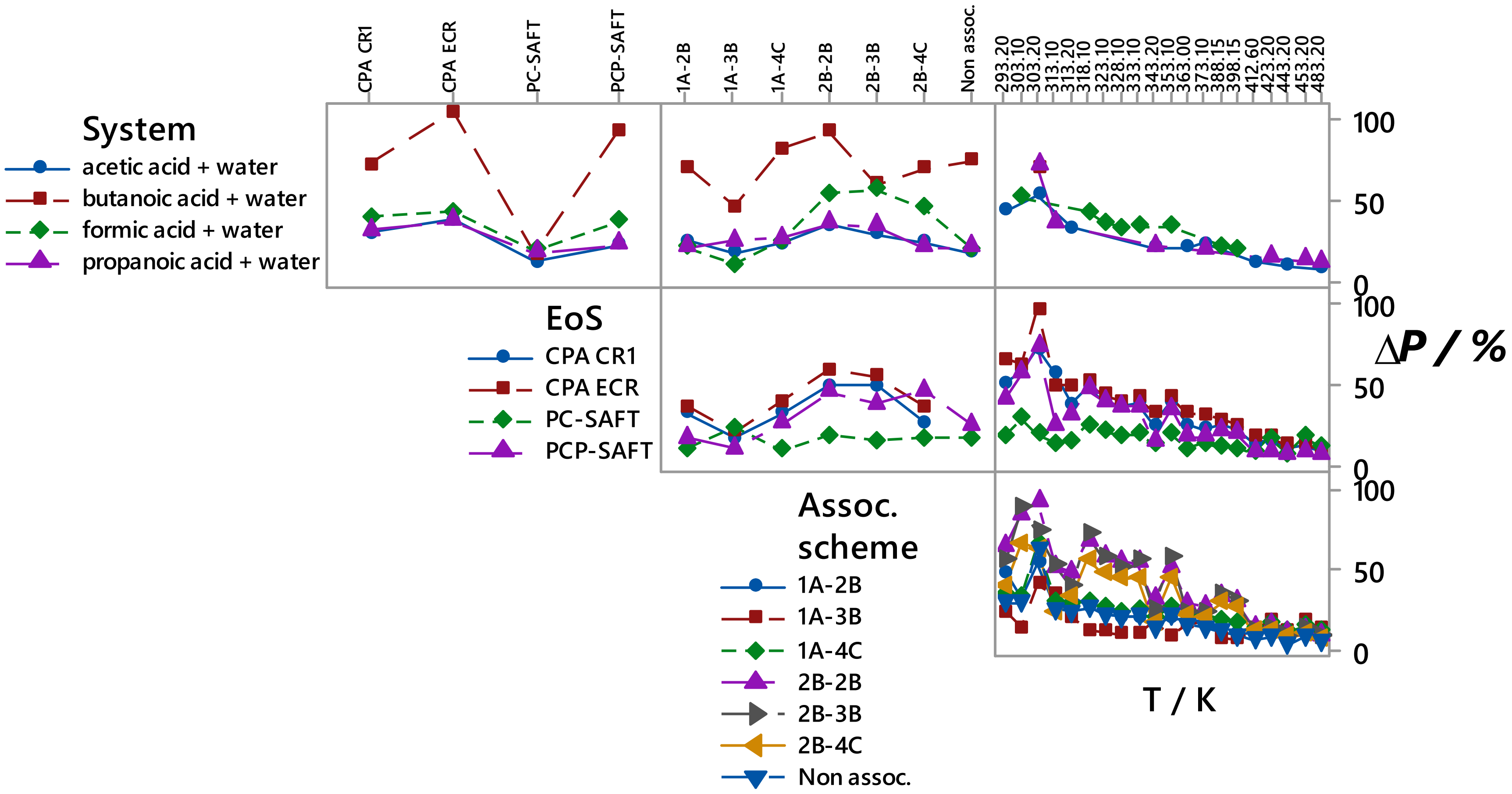

Figure 2. Interaction plot of the average ΔP as a function of System, EoS, Association scheme and T for $k_{ij} = 0$.

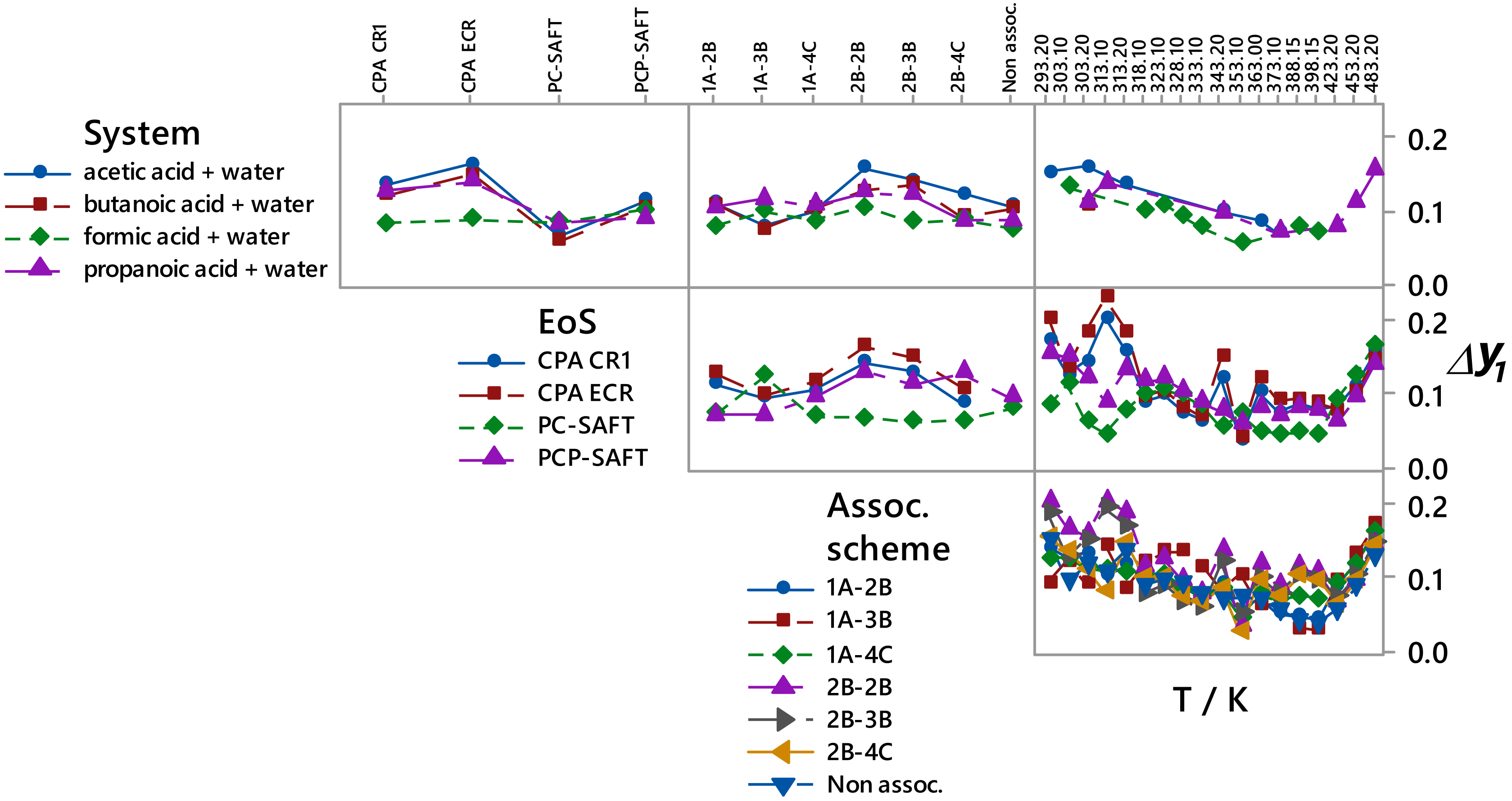

Figure 3. Interaction plot of the average Δy_1 as a function of System, EoS, Association scheme and T for $k_{ij} = 0$.

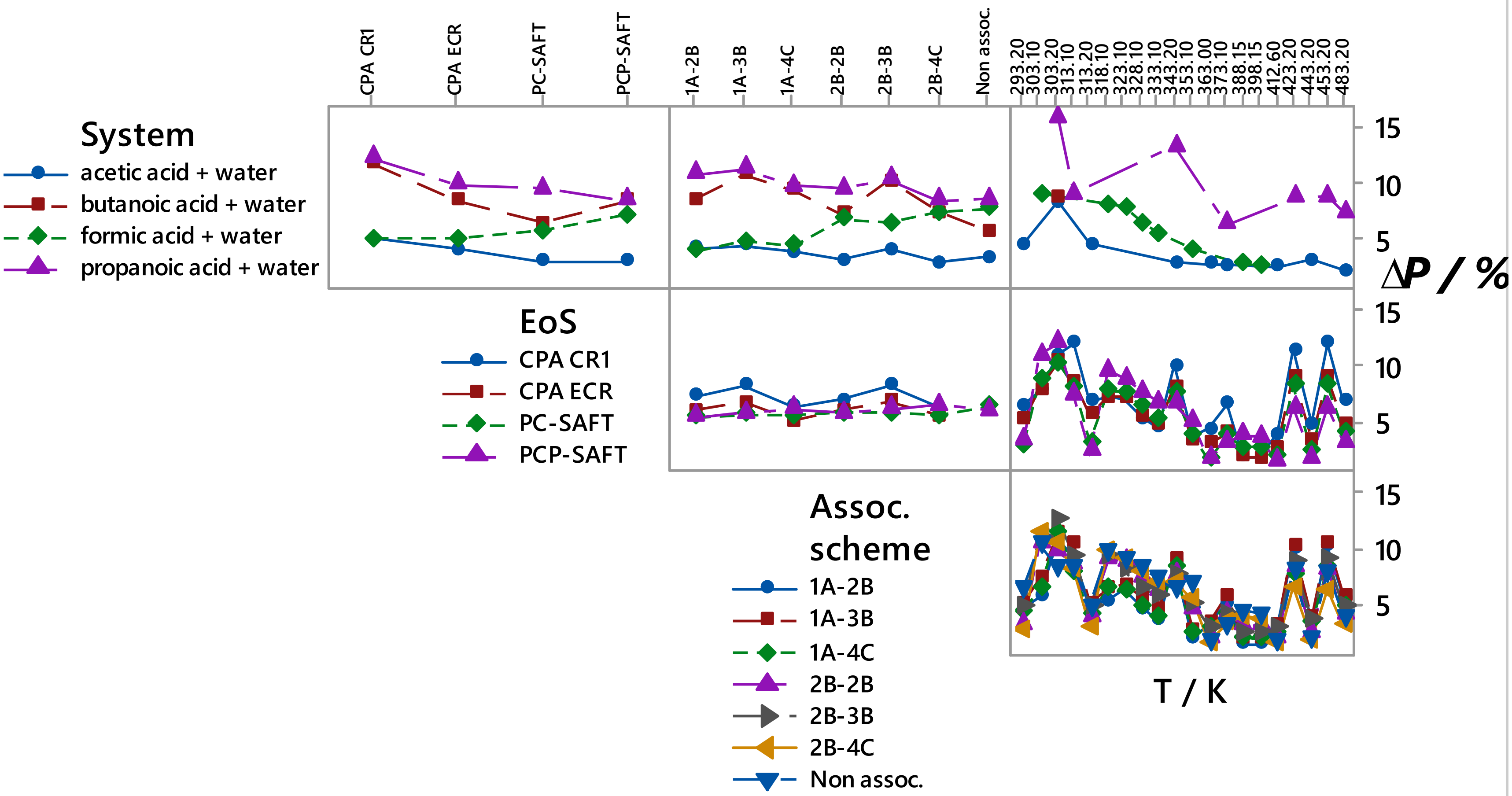

Figure 4. Interaction plot of the average ΔP as a function of System, EoS, Association scheme and T for $k_{ij} = A_{ij} + B_{ij}T$.

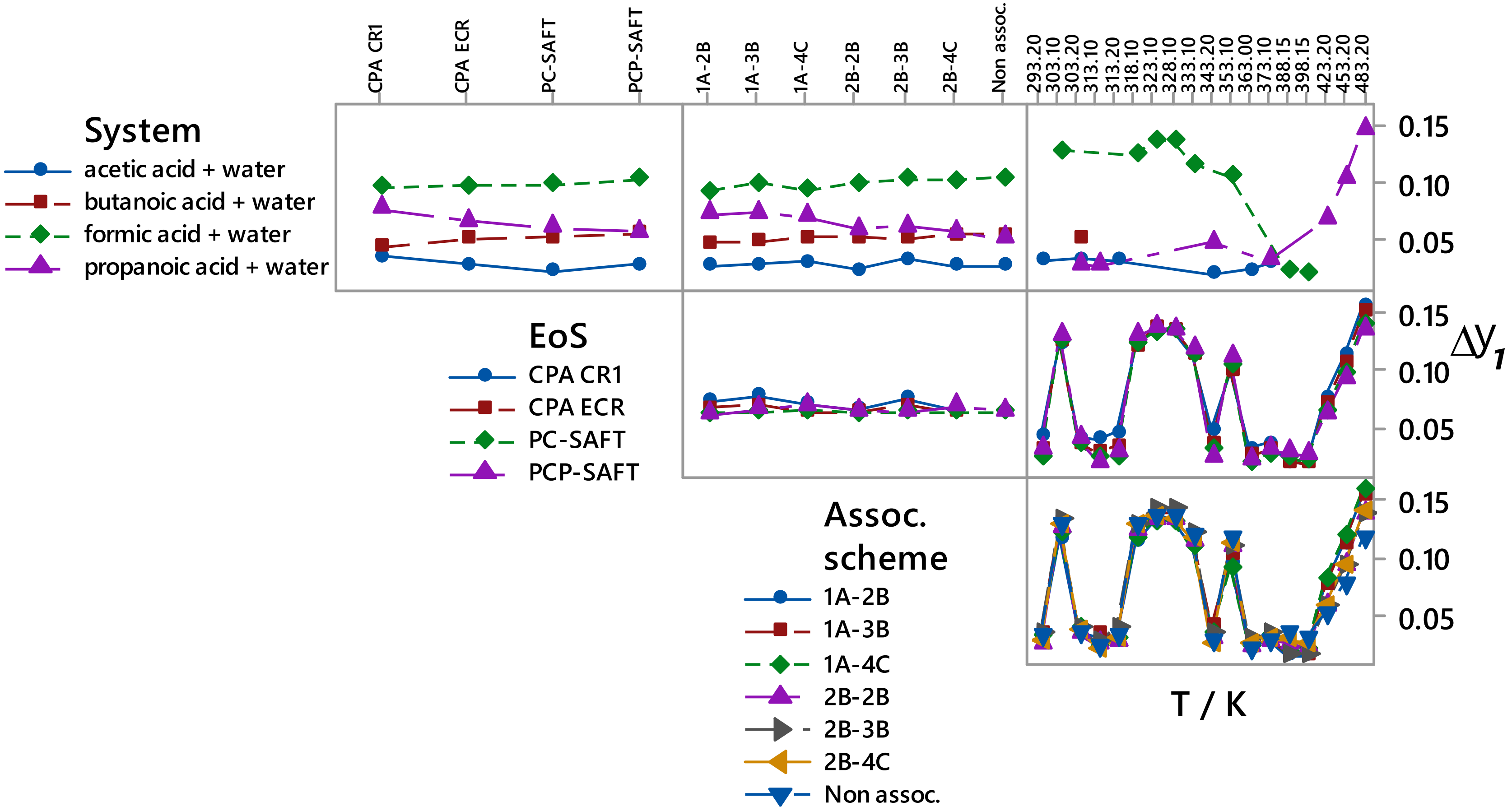

Figure 5. Interaction plot of the average Δy_1 as a function of System, EoS, Association scheme and T for $k_{ij} = A_{ij} + B_{ij}T$.

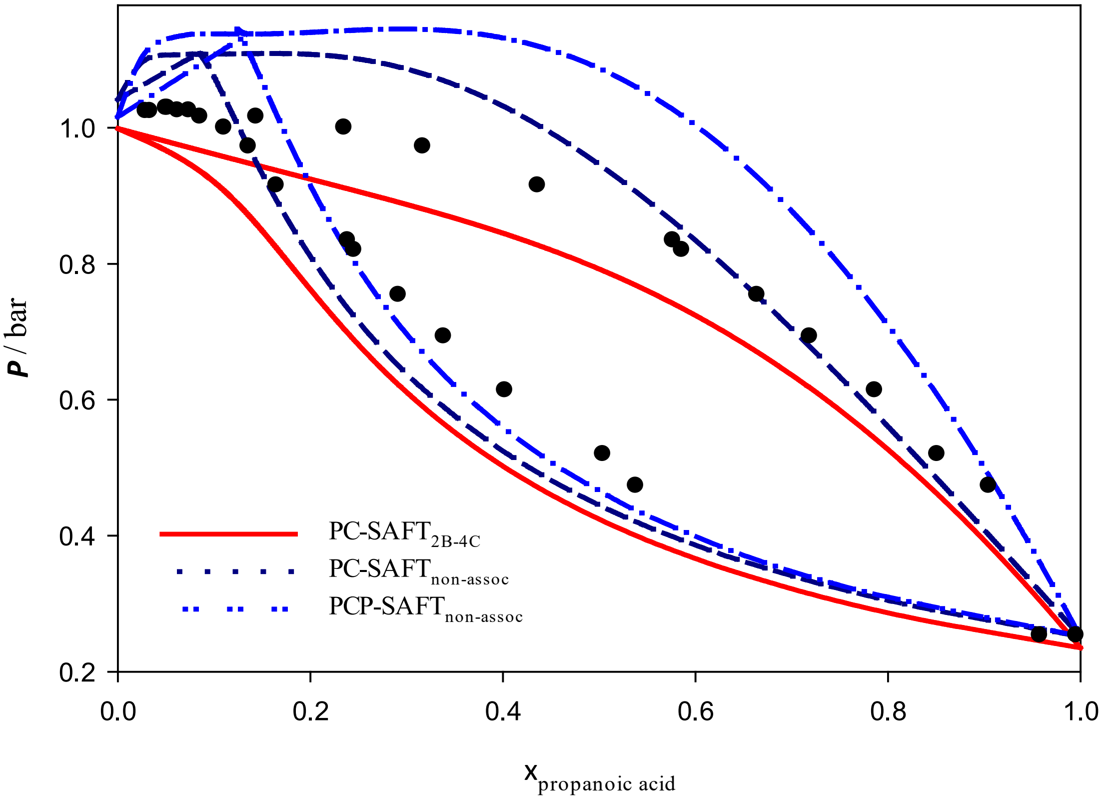

Figure 6. Propanoic acid + water VLE diagram at 373.1 K. Symbols: experimental data (Rafflenbeul and Hartmann 1978). Lines: EoS predictions ($k_{ij} = 0$).

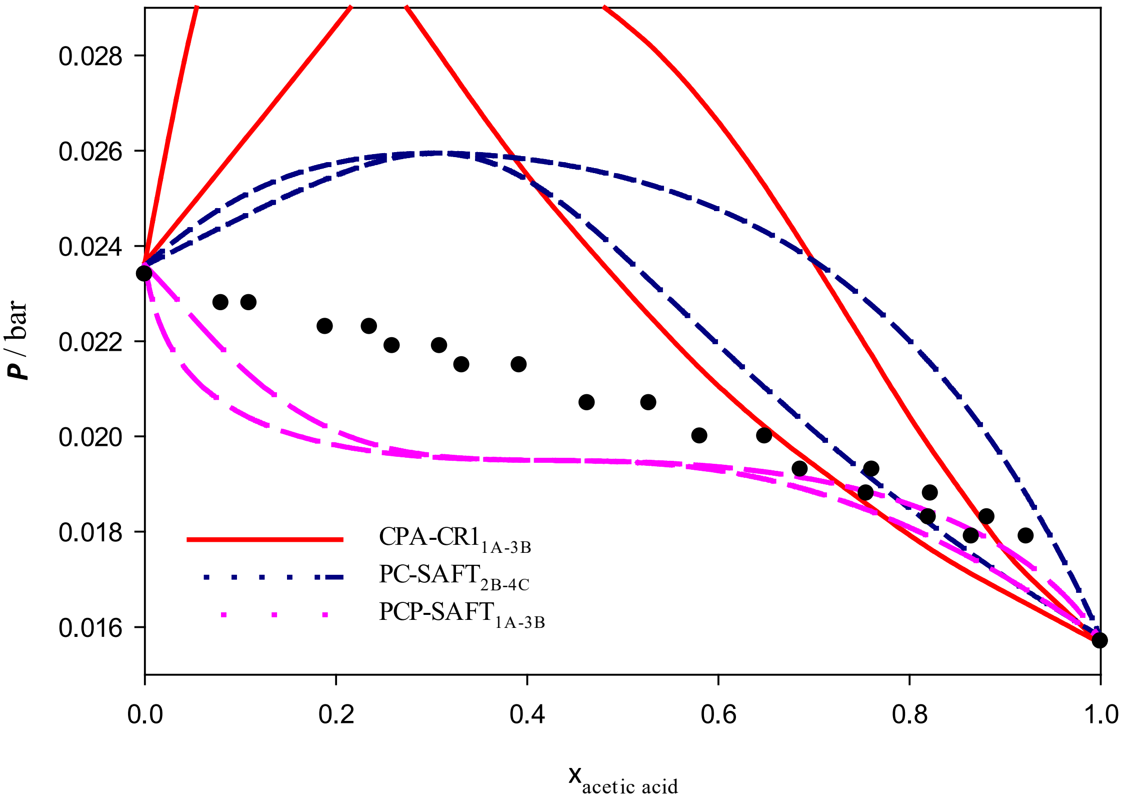

Figure 7. Acetic acid + water VLE diagram at 293.2 K. Symbols: experimental data (Lazeeva and Markuzin 1973). Lines: EoS predictions ($k_{ij} = 0$).

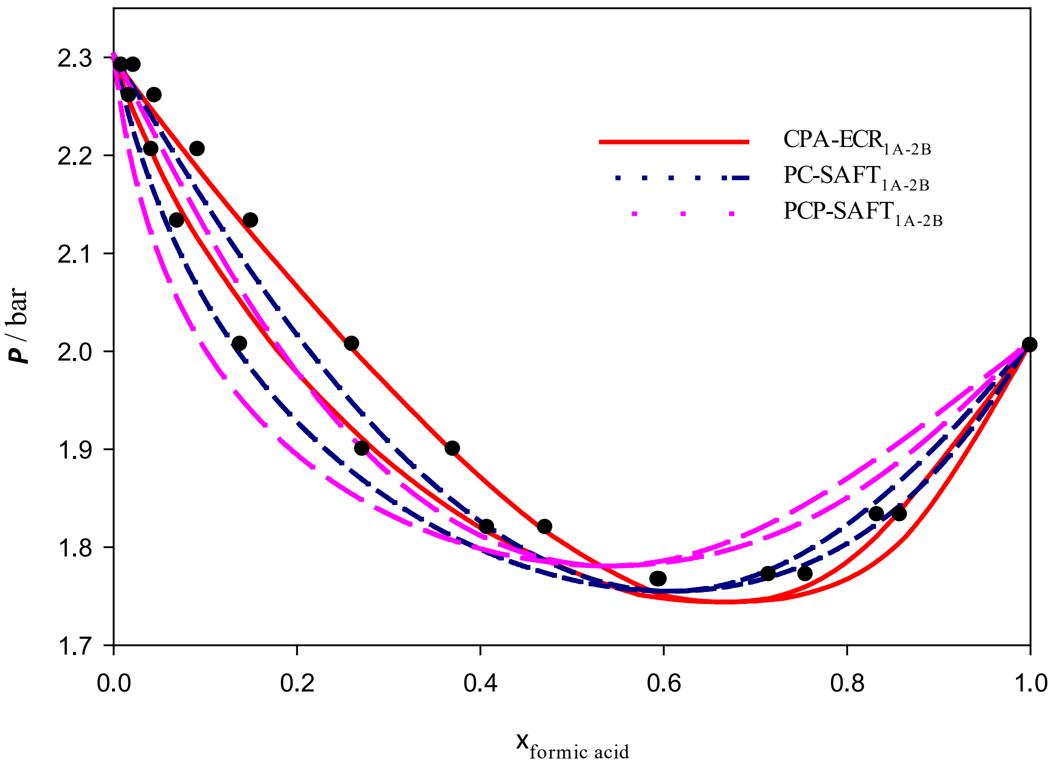

Figure 8. Formic acid + water VLE diagram at 398.2 K. Symbols: experimental data (Sommer et al. 2016). Lines: EoS correlations ($k_{ij} = A_{ij} + B_{ij}T$).

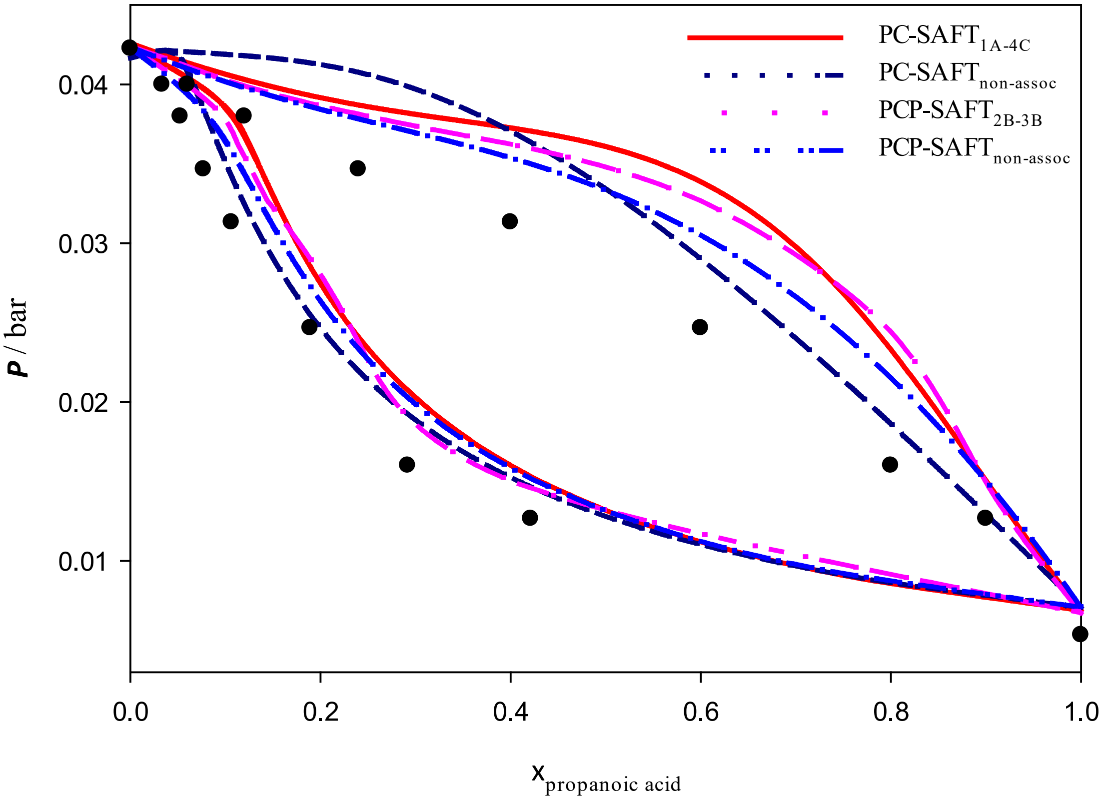

Figure 9. Propanoic acid + water VLE diagram at 303.2 K. Symbols: experimental data (Wright and Akhtar 1970). Lines: EoS correlations ($k_{ij} = A_{ij} + B_{ij}T$).

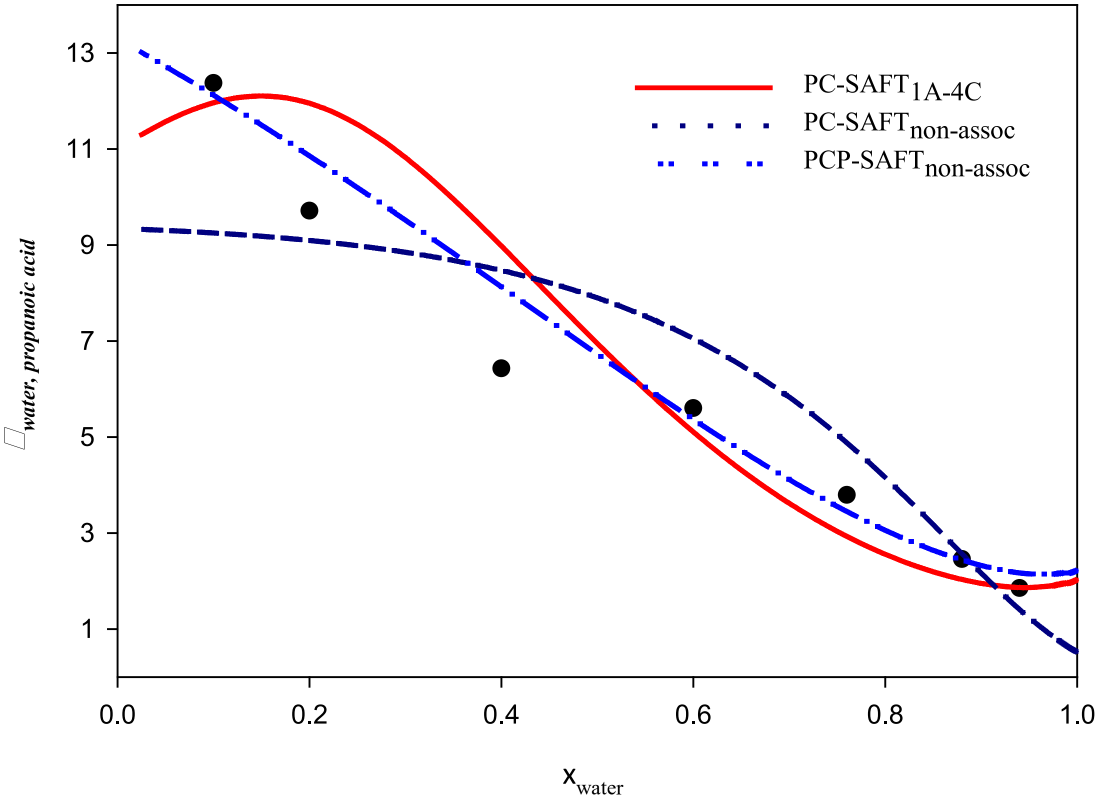

Figure 10. Relative volatility (α) at 303.2 K. Symbols: experimental data (Wright and Akhtar (1970). Lines: EoS correlations ($k_{ij} = A_{ij} + B_{ij}T$).

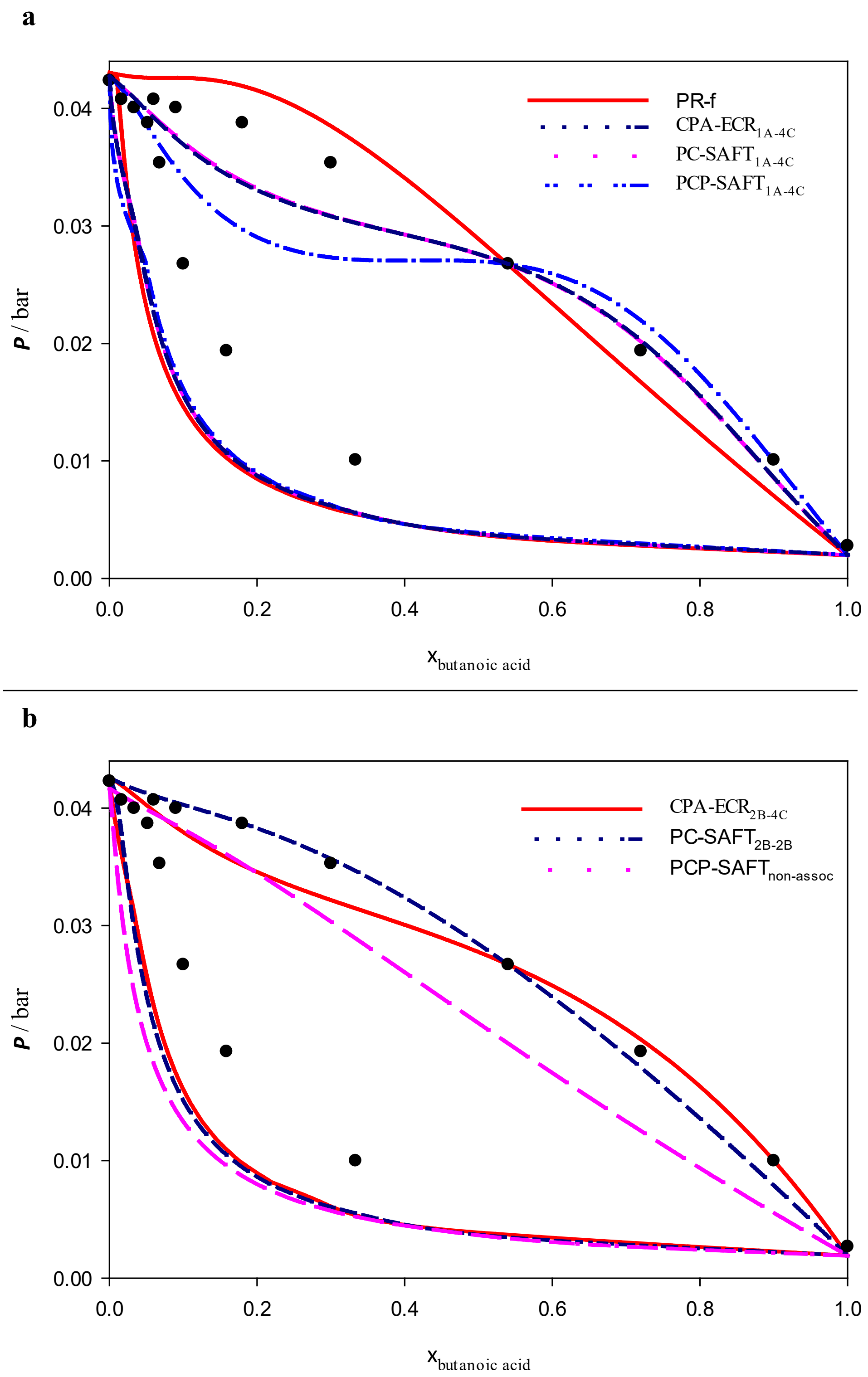

Figure 11. Butanoic acid + water VLE diagram at 303.2 K. Symbols: experimental data (Wright and Akhtar 1970). Lines: EoS correlations ($k_{ij} = A_{ij} + B_{ij}T$).