

Capabilities, limitations and challenges of a simplified PC-SAFT equation of state

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Abstract

PC-SAFT (perturbed-chain statistical associating fluid theory) is a novel equation of state, proposed by Gross and Sadowski in 2001 [J. Gross, G. Sadowski, Perturbed-chain SAFT: an equation of state based on a perturbation theory for chain molecules, *Ind. Eng. Chem. Res.* 40 (2001) 1244]. It is a variant of the SAFT family and has already found several successful applications, especially for polymer and co-polymer solutions at both low and high pressures. Recently, a simplified version of PC-SAFT proposed by von Solms et al. [N. von Solms, M.L. Michelsen, G.M. Kontogeorgis, Computational and physical performance of a modified PC-SAFT equation of state for highly asymmetric and associating mixtures, *Ind. Eng. Chem. Res.* 42 (2003) 1098.] has been applied to several complex polymer–solvent systems, including vapor–liquid equilibria, liquid–liquid equilibria and gas solubilities for both single-solvent and mixed-solvents (ternary) systems. This manuscript briefly reviews previous successful applications of PC-SAFT, illustrates the capabilities of the model and indicates some problems and limitations in specific areas, especially aqueous systems and blends, as well as challenges that need to be addressed in the future for describing various systems of practical significance.

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1. Introduction—current status

While most SAFT versions use hard spheres as a reference fluid, PC-SAFT uses a more realistic dispersion term, accounting for dispersive interactions between chains. First, hard-sphere chains are formed from hard spheres and then a chain dispersion term is added (rather than adding dispersion to the individual spheres). The chain and association terms are both given by Wertheim's theories [1–4] as in the original SAFT versions. The radial distribution and hard-sphere Helmholtz energy function

of the original and simplified PC-SAFT are as follows: Original PC-SAFT [5]:

$$g_{ij}^{\text{hs}}(d_{ij}^+) = \frac{1}{1 - \zeta_3} + \left(\frac{d_i d_j}{d_i + d_j} \right) \frac{3\zeta_2}{(1 - \zeta_3)^2} + \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2\zeta_2^2}{(1 - \zeta_3)^3} \quad (1)$$

$$a^{\text{hs}} = \frac{1}{\zeta_0} \left[\frac{3\zeta_1 \zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1 - \zeta_3) \right] \quad (2)$$

Simplified PC-SAFT [6]:

$$g^{\text{hs}}(d^+) = \frac{1 - \eta}{(1 - \eta)^3} \quad (3)$$

$$a^{\text{hs}} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \quad (4)$$

Abbreviations: BR, butadiene rubber; LLE, liquid–liquid equilibria; PB, polybutene; PBA, polybutylacrylate; PBMA, polybutylmethacrylate; PC-SAFT, perturbed-chain statistical association fluid theory; PE, polyethylene; PEA, polyethylacrylate; PEG, polyethylene glycol; PIB, polyisobutylene; PMA, polymethyl acrylate; PMMA, polymethylmethacrylate; PP, polypropylene; PPA, polypropylacrylate; PS, polystyrene; PVAc, polyvinyl acetate; SLE, solid–liquid equilibria; SRK, Soave–Redlich–Kwong; VLE, vapor–liquid equilibria

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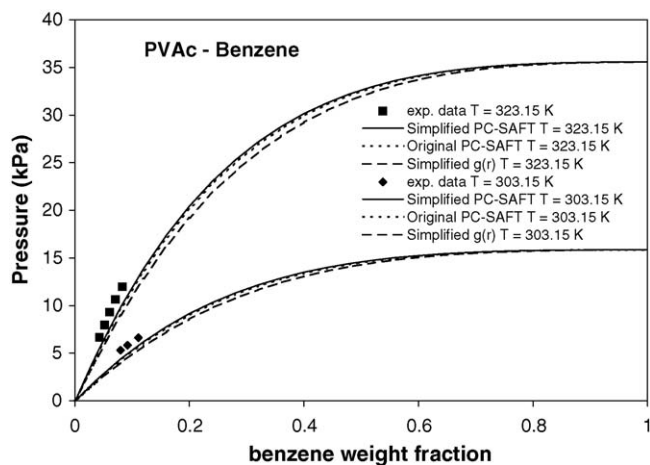


Fig. 1. Prediction of vapor–liquid equilibria for polyvinyl acetate (PVAc)–benzene with various PC-SAFT variants at 303.15 and 323.15 K. Experimental data are from [52].

where

$$\eta \equiv \zeta_3 \rightarrow d = \left(\frac{\sum_i x_i m_i d_i^3}{\sum_i x_i m_i} \right)^{1/3} \quad (5)$$

The simpler radial distribution function affects both the chain and association terms, since the radial distribution function appears in both terms. The justification for the simplified PC-SAFT is that the segment diameter values of different molecules are very similar, as seen by the parameter values published by Gross and Sadowski [5]. Both models typically employ a single interaction parameter in the dispersion term, a^{disp} :

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} (1 - k_{ij}) \quad (6)$$

In most cases studied, the results with the various PC-SAFT variants are very similar, as can be seen for a typical prediction result in Fig. 1, which shows VLE in the system Polyvinyl acetate–benzene. Original PC-SAFT employs Eqs. (1) and (2) above; simplified PC-SAFT employs Eqs. (3) and (4). The lines marked “simplified $g(r)$ ” show the results of an intermediate simplification where the simpler radial distribution function Eq. (3) is used, but the full expression for the Helmholtz energy Eq. (1) is still used. More results have been recently reported [7], which demonstrate that the predictions of the two versions of the model are comparable. With the use of a (possibly different) non-zero interaction parameter k_{ij} , whatever small differences exist in the predictions tend to disappear.

PC-SAFT has already found widespread application, as indicated in several recent reviews [8,9] with great success, e.g. in simultaneous description of VLE and LLE for alcohol–alkanes, polar systems such as ketone–alkanes (using additional term for polar interactions) and high pressure polymer and co-polymer systems. PC-SAFT is available in commercial simulators/software: ASPEN-Plus (<http://www.aspentech.com/>), Infochem (<http://www.infochemuk.com/>), VLXE (<http://www.vlxe.com/>). It is also available online: PE 2000 software ([\[harburg.de/vt2/pe2000/\]\(http://harburg.de/vt2/pe2000/\)\), and in various other software, e.g. SPECS by IVC-SEP, Technical University of Denmark and as a CAPE-OPEN module, e.g. by IVC-SEP, thus ensuring use in commercial simulators.](http://www.tu-</p>
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A list of applications of PC-SAFT is provided in Table 1. This list may not be complete as numerous applications appear continuously, but provides an indication of the wide variety of applications of the PC-SAFT model in the short time since its conception.

1.1. Parameter estimation for polymers

While the PC-SAFT parameters for low molecular weight compounds are estimated from vapor pressures and liquid densities, the situation is more complex for polymers, which are non-volatile. Thus, critical properties and vapor pressures typically do not have a physical meaning. Sadowski and co-workers have proposed a method for estimating such polymer parameters based on density data and a single LLE polymer–solvent system. The obtained polymer parameters have been shown to yield successful results in many cases, including polymer–solvent and copolymer solvent VLE and LLE [7]. However, such parameters which require phase equilibria data for mixtures are not unique. Recently, Kouskoumvekaki et al. [10] presented a method for estimating the PC-SAFT parameters of polymers without use of mixture data. The method is based on the principle of using the monomer parameters and a suitable extrapolation equation. Very successful LLE results have been presented and a typical result is shown in Fig. 2, which shows LLE in the system polybutadiene–diisobutyl ketone for a polymer molecular weight ranging from 22,700 to 6,000,000.

Table 2 presents the segment diameters (in Å) for various polymers from the method of Kouskoumvekaki et al. [10] and the method of Sadowski. The errors in density are also given. We notice that the segment diameters obtained with the two methods are very similar (although the other two EoS parameters may be quite different). The performance of the PC-SAFT with the new

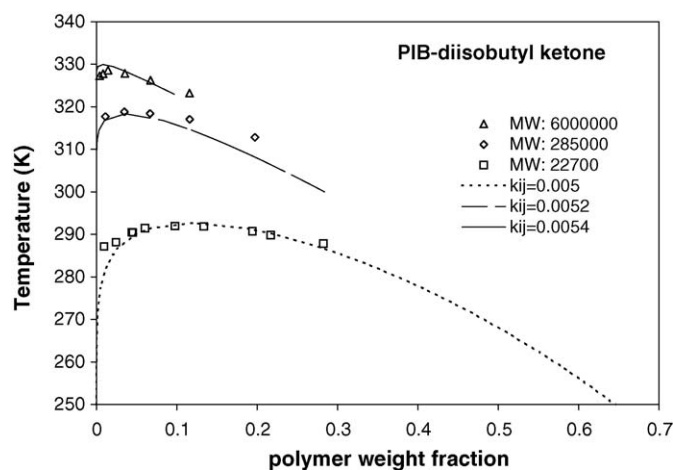


Fig. 2. Liquid–liquid equilibria for polyisobutylene (PIB)/diisobutyl ketone with simplified PC-SAFT using the parameters estimated with the method proposed by Kouskoumvekaki et al. [10]. The binary interaction parameter is a weak function of molecular weight. Experimental data are from [53].

Table 1
Applications of the PC-SAFT equation of state (2001–2005)

PC-SAFT variant	Application	Reference
Original	High pressure polymer–solvent, CO ₂ –alkanes, alkanes VLE, parameters for 78 non-associating compounds	[5]
Original	Polymers: 6 polymers parameters (polyolefins, PS), LLE for polymer–light solvent, high and low pressures, polymer–solvent VLE, ternary polymer–CO ₂ –solvent	[11]
Original	Polymers (PVAc parameters), PE–CO ₂ , co-polymers	[43]
Original	Associating systems (18 compounds) – all described as two-site (2B) molecules, VLE & LLE for alcohol–alkanes, water–pentanol	[21]
Original	Co-polymers (PMA parameters), VLLE, LLE, high pressures	[64]
Original	Ethylene–methacrylate co-polymers (PBMA, PMMA, PPA, PBA, PEA parameters)	[56]
Polar	Ketones–alkanes VLE	[36]
Polar	Ketones–alkanes VLE	[57]
Original	VLE for asymmetric alkane systems	[57]
Original	Gas solubilities in alkanes	[58]
Simplified	Gas–alkanes, associating systems, computing times	[6]
Simplified	Polymers–solvents VLE	[7]
Simplified	Polymers–solvents LLE	[59]
Simplified	Polymers–mixed solvents LLE	[13]
Simplified	Ketones, esters treated as associating molecules	[38]
Simplified	Nylon systems	[33]
Simplified	Polymers–gases at high pressure	[60]
Simplified	Polymer–solvent LLE, method to estimate pure polymer parameters	[10]
Original	CO ₂ –benzenes, N ₂ systems	[61]
Original	CO ₂ –PEG	[62]
Quadrupolar, polar, electrolyte	CO ₂ –alkanes, polar systems electrolytes	[25,55]

polymer parameter estimation method is, in terms of density calculations, very satisfactory, although only a single parameter (the diameter) has been fitted to available density data in the whole range of pressure and temperature. The investigation has shown that the value of the segment diameter parameter is crucial for accurate density calculations.

PC-SAFT has been applied to multicomponent polymer–solvent LLE as well, e.g. [11,12]. Lindvig et al. [13] have tested several models (including the original SAFT) for polymer–mixed solvent VLE as well. PC-SAFT was not included in this evaluation. Some sample calculations with

Table 2
The segment diameter of PC-SAFT for several polymers as obtained by the new method of Kouskoumvekaki et al. [10] and the method of Sadowski

Polymer	Solvent	Segment (Å)	
		New method	Sadowski
PS	Ethylbenzene	4.152 (0.6)	4.107 (1.2)
PIB	Isobutene	4.117 (1.4)	4.100 (0.95)
PP	Propane	4.132 (1.1)	4.100 (5.5)
PVAc	Ethylacetate	3.463 (0.4)	3.589; 3.397 (5.9; 6.1)
PE	Ethane	4.107 (1.0)	4.022 (1.1–1.6)
PMMA	Methylisobutyrate	3.553 (1.0)	3.60
PBMA	Isobutylisobutyrate	3.884 (1.0)	3.75
BR	2-Butene	4.008 (1.0)	
PMA	Methylpropionate	3.511 (0.5)	3.535; 3.50 (3.3)
PB	Butane	4.144 (0.9)	4.200 (30)

The percentage errors in density over the whole experimental temperature and pressure range are given in parenthesis with the two methods. The “solvent” indicates the solvent used for estimating the polymer parameters in the method of Kouskoumvekaki et al. [10].

simplified PC-SAFT are shown in Table 3. Table 3 shows predictions of vapour liquid equilibrium (VLE) in the ternary system polystyrene(1)–chloroform(2)–carbon tetrachloride(3). The three binary interaction parameters used to model the data were $k_{12} = -0.025$, $k_{13} = -0.01$ and $k_{23} = 0.006$. These three parameters were obtained by fitting each of the k_{ij} 's to experimental VLE data for the three binary systems. Pure-component parameters for chloroform and carbon tetrachloride are from [7]. The results with PC-SAFT for this system are similar to those of SAFT and other models, as presented by Lindvig et al. [13]. However, experimental measurements for mixed solvent–polymer VLE data are often associated with large uncertainties [13].

Despite this impressive number of applications, the potential of the PC-SAFT model has still not been fully investigated and further investigations presented in this work reveal both capabilities and limitations of the equation of state. In addition, future challenges are briefly discussed.

Table 3
Ternary vapor–liquid equilibrium in the system polystyrene(1)–chloroform(2)–carbon tetrachloride(3)

Experimental data				Simplified PC-SAFT		% Deviation	
w_2	w_3	y_2	P (kPa)	y_2	P (kPa)	y_2	P
0.154	0.175	0.44	40.13	0.615	35.72	29.1	12.3
0.188	0.203	0.45	44.22	0.629	40.12	28.3	10.2
0.206	0.237	0.43	47.44	0.615	42.41	30.2	11.9
0.234	0.257	0.44	50	0.628	45.28	29.4	10.4

w_i is the weight fraction of i in the liquid phase and y_i is the mol fraction of i in the vapour phase. Experimental data from [63].

2. The chain term of PC-SAFT: activity coefficients for athermal asymmetric systems

The chain term of PC-SAFT (and other SAFT variants) is strongly dependent on the radial distribution function employed. One way to test the chain (and dispersion) term of a model is by performing calculations for nearly athermal systems such as alkane solutions for which these effects are predominant and other contributions (polarity, association) are essentially non-existent. Three types of calculations have been performed with both the original and simplified PC-SAFT models and compared to experimental data and state-of-the-art free-volume based activity coefficient models:

- infinite dilution activity coefficient calculations (γ_1^∞) of short-chain alkanes (C₄–C₁₀) in long-chain ones (C₃₀ and C₃₆) without interaction parameters ($k_{ij} = 0$);
- infinite dilution activity coefficient calculations (γ_2^∞) of long-chain hydrocarbons (C₁₂–C₃₆) in short-chain ones (hexane, cyclohexane and heptane) without interaction parameters ($k_{ij} = 0$);
- calculations using an optimum interaction parameter k_{ij} in order to evaluate the sensitivity of PC-SAFT to the value of the interaction parameter. The optimization was based on fitting the interaction parameter to the single experimental value of γ_1^∞ for each short-chain alkane (C₄–C₁₀)–C₃₆ system. These systems were chosen because the experimental γ_1^∞ data show a uniform trend and are not scattered, as is often the case for the γ_2^∞ data;
- for comparison purposes, calculations with two successful free-volume (FV)-based activity coefficient models have been made—the entropic-FV activity coefficient model [14] and the modified entropic-FV model proposed by Kouskoumvekaki et al. [15].

These types of calculations can help us evaluate the chain term of the model and its ability to describe effects when long-chain molecules are involved. In particular, as experimental polymer activities are not available, the γ_2^∞ data provide a way to test the model in the “polymer” end, which is of importance, e.g. for liquid–liquid equilibrium calculations in polymer mixtures, where the activities of all the components in the mixture are involved. Tables 4 and 5 summarize the results, while some characteristic results are shown in Figs. 3–5. The following points summarize our observations:

Table 4

Average percentage absolute deviations (% AAD) between experimental data and predicted activity coefficients at infinite dilution with two versions of PC-SAFT and the entropic-FV model (original and modified versions)

% AAD	Simplified PC-SAFT	Original PC-SAFT	Entropic-FV	Modified entropic-FV
C ₁₂ –C ₃₆ in hexane	16	8	29	12
C ₁₆ –C ₃₂ in cyclohexane	30	15	50	41
C ₁₈ –C ₃₆ in heptane	15	6	31	13
C ₄ –C ₁₀ in C ₃₀	5	3	7	5
C ₄ –C ₁₀ in C ₃₆	6	2	8	5

C_X indicates an *n*-alkane with X carbon atoms. The results are predictions ($k_{ij} = 0$).

Table 5

Optimum k_{ij} values fitted to the experimental γ_1^∞ of each system (for the simplified PC-SAFT EoS)

System	Optimum k_{ij}
C ₄ in C ₃₆	–0.006
C ₅ in C ₃₆	–0.0043
C ₆ in C ₃₆	–0.00295
C ₇ in C ₃₆	–0.0031
C ₈ in C ₃₆	–0.0021
C ₉ in C ₃₆	–0.001
C ₁₀ in C ₃₆	–0.00075

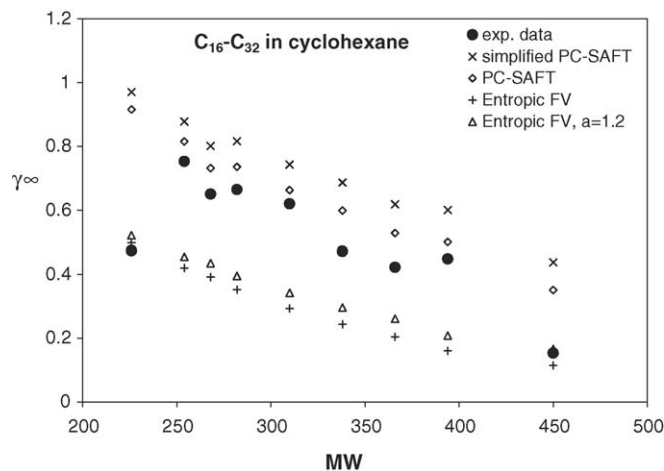


Fig. 3. Experimental and predicted activity coefficients at infinite dilution for heavy alkanes in cyclohexane against the molecular weight of the heavy alkane.

1. In general, both simplified PC-SAFT and original PC-SAFT provide very good results, in satisfactory agreement with the experimental data. The simplified PC-SAFT typically overestimates the experimental data.
2. Original PC-SAFT in general performs slightly better for the activity coefficients of low alkanes in heavy alkanes as well as for the “heavy end”, i.e. the activity coefficients of heavy alkane solutes in small alkanes. These infinite dilution activity coefficients are obtained from extrapolation of SLE data and are often associated with high errors (often more than 20%—[16]).
3. The results of both PC-SAFT versions compare favorably and are often better than the two activity coefficient models, which are among the best models for such calculations [15]. For comparison purposes, it can be mentioned that the clas-

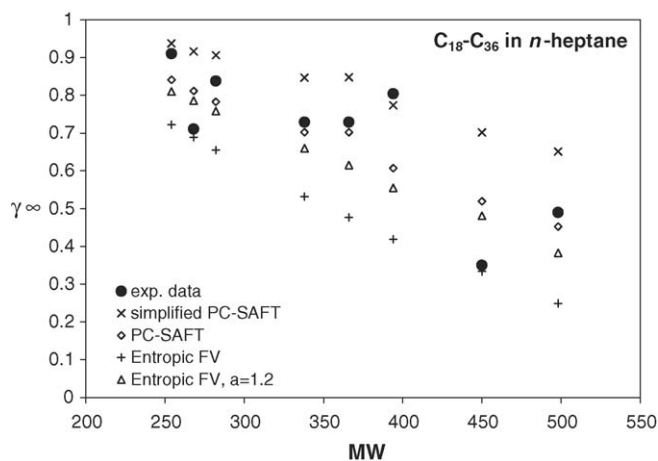


Fig. 4. Experimental and predicted activity coefficients at infinite dilution for heavy alkanes in *n*-heptane against the molecular weight of the heavy alkane.

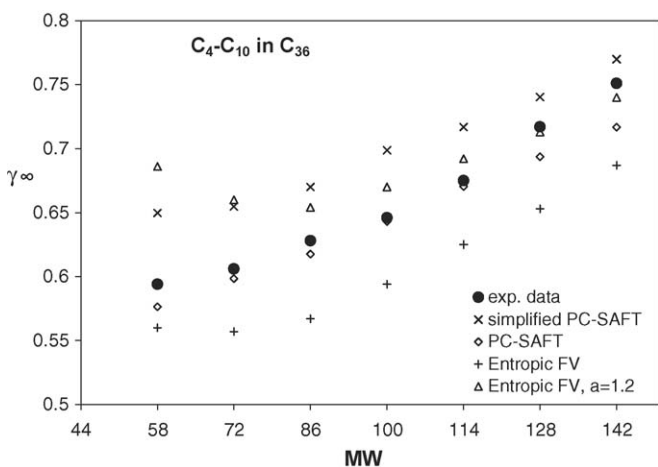


Fig. 5. Experimental and predicted activity coefficients at infinite dilution for low molecular weight alkanes in *n*-C₃₆ against the molecular weight of the alkane.

sical UNIFAC-FV model of Oishi and Prausnitz [17] has a mean deviation of about 50% for the infinite dilution activity coefficients of heavy alkanes, compared to 38% for the original entropic-FV model. PC-SAFT performs even better than this.

- The optimum interaction parameters are small but rather system specific, as can be seen in Table 4.

3. Polymer blends

Mixtures of polymers (polymer blends) are of importance in numerous practical applications. Various models have been systematically employed to blends including solubility parameters and the Flory–Huggins model [18] and cubic equations of state like the van der Waals EoS [19]. Recently, Voutsas et al. [20] have presented a systematic investigation of various models (entropic-FV, Peng–Robinson, Sanchez–Lacombe EoS) for blends. They have shown that it is difficult to correlate simultaneously the variation of the binodal curves with respect to molecular weight and the concentration. A typical result for polystyrene–butyl rubber

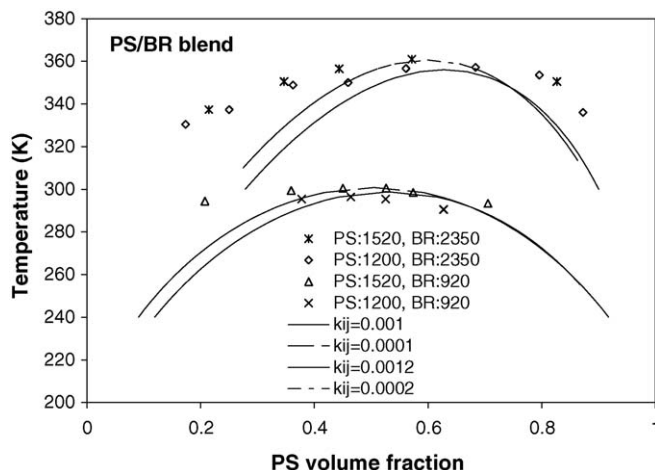


Fig. 6. Liquid–liquid equilibria for a polystyrene (PS)–butadiene rubber (BR) blend with simplified PC-SAFT. Results are shown with various values for the interaction parameter. The numbers refer to the molecular weight of the polymer. Experimental data are from [54].

with simplified PC-SAFT is shown in Fig. 6, demonstrating that this model suffers from the same limitation.

4. Aqueous systems

4.1. Previous applications

Aqueous systems are very important in numerous applications, and PC-SAFT parameters for water have only recently been published (assuming water to be a two-site, 2B, molecule [21]). Thus, PC-SAFT has not yet been extensively applied to aqueous systems.

However, other SAFT-variants have been used for various types of aqueous systems. The limitations of the SAFT approach for aqueous systems such as water–alkanes LLE is well-documented in the literature [22]. As shown in that work, none of the association schemes for water employed and mixing rules in the physical term improved the results. A possible explanation for the limitations of the SAFT approach to aqueous systems is the missing polar term, and an effort for accounting explicitly for polarity in SAFT has recently been initiated [23]. Preliminary results for pure water using the polar term of Rushbrook et al. [24] have been positive (see for example [25]).

However, another explanation for these problems may be the complexity of the physical term of SAFT. Indeed, models like APACT employing the same association term as SAFT but different physical terms have been shown to perform much better than SAFT, yielding satisfactory LLE for water–alkane systems, including both the water solubility and the alkane solubility using a single k_{ij} [26]. A three-site association scheme performed better than a two-site scheme for water. It must be emphasized that different results with APACT (much worse) were presented for water–alkanes in subsequent publication by Economou and Tsonopoulos [22]). Thus the validity of the APACT model cannot be fully assessed.

Although most SAFT variants do not perform well for aqueous systems, in a few cases, e.g. soft-SAFT [27] some

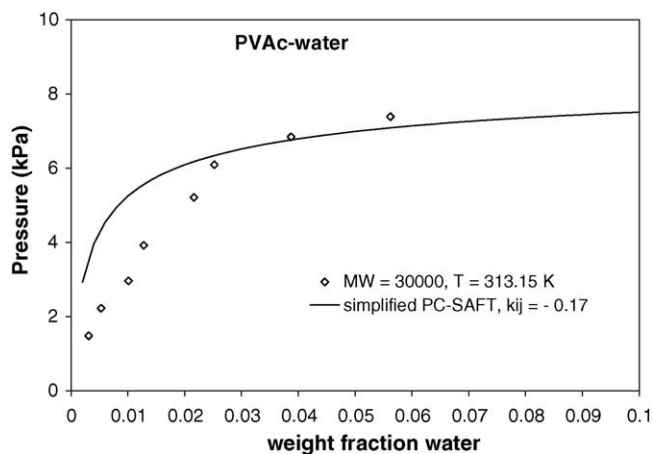


Fig. 7. Vapor-liquid equilibria for polyvinylacetate (PVAc)-water with simplified PC-SAFT at 313.15 K. The correlation is poor, even with a large negative binary interaction parameter $k_{ij} = -0.17$.

success has been reported in modeling water-alkane systems. More investigation is required as the results seem to be highly sensitive to the optimization of the water solubility in the hydrocarbon phase for water-alkane systems. Other models which use a Wertheim term to model association, such as the Elliott-Suresh-Donohue equation of state [28] or the Cubic-Plus-Association equation of state [29–31] have been shown to provide rather good results for water-alkane systems. In general, although the only water PC-SAFT parameters published assume a two-site model, in most SAFT publications, best results are obtained when water is treated as a four-site molecule [27,32].

4.2. Simplified PC-SAFT for various types of aqueous systems

We present in this section a number of different applications of simplified PC-SAFT for aqueous systems, aiming to illustrate both strengths and limitations of the approach. The published PC-SAFT parameters are employed.

Fig. 7 shows that poor agreement is obtained in correlating the water activity in polyvinylacetate (PVAc), even with a large negative binary interaction parameter. Similarly, Kouskoumvekaki et al. [33] have reported rather high values for caprolactam-water and nylon-water systems (around 0.07–0.1, typically negative). VLE and LLE for aqueous polymer systems are very difficult to describe even for explicit free-volume activity coefficient models employing several adjustable parameters, as shown recently by Tritopoulou et al. [34]. These authors investigated PEG-water systems and found that accounting for the end groups is essential for obtaining good results. Simultaneous VLE and LLE is impossible even with several adjustable parameters.

In general, aqueous polymer systems are very difficult to describe with simplified PC-SAFT (and other thermodynamic models). The free-volume effects are not very pronounced for such systems, as water and polymers have similar free-volume percentages. Thus, even small errors in describing the complex energetic interactions (which could have been masked in

Table 6

Experimental and predicted infinite dilution activity coefficients with simplified PC-SAFT for polystyrene (MW 20,000)-water at various temperatures

Temperature (K)	Experimental	Predicted ($k_{ij} = 0$)	k_{ij} fitted at 435.5 K ($k_{ij} = -0.275$)
435.5	250.98	1168	251
445.0	180.19	1245	281
492.9	76.84	1639	458
502.6	76.58	1719	499

other polymer-solvent systems due to large free-volume differences) may significantly affect the results. These problems are further illustrated by the results shown in Table 6, which provides a comparison of infinite dilution activity coefficients for water-polystyrene systems. The agreement is not satisfactory, the temperature dependency is wrong, and the performance cannot be improved with the use of a single interaction parameter. Apparently, k_{ij} should have a high negative value, possibly decreasing with increasing temperature.

Non-polymeric aqueous systems are of great practical importance in applications in oil and gas and in the chemical industry. Few calculations for aqueous non-polymeric systems have been presented in the literature. Gross and Sadowski [21] have shown that PC-SAFT can, using a single k_{ij} , describe satisfactorily (and better than SAFT) VLE and LLE of water-pentanol. Kouskoumvekaki et al. [33] have shown that simplified PC-SAFT can rather satisfactorily correlate the VLE of water-acetic acid (with a $k_{ij} = -0.07$), using the published PC-SAFT parameters for water and a new set of parameters for acetic acid. Other SAFT-variants have also been applied to water-alcohol-alkane systems [35] but only very few such investigations have been reported.

On the other hand, simplified PC-SAFT performs very well for other type of sensitive calculations in aqueous systems such as solubility of water in CO₂ at 298 K, as shown in Fig. 8. A comparison with SRK is also provided. The performance in both models is quite satisfactory up to the vapor pressure of CO₂. SRK

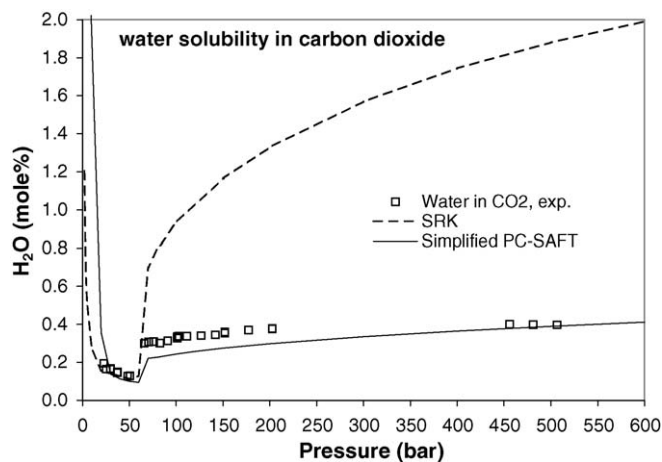


Fig. 8. Prediction ($k_{ij} = 0$) of the water solubility in CO₂ at various pressures with the SRK and simplified PC-SAFT equations of state at 298.15 K. Water has been assigned a 2B association scheme in PC-SAFT.

greatly overestimates the solubility after the discontinuity point and progressively deviates from the experimental data as the pressure increases. Simplified PC-SAFT slightly underestimates the water solubility after the discontinuity point but gradually gets better as the pressure is increased.

5. Sensitive calculations

5.1. Separation factors in ketone–alkane systems

If acetone and other ketones are treated as inert (non-self-associating) compounds, then satisfactory description with SAFT variants of ketone–alkane VLE requires additional contributions to account for the polarity of the ketones [36,37]. Recently, von Solms et al. [38] showed that by treating acetone as a self-associating compound, excellent agreement is obtained for ketone–alkane systems, as can be seen in Fig. 9 at 25 °C, even without the use of any interaction parameter. The same excellent prediction was obtained by Jog et al. [39] by adding a polar term to the SAFT model. Less satisfactory results are obtained, at the same temperature, for the separation factor (relative volatilities), as seen in Fig. 10, although the performance of the model is clearly improved at higher temperatures (Fig. 11).

5.2. The azeotrope of the methanol–propane system at 20 °C

The system methanol–propane at 20 °C is quite interesting, as industrial evidence suggests the existence of azeotropic behaviour at very low methanol concentrations. This azeotropic behaviour creates problems in propane–propene separations when traces of methanol are present. As can be seen in Fig. 12, PC-SAFT can predict this behaviour without use of binary interaction parameters. The azeotrope is predicted at methanol mole fraction equal to 0.005 similar to that previously reported for SAFT [40].

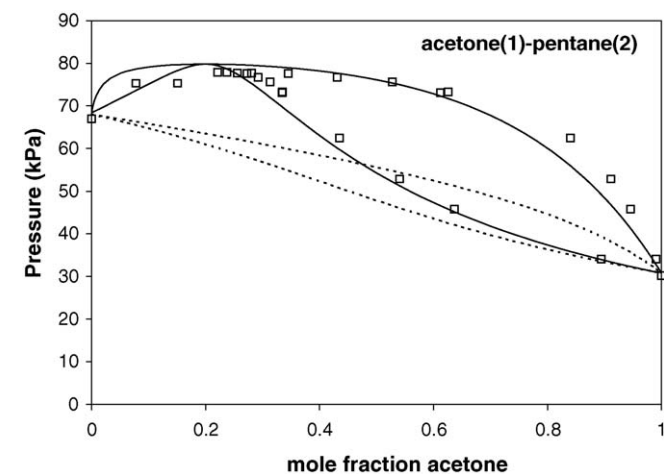


Fig. 9. Vapour–liquid equilibrium prediction for acetone–pentane using simplified PC-SAFT at 25 °C. Acetone is considered as a self-associating compound for the solid line. Acetone as a non-associating compound predicts the more ideal behaviour evident in the dotted line.

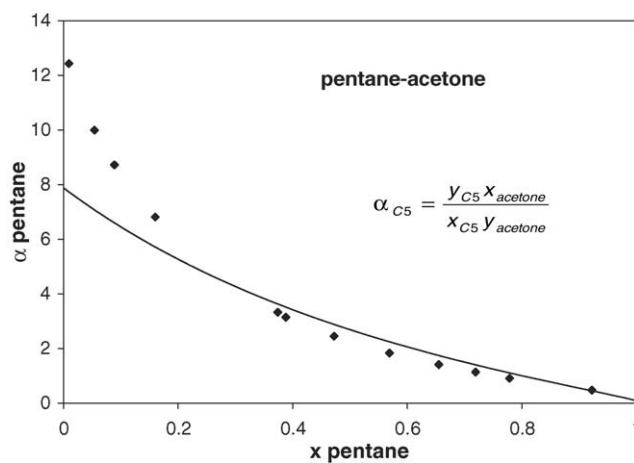


Fig. 10. Pentane separation factor for acetone–pentane at 25 °C using simplified PC-SAFT. Acetone is considered as self-associating compound.

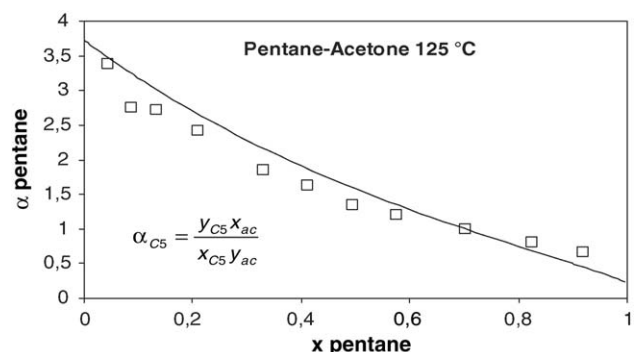


Fig. 11. Pentane separation factor for acetone–pentane at 125 °C using simplified PC-SAFT. Acetone is considered as self-associating compound.

5.3. The effect of quadrupoles in CO₂-systems

CO₂ is a molecule of great importance, both in a positive sense (an excellent “inert” solvent, of major importance in supercritical fluid extraction processes) and in a negative

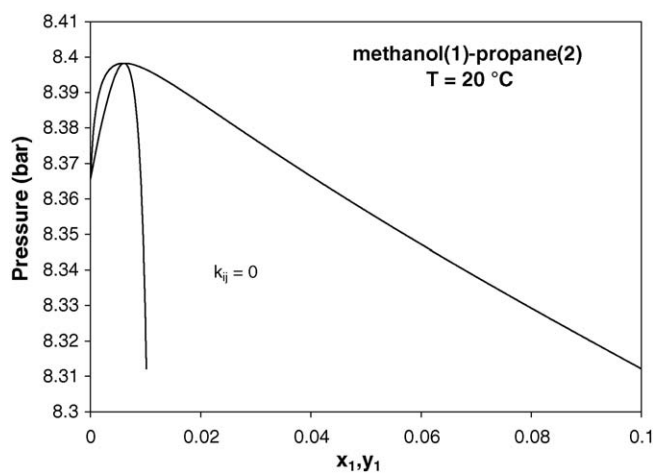


Fig. 12. P - x - y plot for methanol–propane at 20 °C using simplified PC-SAFT without use of binary interaction parameters ($k_{ij} = 0$). An azeotrope at very low methanol concentrations is correctly predicted.

sense (removal of CO₂ from fuel gases, greenhouse effect). Although quadrupolar effects are much less important compared to dipolar forces and of course hydrogen bonding, they are especially pronounced at low temperatures, often causing problems in thermodynamic modeling. This can be seen, e.g. in the results obtained with conventional models (cubic EoS like PR and SRK). Especially at low temperatures, large k_{ij} values are required and the results are often not satisfactory. For example, for CO₂–ethane systems, at 263 and 223 K very high k_{ij} values are required in both cases: 0.124 for PR and 0.1304 for SRK, respectively [41,42]. Without interaction parameters, the two cubic EoS cannot represent the azeotropic behaviour and even when k_{ij} 's are used the behavior is not satisfactory at the very low temperature.

Gross and Sadowski [6] have applied PC-SAFT to CO₂–alkanes (cyclohexane, decane) and an interaction parameter equal to 0.13 is required for good results. We observe that k_{ij} is of the same order as that for PR EoS. Tumakaka et al. [43] have also shown that a $k_{ij}=0.18$ is required for CO₂–polyethylene systems, compared to 0.24 for SAFT. Despite the more sound physical term compared to cubic equations of state, PC-SAFT requires rather high k_{ij} values for CO₂-containing systems, indicating the need to account properly for the quadrupolar effects. Successful efforts in this direction have been reported by Gross [25].

6. Limitations and challenges

Based on the results showed in this work and further investigations, a number of important areas where serious limitations of simplified PC-SAFT (and of the SAFT approach in general) have been identified. In addition, further challenging research areas are reported below. The areas where serious limitations exist require primary attention for improving the capabilities of the model for future applications.

6.1. Serious limitation

Aqueous systems, e.g. water–polymers and simultaneous representation of water and hydrocarbon solubilities in water–alkane systems including the minimum of hydrocarbon solubility with respect to temperature. While some equations of state can provide good simultaneous representation of water and hydrocarbon solubilities in water–alkane systems [30], it should be admitted that no equation of state can reproduce the minimum of hydrocarbon solubility with respect to temperature.

6.2. Other limitations

1. Limitations of Wertheim's approach, e.g. accounting for co-operativity, intramolecular association, cyclic aggregates [44,45].
2. A systematic method for estimating polymer parameters without the use of mixture data—including associating polymers. If possible such a general method should be based on data which are readily available for polymers e.g. solubility parameters.

3. A systematic method for estimating parameters for compounds, e.g. pesticides or pharmaceuticals where extensive vapor pressure and liquid density data are not available.

7. Further future challenges

1. Estimation of SAFT parameters from “first principles” (ab-initio calculations, spectroscopy)—establishment of the physical meaning of the equation of state parameters (both those related to the “physical” and the “association” terms). Several attempts in this direction have been reported by Sandler and co-workers [46–50].
2. Extension to charged (bio)molecules. An initial effort in this direction has recently been published by Cameretti et al. [51].
3. Clear proof of the superiority of the “physical” term of SAFT over that of e.g. cubic equations of state—comparison of the “various physical terms” used in PC-SAFT and the other SAFT variants.
4. Study of relative importance of terms (dispersion, chain, repulsive, association) in the SAFT model.
5. The description of cross-associating systems including “complex solvation” when one or more compounds do not self-associate (acetone/water or acetone/chloroform).
6. The necessity of additional contributions, e.g. to account for polar and quadrupolar effects. Can such systems be described satisfactorily without incorporating additional terms?
7. Establishment of the “correct” association schemes, especially for “difficult” multifunctional molecules, e.g. alkanolamines and glycols or molecules not previously studied (pyridine, sulfolane, . . .).
8. Simultaneous prediction of phase equilibria and enthalpies.
9. Limitations in the description of the critical area.
10. Model validation for “difficult” multicomponent systems, e.g. water–alcohol (glycol)–alkanes of importance in the design of gas hydrate inhibitor systems as well as polymer–mixed solvents of importance in design of paints and membrane technology.

8. Conclusions

The applications of the simplified PC-SAFT equation of state have been reviewed and several “key” areas have been discussed, illustrated by sample calculations. These areas are polymer–mixed solvent phase equilibria, asymmetric athermal alkane systems, aqueous polymer solutions and water solubility in CO₂, polymer blends as well as a number of sensitive calculations. Both the capabilities and limitations of simplified PC-SAFT have been presented and discussed. Finally, we have identified areas where serious improvements are required and/or where future challenges exist. In short, despite the great applicability and success of simplified PC-SAFT in many cases, e.g. the satisfactory representation of asymmetric systems including polymer–mixed solvents, future “survival” of the model will largely depend on tackling the existing serious limitations for aqueous systems and the parameter estimation for “diffi-

cult” compounds for which reliable pure compound data are not available such as polymers and multifunctional compounds. Moreover, a careful comparative analysis of the various terms of PC-SAFT may indicate where improvements are needed and in which cases additional terms, e.g. to account for polarity are required.

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