Heat Capacities of Fluids: The Performance of Various Equations of State

Zhu, Chenyang; Liu, Xiangyang; He, Maogang; Kontogeorgis, Georgios M.; Liang, Xiaodong

Published in:
Journal of Chemical and Engineering Data

Link to article, DOI:
[10.1021/acs.jced.0c00649](https://doi.org/10.1021/acs.jced.0c00649)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Zhu, C., Liu, X., He, M., Kontogeorgis, G. M., & Liang, X. (2020). Heat Capacities of Fluids: The Performance of Various Equations of State. *Journal of Chemical and Engineering Data*, 65(12), 5654–5676.
<https://doi.org/10.1021/acs.jced.0c00649>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Abstract

Heat capacities are fundamental properties of fluids for heat transfer applications. Accurate data can be generally obtained by experimental methods, which are usually expensive, difficult and time-consuming. In terms of the calculations of heat capacities, many models have been proposed in literature. Equations of state represent one of the most promising methods, but their performance has not been systematically studied and extensively reviewed. In this work, calculations and performance of various equations of state for heat capacities are reviewed, and the different contributions to heat capacities are also discussed. The accuracy of the calculated heat capacities, as presented in literature, is also compared for some specific compounds, and the effects of different parametrization strategies as well as association schemes are analyzed. Finally, calculations for both associating and non-associating compounds are performed using two association models, Cubic Plus Association and Perturbed-Chain Statistical Associating Fluid Theory equations of state, for a wide range of compounds for which the heat capacity results from literature are available.

1. Introduction

Heat capacities, including both isochoric and isobaric one, belong to the most important thermophysical properties of fluids. They are related to the temperature derivatives of fundamental thermodynamic functions and they can, therefore, be used to derive other properties such as enthalpy and entropy.¹⁻⁴ In the context of equations of state (EoS), heat

capacities are of interest also for testing the performance limits of such models.⁵ Variations in heat capacities are also required for understanding the changes of the fluid structures^{1,4} and heat transfer processes in the industrial aspects.⁶

Equations of state are effective tools for representing the thermophysical properties of fluids including heat capacities, which can be calculated by the following two equations:

$$C_v = -T \left(\frac{\partial^2 F^{\text{res}}}{\partial T^2} \right)_V + C_p^{\text{id}} - R \quad (1)$$

$$C_p = C_v - T \frac{(\partial p / \partial T)_V^2}{(\partial p / \partial V)_V} \quad (2)$$

where C_v , C_p and C_p^{id} represent the isochoric, isobaric and ideal gas heat capacities, respectively. F^{res} is the residual molar Helmholtz free energy, and R is the universal gas constant. At present, EoS based on the perturbation theory are considered among the most popular tools for thermodynamic calculations. Examples of such models are the Statistical Associating Fluid Theory (SAFT) and the Cubic Plus Association (CPA) EoS. The former model was proposed by Chapman et al.^{7,8} Following these original studies, many different EoS based on the SAFT framework were developed.^{9–15} The CPA equation of state (EoS) is a combination of cubic EoS, e.g. Soave–Redlich–Kwong (SRK) and the association contribution from SAFT. It was first developed by Kontogeorgis et al.¹⁶ in an attempt to balance the accuracy and simplicity of an EoS.¹⁷ The parameters of SAFT and CPA are obtained from experimental data, most often saturated densities and vapor pressures. Therefore, these models can usually give a satisfactory representation for these two properties, while for some thermodynamic derivative properties e.g. heat capacities, the

performance may get unsatisfactory.

In some cases, heat capacities are calculated in order to test the predictive ability of an EoS for second-order thermodynamic derivative properties. For this reason, isochoric (C_v) and isobaric (C_p) heat capacities have been calculated by several researchers using different EoS, and the results are summarized in Table 1. Some of the most important studies are discussed hereafter.

Palma et al.^{18–20} modified the CPA EoS with a five-parameter function in the attractive term (the so-called α function) and a volume shift, and they analyzed its performance for the estimation of saturated C_v , C_p , and residual C_p (C_p^{res}) for water and alcohols. Then, they compared their results with the original CPA. Polishuk and co-workers^{15,21–27} attached the attractive term of cubic EoS to the SAFT EoS, and they calculated the C_v and C_p of both associating and non-associating compounds using two SAFT-type models (PC-SAFT, SAFT-VR-Mie) and also, CPA, SBWR and PR for comparison. In addition, the performance of another EoS within the PC-SAFT framework named CP-PC-SAFT for heat capacities of several fluids was also tested by Polishuk and co-workers^{28–30}. In their studies, it was mentioned that the available C_p data might have noticeable uncertainties, which make the evaluation of the performance of these models difficult.^{22,30} Liang et al.,³¹ Diamantonis and Economou,³² and de Villiers et al.³³ compared the accuracy of the PC-SAFT, SAFT and CPA EoS for the calculation of C_v , C_p , and their residual values. Different parameter sets for these EoS and association schemes of associating compounds were analyzed. In the work of de Villiers et al.³³, the performance of these models for derivatives

of pressure by volume (dp/dV) and temperature (dp/dT), which are linked to the isobaric heat capacity, were also discussed. Burgess et al.³⁴ tested a new PC-SAFT EoS with a “hybrid” group contribution method by calculating the C_p of some non-associating substances. Their calculations were performed at both low-pressure (lower than 7 MPa) and high-pressure (up to 276 MPa) conditions. Lafitte et al.³⁵ calculated the C_p and C_p^{res} of alcohols and their binary mixtures with alkanes through a SAFT-VR EoS based on the Mie potential (SAFT-VR-Mie). The performance of the model for pure alkanes was compared with the SAFT-VR-SW EoS over a wide pressure range.³⁶ Following this work, a modified SAFT-VR-Mie with a higher-order perturbation term was then developed by Lafitte et al.,³⁷ and the performance of the new model was tested by several properties including the isobaric heat capacity. The accuracy of calculated C_p with SAFT-VR-Mie for the mixtures of fatty acid methyl esters (FAMES) was analyzed by Perdomo and Gil-Villegas.³⁸ A simple mixing rule with a binary interaction parameter fitted to the density and sound velocity data was used in their work. Vega and co-workers^{39–42} estimated the heat capacities of several substances and their mixtures in the subcritical and critical regions using soft-SAFT. A crossover approach on the basis of the renormalization group theory was used in order to improve the performance in the critical region. Maghari et al.^{43,44} investigated the predictive ability of SAFT-BACK for heat capacities and their residual values. In their studies, both alkanes and their mixtures were considered over wide pressure ranges, up to 300 MPa for alkane mixtures. Another model in the PC-SAFT framework, which is named ePC-SAFT with a Coulomb interaction term for charged species and applicable to ionic

liquids (ILs), was studied by Shen et al.⁴⁵ In their study, the IL molecule is considered as a combination of IL-cation and IL-anion rather than a complete molecule. Except for the CPA- and SAFT-type EoS, there are some other types of EoS being used for heat capacities estimation. Diedrichs et al.⁴⁶ calculated the liquid C_p for 33 pure compounds including associating fluids through a group contribution VTPR (Volume Translated Peng-Robinson) EoS, and different parametrization strategies were considered for comparison. Using the PHTC (Perturbed Hard-Trimer-Chain) EoS, Alavianmehr et al.⁴⁷ predicted the C_p of several fatty acid ethyl esters (FAEEs) at pressures up to 100 MPa, and the results were compared with the calculated data from literature.

The equation of state approach is generally considered as an indirect method for heat capacity estimation and can also be used to calculate other required properties of fluids. In addition, methods specifically developed for heat capacity have also been proposed, such as group contribution (GC) methods^{48–52}, corresponding states methods^{52,53} and some innovative methods based on quantum mechanics.^{54–56} These methods have been used for the calculations of heat capacities for several compounds, and good agreement between the calculated values and the experimental data was observed. However, the group contribution and corresponding states methods are generally empirical and applicable to the properties at atmospheric pressure and temperatures far from the critical points, while for a global calculation method of heat capacities with a physically sound background, EoS are usually preferred. Therefore, the remainder of this study is focused on EoS, especially those based on the SAFT framework. First, the overall performance of each EoS on heat capacities is

114 presented according to the literature studies. Then, different equations are compared for
115 some specific compounds containing *n*-alkanes, 1-alcohols and water. Next, the
116 performance of the CPA and PC-SAFT EoS is systematically evaluated and discussed via
117 the calculations of the heat capacities of many compounds in the compressed and critical
118 isothermal regions. At last, the manuscript is completed with our conclusions.

Table 1. Literature studies for the calculation of heat capacities using equations of state

Author	Model	T/K^a	p/MPa	Substance	Property	Ref.
Palma et al.	Modified CPA	251–533	Saturation	Alcohol	C_p	18
	Modified CPA	260–576	Saturation	Water	C_v, C_p	19
	Modified CPA	260–490	Saturation	1-Alcohol	C_v, C_p, C_p^{res}	20
Polishuk and co-workers	SAFT + Cubic,	150–1400	Saturation,	Water, methanol, carbon dioxide,	C_v, C_p	15
	SAFT-VR-Mie, PR		0.1–1000			
	SAFT + Cubic	293–413	0.1–160	Di-isodecyl Phthalate	C_v	21
	SAFT + Cubic, PC-SAFT	298–433	0.1–240	1-Alkene	C_v, C_p	22
	SAFT + Cubic, PC-SAFT	80–500	Saturation	Halomethane	C_v, C_p	23
	SAFT + Cubic, PC-SAFT	150–420	Saturation,	Haloethane	C_v, C_p	24
			0.1–120			
	SAFT + Cubic, PC-SAFT	299–433	0.1–1000	n -Octane, n -octane + n -hexadecane	C_v, C_p	25
	SAFT + Cubic, SBWR	243–503	Saturation,	n -Hexane	C_v	26
			0.1–1000			
	SAFT + Cubic,	298–323	0.1–150	Ionic liquid	C_v, C_p	27
	PC-SAFT, CPA					
	CP-PC-SAFT	250–550	0.1	Ionic liquid	C_v, C_p	28
	CP-PC-SAFT, PC-SAFT	270–1273	Saturation,	Water	C_v, C_p	29
			30–1000			
Liang et al.	CPA, PC-SAFT	280–620	Saturation	Water	C_v^{res}, C_p^{res}	31
Diamantonis and Economou	SAFT, PC-SAFT	80–695	0.1–20	Carbon dioxide, nitrogen, oxygen, methane, water, hydrogen sulfide	C_v, C_p, C_v^{res}	32
de Villiers et al.	CPA, SAFT, PC-SAFT	0.5–1.1 T_c ,	0.01–100,	n -Alkane, 1-alcohol	C_v, C_p	33
		325–570	10–30			
Burgess et al.	GC-PC-SAFT	323–533	0.1–276	Toluene, 2-methylbutane, n -decane	C_p	34

Author	Model	T/K ^a	p/MPa	Substance	Property	Ref.
Lafitte et al.	SAFT-VR-Mie	298–570	0.1–60	Alcohol, n -alkane + 1-alcohol	C_p, C_p^{res}	35
	SAFT-VR-Mie,	298–403	0.1–100	n -Alkane	C_p, C_p^{res}	36
	SAFT-VR-SW					
	Modified SAFT-VR-Mie	100–470	0.1–150	n -Alkane, 1-alcohol, perfluoroalkane	C_v, C_p	37
Perdomo and Gil-Villegas	SAFT-VR-SW	300–700	0.1	FAME mixture	C_v	38
Vega and co-workers	soft-SAFT	293–500	0.1–50	n -Alkane, perfluoroalkane, 1-alcohol, water	$C_p, C_v^{res}, C_p^{res}$	39
	(crossover) soft-SAFT	1.1–1.5 T_c , 280–573	0.1–60	n -Alkane, 1-alcohol	$C_v, C_p, C_v^{res}, C_p^{res}$	40
	(crossover) soft-SAFT	1.1–1.25 T_c , 280–330	--	Isobutene, propane + isobutene, n -alkane + 1-alcohol	$C_v, C_p, C_v^{res}, C_p^{res}$	41
	(crossover) soft-SAFT	225–500	0.1–30	Perfluoroalkane	$C_v, C_p, C_v^{res}, C_p^{res}$	42
Maghari et al.	SAFT-BACK	150–675	--	n -Alkane	C_v, C_p, C_v^{res}	43
	SAFT-BACK	300–400	0.1–300	n -Alkane mixture	$C_v, C_p, C_v^{res}, C_p^{res}$	44
Shen et al.	ePC-SAFT	273–413	0.1–150	Ionic liquid	C_v, C_p	45
Diedrichs et al.	VTPR	90–480	Saturation	Alkane, ketone, water, etc.	C_p	46
Alavianmehr et al.	PHTC	286–341	0.1–100	FAEE	C_p	47

120 ^a Temperature and pressure ranges are only for heat capacities.

2. Discussion of the Performance of Different Equations of State

The present study is mainly focused on isochoric and isobaric heat capacities, while the accuracy of other calculated properties, such as vapor-liquid equilibrium (VLE) properties, compressed density, and speed of sound, is also discussed, as ideally we would like to have EoS which can represent a wide range of properties. The performance of various EoS, as presented in literature, for heat capacities and selected additional thermodynamic properties is discussed in this section. The details of calculated results with different models can be found in Table 2, in which the association schemes, the properties used in the parameter estimation methods, and the average absolute relative deviation (AAD), which is defined by the eq 3, for the various properties and models are also presented.

$$\text{AAD}(\%) = \frac{1}{N} \sum_{i=1}^N \left| \frac{100(X_{\text{cal}} - X_{\text{exp}})}{X_{\text{exp}}} \right| \quad (3)$$

where X is the investigated property, N is the number of data, and subscripts cal and exp represent the calculated and experimental values, respectively.

2.1 Results with Equations of State

2.1.1 CPA EoS

Palma et al.^{18–20} proposed a modified CPA EoS to calculate the C_v , C_p , C_v^{res} and C_p^{res} of alcohols and water at saturation. In their works, the original α function (one parameter) was replaced by a 5-parameter function, and two different kinds of (T -independent and T -dependent) volume shifts were added to the EoS. The energy parameter and co-volume were obtained by solving the corresponding equations at the critical points in order to

improve the accuracy of the critical properties. Generally, their modified CPA shows satisfactory performance for heat capacities and their residual properties, and the only exception is for the C_p of glycerol with an AAD of 15%.^{19,20} The T -independent volume shift used in the modified CPA has no influence on heat capacity calculations, while the C_v of several alcohols can be better described with a T -dependent volume shift.

Liang et al.³¹ calculated the C_v^{res} and C_p^{res} of water at the saturated condition with CPA, and only the vapor pressure (p_{sat}) and saturated liquid density data were used in the parameter estimation procedure. The results show good agreement for p_{sat} and $\rho_{\text{sat,l}}$, while the accuracy of C_v^{res} and C_p^{res} at the reduced temperature (T_r) up to 0.96 is not as good as p_{sat} and $\rho_{\text{sat,l}}$. Using the CPA EoS, de Villiers et al.³³ investigated the heat capacities and speed of sound (u) for n -alkanes and 1-alcohols at high pressures. For n -alkanes, the AADs of C_v , C_p and u are lower than 4% near the critical region (1.06 – $1.1T_c$), while the performance on C_v and u deteriorates when a lower temperature (0.5 – $0.9T_c$) and higher pressure (up to 100 MPa) region is considered, especially for u with an AAD of 9.3%. Two association schemes (2B and 3B) were used for 1-alcohols by de Villiers et al.³³ Both schemes, when used in CPA, perform poorly for u , with the AAD higher than 12%. Nevertheless, the performance for C_p with CPA and both schemes is much better, with the AAD lower than 4.1%. Considering a 2B scheme, Polishuk²⁷ tested the performance of CPA for two ionic liquids ($[\text{C}_2\text{mim}][\text{NTf}_2]$ and $[\text{C}_4\text{mim}][\text{NTf}_2]$). The CPA EoS shows high accuracy of density for these two ILs, while the accuracy of derivative properties for

[C₄mim][NTf₂] is not satisfactory, with the deviations of 16% and 21% for C_p and u , respectively.

To sum up these literature studies for CPA, using a more flexible α function with 5 parameters, the modified CPA has good performance for heat capacities at the saturated condition, without sacrificing too much the accuracy of other properties. The T -dependent volume shift can improve the accuracy of C_v , but such volume shift may lead to the crossing of isotherms in the p - V plane and negative heat capacities.⁵⁷ Therefore, it is not recommended to use a T -dependent volume shift in an EoS for improving its T -dependent performance. It should be noticed that, from Table 2, the performance of the original CPA may be only acceptable in some cases, but overall, it predicts rather well the heat capacities of alkanes and alcohols over relatively wide pressure ranges, while the AADs of u are much higher. This may be due to the inadequacy of the model for the description of the dp/dV .

2.1.2 Original SAFT EoS

Diamantonis and Economou³² studied the performance of original SAFT for heat capacities of some non-associating compounds. The results show satisfactory agreement between the calculated properties for methane, nitrogen, and oxygen, while the accuracy of heat capacities and u for carbon dioxide is barely acceptable. Particularly, the AAD of C_v for carbon dioxide is 5.9%, while the accuracy of C_v^{res} is much lower with an AAD of 49%. In the work of Diamantonis and Economou, the heat capacities of hydrogen sulfide and water were also estimated with different association schemes.³² For hydrogen sulfide, a one-associating site model (1A) was used to describe the hydrogen bond in H₂S dimers.

The AAD of C_v with 1A scheme is 4.7%, while the accuracy of C_p and u gets worse, with both AAD higher than 8.5%. Considering hydrogen sulfide as an inert compound (less parameters than 1A scheme), satisfactory performance for VLE properties, compressed ρ , and u can still be obtained, while the AAD of both heat capacities is higher than 6%. For water with two association schemes (2B and 4C), neither of them can give good accuracy of second-order derivative properties, especially for the speed of sound, with the AAD of 19% using the 2B scheme.

The heat capacities of n -alkanes and 1-alcohols were also estimated by de Villiers et al.³³ using the original SAFT EoS. The results are similar to those with CPA: High accuracy of n -alkanes for C_v , C_p and u is obtained near the critical region, while the AAD of these properties increase when a wider pressure region is considered. The original SAFT coupled with the 2B scheme shows good performance for the C_p of 1-alcohols, while the description of u using both 2B and 3B schemes is not satisfactory (deviation around 15%).

In summary, the original SAFT can accurately describe the VLE properties and compressed ρ for both associating and non-associating compounds, but it fails to give a satisfactory description of u for most substances. In addition, the heat capacities of water cannot be well predicted by original SAFT, indicating the need of either a better EoS or an improved parameter estimation method.

2.1.3 PC-SAFT EoS

Using the PC-SAFT EoS, Liang et al.³¹ calculated the thermophysical properties of water at $T_r=0.43-0.96$ and vapor pressures. The accuracy of VLE properties is quite satisfactory,

but the deviation for the residual heat capacities is in all cases higher than 20%. The high AAD of C_p^{res} and u may be, to some extent, due to the inaccurate description of dp/dV , which has an AAD of almost 50%. Polishuk et al.^{23,24} estimated the C_p of halomethanes and haloethanes at both saturated and compressed conditions. The AAD of C_p are not given in their studies, but we can nevertheless conclude that PC-SAFT can give accurate results for the C_p for halomethanes and haloethanes far from the critical points. Using PC-SAFT, Polishuk²⁷ calculated the density, heat capacities, and speed of sound for several ILs. The results show good agreement between the calculations and experiments for ρ and u , while the AAD of heat capacities can be higher than 43%.

Diamantonis and Economou³² also calculated the thermophysical properties of some associating and non-associating compounds using PC-SAFT. For non-associating fluids, and for all studied properties, there is very good agreement between the calculated values and experimental data, while the C_v^{res} still has a large AAD of 41% for carbon dioxide. For hydrogen sulfide with 1A and non-associating schemes, all properties are well estimated by PC-SAFT, no matter whether the association is considered. Although a more rigorous association scheme with four associating sites (4C) is used, the AAD of heat capacities for water are still about 10%, and only the sound velocity data are successfully described by PC-SAFT with 4C scheme among the studied second-order derivative properties of water. However, when the supercritical water over wider temperature (up to 1273 K) and pressure (up to 1000 MPa) ranges is considered, PC-SAFT with 4C scheme provides lower AAD of C_v and C_p , which are 6.3% and 7.1%, respectively, while the deviation of u can increase to

224 9.0%.²⁹

225 The performance of PC-SAFT for the heat capacities of *n*-alkanes and 1-alcohols was
226 also tested by de Villiers et al.³³ The C_p of *n*-alkanes is well described by PC-SAFT,
227 although the model shows less accuracy in the vicinity of critical points than over a lower
228 temperature and higher pressure region. Furthermore, the overall performance for C_v of *n*-
229 alkanes is satisfactory, while the predicted results of u over a wide temperature and pressure
230 region still need improvement. For 1-alcohols, PC-SAFT with both 2B and 3B schemes
231 shows high accuracy of C_p data but low accuracy for u , with the AAD lower than 3% and
232 higher than 6%, respectively.

233 Except for the original PC-SAFT, some new EoS within the PC-SAFT framework were
234 developed and used to estimate the heat capacities of fluids. By means of the CP-PC-SAFT
235 (Critical Point-based Modified PC-SAFT) and GC-PPC-SAFT (Group Contribution Polar
236 PC-SAFT) EoS, Polishuk and co-workers³⁰ calculated the thermophysical properties of
237 alcohols, ketones, ethers, and esters. The former model does not include the association
238 contribution to the residual Helmholtz energy, and the parameters are obtained by solving
239 three equations at the critical points and one equation at the triple point. It is found that CP-
240 PC-SAFT shows superior performance for compressed ρ and u than GC-PPC-SAFT at
241 pressures up to 861 MPa, although the latter one considers both associating and polar
242 interactions. However, CP-PC-SAFT and GC-PPC-SAFT cannot give satisfactory
243 descriptions of C_p at saturated conditions. The density and derivative properties of water
244 and ILs were also calculated by Polishuk et al. with CP-PC-SAFT.^{28,29} For water, the model

shows satisfactory accuracy for density and speed of sound and acceptable performance for heat capacities, while it substantially underestimates these properties at the saturated conditions.²⁹ For ionic liquids at the atmospheric pressure, CP-PC-SAFT gives higher deviations of heat capacities ($\leq 7.5\%$) than speed of sound ($\leq 4.3\%$) and density ($\leq 0.3\%$). Nevertheless, as concluded by the authors, the model still gives a robust estimation of C_p data considering their relatively high uncertainty.²⁸ Without considering the polar and association terms in GC-PPC-SAFT, Burgess et al.³⁴ calculated the C_p and u of three non-associating compounds. Both properties are well described by GC-PC-SAFT, especially in the low-pressure region. In order to estimate the thermophysical properties of ILs, Shen et al.⁴⁵ added the Coulomb interaction term to the PC-SAFT EoS. The parameters in their model (the so-called ePC-SAFT) are only correlated by compressed ρ data, since accurate vapor pressure data of ILs are not available. Although better results are obtained by regarding an IL as a combination of IL-cation and IL-anion than treating it as a single molecule, the performance of ePC-SAFT for heat capacities is still poor. The authors concluded that such large deviations could be due to the lack of experimental ideal gas data, which were estimated using a statistical thermodynamic method in their work.

In conclusion, it can be seen that in Table 2, with some exceptions, PC-SAFT can generally show high accuracy for heat capacities, and even give quite satisfactory accuracy of u for some compounds including carbon dioxide, nitrogen, oxygen, methane, hydrogen sulfide, ionic liquids, and water (with 4C scheme).

2.1.4 SAFT-VR EoS

Another SAFT-type EoS based on the attractive potentials of variable range (the so-called SAFT-VR) has been also applied for the calculation of heat capacities. Lafitte et al.^{35,36} calculated the heat capacities of alkanes and alcohols using two versions of SAFT-VR combined with either square well (SAFT-VR-SW) or Mie potentials (SAFT-VR-Mie). The results of all of the investigated properties with SAFT-VR-Mie show very good agreement with the experimental data for both 1-alcohols and branched alcohols. The AAD of C_p and u for all alcohols are lower than 1.5% and 3.0%, respectively, and the AAD of C_p^{res} for methanol in a wide temperature range ($T=300\text{--}700$ K) and at 50 MPa is only 6.2%. The performance of SAFT-VR-Mie on VLE properties and compressed ρ for n -alkanes is mostly satisfactory for compounds with the carbon atom numbers less than 22, while the AAD of p_{sat} can reach to 18% for hexatriacontane. The SAFT-VR-SW EoS even shows high inaccuracy of p_{sat} for decane with the AAD of 47%. Both SAFT-VR-Mie and SAFT-VR-SW cannot give high accuracy of heat capacity for n -alkanes, and the AAD of C_p and C_p^{res} are within the ranges of 5.4–8.7% and 23–40%, respectively. A modified SAFT-VR-Mie with a higher-order perturbation term was also proposed and used to calculate the VLE and derivative properties for n -alkanes, 1-alcohols and perfluoroalkanes by Lafitte et al.³⁷ This new SAFT-VR-Mie shows satisfactory accuracy for most substances in the compressed liquid phase, while the AAD of C_p for methanol and u for perfluoromethane are still noticeable (about 7-9%).

The properties of mixtures of n -alkane + 1-alcohol were also calculated by Lafitte et al.³⁵ using the SAFT-VR-Mie EoS at atmospheric pressure. High accuracy is obtained for

compressed ρ , C_p , C_p^{res} , and u without any adjustable interaction parameters. Perdomo and Gil-Villegas³⁸ estimated the C_v and u values of the mixtures of fatty acid methyl esters (FAMES) at $p=0.1$ MPa. They have considered association contributions for these compounds in their work. The C_v of FAME mixtures are well described by SAFT-VR-SW. However, the accuracy of u is still not satisfactory, although the data of this property are included in the objective function for the parameter estimation.

In brief, the SAFT-VR-Mie EoS shows a great potential for calculating the heat capacities and u of alcohols and their mixtures with alkanes. For pure n -alkanes, the u data can be accurately reproduced by adding them to the parametrization process, while the accuracy of C_p still needs improvement. This inaccuracy may be alleviated by including C_p data in the parameter estimation procedure or using a higher-order perturbation term.

2.1.5 soft-SAFT EoS

The soft-SAFT EoS is a variant of SAFT EoS with the reference term of a Lennard-Jones (LJ) fluid, which includes both the repulsive and attractive interactions for chains formation. By means of the soft-SAFT EoS, Vega and co-workers³⁹ investigated the heat capacities and their residual values for both associating and non-associating fluids at high pressures. For non-associating compounds (n -alkanes and perfluoroalkanes), in most cases, it seems sufficient to obtain good results of VLE properties and heat capacities at $T_r=0.7-0.9$ and pressure up to 30 MPa only to use the VLE data in the parameter estimation. For the associating substances of 1-achohols and water, the C_p data should be added to the parameter estimation procedure for obtaining better results of heat capacities. For example,

the AAD of C_p for 1-hexanol can reach to 13% without correlating the parameters to C_p data, while such deviation can be reduced to 5.4% when the parameters are refitted to both VLE properties and C_p . However, although soft-SAFT can give high accuracy of calculated heat capacities, the description of the C_v^{res} and the C_p^{res} near the critical points is still poor.

A crossover soft-SAFT EoS with a renormalization group (RG) method was also developed by Vega and co-workers,^{40–42} and the model showed rather good accuracy of VLE properties for n -alkanes, isobutene and perfluoroalkanes. In addition, satisfactory performance for heat capacities for perfluoroethane is observed at the gas and liquid subcritical conditions ($T_r=0.77–0.94$ and $p=0.1–30$ MPa), with the AAD about 5% for both C_v and C_p . The crossover soft-SAFT EoS coupled with mixing rules which include two binary parameters, was also applied to the calculations of heat capacities for propane + isobutene and n -alkane + 1-alcohol.⁴¹ It can be observed that both C_v and C_p are precisely represented at atmospheric pressure.

Considering the high accuracy for C_p^{id} , the soft-SAFT EoS can be regarded as a good tool for describing the heat capacities for non-associating compounds. As for associating fluids, one of the prerequisites for getting acceptable accuracy of heat capacity is correlating the adjustable parameters to C_p data, although this is not necessary for non-associating compounds like n -alkanes. Furthermore, for the residual heat capacities, the calculated results with soft-SAFT show significant deviations from the experiments, especially for the values in the vicinity of the critical points.

2.1.6 Other EoS

To avoid the numerical pitfalls of the EoS and give a better description on critical data, Polishuk and co-workers^{15,21–26} added an attractive term of cubic EoS to SAFT and developed a new equation of state named SAFT + Cubic. Using the proposed model, they calculated the thermophysical properties of several fluids at both saturated and compressed conditions, but the values of AAD were not given. Generally, as shown in their works, the SAFT + Cubic EoS describes better compressed ρ , k_T , C_v and u than PC-SAFT and better compressed ρ and u than SAFT-VR-Mie, while its performance for saturated C_v of n -hexane is worse than the SBWR (Soave–Benedict–Webb–Rubin) EoS. In addition, although the results with SAFT + Cubic are better than PC-SAFT and SAFT-VR-Mie, it still shows large deviations for C_v , and its performance on heat capacity deteriorates with the increase of ρ .¹⁵ Nevertheless, it should be emphasized again that, as stated by the authors, the used C_p data may have significant uncertainties, thus a precise comparison of models may be difficult.^{22,30} In order to describe the properties of ionic liquids, a generalized version of SAFT + Cubic were developed and used by Polishuk.²⁷ With the parameters only obtained by two density data, very impressive performance of the model can be observed, and the values of AAD for all investigated properties are lower than 3.1%. In conclusion, the performance of SAFT + Cubic for heat capacities requires further study as well as the effects of different parametrization methods with this model.

Combining the BACK and SAFT EoS, the performance of the so-called SAFT-BACK on second-order derivative properties was tested by Maghari et al.^{43,44} The results for C_v , C_p , C_v^{res} , C_p^{res} , and u for n -alkanes and their mixtures indicate good agreement with

experimental data, and no interaction parameter is used for mixtures. Using the volume translated Peng-Robinson (VTPR) EoS, Diedrichs et al.⁴⁶ estimated the saturated properties of some pure compounds including alkanes, ketones, water, etc. In their work, an exponential α function and a T -independent volume shift were used, and the parameters of the EoS were correlated to p_{sat} and C_p data. The accuracy of VTPR for p_{sat} , ΔH_{vap} and C_p is very good, with the AAD of 0.9%, 1.2%, and 0.8%, respectively. This good agreement between the calculated C_p and the experimental values can be partially explained by the fact that the parameters of VTPR are correlated to the C_p data. However, it should be noted that, in the study of Diedrichs et al, these properties are sometimes calculated over relatively low reduced temperature ranges. For example, the temperatures of water in their work are from 273 to 373 K, corresponding to a reduced temperature range of 0.42–0.58. Alavianmehr et al.⁴⁷ calculated the properties of fatty acid ethyl esters (FAEEs) with the perturbed hard-trimer-chain (PHTC) EoS, for which the parameters were only fitted to the compressed ρ . A satisfactory accuracy of ρ , C_p , and u can be observed in their study. However, their study is mostly performed over a narrow temperature range, with the conditions of FAEEs commonly far from their critical points. Therefore, a further study at a wider temperature range would be relevant for a more complete evaluation of the performance of the model.

2.2 Other Results

In many cases, the heat capacities of fluids can be estimated with rather low deviations, but higher deviations can be seen, as expected, when we focus only on the residual values

which are obtained from the thermodynamic models. The overall good results are due to the accurate values of the ideal heat capacity (C_p^{id}), which is most often the main contribution.^{18,35,46} In order to illustrate the above, we calculated the percentage of C_p^{id}/C_p for water with the results from the NIST chemistry webbook⁵⁸ at saturated condition and different pressures. The results are shown in Figure 1.

Figure 1. The percentage of ideal gas heat capacity to heat capacity for water with respect to temperature: (---) Saturated liquid, (-.-) Saturated vapor, (—) 0.1 MPa (red), (—) 10 MPa (blue), (—) 20 MPa (green), (—) 30 MPa (pink), (—) 40 MPa (orange), (—) 50 MPa (brown).

From Figure 1, It is obvious that, at temperatures much lower than the critical temperature, the proportions of C_p^{id}/C_p at different pressures are almost identical, with the value of 44% or so. This reflects that the pressure can only have a negligible influence on heat capacity in this region. According to Figure 1 and ref. 59, we can know that the liquid

C_p at constant pressure and vapor pressure are in close numerical agreement at low reduced temperatures. Therefore, if the liquid saturated C_p can be well described using an EoS, the performance for C_p at different pressures and low temperatures will also be satisfactory. This can partially explain the reason that the saturated C_p data are required in parametrization process in some cases. At temperatures close to the pseudocritical temperatures (at which C_p maximum can be obtained along supercritical isobars), the percentages of C_p^{id}/C_p decline rapidly to low values. This is the reason that the calculated heat capacities can only achieve quite low accuracy in these regions. Furthermore, with the increase of temperature, the proportions then rise up to higher than 70% even at high pressures. Obviously, the C_p data at higher temperatures are much easier to be well-described with an equation of state.

From the above, we can conclude that the residual contribution is significant in the liquid and near-pseudocritical regions, but at high temperatures, it becomes less important.³² For non-associating compounds, the dispersion contribution to the residual heat capacities is dominant.⁴³ According to this, the calculation of higher-order perturbation terms in EoS is probably required for a better description of heat capacities.³⁶ For associating compounds, the association plays the most important role in the residual heat capacities for relatively short associating chains, such as methanol.⁴⁰ However, with the increase of temperature or molecular length, the contribution of the association term decreases, while the dispersion contribution becomes more significant.

Then, as the calculations of speed of sound need both C_v and C_p , we now turn our

406 attention to the description of u . In some cases, such as ePC-SAFT for ILs,⁴⁵ PC-SAFT for
407 water and the original SAFT for hydrogen sulfide,³² the AAD of C_v and C_p are relatively
408 large, while the deviations of u are much lower. The high accuracy of u may be not because
409 of the accurate description of interactions between molecules with the EoS but arise from
410 a compensation of the errors on the C_v and C_p , since the results of u are related to the values
411 of C_p/C_v .²⁴

Table 2. Summary of the results with different equations of state as presented in literature

EoS	Substance	T/K ^a	p/MPa	Scheme	Fitted properties ^b								AAD/%							Ref.	
					p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_p	u	CP ^c	p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_v	C_v^{res}	C_p	C_p^{res}		u
Modified CPA	Alcohol	251–533	Saturation	2B	✓				✓		✓	≤1.61	≤1.68	≤3.00				≤15.3			18
	Water	260–450	Saturation	4C	✓				✓		✓	0.05	2.28	0.42				0.84			19
CPA	1-Alcohol	260–490	Saturation	2B	✓	✓			✓		✓	≤0.79	≤1.94	≤1.91				≤2.25	≤5.52		20
	Water	260–450	Saturation	4C	✓	✓						1.17	1.10	1.45				7.43			19
	1-Alcohol	260–490	Saturation	2B	✓	✓			✓		✓	≤0.95	≤1.25	≤1.75				≤5.31	≤12.6		20
	Water	280–620	Saturation	4C	✓	✓						0.75	1.16				15.1		11.0	9.05	31
	<i>n</i> -Alkane	0.5–0.9 T_c	0.01–100		✓	✓										5.50		3.24		9.31	33
	<i>n</i> -Alkane	1.06–1.1 T_c	0.1–3 p_c		✓	✓										2.02		3.46		3.43	33
	1-Alcohol	325–570	10–30	2B	✓	✓												4.07		12.5	33
		325–570	10–30	3B	✓	✓	✓		✓									0.93		14.2	33
	Ionic liquid	298–323	0.1–150	2B	✓				✓						0.95	6.55		15.8		21.0	27
SAFT	Carbon dioxide, nitrogen, oxygen, methane	80–695	0.1–20		✓	✓						≤1.58	≤1.84		≤2.20	≤5.90	48.8	≤8.50		≤5.10	32
SAFT	Hydrogen sulfide	190–510	0.1–20		✓	✓						1.80	2.11		1.60	6.10		6.90		3.70	32
		190–510	0.1–20	1A	✓	✓						2.19	2.76		1.20	4.70		9.10		8.60	32
	Water	275–695	0.1–20	2B	✓	✓						1.19	3.08		2.40	14.8		7.80		18.8	32
		275–695	0.1–20	4C	✓	✓						1.09	2.38		1.80	13.4		7.30		8.50	32
	<i>n</i> -Alkane	0.5–0.9 T_c	0.01–100		✓	✓										3.04		4.33		17.6	33
	<i>n</i> -Alkane	1.06–1.1 T_c	0.1–3 p_c		✓	✓										2.79		3.61		6.58	33
	1-Alcohol	325–570	10–30	2B	✓	✓												2.17		15.0	33
		325–570	10–30	3B	✓	✓	✓											5.59		16.0	33
	PC-SAFT	Water	280–620	Saturation	4C	✓	✓					1.46	2.14				21.8		20.6	21.1	31

EoS	Substance	T/K^a	p/MPa	Scheme	Fitted properties ^b								AAD/%								Ref.
					p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_p	u	CP ^c	p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_v	C_v^{res}	C_p	C_p^{res}	u	
CP-PC-SAFT	Halomethane	80–500	Saturation		✓	✓															23
	Haloethane	150–420	Saturation, 0.1–120		✓	✓															24
	Carbon dioxide, nitrogen, oxygen, methane	80–695	0.1–20		✓	✓						≤0.49	≤1.92		≤1.00	≤4.50	40.80	≤3.50		≤2.30	32
	Hydrogen sulfide	190–510	0.1–20		✓	✓						0.38	1.90		0.70	3.30		4.00		2.30	32
		190–510	0.1–20	1A	✓	✓						0.63	0.41		0.90	4.40		3.60		3.10	32
	Water	275–695	0.1–20	2B	✓	✓						1.18	3.92		2.90	10.8		5.60		23.9	32
		275–695	0.1–20	4C	✓	✓						1.98	0.83		1.00	11.6		9.80		3.10	32
		270–1273	30–1000	4C	✓	✓									6.03	6.31		7.09		8.97	29
	<i>n</i> -Alkane	0.5–0.9 T_c	0.01–100		✓	✓										5.25		1.46		9.93	33
	<i>n</i> -Alkane	1.06–1.1 T_c	0.1–3 p_c		✓	✓										2.74		4.21		2.32	33
	1-Alcohol	325–570	10–30	2B	✓	✓												2.91		6.91	33
		325–570	10–30	3B	✓	✓	✓											1.33		8.40	33
	Ionic liquid	298–323	0.1–150					✓							0.09	43.2		44.5		3.48	27
	Water	270–1273	30–1000	4C				✓			✓				2.62	6.14		5.42		3.91	29
	Ionic liquid	250–550	0.1					✓							≤0.33	≤7.19		≤7.48		≤4.29	28
	Alcohol, ketone, ether, ester	150–450	Saturation								✓				0.88					4.07	30
GC-PPC-SAFT	Alcohol, ketone, ether, ester	150–450	Saturation		✓	✓									1.46					8.85	30
GC-PC-SAFT	Toluene, <i>n</i> -decane, 2-methylbutane	323–533	0.1–276		✓	✓		✓							≤1.00			≤5.00		≤4.00	34
ePC-SAFT	Ionic liquid	273–413	0.1–150					✓							≤1.20	≤21.1		≤20.5		≤7.69	45

EoS	Substance	T/K ^a	p/MPa	Scheme	Fitted properties ^b								AAD/%							Ref.	
					p_{sat}	$\rho_{\text{sat,l}}$	ΔH_{vap}	ρ	C_p	u	CP ^c	p_{sat}	$\rho_{\text{sat,l}}$	ΔH_{vap}	ρ	C_v	C_v^{res}	C_p	C_p^{res}		u
Modified	1-Alcohol	248–470	0.1–12	2B	✓	✓						≤1.56	≤0.29	≤2.51	≤0.22			≤8.82		≤4.35	37
SAFT-VR-Mie	<i>n</i> -Alkane	100–413	0.1–150		✓	✓						≤1.86	≤1.46	≤4.09	≤1.65			≤4.73		≤2.60	37
	Perfluoroalkane	150–400	0.1–50		✓	✓						≤0.92	≤1.75	≤1.48	≤1.34			≤0.92		≤7.38	37
SAFT-VR-Mie	1-Alcohol	298–570	0.1–30	3B	✓	✓	✓	✓		✓		≤1.70	≤1.38	≤1.86	≤1.00			≤1.40	6.20	≤2.98	35
	Alcohol	333–421	10–60	3B	✓	✓	✓	✓		✓		≤1.55		≤2.75	≤0.63			≤1.50		≤2.92	35
	<i>n</i> -Alkane	298–403	0.1–100		✓	✓		✓		✓		≤17.7	≤1.19		≤1.17			≤7.25	≤33.3	≤2.75	36
	<i>n</i> -Alkane + 1-alcohol	303–308	0.1	3B	✓	✓	✓	✓		✓					≤0.63					≤4.96	35
SAFT-VR-SW	<i>n</i> -Alkane	298–403	0.1–100		✓	✓						≤58.2	≤3.72		≤2.30			≤8.72	≤40.3	≤16.5	36
	FAME mixture	300–700	0.1		✓	✓		✓		✓											38
soft-SAFT	<i>n</i> -Alkane	0.7–0.9 T_c	0.1–30		✓	✓						≤3.24	≤1.73					≤3.23			39
	Perfluoroalkane	0.7–0.9 T_c	0.1–30		✓	✓						≤2.71	≤1.59					≤6.21			39
	1-Achohol	300–500	0.1–30	2B	✓	✓				✓		≤3.88	≤1.63					≤5.38			39
	Water	293–500	0.1–50	4C	✓	✓				✓		2.01	0.97					1.20			39
	<i>n</i> -Alkane	1.1–1.5 T_c	--		✓	✓										≤4.26	≤55.9	≤4.61	≤24.0		40
	1-Achohol	280–573	0.1–30	2B	✓	✓												≤18.1	≤30.0		40
Crossover	<i>n</i> -Alkane	1.1–1.5 T_c	--		✓	✓														≤13.5	40
soft-SAFT	Isobutene	1.1–1.25 T_c	--		✓	✓															41
	Perfluoroethane	225–500	0.1–30		✓	✓										5.00		5.00			42
	Propane + isobutene	280–330	0.1		✓	✓										3.00					41
	<i>n</i> -Alkane + 1-alcohol	280–318	0.1	2B	✓	✓															41
SAFT-BACK	<i>n</i> -Alkane	150–675	--		✓	✓					✓					1.90		1.20		2.30	43
	<i>n</i> -Alkane mixture	300–400	0.1–300		✓	✓					✓				≤1.00					≤3.50	44

EoS	Substance	T/K ^a	p/MPa	Scheme	Fitted properties ^b								AAD/%								Ref.
					p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_p	u	CP ^c	p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_v	C_v^{res}	C_p	C_p^{res}	u	
SAFT + Cubic	Halomethane	80–500	Saturation		√	√					√										23
	Haloethane	150–420	Saturation, 0.1–120		√	√					√										24
	Water, methanol	150–1400	Saturation, 0.1–1000	4C, 3B	√	√					√										15
	Carbon dioxide, <i>n</i> -pentadecane	200–1200	Saturation, 0.1–800		√	√					√										15
	<i>n</i> -Hexane	243–503	Saturation, 0.1–1000			√					√										26
	Di-isodecyl phthalate	293–413	0.1–160								√										21
	1-Alkene	298–433	0.1–240		√	√					√										22
	<i>n</i> -Octane	299–385	0.1–1000			√					√										25
	<i>n</i> -Octane + <i>n</i> -hexadecane	313–433	0.1–120			√					√										25
	Ionic liquid	298–323	0.1–150					√							0.10	2.06		3.10		1.34	27
	Alkane, ketone, water, etc.	90–480	Saturation		√				√			0.90		1.21				0.78			46
	<i>n</i> -Hexane	243–503	Saturation, 0.1–1000		√	√															26
PHTC	FAEE	286–341	0.1–100					√							0.11			0.91		2.71	47

413 ^a Temperature and pressure ranges are only for heat capacities; ^b Properties used in parameter estimation; ^c CP: critical point.

3. Comparisons of Literature Models for Selected Compounds

Following our discussion of the general performance of each EoS, it is of relevance to comparatively evaluate the different models for specific compounds. Table 3 classifies the EoS according to specific families of compounds of *n*-alkanes, 1-alcohols, water, and other compounds (carbon dioxide and hydrogen sulfide). In Table 3, different temperature and pressure ranges studied with different EoS are shown, and this makes it hard to give an overall comparison of all models. Therefore, in this work, only the EoS used at the similar conditions will be discussed.

3.1 *n*-Alkanes

For *n*-alkanes at evaluated pressures, the accuracy of CPA, original SAFT and PC-SAFT were compared.³³ The results show that the C_v data are best described by the original SAFT, and the most accurate C_p and u results can be obtained with CPA and PC-SAFT, respectively. Overall, the original SAFT EoS has the best performance for heat capacities with the AAD of both C_v and C_p lower than 5%, while its accuracy of u is the lowest among the three EoS. In the near critical region ($T_r=1.06-1.10$), all three EoS have satisfactory accuracy for heat capacities, while the AAD of u calculated by the original SAFT is relatively large, reaching to about 6.6%. From Table 3, we can conclude that PC-SAFT gives a best balance between the heat capacities and sound velocity, but none of the three EoS can simultaneously give satisfactory descriptions of all of these properties. Therefore, some attempts, such as re-estimating the parameters and even universal constants for PC-SAFT with the C_p or u data may be of interest.⁶⁰

Two SAFT-VR models with the SW and Mie potentials were used to calculate the properties of *n*-alkanes.³⁶ The SAFT-VR-Mie EoS is superior to SAFT-VR-SW for all studied properties, especially p_{sat} and u . The high accuracy of u with the former model may be due to including u data in the parameter estimation procedure, but this method cannot improve the predictive ability for C_p remarkably. However, when a higher-order perturbation term is included in SAFT-VR-Mie, the performance for both VLE and derivative properties can be improved significantly.³⁷ Specially, although the parameters of modified SAFT-VR-Mie are only fitted to p_{sat} and $\rho_{\text{sat},l}$, the AAD of u can still be lower than 2.6%.

The soft-SAFT EoS can give rather good performance for C_v and C_p , while the deviations of their residual values are quite large.⁴⁰ Coupling with the RG approach, a crossover soft-SAFT EoS was also used to calculate the heat capacities of *n*-alkanes. The accuracy of C_v^{res} and C_p^{res} at $T_r=1.1-1.5$ with this crossover EoS is obviously improved, while the AAD of C_v^{res} in the vicinity of the critical point ($T_r=1.1$) can still reach 11% for propane and 38% for heptane, respectively. Such results indicate that a crossover equation may increase the accuracy of residual heat capacities, but the basic performance of soft-SAFT may still pose some limitations.

Finally, it can be seen that the SAFT-BACK EoS can describe well the heat capacities and sound velocity of *n*-alkanes in both subcritical and supercritical regions, giving a best performance for this kind of compounds among these EoS.

3.2 1-Alcohols

For the properties of 1-alcohols, the original CPA and the modified CPA with 5-parameter α function were tested.²⁰ A two-site association scheme (2B) was chosen, and the parameters of two models were obtained from VLE properties, heat capacity, and critical properties. In Table 3, we can see that the modified CPA shows similar performance for VLE properties compared to the original CPA and much better performance for C_p and C_p^{res} . This indicates that a more flexible α function can increase the correlation ability of this type of EoS for heat capacities. In addition, the original CPA shows lower AAD of the saturated liquid density ($\rho_{\text{sat,l}}$) for short-chain alcohols than the modified model, while the deviations increase with the increase of carbon numbers.

Then, the performance of the original CPA, the original SAFT and PC-SAFT at pressures up to 30 MPa with two different association schemes is compared.³³ The best balance between C_p and u is given by PC-SAFT, which gives an AAD of u lower than 9% with both the 2B and 3B schemes. Generally, the three models using the 3B scheme have lower AAD of C_p but higher AAD of u compared to 2B. The only exception is with original SAFT for C_p , with which the 2B model provides higher accuracy. In addition, it should be noticed that the original CPA with the 3B scheme provides a rather satisfactory performance on C_p , with the AAD of 0.9%. This may be because the parameters of the EoS are correlated not only to the VLE properties, but also to the C_p data. However, as mentioned by de Villiers et al.,³³ the same parameter regression strategy applied to the original SAFT and PC-SAFT cannot give the same improvements compared to CPA. In conclusion, it should be realized that although a more rigorous association scheme (3B) for 1-alcohols is used, the higher

accuracy of the calculated C_p and u can still not be obtained simultaneously, indicating the limitations of the EoS. Furthermore, it can be seen that one parameter regression strategy for different EoS might have different effects on properties of fluids, thus the selection of the most suitable fitting procedure shall depend on the equation of state used, when going beyond vapor pressure and liquid density

By including VLE, compressed ρ and u data in the parameter estimation, SAFT-VR-Mie provides an excellent representation of these properties.³⁵ Unlike n -alkanes, both the calculated C_p and C_p^{res} for 1-alcohols have rather low deviations from the experimental data, and the overall performance for u and C_p is better than PC-SAFT. With model parameters only correlated to VLE properties, the modified SAFT-VR-Mie with a higher-order perturbation term can still give acceptable performance for C_p and u , with methanol for C_p being the only exception.³⁷ But it should be pointed out that the calculated C_p for methanol with original SAFT-VR-Mie in ref. 16 is only at one point, while the results with the modified EoS are obtained over wider temperature and pressure ranges. The performance of soft-SAFT with two different parametrization strategies⁴⁰ is also compared in Table 3. The soft-SAFT EoS seems to have worse accuracy of C_p than the most aforementioned EoS, no matter whether the C_p data are used in the parametrization process.

3.3 Water

Compared with the original CPA EoS, the modified CPA proposed by Palma et al. gives much higher accuracy for the C_p for water, while the AAD of $\rho_{\text{sat,l}}$ increases as the data of this property are not included in the fitting procedure.¹⁹ In Table 3 are also presented and

compared the saturated properties of water obtained from the original CPA and PC-SAFT at reduced temperatures up to 0.96.³¹ Both EoS can accurately reproduce the VLE data. The original CPA is superior to PC-SAFT for all the investigated properties, especially for the residual heat capacities and speed of sound. Nevertheless, both CPA and PC-SAFT cannot give satisfactory results of these second-order derivative properties, and the C_v and u data are even not qualitatively described. Finally, the VTPR EoS gives similar AAD of C_p compared to the modified CPA.⁴⁶

For water at evaluated pressures up to 20 MPa, two different association schemes (2B and 4C) with the original SAFT and PC-SAFT were tested by estimating its thermophysical properties.³² The original SAFT with the 4C scheme has better performance for all the studied properties compared to the 2B scheme, while the descriptions of heat capacities and sound velocity are still unsatisfactory. The PC-SAFT EoS with the 4C scheme shows higher accuracy for C_v and u than with the original SAFT. Furthermore, PC-SAFT provides higher AAD of heat capacities with 4C scheme than with 2B scheme. Therefore, for water, a similar conclusion as for 1-alcohols' can be made: A more rigorous association scheme is not a sufficient condition for better descriptions of thermophysical properties, as the accuracy of the calculated results is also deeply influenced by the selected EoS itself. Considering the 4C scheme, the performance of PC-SAFT and CP-PC-SAFT for water was compared over a wide temperature and pressure ranges ($T=270\text{--}1273$ K, $p=30\text{--}1000$ MPa).²⁹ It can be concluded that the latter is superior to the former for all properties at the compressed regions, while CP-PC-SAFT is a worse estimator than PC-SAFT for saturated

density near the critical point. Finally, the soft-SAFT EoS with parameters fitted to VLE and C_p reproduces rather well these properties, with the AAD lower than 2.1%.³⁹ However, a wider temperature range still needs to be considered for soft-SAFT in order to compare its performance for C_p with the original SAFT and PC-SAFT.

3.4 Other Compounds

Except for *n*-alkanes, 1-alcohols and water, the calculated heat capacities of some other fluids are also compared using various equations of state. The properties of carbon dioxide, nitrogen, oxygen and methane were estimated with the original SAFT and PC-SAFT models,³² and the results demonstrate that the latter model has better performance for most considered properties. The only exception is for saturated liquid density, with the AAD of 1.9% for PC-SAFT and 1.8% for SAFT, respectively.

Using the original SAFT and PC-SAFT, the properties of hydrogen sulfide were calculated with two different association schemes.³² It can be seen that PC-SAFT is superior to the original SAFT for all properties no matter whether the association is considered or not. As for the effect of the association scheme, compared with the non-associating model, the original SAFT EoS with the 1A scheme shows a small effect on VLE properties and compressed ρ . The AAD using the 1A scheme provides better accuracy of C_v and worse accuracy of C_p and u than without considering the association contribution. Unlike the original SAFT EoS, PC-SAFT combined with the 1A scheme of hydrogen sulfide has similar performance for most properties compared to using the non-associating model, even though more parameters are involved in the former one.

For the performance for ILs, five EoS have been tested in the literature.^{27,28,45} Different contributions to Helmholtz energy are considered in each model: For CPA, ILs are regarded as associating compounds with 2B scheme. Five positive sites and five negative sites are considered in the association contribution of PC-SAFT. No association term is included in the SAFT + Cubic, CP-PC-SAFT, and ePC-SAFT EoS for ILs, while the Coulomb interaction contribution is considered in the last model. Overall, at the pressures up to 150 MPa, SAFT + Cubic shows the best performance for both heat capacities and speed of sound, and PC-SAFT and CPA give the lowest accuracy of heat capacity and speed of sound, respectively. The description of heat capacities with ePC-SAFT is also not satisfactory, with the AAD lower than 21%. It is worth mentioning that, with comparison to CP-PC-SAFT, the performance of ePC-SAFT for ILs at the atmospheric pressure is still worse.²⁸

Some conclusions are drawn from the above discussion. First, although the PC-SAFT EoS may not give the best results in some cases, it exhibits a better overall performance for investigated properties (heat capacities, speed of sound, VLE, and compressed density) and fluids than the original CPA and SAFT. Second, a more rigorous association scheme may not always lead to a better description of thermophysical properties, as the accuracy depends a lot on the overall model (EoS) considered. Finally, the parametrization method where C_p or u data are used in the parameter estimation cannot always improve the accuracy of calculated second-order derivative properties. On the other hand, we can state based on the literature studies that for the models of VTPR, CPA, and SAFT-VR-Mie, very good results are obtained by including the C_p or u data in the parameter estimation procedure.

Table 3. Summary of the results for several compounds and families of compounds

Substance	EoS	T/K ^a	p/MPa	scheme	Fitted properties ^b								AAD/%							Ref.	
					p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_p	u	CP ^c	p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_v	C_v^{res}	C_p	C_p^{res}		u
<i>n</i> -Alkane	CPA	0.5–0.9 T_c	0.01–100		√	√										5.50		3.24		9.31	33
		1.06–1.1 T_c	0.1–3 p_c		√	√										2.02		3.46		3.43	33
	SAFT	0.5–0.9 T_c	0.01–100		√	√										3.04		4.33		17.6	33
		1.06–1.1 T_c	0.1–3 p_c		√	√										2.79		3.61		6.58	33
	PC-SAFT	0.5–0.9 T_c	0.01–100		√	√										5.25		1.46		9.93	33
		1.06–1.1 T_c	0.1–3 p_c		√	√										2.74		4.21		2.32	33
	Modified	100–413	0.1–150		√	√					≤1.86	≤1.46	≤4.09	≤1.65				≤4.73		≤2.60	37
	SAFT-VR-Mie																				
	SAFT-VR-Mie	298–403	0.1–100		√	√		√		√	≤17.7	≤1.19		≤1.17				≤7.25	≤33.3	≤2.75	36
	SAFT-VR-SW	298–403	0.1–100		√	√					≤58.2	≤3.72		≤2.30				≤8.72	≤40.3	≤16.5	36
	soft-SAFT	0.7–0.9 T_c	0.1–30		√	√					≤3.24	≤1.73						≤3.23			39
		1.1–1.5 T_c	--		√	√										≤4.26	≤55.9	≤4.61	≤24.0		40
	Crossover	1.1–1.5 T_c	--		√	√											≤38.2		≤13.5		40
	soft-SAFT																				
	SAFT-BACK	150–675	--		√	√				√						1.90		1.20		2.30	43
1-Alcohol	Modified CPA	260–490	Saturation	2B	√	√			√	√	≤0.79	≤1.94	≤1.91				≤2.25	≤5.52		20	
	CPA	260–490	Saturation	2B	√	√			√	√	≤0.95	≤1.25	≤1.75				≤5.31	≤12.6		20	
		325–570	10–30	2B	√	√												4.07		12.5	33
		325–570	10–30	3B	√	√	√		√									0.93		14.2	33
	SAFT	325–570	10–30	2B	√	√												2.17		15.0	33
		325–570	10–30	3B	√	√	√											5.59		16.0	33
	PC-SAFT	325–570	10–30	2B	√	√												2.91		6.91	33
		325–570	10–30	3B	√	√	√											1.33		8.40	33

Substance	EoS	T/K^a	p/MPa	scheme	Fitted properties ^b								AAD/%								Ref.
					p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_p	u	CP ^c	p_{sat}	$\rho_{sat,l}$	ΔH_{vap}	ρ	C_v	C_v^{res}	C_p	C_p^{res}	u	
Water	Modified	248–470	0.1–12	2B	√	√						≤1.56	≤0.29	≤2.51	≤0.22			≤8.82		≤4.35	37
	SAFT-VR-Mie																				
	SAFT-VR-Mie	298–570	0.1–30	3B	√	√	√	√		√		≤1.70	≤1.38	≤1.86	≤1.00			≤1.40	6.20	≤2.98	35
	soft-SAFT	300–500	0.1–30	2B	√	√			√			≤3.88	≤1.63					≤5.38			39
		280–573	0.1–30	2B	√	√												≤18.1	≤30.0		40
	Modified CPA	260–450	Saturation	4C	√				√		√	0.05	2.28	0.42				0.84			19
	CPA	260–450	Saturation	4C	√	√						1.17	1.10	1.45				7.43			19
		280–620	Saturation	4C	√	√						0.75	1.16				15.1		11.0	9.05	31
	VTPR	273–373	Saturation		√				√			0.55		0.85				0.93			46
	SAFT	275–695	0.1–20	2B	√	√						1.19	3.08		2.40	14.8		7.80		18.8	32
		275–695	0.1–20	4C	√	√						1.09	2.38		1.80	13.4		7.30		8.50	32
	PC-SAFT	280–620	Saturation	4C	√	√						1.46	2.14				21.8		20.6	21.1	31
		275–695	0.1–20	2B	√	√						1.18	3.92		2.90	10.8		5.60		23.9	32
		275–695	0.1–20	4C	√	√						1.98	0.83		1.00	11.6		9.80		3.10	32
		270–1273	30–1000	4C	√	√									6.03	6.31		7.09		8.97	29
Carbon dioxide, nitrogen, oxygen, methane	CP-PC-SAFT	270–1273	30–1000	4C							√				2.62	6.14		5.42		3.91	29
	soft-SAFT	293–500	0.1–50	4C	√	√			√			2.01	0.97					1.20			39
	SAFT	80–695	0.1–20		√	√						≤1.58	≤1.84		≤2.20	≤5.90	48.8	≤8.50		≤5.10	32
	PC-SAFT	80–695	0.1–20		√	√						≤0.49	≤1.92		≤1.00	≤4.50	40.8	≤3.50		≤2.30	32
	SAFT	190–510	0.1–20		√	√						1.80	2.11		1.60	6.10		6.90		3.70	32
Hydrogen sulfide		190–510	0.1–20	1A	√	√						2.19	2.76		1.20	4.70		9.10		8.60	32
	PC-SAFT	190–510	0.1–20		√	√						0.38	1.90		0.70	3.30		4.00		2.30	32
		190–510	0.1–20	1A	√	√						0.63	0.41		0.90	4.40		3.60		3.10	32

Substance	EoS	T/K ^a	p/MPa	scheme	Fitted properties ^b										AAD/%					Ref.	
					p_{sat}	$\rho_{\text{sat,l}}$	ΔH_{vap}	ρ	C_p	u	CP ^c	p_{sat}	$\rho_{\text{sat,l}}$	ΔH_{vap}	ρ	C_v	C_v^{res}	C_p	C_p^{res}		u
Ionic liquid	CPA	298–323	0.1–150	2B	√			√							0.95	6.55		15.8		21.0	27
	PC-SAFT	298–323	0.1–150					√							0.09	43.2		44.5		3.48	27
	SAFT + Cubic	298–323	0.1–150					√							0.10	2.06		3.10		1.34	27
	ePC-SAFT	273–413	0.1–150					√							≤1.20	≤21.1		≤20.5		≤7.69	45
	CP-PC-SAFT	250–550	0.1					√							≤0.33	≤7.19		≤7.48		≤4.29	28

562 ^a Temperature and pressure ranges are only for heat capacities; ^b Properties used in parameter estimation; ^c CP: critical point.

4. Modelling Results with CPA and PC-SAFT

In order to carry out a fair and comprehensive comparison of two of the most well-known models, we have considered CPA and PC-SAFT and performed in this work a systematic evaluation of them for heat capacities for several associating and non-associating compounds. The parameters of CPA and PC-SAFT for the studied fluids are, in most cases, obtained from literature and they are respectively presented in Tables S1 and S2 in Support Information. For the compounds for which no available parameters were found in the literature, their parameters were determined based on vapor pressure and saturated liquid density data from the DIPPR correlations⁶¹ at reduced temperatures from 0.5 to 0.9. The ideal gas isobaric heat capacity data required in the calculations are also obtained from the DIPPR correlations with the uncertainties mostly lower than 1% (reported by DIPPR).

4.1 Compressed Region

Table 4 presents the AAD of calculated heat capacities, dp/dV , and dp/dT compared to the values from NIST⁵⁸ for some non-associating fluids at pressures up to 100 MPa. From Table 4, it can be seen that, in general, the PC-SAFT EoS has better performance for both C_v and C_p with the overall AAD of 1.2% and 3.2%, respectively (compared to 2.3 and 4.3% for CPA). It can also be noted that, for both models, the AAD of C_p are commonly lower than those of C_v over a wide pressure range, which is consistent with the literature results from Tables 2 and 3. The other two derivative properties in eq 2, i.e. dp/dV and dp/dT are also calculated and presented in Table 4. We can see that the AAD of these two properties with both CPA and PC-SAFT are rather high (10-15%), with PC-SAFT performing better.

Such better descriptions of dp/dV with PC-SAFT may be attributed to the more appropriate co-volume values established by SAFT models than by the cubic equations.^{62,63} The largest deviation of the calculated dp/dV and dp/dT observed in Table 4 is the AAD of dp/dV for 2-methylpentane with CPA, reaching to 44%, while the AAD of C_p for this substance with CPA is only 3.6%. This is actually not surprising since the average ratio of C_p^{id}/C_p is higher than 80% at the investigated conditions, and this means that the accuracy of the calculated heat capacity depends more on the ideal gas contribution, as we have discussed in the previous section.

Table 4. AAD of heat capacities for non-associating compounds with CPA and PC-SAFT

Compound	T/K	p/MPa	CPA/%				PC-SAFT/%				No. of points
			C_p	C_v	dp/dV	dp/dT	C_p	C_v	dp/dV	dp/dT	
Methane	100–400	0.1–100	0.86	3.25	6.71	4.64	1.44	2.76	3.16	3.07	134
Ethane	200–500	0.1–70	1.46	4.67	9.70	9.11	1.44	4.00	5.02	5.12	105
Propane	200–500	0.1–100	3.06	4.18	10.7	12.4	1.04	4.93	8.12	9.29	147
Butane	250–550	0.1–65	1.95	4.71	9.41	13.5	1.24	4.11	8.90	9.08	98
Pentane	300–600	0.1–100	1.40	4.63	11.7	16.7	0.58	3.25	10.2	11.8	147
Hexane	300–600	0.1–100	2.07	4.01	13.7	18.3	0.64	3.09	9.69	12.0	147
Heptane	300–600	0.1–100	2.26	3.94	15.6	20.7	0.52	2.71	12.7	14.0	147
Octane	300–600	0.1–100	2.29	3.61	18.4	20.3	0.55	2.04	12.3	13.7	147
Nonane	250–550	0.1–100	3.22	4.76	23.0	25.9	0.54	3.44	15.1	18.4	136
Decane	350–650	0.1–100	1.66	4.36	20.0	23.7	0.63	2.05	13.7	15.4	147
Dodecane	400–700	0.1–100	2.25	2.93	22.7	23.8	1.42	0.96	11.3	14.2	147
Isobutane	250–550	0.1–35	1.76	3.91	13.5	14.2	1.18	3.31	8.82	7.72	56
2-Methylpentane	250–550	0.1–100	3.56	4.20	44.2	7.76	0.68	4.14	13.2	15.7	147
Cyclohexane	400–700	0.1–80	2.05	2.71	11.1	16.9	1.51	1.77	11.3	10.7	119
Propylene	200–500	0.1–100	2.41	5.68	12.0	11.7	1.14	5.20	6.36	8.61	147
Benzene	300–600	0.1–75	3.23	6.12	11.6	19.7	1.95	5.18	9.14	12.7	103
Toluene	400–700	0.1–100	1.66	3.56	11.2	17.1	0.78	2.33	10.2	10.3	147
Carbon dioxide	250–550	0.1–100	3.46	5.46	9.51	7.78	4.42	3.63	4.16	4.62	147

Compound	T/K	p/MPa	CPA/%				PC-SAFT/%				No. of points
			C_p	C_v	dp/dV	dp/dT	C_p	C_v	dp/dV	dp/dT	
Nitrogen	100–400	0.1–100	1.72	4.56	5.98	4.11	1.47	3.07	2.18	2.45	147
Overall			2.25	4.26	15.1	15.3	1.20	3.22	9.32	10.7	

593 Figure 2 compares the four calculated derivative properties for dodecane from the
 594 models and the values from NIST. It can be seen that the PC-SAFT EoS tends to
 595 overestimate dp/dV , while the CPA EoS usually underestimates this property at high
 596 pressures. As for dp/dT , both EoS give lower values than the values from NIST with PC-
 597 SAFT being more accurate than CPA. It can also be observed in Figure 2c that both CPA
 598 and PC-SAFT show satisfactory performance for the calculation of C_v , again with PC-
 599 SAFT being the better of the two. In Figure 2d, Similar results are also obtained for C_p , for
 600 which the PC-SAFT EoS shows higher accuracy than CPA, especially at low temperatures.
 601 For supercritical fluids, the tendency of C_p can be well described by CPA and PC-SAFT,
 602 although there are some deviations at the pseudocritical temperatures. However, both
 603 models fail to capture the C_v maxima at the supercritical conditions, and these results can
 604 also be obtained for other compounds, such as toluene, as shown in Figure 3. In fact, the
 605 failure in the description of C_v maxima is quite common for analytical models.⁶⁴ From
 606 Figures 2 and 3, we can conclude again that the PC-SAFT EoS has better performance than
 607 CPA for all four derivative properties for non-associating fluids.

(a)

(b)

(c)

(d)

Figure 2. Derivative properties of dodecane with CPA and PC-SAFT: (a) dp/dV , (b) dp/dT ,
(c) C_v , (d) C_p . Symbols:⁵⁸ (●) 400 K, (▲) 500 K, (◆) 600 K, (■) 700 K; (—) CPA (red), (—
—) PC-SAFT (blue).

(a)

(b)

(c)

(d)

Figure 3. Derivative properties of toluene with CPA and PC-SAFT: (a) dp/dV , (b) dp/dT ,
(c) C_v , (d) C_p . Symbols:⁵⁸ (●) 400 K, (▲) 500 K, (◆) 600 K, (■) 700 K; (—) CPA (red), (—
—) PC-SAFT (blue).

The relative deviations (RDs) of heat capacities for pentane with the two EoS are shown
in Figures 4 and 5, in which the deviations in liquid and supercritical phases are considered
separately. It is obvious that the two EoS can give lower deviations of both C_v and C_p at

617 supercritical conditions than at subcritical ones. This is because, as shown in Figure 1, the
618 percentage of C_p^{id}/C_p is larger at higher temperatures. Furthermore, the CPA EoS tends to
619 underestimate the liquid C_p , and deviations increase with the temperature until positive
620 deviations may be obtained in the supercritical regions. On the other hand, the RDs of C_v
621 show that this property is typically overestimated by the two EoS for liquid pentane, and
622 the deviations reduce with increasing temperature. Finally, it should be emphasized that,
623 although the above results summarized in Figures 4 and 5 are for pentane, they are actually
624 almost general for most compounds studied in this work.

625
626 Figure 4. Relative deviations of heat capacities with CPA for liquid pentane: (●) C_v (red),
627 (◆) C_p (blue) and supercritical pentane: (▲) C_v (green), (■) C_p (orange).

Figure 5. Relative deviations of heat capacities with PC-SAFT for liquid pentane: (●) C_v (red), (◆) C_p (blue) and supercritical pentane: (▲) C_v (green), (■) C_p (orange).

Next, the heat capacities of some associating fluids are also calculated using CPA and PC-SAFT, and the results are shown in Table 5. Overall, unlike the results for non-associating compounds, the AAD of heat capacities for fluids in Table 5 with CPA are lower than with PC-SAFT. The accuracy of dp/dT with the CPA EoS is similar to that with PC-SAFT, but PC-SAFT is more accurate for the calculation of dp/dV . According to eq 2, it can be realized that the accuracy of C_p is determined by C_v , dp/dT , and dp/dV . Therefore, in some cases, the performance for C_v , dp/dT , and dp/dV may not be satisfactory, but the high accuracy of C_p can still be obtained. For example, the AAD of C_v , dp/dT , and dp/dV for hydrogen sulfide with CPA and the three-sites association scheme is higher than with PC-SAFT, but the CPA provides a better description of C_p . This is because the deviations of three properties (C_v , dp/dT , and dp/dV) are somewhat counterbalanced, leading to a

lower AAD of 1.4% with CPA compared to an AAD of 3.5% with PC-SAFT. In addition,
 the equations of state with different association schemes proposed by Huang and Radosz⁹
 are also considered in Table 5. As we have mentioned before, a more rigorous scheme (in
 the terminology used by Huang and Radosz) may not always give better performance for
 the heat capacities. For example, in Table 5, although the accuracy of C_v for water with
 both CPA and PC-SAFT coupled with the 4C scheme is higher than that with the 3B scheme,
 the performance for C_p with the more rigorous scheme for water (4C) deteriorates.
 Specially, hydrogen sulfide is considered as both inert compound and associating
 compound with three different schemes. Although less parameters are included, both
 models without considering the association still can give good performance for heat
 capacities, with the AAD of 3% or so, and this is consistent with the results in ref. 32.
 Furthermore, among the eight scenarios, CPA without the association shows the lowest
 AAD, which is 2.8%, for C_v . Figure 6 shows the derivative properties of water with two
 EoS at 400 K. From Figures 6a and 6b, we can observe that the calculated dp/dV and dp/dT
 with the 3B scheme show the largest deviations from the NIST values among the three
 schemes, and such deviations decrease significantly when the 4C scheme is used. This
 result is also shown in Table 5, in which the AAD of dp/dT for water with PC-SAFT and
 3B scheme is even higher than 96%, while the AAD with 4C scheme can reduce to 23%.
 Furthermore, in Figures 6a and 6b, each model with different association schemes gives
 the same slope of dp/dV or dp/dT curves. The PC-SAFT EoS can give better description of
 the slopes compared to the results from NIST than CPA. As for the heat capacities, the CPA

663 EoS with the 4C and 2B schemes respectively describes the C_v and C_p data best among the
 664 six calculation scenarios. Surprisingly, the PC-SAFT EoS with 4C scheme just slightly
 665 improves the results of C_v compared with the EoS with 3B scheme, and even has a worse
 666 performance for C_p . It should be emphasized that the performance of CPA with the 4C
 667 scheme for heat capacities seems quite satisfactory in Figure 6 at $T=400$ K, but the AAD
 668 of C_v and C_p for water over a wider temperature range are relatively large, reaching to 5.4%
 669 and 7.9%, respectively.

670 Table 5. AAD of heat capacities for associating compounds with CPA and PC-SAFT

Compound	T/K	p/MPa	Scheme	CPA/%				PC-SAFT/%				No. of points
				C_p	C_v	dp/dV	dp/dT	C_p	C_v	dp/dV	dp/dT	
Water	300–700	0.1–100	2B	3.41	10.3	38.6	72.8	11.9	12.2	49.2	49.4	189
			3B	4.97	12.6	46.3	80.5	8.11	15.3	82.6	96.8	189
			4C	5.37	7.92	12.8	28.4	9.68	11.4	9.08	22.9	189
Hydrogen sulfide	200–500	0.1–100		3.07	2.82	9.41	5.68	3.14	2.98	5.08	1.72	132
			1A	3.37	17.1	7.03	14.2	4.09	5.73	4.60	1.76	132
			2B	0.97	13.3	5.25	11.6	2.59	2.96	4.69	1.62	132
			3B	1.40	8.81	5.19	6.92	3.45	4.21	4.55	1.86	132
Ammonia	250–550	0.1–100	3B	2.59	5.21	6.56	6.84	5.68	10.1	5.74	4.14	147
			4B	2.39	5.82	6.73	7.68	5.65	12.6	5.40	5.22	147
Methanol	300–600	0.1–100	2B	7.83	5.60	6.15	11.0	12.2	12.5	8.92	12.2	147
			3B	5.24	8.07	18.2	14.5	4.61	17.9	17.7	29.2	147
Overall ^a				3.77	7.64	11.0	15.5	6.17	11.7	9.28	15.7	

671 ^a Only the most rigorous schemes (bold) for each compound are included in the overall
 672 AAD.

(a)

(b)

(c)

(d)

Figure 6. Derivative properties of water with CPA and PC-SAFT at $T=400$ K: (a) dp/dV ,
 (b) dp/dT , (c) C_v , (d) C_p . (●) NIST values,⁵⁸ (····) CPA-2B (pink), (— · —) PC-SAFT-2B
 (brown), (—) CPA-3B (red), (— —) PC-SAFT-3B (blue), (— · — ·) CPA-4C (orange), (— · —) PC-
 SAFT-4C (green).

In the previous section, it is mentioned that some EoS cannot give good performance for
 both the heat capacity and speed of sound. As seen from the results of Table 5, PC-SAFT

cannot always provide good descriptions of both C_v and C_p . To analyze this further, we have considered the case of ammonia. Table 6 provides six sets of parameters for PC-SAFT for ammonia, and Table 7 gives the results of VLE and derivative properties using these parameter sets, which were fitted to the vapor pressure and saturated liquid density data at $T_r=0.5-0.9$ in this work. The calculated VLE and derivative properties are compared with the values from DIPPR⁶¹ and NIST⁵⁸, respectively. The results show that, with sets 1–3 (in which the association volume κ^{AB} increases) with 3B scheme, the AAD of VLE and C_p decrease, while the AAD of C_v increases. Similar results can also be observed when the 4B scheme is used. This indicates that no matter which association scheme and parameter set are adopted, the PC-SAFT EoS cannot give both good descriptions of both C_v and C_p for ammonia.

Table 6. PC-SAFT parameters for ammonia

Set	Scheme	m	σ (Å)	ε/k (K)	ε^{AB}/k (K)	κ^{AB}
1	3B	2.8587	2.1923	124.04	1084.5	0.4435
2		3.3790	2.0738	123.62	835.2	0.9133
3		3.8627	1.9840	123.65	580.1	1.9543
4	4B	3.2723	2.0906	120.93	933.6	0.4567
5		3.7231	2.0044	121.23	706.1	0.8810
6		4.0257	1.9538	121.47	536.9	1.4935

Table 7. AAD of VLE and derivative properties for ammonia with PC-SAFT at

$T=200-500$ K and $p=0.1-100$ MPa

Set	Scheme	AAD/%					
		p_{sat}	$\rho_{\text{sat},l}$	C_p	C_v	dp/dV	dp/dT
1	3B	1.04	0.22	8.18	5.90	9.83	6.97

Set	Scheme	AAD/%					
		p_{sat}	$\rho_{\text{sat,l}}$	C_p	C_v	dp/dV	dp/dT
2	4B	0.41	0.14	5.68	10.12	5.74	4.14
3		0.05	0.09	4.32	13.96	6.28	8.02
4		0.72	0.11	7.63	9.04	8.10	5.22
5		0.24	0.08	5.65	12.60	5.40	5.22
6		0.04	0.06	4.68	14.99	6.68	8.85

In addition to methanol presented in Table 5, the isobaric heat capacities of other alcohols were also calculated with CPA and PC-SAFT. The deviations of the calculated C_p from the experimental data^{65–80} are shown in Table 8. Two association schemes (2B and 3B) are considered with the two EoS. The results show that the different schemes with CPA may affect the C_p calculation for each compound, but the effect on the overall performance is small. Compared to CPA, PC-SAFT provides a slightly lower AAD with 3B scheme (5.0%) and almost an identical AAD with 2B scheme (5.9%). Therefore, we can conclude that, the two EoS with two different association schemes have the similar overall accuracy of C_p for alcohols. Figure 7 shows the relative deviations of C_p with the two EoS and two schemes for pentanol at atmospheric pressure. We can see that all four scenarios have almost identical and low deviations in the gas region, with an average deviation about 2%, and the RDs in the liquid region show similar distributions. This conclusion can also be given from Figure 8, in which the calculated C_p for 2-butanol is compared with the experimental data from refs 68 and 78 at $p=0.1$ MPa. The identical C_p results at the gas state can be observed in Figure 8, since the four curves nearly overlap in this region.

Table 8. AAD of C_p for alcohols with CPA and PC-SAFT

Compound	T/K	p/MPa	CPA/%		PC-SAFT/%		No. of Points	Ref.
			2B	3B	2B	3B		
Ethanol	265–591	0.1–25.1	11.3	11.9	1.90	4.09	80	65–68
Propanol	154–603	0.1	6.12	6.18	6.36	6.34	64	68, 69
Butanol	188–603	0.1–50	4.59	5.09	6.09	7.11	119	68, 70–72
Pentanol	200–574	0.1	4.19	4.12	8.12	3.43	65	68, 69
Hexanol	326–571	2–30	3.88	1.24	1.94	1.31	66	73
Heptanol	326–571	2–30	4.58	1.93	6.48	3.00	68	73
Octanol	326–571	2–30	6.29	5.54	2.85	2.47	66	73
Nonanol	281–330	0.1	4.54	11.0	11.2	10.9	24	74
Decanol	326–571	2–30	2.63	3.12	2.03	3.37	68	73
2-Propanol	253–573	0.1–40	7.26	8.47	8.27	8.27	167	75–77
2-Butanol	188–583	0.1–25	10.3	8.57	14.9	10.3	84	68, 78, 79
iso-Butanol	298–493	0.1–4	5.24	4.92	7.40	3.49	97	69, 77
tert-Butanol	353–453	1–4	2.46	2.35	1.25	1.36	62	77
tert-Pentanol	298–369	0.1	1.92	1.55	1.38	1.22	73	80
Overall			5.67	5.57	5.90	4.99

709

710 Figure 7. Relative deviations of C_p with CPA and PC-SAFT for pentanol at $p=0.1$ MPa: ($\circ$)711 CPA-2B (red), (Δ) PC-SAFT-2B (blue), ($\diamond$) CPA-3B (orange), ($\square$) PC-SAFT-3B (green).

Figure 8. C_p of 2-butanol with CPA and PC-SAFT at $p=0.1$ MPa: ($\circ$) Experiment^{68,78}, (—) CPA-2B (red), (---) PC-SAFT-2B (blue), (-.-) CPA-3B (orange), (-.-.-) PC-SAFT-3B (green).

Figure 9 shows the relative deviations of C_p and residual C_p with PC-SAFT and the 3B scheme for butanol at atmospheric pressure. In the liquid phase, the RD values of C_p are almost half of the RD of C_p^{res} , while the differences between the RD values of C_p and C_p^{res} become much larger for the gaseous butanol. This is because the percentage of C_p^{res} in C_p is about 50% for the liquid butanol, while this value decrease to lower than 10% in the gas phase. The similar results can also be observed for water in Figure 1. In fact, as the contribution of the association interaction to C_p is noticeable in the liquid phase, the ratio of C_p^{id}/C_p for associating fluids is generally lower than that for non-associating substances, while it becomes much higher in the gaseous region with the break of hydrogen bond, leading to a dominant contribution from ideal gas C_p . This can also explain why CPA and

PC-SAFT with both 2B and 3B schemes show the same and good performance on C_p at the gas condition in Figures 7 and 8.

Figure 9. Relative deviations of C_p and C_p^{res} with PC-SAFT and 3B scheme for butanol at $p=0.1$ MPa: (■) C_p (blue), (■) C_p^{res} (orange).

4.2 Critical Isotherms

The derivative properties at reduced temperature $T_r=T/T_c=1$ and pressures up to $2p_c$ are also estimated with CPA and PC-SAFT in this work, and the AAD compared to the NIST values⁵⁸ are shown in Table 9. It should be noted that, for a fair comparison, the above critical temperature and pressure for NIST values are from experiments (the “real” T_c and p_c), while the critical properties for each model are calculated by the model itself. Only some of previously studied compounds from Tables 4 and 5 are considered, as not all the correlations from NIST can be used for fluids near the critical points. From Table 9, it is obvious that CPA is somewhat more accurate on the estimation of heat capacities at critical

isotherms with the overall AAD of 6.7% (compared to 7.8% for PC-SAFT), while PC-SAFT gives lower deviations of dp/dV and dp/dT with the overall AAD of 24% and 7.2%, respectively. The calculated results for dodecane and toluene are plotted in Figures 10 and 11, respectively, in which the dp/dV is given as $\ln(-dp/dV)$ for a clear illustration at the gas condition. On the basis of Figures 10 and 11, the following conclusions can be obtained: First, compared with CPA, there is a superiority of PC-SAFT in dp/dV and dp/dT at the liquid state. Second, neither of the two EoS can capture the C_v divergence at the critical point. Third, the performance of the two EoS for C_p is quite similar at $T_r=1$, and both models give rather satisfactory descriptions outside of the critical regions, while the deviations become much larger in the vicinity of the critical points.

Table 9. AAD of heat capacities with CPA and PC-SAFT at $T_r=1$

Compound	Scheme	CPA/%				PC-SAFT/%				No. of points
		C_p	C_v	dp/dV	dp/dT	C_p	C_v	dp/dV	dp/dT	
Methane		6.89	5.90	20.5	8.11	11.4	4.90	14.7	3.05	91
Butane		4.80	2.35	28.1	9.41	5.82	1.75	19.7	3.38	75
Dodecane		4.56	0.97	38.4	9.74	4.57	1.56	33.1	14.4	36
Isobutane		5.83	2.38	26.4	8.89	6.94	2.03	19.7	3.11	73
Toluene		6.00	1.64	28.6	7.56	6.47	2.04	22.4	8.07	82
Carbon dioxide		8.59	8.81	25.6	8.12	7.20	13.3	18.2	3.92	74
Nitrogen		7.32	6.73	20.2	7.91	11.5	5.79	14.8	3.31	67
Water	2B	6.95	12.0	42.4	12.8	11.9	7.96	103	33.1	88
	3B	8.49	13.6	49.3	16.2	16.3	20.7	108	35.5	88
	4C	8.07	6.16	48.5	19.3	6.73	8.74	53.4	20.3	88
Overall ^a		6.66	4.61	29.3	10.1	7.79	5.27	24.4	7.24	

^a Only the 4C scheme for water is included in the overall AADs.

Figure 10. Derivative properties of dodecane with CPA and PC-SAFT at $T_r=1$: (a) dp/dV ,

(b) dp/dT , (c) C_v , (d) C_p . (○) NIST values,⁵⁸ (—) CPA (red), (---) PC-SAFT (blue).

Figure 11. Derivative properties of toluene with CPA and PC-SAFT at $T_r=1$: (a) dp/dV , (b) dp/dT , (c) C_v , (d) C_p . ($\circ$) NIST values,⁵⁸ (—) CPA (red), (---) PC-SAFT (blue).

In Figure 12 is compared the performance of the two EoS with 2B, 3B, and 4C schemes for the heat capacities of water. It is shown that CPA with the 2B scheme and PC-SAFT with the 4C scheme have the similar good accuracy for C_p , with the AAD of both models lower than 7%. The CPA EoS with the 4C scheme gives the best description of C_v among

760 the six scenarios, with the AAD of 6.2%. For both models, the worst overall performance
 761 can be observed when the 3B scheme is considered. Similar to dodecane and toluene, the
 762 deviations of C_p for water are also quite low at the region far from the critical point, and
 763 become much higher when close to the critical region. This is because both CPA and PC-
 764 SAFT are developed on the basis of the mean-field theory, in which the density fluctuations
 765 in the vicinity of critical point are not considered. As for the C_v , it is encouraging that both
 766 EoS with the 4C scheme can slightly reproduce the C_v maxima at their critical points, and
 767 this is not observed for other compounds. However, none of the models can successfully
 768 describe the dp/dV of gaseous water, and the RDs for this property in the gas phase are
 769 usually higher than 80% and even reach to 160% with PC-SAFT and the 3B scheme.

Figure 12. Derivative properties of water with CPA and PC-SAFT at $T_r=1$: (a) dp/dV , (b) dp/dT , (c) C_v , (d) C_p . ($\circ$) NIST values,⁵⁸ ($\cdots$) CPA-2B (pink), ($-\cdots-$) PC-SAFT-2B (brown), ($---$) CPA-3B (red), ($---$) PC-SAFT-3B (blue), ($-\cdots-$) CPA-4C (orange), ($---$) PC-SAFT-4C (green).

Next, the RD distributions of four properties in eq 2 with CPA for nitrogen are analyzed in Figure 13, from which we can see that the deviations are larger when we are closer to the critical point. Furthermore, we can observe that the RDs of C_v and C_p show similar trends in the gas phase, especially in the region far away from the critical point. This is due to the significant values of the ideal gas contributions to heat capacities at this condition, and the values are all higher than 70% at $p_r < 0.5$ for both C_v and C_p . In addition, it can also be noted that although the ratio of C_p^{id}/C_p is only about 30% at $p_r > 1$, the large deviations of dp/dV and dp/dT can be somewhat counterbalanced, leading to relatively low deviations for C_p . This can explain why CPA has worse performance for dp/dV and dp/dT but still may

783 provide a higher accuracy for C_p than PC-SAFT.

784

785 Figure 13. Relative deviations of derivative properties for nitrogen with CPA at $T_r=1$: (■)

786 C_p , (—) C_v (green), (—·—) dp/dV (red), (---) $(dp/dT)^2$ (blue).

787 Closing this section, some key points can be summarized. First, for non-associating
 788 compounds at the compressed conditions, PC-SAFT shows better performance for the heat
 789 capacities than CPA. For associating fluids with the most rigorous schemes (i.e. the scheme
 790 with the most associating sites), the two EoS show similar accuracy for the description of
 791 C_p for alcohols, while CPA gives higher accuracy for other associating fluids, such as water,
 792 hydrogen sulfide and ammonia. Second, for the investigated fluids along the critical
 793 isotherms, the overall accuracy of heat capacities with CPA is higher than that with PC-
 794 SAFT, although the latter have lower AAD of C_p for carbon dioxide and water. Third,
 795 although the most rigorous schemes are considered, the heat capacities may still not be
 796 better estimated with EoS compared to when an “approximate” association scheme is used.

Our fourth comment is that, in some cases, the C_v and C_p cannot be both well represented via an EoS. Fifth, the C_v maxima can usually not be captured using EoS. Our final comment is that the ideal gas contributions to heat capacities are particularly high at the gaseous and supercritical conditions far away from the critical point, thus, in these cases, satisfactory results of heat capacities can be obtained if accurate ideal gas heat capacities are available.

5. Conclusions

In this work we have presented a systematic evaluation of the performance of CPA, PC-SAFT and other models (mostly SAFT-related) with respect to heat capacities and a few other properties. From the literature studies, the most important conclusion is, except for the EoS (SAFT-BACK, VTPR, and PHTC) only been tested by a few substances, none of the studied EoS can give good performance in all cases. Among the CPA, original SAFT and PC-SAFT EoS, CPA may show the highest accuracy of C_v and C_p in some cases, but PC-SAFT can give the best balance between the performance on heat capacities and speed of sound. EoS with higher order perturbation terms, e.g. the modified SAFT-VR-Mie can be a potential tool for the calculation of heat capacities. Furthermore, the performance of soft-SAFT for C_p for alcohols is not as good as other EoS.

An important observation is about the relative significance of the ideal and residual heat capacity contributions, and we conclude that the ideal gas contribution, which can usually be well estimated, often plays a dominant role in heat capacities at the gas and supercritical conditions far from the critical points. Therefore, in these regions, the heat capacities are

easier to be well described by an EoS, even though the performance for the residual values is unsatisfactory. In terms of the contributions to residual heat capacities, for associating compounds, the contribution of the association term is quite significant, while it becomes much weaker at higher temperatures and/or for longer molecules. For non-associating fluids, the dominant contribution is from the dispersion term. Thus, a higher-order perturbation term for an EoS may be required for a better description of residual heat capacities.

Finally, from the calculations performed in this study, we observe that PC-SAFT shows higher accuracy of the heat capacities for non-associating compounds than CPA, while the differences between the two models and different schemes for alcohols are not significant. In addition, the C_v at critical isotherms cannot well described by both CPA and PC-SAFT, and the deviations of C_p are more significant when we are closer to the critical points. Therefore, we conclude that the performance of CPA and PC-SAFT for residual heat capacities still needs improvement, especially in the region near the critical point.

Acknowledgement

The support provided by the National Science Fund for Distinguished Young Scholars of China (No. 51525604), the Foundation for Innovative Research Groups of the National Natural Science Foundation of China (No. 51721004), and the China Scholarship Council (No. 201906280322) for the completion of the present work is gratefully acknowledged.

Supporting Information

Parameters of the CPA and PC-SAFT EoS.

References

- [1] Zábanský, M.; Růžicka Jr, V.; Domalski, E. S. Heat capacity of liquids: critical review and recommended values. Supplement I. *J. Phys. Chem. Ref. Data* **2001**, *30*, 1199–1689.
- [2] Wilhelm, E. What you always wanted to know about heat capacities, but were afraid to ask. *J. Solut. Chem.* **2010**, *39*, 1777–1818.
- [3] Wilhelm, E. Heat capacities: introduction, concepts and selected applications. In *heat capacities. liquids, solutions and vapours*; Wilhelm, E., Letcher, T. M., Eds.; RSC Publishing: Cambridge, U.K., 2010.
- [4] Segovia, J. J.; Vega-Maza, D.; Chamorro, C. R.; Martín, M. C. High-pressure isobaric heat capacities using a new flow calorimeter. *J. Supercrit. Fluids* **2008**, *46*, 258–264.
- [5] Deiters, U. K.; De Reuck, K. M. Guidelines for publication of equations of state-I. Pure fluids. *Fluid Phase Equilib.* **1999**, *161*, 205–219.
- [6] Zhu, C.; Xue, S.; Ikram, R.; Liu, X.; He, M. Experimental study on isobaric molar heat capacities of a deep eutectic solvent: choline chloride + ethylene glycol. *J. Chem. Eng. Data* **2020**, *65*, 690–695.
- [7] Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. SAFT: Equation-of-state solution model for associating fluids. *Fluid Phase Equilib.* **1989**, *52*, 31–38.

- 860 [8] Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New reference equation of
861 state for associating liquids. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709–1721.
- 862 [9] Huang, S. H.; Radosz, M. Equation of state for small, large, polydisperse, and
863 associating molecules. *Ind. Eng. Chem. Res.* **1990**, *29*, 2284–2294.
- 864 [10] Gross, J.; Sadowski, G. Perturbed-chain SAFT: An equation of state based on a
865 perturbation theory for chain molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260.
- 866 [11] Gil-Villegas, A.; Galindo, A.; Whitehead, P. J.; Mills, S. J.; Jackson, G.; Burgess, A.
867 N. Statistical associating fluid theory for chain molecules with attractive potentials of
868 variable range. *J. Chem. Phys.* **1997**, *106*, 4168–4186.
- 869 [12] Galindo, A.; Davies, L. A.; Gil-Villegas, A.; Jackson, G. The thermodynamics of
870 mixtures and the corresponding mixing rules in the SAFT-VR approach for potentials
871 of variable range. *Mol. Phys.* **1998**, *93*, 241–252.
- 872 [13] Blas, F. J.; Vega, L. F. Thermodynamic behaviour of homonuclear and heteronuclear
873 Lennard-Jones chains with association sites from simulation and theory. *Mol. Phys.*
874 **1997**, *92*, 135–150.
- 875 [14] Chen, J.; Mi, J. G. Equation of state extended from SAFT with improved results for
876 non-polar fluids across the critical point. *Fluid Phase Equilib.* **2001**, *186*, 165–184.
- 877 [15] Polishuk, I. Hybridizing SAFT and cubic EOS: what can be achieved? *Ind. Eng. Chem.*
878 *Res.* **2011**, *50*, 4183–4198.
- 879 [16] Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. An equation of
880 state for associating fluids. *Ind. Eng. Chem. Res.* **1996**, *35*, 4310–4318.

- 881 [17] Kontogeorgis, G. M.; Folas, G. K. *Thermodynamic Models for Industrial Applications:*
882 *from Classical and Advanced Mixing Rules to Association Theories*. John Wiley &
883 Sons: Chichester, U.K., 2009.
- 884 [18] Palma, A. M.; Oliveira, M. B.; Queimada, A. J.; Coutinho, J. A. Evaluating cubic
885 plus association equation of state predictive capacities: A study on the transferability
886 of the hydroxyl group associative parameters. *Ind. Eng. Chem. Res.* **2017**, *56*,
887 7086–7099.
- 888 [19] Palma, A. M.; Queimada, A. J.; Coutinho, J. A. Improved prediction of water
889 properties and phase equilibria with a modified cubic plus association equation of state.
890 *Ind. Eng. Chem. Res.* **2017**, *56*, 15163–15176.
- 891 [20] Palma, A. M.; Oliveira, M. B.; Queimada, A. J.; Coutinho, J. A. Re-evaluating the CPA
892 EoS for improving critical points and derivative properties description. *Fluid Phase*
893 *Equilib.* **2017**, *436*, 85–97.
- 894 [21] Polishuk, I. Generalization of SAFT + Cubic equation of state for predicting and
895 correlating thermodynamic properties of heavy organic substances. *J. Supercrit. Fluids*
896 **2012**, *67*, 94–107.
- 897 [22] Polishuk, I.; Perel, A. Implementation of PC-SAFT and SAFT + Cubic for modeling
898 thermodynamic properties of eight 1-alkenes and their mixtures. *J. Chem. Thermodyn.*
899 **2012**, *54*, 155–164.
- 900 [23] Polishuk, I.; Katz, M.; Levi, Y.; Lubarsky, H. Implementation of PC-SAFT and SAFT
901 + Cubic for modeling thermodynamic properties of haloalkanes. I. 11 halomethanes.

902 *Fluid Phase Equilib.* **2012**, 316, 66–73.

903 [24]Polishuk, I.; Assor, E.; Cohen, N.; Potievsky, R. Implementation of PC-SAFT and
 904 SAFT + Cubic for modeling thermodynamic properties of haloalkanes. II. 7
 905 Haloethanes and their mixtures. *Int. J. Refrig.* **2013**, 36, 980–991.

906 [25]Polishuk, I. Implementation of SAFT + Cubic and PC-SAFT for comprehensive
 907 description of thermodynamic properties of n-octane and its mixtures. *J. Supercrit.*
 908 *Fluids* **2012**, 62, 47–54.

909 [26]Polishuk, I. Semi-Theoretical Versus Entirely Empirical: Comparing SAFT + Cubic
 910 and Soave-Benedict-Webb-Rubin (SBWR) Equations of State. *Ind. Eng. Chem. Res.*
 911 **2011**, 50, 11422–11431.

912 [27]Polishuk, I. Implementation of perturbed-chain statistical associating fluid theory (PC-
 913 SAFT), generalized (G) SAFT + Cubic, and cubic-plus-association (CPA) for
 914 modeling thermophysical properties of selected 1-alkyl-3-methylimidazolium ionic
 915 liquids in a wide pressure range. *J. Phys. Chem. A* **2013**, 117, 2223–2232.

916 [28]Polishuk, I. Implementation of CP-PC-SAFT for predicting thermodynamic properties
 917 and gas solubility in 1-alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide
 918 ionic liquids without fitting binary parameters. *Ind. Eng. Chem. Res.* **2017**, 56,
 919 7845–7857.

920 [29]Polishuk, I.; Sidik, Y.; NguyenHuynh, D. Predicting phase behavior in aqueous
 921 systems without fitting binary parameters I: CP-PC-SAFT EOS, aromatic compounds.
 922 *AIChE J.* **2017**, 63, 4124–4135.

- 923 [30]Lubarsky, H.; Polishuk, I.; NguyenHuynh, D. The group contribution method (GC)
924 versus the critical point-based approach (CP): predicting thermodynamic properties of
925 weakly-and non-associated oxygenated compounds by GC-PPC-SAFT and CP-PC-
926 SAFT. *J. Supercrit. Fluids* **2016**, *110*, 11–21.
- 927 [31]Liang, X.; Tsivintzelis, I.; Kontogeorgis, G. M. Modeling water containing systems
928 with the simplified PC-SAFT and CPA equations of state. *Ind. Eng. Chem. Res.* **2014**,
929 *53*, 14493–14507.
- 930 [32]Diamantonis, N. I.; Economou, I. G. Evaluation of statistical associating fluid theory
931 (SAFT) and perturbed chain-SAFT equations of state for the calculation of
932 thermodynamic derivative properties of fluids related to carbon capture and
933 sequestration. *Energy Fuels* **2011**, *25*, 3334–3343.
- 934 [33]De Villiers, A. J.; Schwarz, C. E.; Burger, A. J.; Kontogeorgis, G. M. Evaluation of the
935 PC-SAFT, SAFT and CPA equations of state in predicting derivative properties of
936 selected non-polar and hydrogen-bonding compounds. *Fluid Phase Equilib.* **2013**, *338*,
937 1–15.
- 938 [34]Burgess, W. A.; Tapriyal, D.; Gamwo, I. K.; Wu, Y.; McHugh, M. A.; Enick, R. M.
939 New group-contribution parameters for the calculation of PC-SAFT parameters for use
940 at pressures to 276 MPa and temperatures to 533 K. *Ind. Eng. Chem. Res.* **2014**, *53*,
941 2520–2528.
- 942 [35]Lafitte, T.; Piñeiro, M. M.; Daridon, J. L.; Bessièrès, D. A comprehensive description
943 of chemical association effects on second derivative properties of alcohols through a

SAFT-VR approach. *J. Phys. Chem. B* **2007**, *111*, 3447–3461.

[36] Lafitte, T.; Bessieres, D.; Piñeiro, M. M.; Daridon, J. L. Simultaneous estimation of phase behavior and second-derivative properties using the statistical associating fluid theory with variable range approach. *J. Chem. Phys.* **2006**, *124*, 024509.

[37] Lafitte, T.; Apostolakou, A.; Avendano, C.; Galindo, A.; Adjiman, C. S.; Müller, E. A.; Jackson, G. Accurate statistical associating fluid theory for chain molecules formed from Mie segments. *J. Chem. Phys.* **2013**, *139*, 154504.

[38] Perdomo, F. A.; Gil-Villegas, A. Predicting thermophysical properties of biodiesel fuel blends using the SAFT-VR approach. *Fluid Phase Equilib.* **2011**, *306*, 124–128.

[39] Oliveira, M. B.; Llovell, F.; Coutinho, J. A. P.; Vega, L. F. New procedure for enhancing the transferability of statistical associating fluid theory (SAFT) molecular parameters: the role of derivative properties. *Ind. Eng. Chem. Res.* **2016**, *55*, 10011–10024.

[40] Llovell, F.; Vega, L. F. Prediction of thermodynamic derivative properties of pure fluids through the soft-SAFT equation of state. *J. Phys. Chem. B* **2006**, *110*, 11427–11437.

[41] Llovell, F.; Peters, C. J.; Vega, L. F. Second-order thermodynamic derivative properties of selected mixtures by the soft-SAFT equation of state. *Fluid Phase Equilib.* **2006**, *248*, 115–122.

[42] Dias, A. M. A.; Llovell, F.; Coutinho, J. A. P.; Marrucho, I. M.; Vega, L. F. Thermodynamic characterization of pure perfluoroalkanes, including interfacial and

965 second order derivative properties, using the crossover soft-SAFT EoS. *Fluid Phase*
 966 *Equilib.* **2009**, 286, 134–143.

967 [43]Maghari, A.; Sadeghi, M. S. Prediction of sound velocity and heat capacities of n-
 968 alkanes from the modified SAFT-BACK equation of state. *Fluid Phase Equilib.* **2007**,
 969 252, 152–161.

970 [44]Maghari, A.; Hamzehloo, M. Second-order thermodynamic derivative properties of
 971 binary mixtures of n-alkanes through the SAFT-CP equation of state. *Fluid Phase*
 972 *Equilib.* **2011**, 302, 195–201.

973 [45]Shen, G.; Held, C.; Lu, X.; Ji, X. Modeling thermodynamic derivative properties of
 974 ionic liquids with ePC-SAFT. *Fluid Phase Equilib.* **2015**, 405, 73–82.

975 [46]Diedrichs, A.; Rarey, J.; Gmehling, J. Prediction of liquid heat capacities by the group
 976 contribution equation of state VTPR. *Fluid Phase Equilib.* **2006**, 248, 56–69.

977 [47]Alavianmehr, M. M.; El-Shaikh, M.; Akbari, F.; Behjatmanesh-Ardakani, R. A new
 978 equation of state for modeling thermodynamic properties of some fatty acids alkyl
 979 esters, methyl ester-based biodiesels and their blends. *Fluid Phase Equilib.* **2017**, 442,
 980 53–61.

981 [48]Ceriani, R.; Gani, R.; Meirelles, A. J. Prediction of heat capacities and heats of
 982 vaporization of organic liquids by group contribution methods. *Fluid Phase Equilib.*
 983 **2009**, 283, 49–55.

984 [49]Gardas, R. L.; Coutinho, J. A. A group contribution method for heat capacity
 985 estimation of ionic liquids. *Ind. Eng. Chem. Res.* **2008**, 47, 5751–5757.

986 [50] Soriano, A. N.; Agapito, A. M.; Lagumbay, L. J. L. I.; Caparanga, A. R.; Li, M. H. A
 987 simple approach to predict molar heat capacity of ionic liquids using group-additivity
 988 method. *J. Taiwan Inst. Chem. Eng.* **2010**, *41*, 307–314.

989 [51] Valderrama, J. O.; Toro, A.; Rojas, R. E. Prediction of the heat capacity of ionic liquids
 990 using the mass connectivity index and a group contribution method. *J. Chem.*
 991 *Thermodyn.* **2011**, *43*, 1068–1073.

992 [52] Cedeño, F. O.; Prieto, M. M.; Xiberta, J. Measurements and estimate of heat capacity
 993 for some pure fatty acids and their binary and ternary mixtures. *J. Chem. Eng. Data*
 994 **2000**, *45*, 64–69.

995 [53] Anand, K.; Sharma, R. P.; Mehta, P. S. A comprehensive approach for estimating
 996 thermo-physical properties of biodiesel fuels. *Appl. Therm. Eng.* **2011**, *31*, 235–242.

997 [54] Bolmatov, D.; Brazhkin, V. V.; Trachenko, K. The phonon theory of liquid
 998 thermodynamics. *Sci. Rep.* **2012**, *2*, 1–6.

999 [55] Dadgostar, N.; Shaw, J. M. A predictive correlation for the constant-pressure specific
 1000 heat capacity of pure and ill-defined liquid hydrocarbons. *Fluid Phase Equilib.* **2012**,
 1001 *313*, 211–226.

1002 [56] Dadgostar, N.; Shaw, J. M. Predictive correlations for liquid heat capacity—including
 1003 the critical region. *Fluid Phase Equilib.* **2013**, *344*, 139–151.

1004 [57] Jaubert, J. N.; Privat, R.; Le Guennec, Y.; Coniglio, L. Note on the properties altered
 1005 by application of a Péneloux-type volume translation to an equation of state. *Fluid*
 1006 *Phase Equilib.* **2016**, *419*, 88–95.

- 1007 [58] NIST Chemistry Webbook. <http://webbook.nist.gov/chemistry> (accessed May 2020).
- 1008 [59] Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*,
1009 5th ed; McGraw-hill: New York, 2001.
- 1010 [60] Liang, X.; Maribo-Mogensen, B.; Thomsen, K.; Yan, W.; Kontogeorgis, G. M.
1011 Approach to improve speed of sound calculation within PC-SAFT framework. *Ind.*
1012 *Eng. Chem. Res.* **2012**, *51*, 14903–14914.
- 1013 [61] DIPPR 801 database, Design Institute for Physical Property Data. AIChE: New York,
1014 1998.
- 1015 [62] Polishuk, I. Till which pressures the fluid phase EOS models might stay reliable? *J.*
1016 *Supercrit. Fluids* **2011**, *58*, 204–215.
- 1017 [63] Polishuk, I. Addressing the issue of numerical pitfalls characteristic for SAFT EOS
1018 models. *Fluid Phase Equilib.* **2011**, *301*, 123–129.
- 1019 [64] Polishuk, I.; Wisniak, J.; Segura, H. Some observations regarding the prediction of
1020 isochoric heat capacities by engineering EOS models. *Fluid Phase Equilib.* **2009**, *277*,
1021 121–125.
- 1022 [65] Miyazawa, T.; Kondo, S.; Suzuki, T.; Sato, H. Specific heat capacity at constant
1023 pressure of ethanol by flow calorimetry. *J. Chem. Eng. Data* **2012**, *57*, 1700–1707.
- 1024 [66] Zhu, C.; Yang, F.; Liu, X.; He, M. Isobaric molar heat capacities measurement of
1025 binary mixtures containing ethyl laurate and ethanol at high pressures. *J. Mol. Liq.*
1026 **2019**, *280*, 301–306.
- 1027 [67] Vega-Maza, D.; Segovia, J. J.; Martín, M. C.; Villamañán, R. M.; Villamañán, M. A.

1028 Thermodynamic properties of biofuels: Heat capacities of binary mixtures containing
 1029 ethanol and hydrocarbons up to 20 MPa and the pure compounds using a new flow
 1030 calorimeter. *J. Chem. Thermodyn.* **2011**, *43*, 1893–1896.

1031 [68] Stromsoe, E.; Ronne, H. G.; Lydersen, A. L. Heat capacity of alcohol vapors at
 1032 atmospheric pressure. *J. Chem. Eng. Data* **1970**, *15*, 286–290.

1033 [69] Counsell, J. F.; Lees, E. B.; Martin, J. F. Thermodynamic properties of organic oxygen
 1034 compounds. Part XIX. Low-temperature heat capacity and entropy of propan-1-ol, 2-
 1035 methylpropan-1-ol, and pentan-1-ol. *J. Chem. Soc. A* **1968**, 1819–1823.

1036 [70] Counsell, J. F.; Hales, J. L.; Martin, J. F. Thermodynamic properties of organic oxygen
 1037 compounds. Part 16. — Butyl alcohol. *Trans. Faraday Soc.* **1965**, *61*, 1869–1875.

1038 [71] Torín-Ollarves, G. A.; Segovia, J. J.; Martín, M. C.; Villamañán, M. A.
 1039 Thermodynamic characterization of the mixture (1-butanol + iso-octane): Densities,
 1040 viscosities, and isobaric heat capacities at high pressures. *J. Chem. Thermodyn.* **2012**,
 1041 *44*, 75–83.

1042 [72] Naziev, Y. M.; Bashirov, M. M.; Badalov, Y. A. Experimental device for measurement
 1043 of isobaric specific heat of electrolytes at high state parameters. *J. Eng. Phys.* **1986**,
 1044 *51*, 1320–1325.

1045 [73] Fulem, M.; Růžicka, K.; Růžicka, V. Heat capacities of alkanols: Part I. Selected 1-
 1046 alkanols C₂ to C₁₀ at elevated temperatures and pressures. *Thermochim. Acta* **2002**,
 1047 *382*, 119–128.

1048 [74] Domańska, U.; Marciniak, M. Experimental solid–liquid equilibria for systems

1049 containing alkan-1-ol + 1, 3-diaminopropane: Heat capacities of alkan-1-ols and
 1050 amines — Thermodynamic functions of dissociation and enthalpies of melting of the
 1051 congruently melting compounds for the systems (alkan-1-ol + amine). *Fluid Phase*
 1052 *Equilib.* **2005**, *235*, 30–41.

1053 [75] Casás, L. M.; Plantier, F.; Piñeiro, M. M.; Legido, J. L.; Bessièrès, D. Calibration of a
 1054 low temperature calorimeter and application in the determination of isobaric heat
 1055 capacity of 2-propanol. *Thermochim. Acta* **2010**, *507*, 123–126.

1056 [76] Dreher, I. Experimental determination of the isobaric specific heat capacity of propan-
 1057 2-ol up to pressures of 30 MPa and temperatures of 573 K. *J. Chem. Thermodyn.* **1979**,
 1058 *11*, 993–1003.

1059 [77] Hoffman, S.; San Jose, J.; Reid, R. Liquid heat capacity of tert-butyl alcohol, isobutyl
 1060 alcohol, and isopropyl alcohol at high temperature. *J. Chem. Eng. Data* **1977**, *22*,
 1061 385–388.

1062 [78] Andon, R. J. L.; Connett, J. E.; Counsell, J. F.; Lees, E. B.; Martin, J. F.
 1063 Thermodynamic properties of organic oxygen compounds. Part XXVII. (±)-Butan-2-
 1064 ol and (+)-butan-2-ol. *J. Chem. Soc. A* **1971**, 661–664.

1065 [79] Torín-Ollarves, G. A.; Martín, M. C.; Segovia, J. J. Thermophysical properties of 1, 2,
 1066 4-trimethylbenzene in admixtures with 1-butanol or 2-butanol at high pressures. *J.*
 1067 *Chem. Thermodyn.* **2017**, *111*, 41–51.

1068 [80] Dzida, M.; Góralski, P. Molar heat capacities for (2-methyl-2-butanol + heptane)
 1069 mixtures and cyclopentanol at temperatures from (284 to 353) K. *J. Chem. Thermodyn.*

1070 **2009**, *41*, 402–413.

Abstract Graphics ^a

^a For Table of Contents use only;