

Using a Volume Shift in Perturbed-Chain Statistical Associating Fluid Theory To Improve the Description of Speed of Sound and Other Derivative Properties

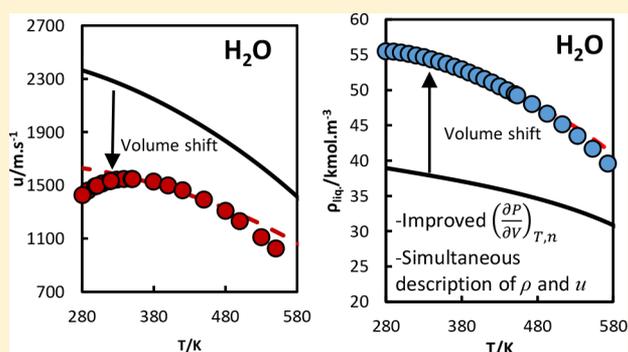
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Supporting Information

ABSTRACT: Volume shifts are commonly applied to cubic equations of state (EoS) to improve the description of densities, since they do not affect the phase equilibria. This concept can in principle be extended to any other EoS, but studies using this approach are scarce for EoS based on perturbation theory, mainly because most of these equations already provide accurate liquid density results. However, as with cubic EoS, most statistical associating fluid theory (SAFT) type EoS have difficulties in describing derivative properties, more noticeably the speed of sound. In this work, we study the use of a volume shift in perturbed-chain statistical associating fluid theory (PC-SAFT). A new parametrization procedure is proposed that involves the use of vapor pressure, the pressure derivative with respect to density obtained from isothermal compressibility, and molar volume data. This last property is only applied to fit a constant Pénélox-type volume shift. It is shown that this approach provides a good description of saturation pressures and liquid densities, as well as an improved description of the speed of sound. The impact of these changes on the performance of PC-SAFT in the description of properties and phase equilibria is further investigated by comparing the results of this methodology with those obtained with the available PC-SAFT parameter sets.



1. INTRODUCTION

Volume shifts have been applied for a long time to cubic equations of state (EoS). This approach, when correctly used, enables a better representation of densities without affecting the phase equilibria. This approach has, however, seldom been applied to EoS based on perturbation theory.^{1–4}

As discussed by Jaubert et al.,^{5,6} and studied in previous works with the cubic-plus-association (CPA) equation of state,^{7–9} the concept of using a volume shift is not restricted to cubic EoS, but also applicable to SAFT-type EoS. In previous studies, the use of a volume shift, using a modified CPA, was analyzed.^{7–9} During these studies it was observed that the main reason for the correct description of density but incorrect description of the speed of sound was the erroneous estimation of the derivative of pressure with respect to volume. The wrong ratio for C_p/C_v also influences this behavior. However, this influence is not as prevalent as that of the derivative, for the cubic EoS and CPA EoS.

In this work, the pure compound parametrization is carried out by fitting the PC-SAFT parameters to the derivative $(\frac{dP}{dV})_T$ close to atmospheric pressure along with the saturation pressure, while the liquid density is used to fit a constant

volume shift, at a reduced temperature of 0.7. The impact of this approach on other pure component properties and mixture phase behavior is further investigated.

2. PROPERTIES IN STUDY AND CONCEPT OF A VS-PC-SAFT

The introduction of a constant, Pénélox-type, volume shift,¹⁰ does not affect the saturation pressure, isobaric heat capacity, heat of vaporization, and both vapor–liquid and liquid–liquid phase equilibria as discussed by Jaubert et al.⁶ and confirmed by the results obtained in this work. The volume shift will, however, impact on the molar volume/density, as well as in the speed of sound and other derivative properties such as the isothermal compressibility and the isobaric expansivity.

The parametrization of the pure components for PC-SAFT¹¹ was carried out using both the saturation pressures and the derivative of pressure in relation to volume close to atmospheric pressure, using different temperature ranges for the two

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Table 1. Data Used in Parametrization

compound	no. P^{sat} values	no. $\left(\frac{dP}{dV}\right)_T$ values	w_{dp}/w_p	T range (K)	
				P^{sat}	$\left(\frac{dP}{dV}\right)_T$
hexane	22	4	2.5	243–453	293–333
benzene	25	5	1.5	280–520	293–333
methanol	24	4	1.5	263–493	293–333
ethanol	25	4	1.5	253–493	293–333
water	32	11	1	273–583	274–372

properties, as presented in Table 1. By minimizing the objective function (OF)

$$\text{OF} = w_p \sum_i^{\text{npsat}} \left(\frac{P_{\text{exp}}^{\text{sat},i} - P_{\text{SAFT}}^{\text{sat},i}}{P_{\text{exp}}^{\text{sat},i}} \right)^2 + w_{\text{dp}} \sum_j^{\text{nder}} \left(\frac{\left(\frac{\partial P}{\partial V}\right)_T^j - \left(\frac{\partial P}{\partial V}\right)_T^{\text{SAFT},j}}{\left(\frac{\partial P}{\partial V}\right)_T^j} \right)^2 \quad (1)$$

where w_p and w_{dp} are weights for the optimization, and w_{dp} ranges from w_p to $2.5w_p$. “nder” and “npsat” are the number of data points applied for the derivative $\left(\frac{dP}{dV}\right)_T$ and saturation pressure, respectively.

During the fitting, the pure component correlations present on Multiflash¹² were used to fit the saturation pressure (except for ethanol, where a correlation on the data from the TRC database¹³ was applied. The value of $\left(\frac{dP}{dV}\right)_T$ was calculated from literature data on k_T at 1 bar (see Figure 3) and the liquid density correlation of Multiflash.¹² The number of values, temperature ranges, and weight for each property used in the parametrization are presented in Table 1.

Saturated liquid volume is not fitted directly, and instead a volume shift is added after the reparametrization, defined as

$$V_t = V_0 - c \quad (2)$$

which is fitted to the saturated liquid density at $0.7T_r$.

For mixtures a linear mixing rule for this parameter is used:

$$c_{\text{mix}} = \sum_i^{\text{ncompounds}} x_i c_i \quad (3)$$

Table 2. Parameter Sets Used in This Work for Hexane, Methanol, Ethanol, and Benzene

	m	σ (Å)	ϵ/k (K)	ϵ^{HB}/k (K)	$K^{\text{HB}} \times 10^2$	c (cm ³ ·mol ⁻¹)
			V_{shift}			
hexane	2.94	3.75	244.1	n.a.	n.a.	-9.26
benzene	2.36	3.61	296.7	n.a.	n.a.	-4.68
methanol	1.65	3.33	215.3	2643.4	2.84	5.44
ethanol	2.33	3.18	197.8	2740.3	2.73	-0.95
			Original ^{11,14}			
hexane	3.06	3.80	236.8	n.a.	n.a.	n.a.
benzene	2.47	3.65	287.4	n.a.	n.a.	n.a.
methanol	1.53	3.23	188.9	2899.5	3.52	n.a.
ethanol	2.38	3.18	198.2	2653.4	3.24	n.a.
			Liang ¹⁶			
hexane ^a	3.04	3.81	237.2	n.a.	n.a.	n.a.
methanol	1.88	3.00	181.8	2738.0	5.47	n.a.
MeOH univ ^a	1.55	3.23	190.7	2864.8	3.59	n.a.

^aThis second methanol set as well as the hexane set considers a reparametrization of the universal constants of PC-SAFT.

3. RESULTS

3.1. Pure Compounds. In this study, the approach presented above is evaluated on five compounds (water, methanol, ethanol, hexane, and benzene) from different families covering aliphatic and aromatic hydrocarbons, alcohols, and water, and their mixtures. It is important to remark that the pure components are reparametrized here, and that the association scheme used for water in this work is 4C. For water, the value of m was restricted to values close to 1.00. The reparametrized parameters along with others previously reported in the literature and used in this work are presented in Tables 2 and 3. Besides the volume shift reparametrization conducted in this work, the original PC-SAFT parameters for these compounds^{11,14} are analyzed, as well as the reparametrizations by Liang et al.^{15,16} The description of water properties is analyzed for five parameter sets: the one from this work, the original PC-SAFT set,^{11,14} the sets from Fuchs et al.¹⁷ and Fouad et al.,¹⁸ and one of the sets proposed by von Solms et al.¹⁹

The results for the liquid densities of the studied compounds using the various parametrizations, along with the predictions for the speed of sound, are presented in Figures 1 and 2. For the results of density in all compounds (except water), only the description of this work and the one from Sadowski and Gross^{11,14} are presented; their deviations are still compared in Table 4. They show that using the new volume shift based parametrization it is possible to obtain an accurate description of the liquid densities and good estimates of the speed of sound in large ranges of temperature, for all these compounds. The water parameters from Fuchs et al.,¹⁷ due to the use of a temperature dependent segment diameter, also represent the water liquid density maximum. However, for the speed of sound, they present high deviations, and while there is a threshold near 330 K, this is not a maximum. Saturation pressure data were used in the parametrization and present good accuracy. Tables 4 and 5 present the %AAD (percentage of average absolute deviation) for this property, as well as for saturated liquid density, when compared to the data of the DIPPR database.²⁴

An evaluation of the results for the derivative properties k_T (isothermal compressibility), α_p (isobaric expansivity), C_p (isobaric heat capacity), and H^{vap} (heat of vaporization) is presented in Figures 3 and 4. Results using the new parametrization are compared with literature PC-SAFT parameters. Summaries of the deviations obtained are presented in Tables 6 and 7.

Table 3. Parameter Sets Used in This Work for Water

	m	σ (Å)	ϵ/k (K)	ϵ^{HB}/k (K)	$k^{\text{HB}} \times 10^2$	c (cm ³ ·mol ⁻¹)	scheme
this work	1.00	3.44	300.9	1691.3	2.52	7.98	4C
original ¹⁴	1.07	3.00	366.5	2500.7	3.49	n.a.	2B
Fuchs ¹⁷	1.20	a	354.0	2425.7	4.50	n.a.	2B
Fouad ¹⁸	1.00	3.04	204.7	1920.0	4.25	n.a.	4C
von Solms ¹⁹	3.00	2.01	182.9	1259.0	42.87	n.a.	4C

^aTemperature-dependent segment diameter: $\sigma = 2.7927 + 10.11 \exp(-0.01775T [\text{K}]) - 1.417 \exp(-0.01146T [\text{K}])$.

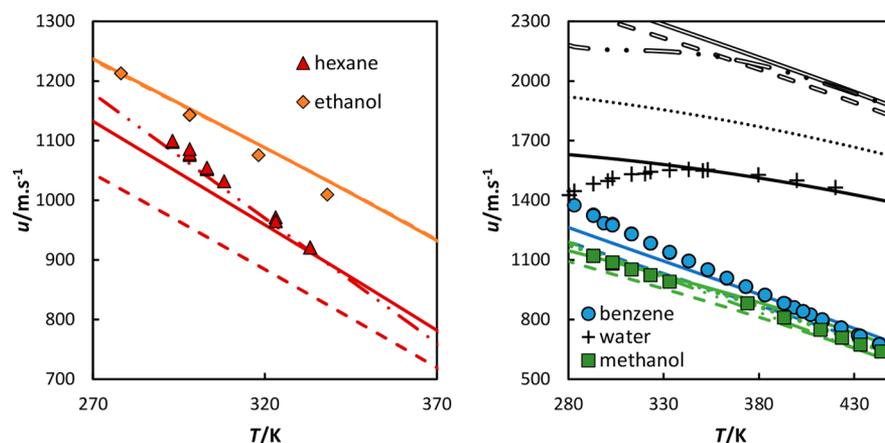


Figure 1. Speed of sound for the five fluids studied. Full lines, volume shifted set; dashed lines, original set;^{11,14} dots and dashes, Liang;¹⁶ double dots and dashes, Fuchs;¹⁷ dots, Liang¹⁶ (MeOH universal); double dashes, Fouad;¹⁸ double line, von Solms.¹⁹ Data from REFPROP,²⁰ +; the TRC database,¹³ ○; Bolotnikov et al.,²¹ △; Pereira et al.,²² □; and Salinas et al.,²³ ◇.

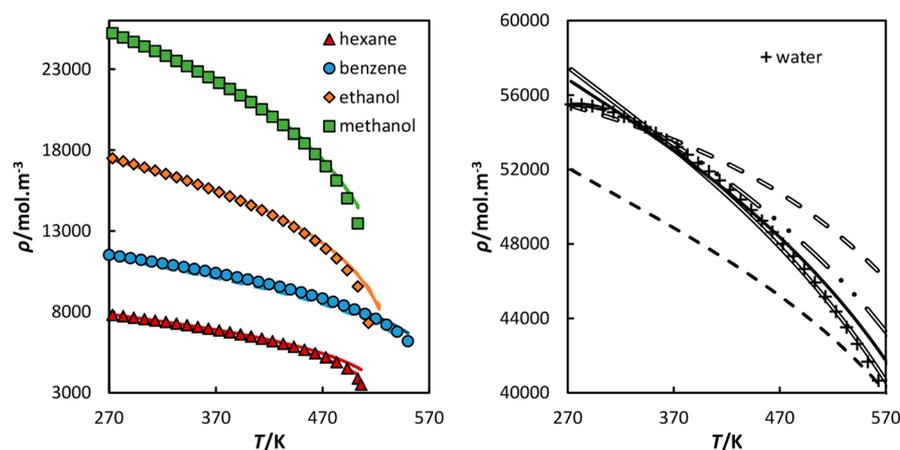


Figure 2. Liquid density for the five fluids studied. Full lines, volume shifted set; dashed lines, original;^{11,14} double dots and dashes, Fuchs;¹⁷ double dashes, Fouad;¹⁸ double line, von Solms.¹⁹ Data from the DIPPR correlations.²⁴

The enhanced performance of the proposed approach in the description of the speed of sound of the liquid phase, results from the use in the parametrization, and consequent improvement in the description of $\left(\frac{\partial p}{\partial V}\right)_T$. However, this improvement in $\left(\frac{\partial p}{\partial V}\right)_T$ leads to a degradation in the description of α_p , while C_p also improves and H^{vap} does not change significantly.

The use of a volume shift has opposite effects on the accuracy of α_p and k_T , due to the improvement of $\left(\frac{\partial p}{\partial V}\right)_T$ being obtained at the cost of a deterioration in the description of $\left(\frac{\partial V}{\partial T}\right)_p$. Methanol and ethanol are exceptions to this behavior with both properties improving in the case of the former, while in the case of the latter the major improvement

was in the description of the saturation pressure. In the cases of C_p and H^{vap} , there is an improvement in the case of methanol, which might be due to the improved description of the saturation pressure data, as these properties are linked. However, the results are very similar for most other compounds (water is an exception), except at higher temperatures, which are probably related to the prediction of the critical temperature of each set being slightly different. When comparing to the results of Fuchs et al.,¹⁷ it is interesting to note that the description of both isobaric expansivity and liquid density are much improved. Both approaches from Liang et al.¹⁶ added the speed of sound to the parametrization and present an accurate description of k_T for methanol. In the case of the set which considers the original PC-SAFT universal constants, the parametrization is also the most accurate of these sets for the α_p data.

Table 4. Average Deviations on P^{sat} and ρ^{liq} ^a

compound	T (K)	original ^{11,14}	%AAD P^{sat}		%AAD ρ^{liq}		
			Liang ¹⁶	V_{shift}	original	Liang ¹⁶	V_{shift}
methanol	243–503	2.26	2.10	1.20	1.15	0.61	0.69
MeOH univ ^b	243–503	–	1.74	–	–	0.55	–
ethanol	243–503	2.67	–	1.04	1.01	–	1.03
hexane	243–503	0.46	1.22 ^b	0.26	1.75	1.69 ^b	1.65
benzene	260–550	0.61	–	0.64	3.11	–	0.95

^aData from DIPPR²⁴ correlations and a correlation on the TRC data (for ethanol).¹³ ^bThis second methanol set as well as the hexane set considers a reparametrization of the universal constants of PC-SAFT.

Table 5. Average Deviations for Water on P^{sat} and ρ^{liq} ^a

set	T (K)	%AAD P^{sat}	%AAD ρ^{liq}
this work		0.44	2.27
original ¹⁴		1.75	6.19
Fuchs ¹⁷	273–623	2.88	3.73
Fouad ¹⁸		2.89	7.23
von Solms ¹⁹		0.30	1.57

^aData from DIPPR²⁴ correlations and a correlation on the TRC data (for ethanol).¹³

Before evaluating the performance of this novel approach for mixtures, it is important to study how the model describes high pressure densities and the speed of sound. Figure 5 presents results for these properties in the case of hexane and water for all parameter sets.

High pressure liquid densities are accurately described, and compare well, with other PC-SAFT parameter sets, while for the speed of sound the better description of this property at low pressures improves the overall description of the property. Nevertheless, there is a degradation with the increase in pressure, mainly for the speed of sound. Also for water, as the speed of sound maximum is not captured (Figure 1), the curve at a lower temperature presents higher speed of sound values than the one at 348 K, which is not experimentally verified. Only the data from the present work are presented for the speed of sound of water, due to the high deviations of the remaining sets for this property at low pressures.

Liang et al.^{15,16} proposed an alternative approach to enhance the description of the speed of sound by changing the universal constants of the PC-SAFT EoS. This approach was applied to

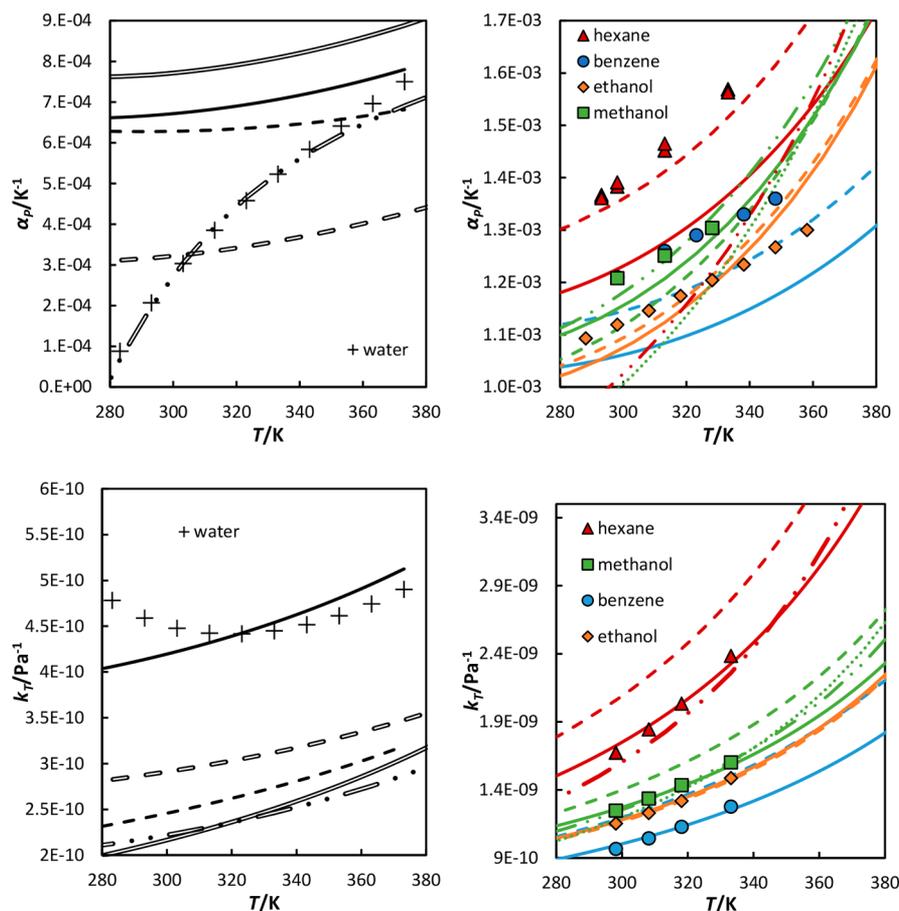


Figure 3. Results for α_p (top) and k_T (bottom). Full lines, volume shifted set; dashed lines, original;^{11,14} dots and dashes, Liang;¹⁶ double dots and dashes, Fuchs;¹⁷ double dashes, Fouad;¹⁸ double line, von Solms.¹⁹ Data from Pereira et al.,²² □; Peña and Tardajos²⁵, ◇ (k_T); Dávila et al.²⁶, ◇ (α_p); Garbajosa et al.²⁷, △; Aicart et al.²⁸, ○; and Kell²⁹, +.

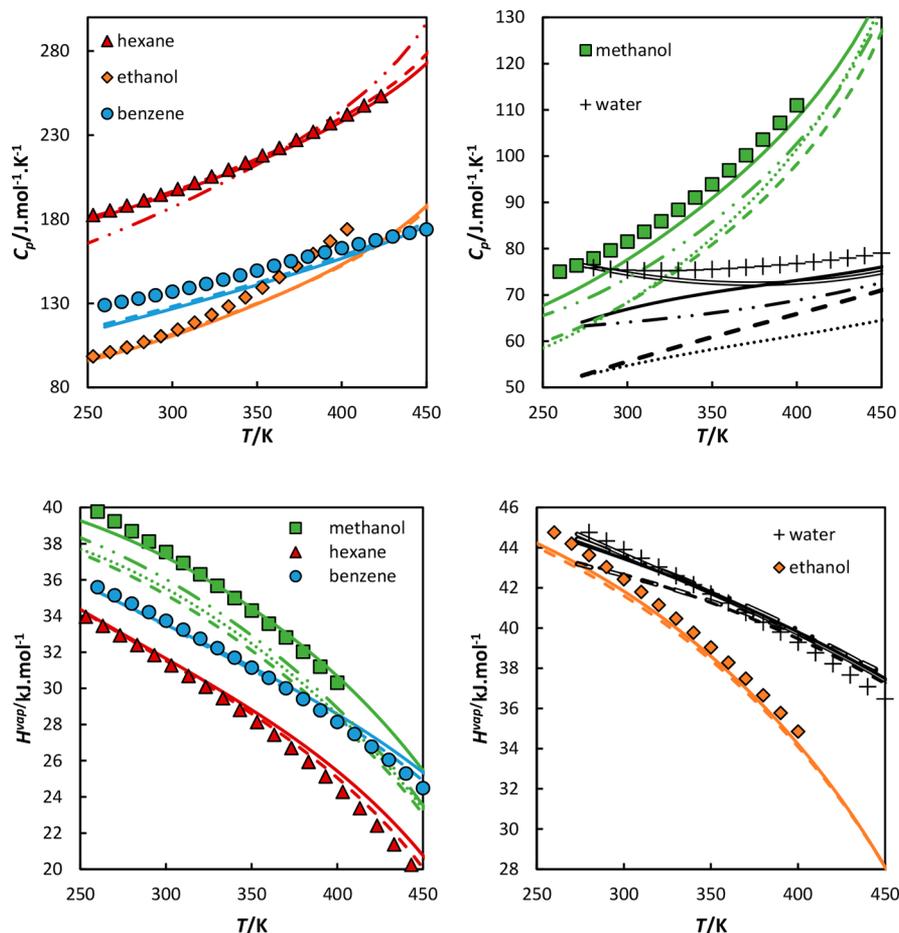


Figure 4. Results for C_p (top) and H^{vap} (bottom). Full lines, volume shifted set; dashed lines, original;^{11,14} dots and dashes, Liang;¹⁶ double dots and dashes, Fuchs;¹⁷ dots, Liang¹⁶ (MeOH universal); double dashes, Fouad;¹⁸ double line, von Solms.¹⁹ Data taken from the pure component correlation of Multiflash¹² and the DIPPR database.²⁴

Table 6. %AAD for Derivative Properties^a

	methanol	MeOH univ ^b	ethanol	hexane	benzene
		V_{shift}			
k_T	0.74	—	0.77	8.02	1.56
C_p	4.62	—	4.74	0.95	5.14
H^{vap}	0.86	—	1.46	2.40	1.10
u	2.86	—	1.24	2.87	5.39
α_p	3.34	—	3.78	12.00	13.69
		Original ^{11,14}			
k_T	10.84	—	0.29	20.38	16.10
C_p	15.22	—	4.13	0.33	4.56
H^{vap}	6.52	—	1.94	1.30	0.74
u	5.02	—	1.25	10.44	6.87
α_p	5.94	—	3.28	2.74	6.76
		Liang et al. ¹⁶			
k_T	0.55	3.11	—	5.58 ^b	—
C_p	9.33	14.58	—	3.79 ^b	—
H^{vap}	4.19	5.51	—	3.04 ^b	—
u	1.49	2.65	—	1.24 ^b	—
α_p	1.79	12.96	—	24.2 ^b	—

^aThe data applied are those shown in Figures 1, 3, and 4. ^bThis second methanol set as well as the hexane set considers a reparametrization of the universal constants of PC-SAFT.

alkanes and alkanols, with good results, as shown in Figure 6 for methanol.

While improving the accuracy of speed of sound, when compared to the original PC-SAFT parameters, the present approach is still not as accurate for this property as either of the reparametrizations from Liang et al.¹⁶ The approach, which uses the original universal constants, presents accuracy similar to the present work at saturation conditions; however, it has a better trend with pressure. This should have to do, at the lower temperatures, with the better description of the isobaric expansivity. Knowing this, and that both are accurate for the isothermal compressibility for such conditions, leads to a better C_p – C_v relation in that set. Thus, while the volume shifted set is more accurate for C_p , the ratio C_p/C_v should be closer to the experimental in the set from Liang et al.,¹⁶ leading to a better overall description of the speed of sound.

To further study the accuracy of the parameters in the description of properties dependent on volume, Figure 7 presents results for k_T and α_p for water, at higher pressures/temperatures than in Figure 3 (which considered results at 0.1 MPa).

The larger temperature range for these data shows that, while the results from Fuchs et al.¹⁷ are accurate for the isobaric expansivity at low temperatures, the accuracy decreases largely at higher temperatures. All sets present an incorrect temperature trend for this property at high temperature conditions. For k_T , the low pressure data are improved with the new set, even at higher temperatures. However, the trend of the property with pressure tends to differ from the experimental data, in all PC-SAFT sets tested.

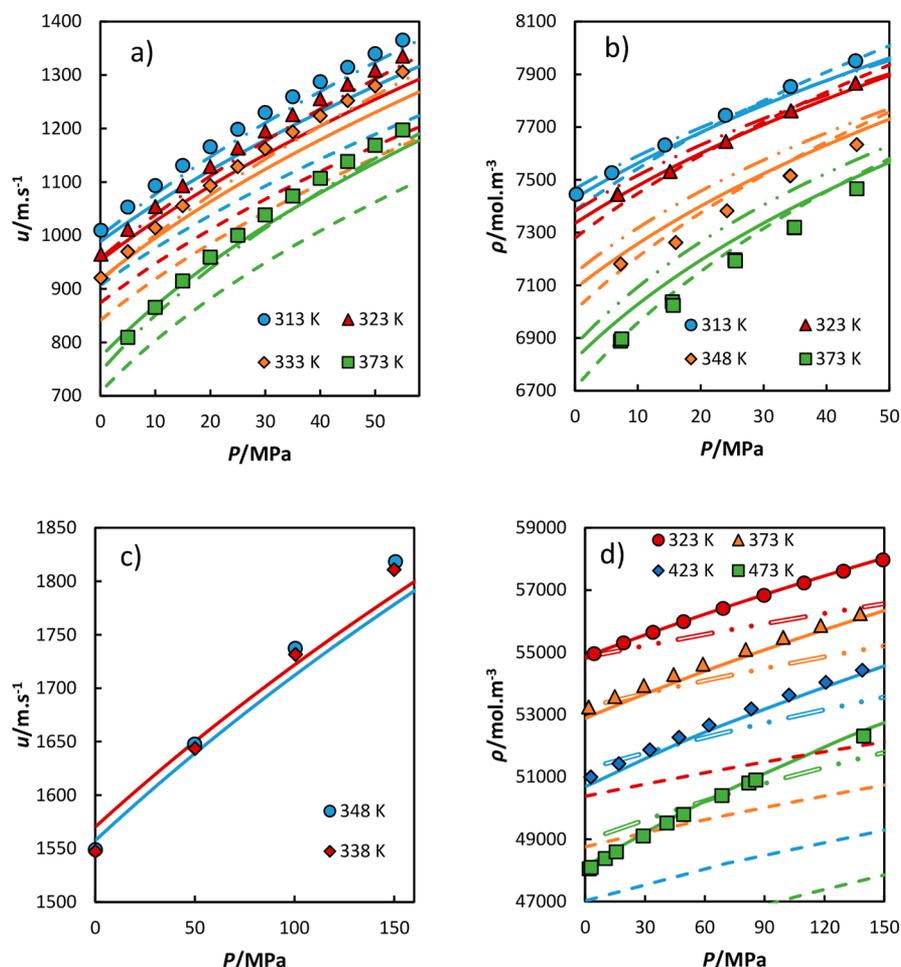


Figure 5. Description of high pressure liquid density and speed of sound in hexane (top) and water (bottom). Full lines, volume shifted set; dashed lines, original;^{11,14} dots and dashes, Liang parameters;¹⁶ double dots and dashes, Fuchs.¹⁷ (For the remaining water sets see the [Supporting Information](#).) Data from Daridon et al.³⁰ (a), Kiran and Sen³¹ (b), Hidalgo Baltasar et al.³² (c), and Tanishita et al.³³ (d).

Table 7. %AAD for Derivative Properties of Water^a

	k_T	C_p	H^{vap}	u	α_p
this work	5.18	6.21	0.95	8.93	121.40
original ¹⁴	40.73	15.04	1.65	45.50	107.68
Fuchs ¹⁷	46.60	10.24	1.24	43.40	5.05
Fouad ¹⁸	32.21	21.26	1.99	27.20	54.38
von Solms ¹⁹	45.89	3.90	0.76	50.14	154.10

^aThe data applied are those shown in [Figures 1, 3, and 4](#).

To finish the analysis on pure component data, monomer fractions and free site fractions are analyzed for water. (See the [Supporting Information](#) for results with methanol.) [Figure 8](#) presents the results with the different sets.

As can be observed in [Figure 8](#), the volume shifted set presents accurate results for these data, comparing well with the set from von Solms et al.¹⁹ Thus, the calculated associative contribution seems to be in close agreement to that of the monomer fraction data. However, it is important to note that there are no experimental uncertainties for monomer fraction data. Liang et al.³⁶ also commented that, for the most applied sets of equations considering association theory, the obtained monomer fraction for water was rather different from the data of Luck.³⁵ An opposite behavior is observed for methanol (see [Supporting Information](#)), where the volume shifted set tends to overestimate the free site

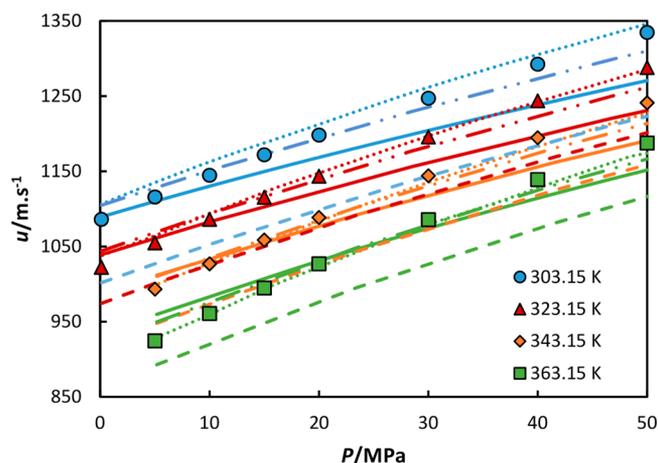


Figure 6. Speed of sound in methanol at constant temperature. Full lines, volume shifted set; dashed lines, original;¹⁴ dots and dashes, Liang;¹⁶ dots, Liang¹⁶ (MeOH universal). Data from Plantier et al.³⁴

fractions at lower temperatures, while the other sets tend to be more accurate.

3.2. Mixtures. Having discussed pure component results, the robustness of the new parametrization procedure needs to be checked for mixtures. For the study of mixture results, three LLE systems are analyzed, as well as three VLE systems.

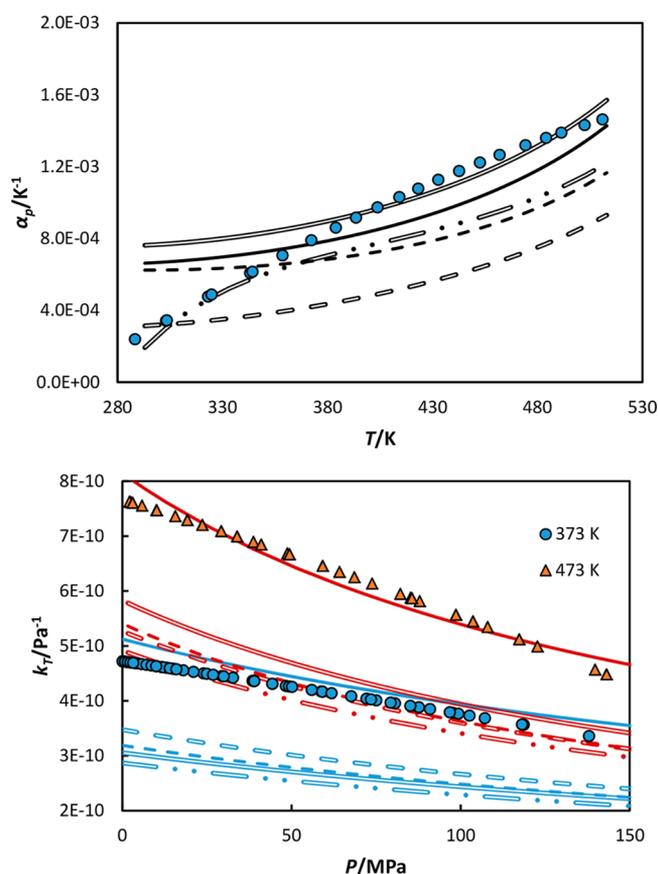


Figure 7. α_p and k_T at 5 MPa and 373/473 K respectively for water. Full lines, volume shifted set; dashed lines, original set;¹⁴ double dots and dashes, Fuchs;¹⁷ double dashes, Fouad;¹⁸ double line, von Solms.¹⁹ Data calculated from liquid volume values available on the TRC database.¹³

The mixtures in this study are methanol + hexane (VLE and LLE), water + hexane (LLE), water + benzene (LLE), ethanol + hexane (VLE), ethanol + benzene (VLE), and ethanol + water (VLE). Figure 9 presents the results for the aqueous mixtures. Tables A1 and A2 of the Supporting Information present the binary interaction parameters used for each mixture. A comparison between the results of this work and

those from Liang et al.¹⁵ for the speed of sound of hexane + ethanol is also presented.

The improvement in the description of the LLE for water-containing mixtures is noticeable when using the 4C association scheme. The present volume shifted set compares well with the other sets from the literature. The sets with a 4C scheme, as discussed by Liang et al.,³⁹ tend to be superior in the description of mixtures of alkanes + water, as 2B presents higher difficulties in the description of water solubility in the hydrocarbon phase. For the 2B sets of water, in the mixture with benzene, it was opted to try to improve the description of the water in the hydrocarbon phase, thus leading to a poor description of benzene in the aqueous phase.

Thus, for these kind of mixtures this new parametrization approach improves the description of some derivative properties while keeping accurate phase equilibria results. It is important to note that a binary interaction parameter for the volume of association was applied in the mixture with benzene, using the same approach as that by Folas et al.⁴⁰ for CPA.⁴¹ No advantages were found in the use of such an approach for the sets of pure parameters using the 2B scheme.

The mixture containing methanol is analyzed in Figure 10.

Using a single binary interaction parameter, as in the case of the original PC-SAFT sets, it is possible to describe both the LLE and VLE for methanol + hexane. It is important to note that the new set tends to slightly overestimate the liquid–liquid critical point, similar to what is obtained with the reparametrization of the universal constants, while improving the description of the alkane-rich phase.

The results for the remaining mixtures are presented in Figures 11 and 12. For both ethanol + hydrocarbon mixtures, the results are accurate, but a binary interaction parameter is needed. No clear differences related to the use of various parameter sets is observed.

For water + ethanol, presented in Figure 12, there are some improvements with the new parameter set when compared with the original set which shows LLE at some of the analyzed conditions. From the other sets, only the sets using the 4C scheme behaved similarly to our new set.

Figure 13 presents the results for the speed of sound of ethanol + hexane at 298.15 and 318.15 K. As previously discussed, the present approach, while greatly improving the description of the speed of sound, is still not as powerful in the

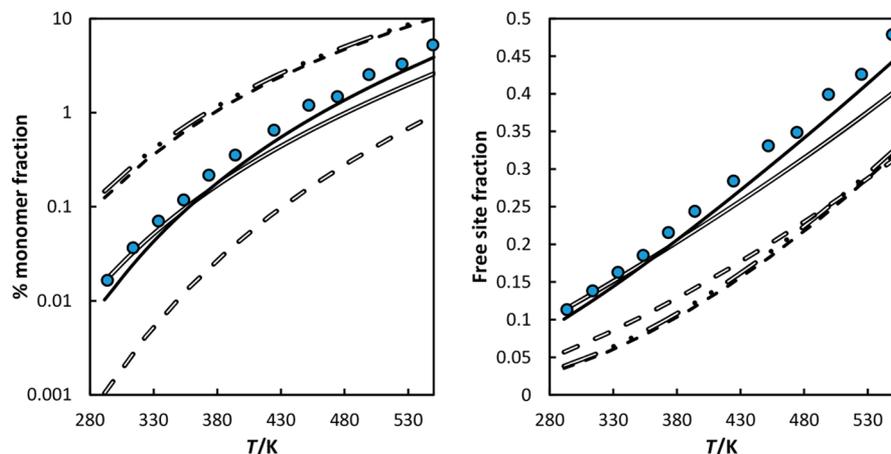


Figure 8. Percent monomer fraction and free site fraction for water. Full lines, volume shifted set; dashed lines, original set;¹⁴ double dots and dashes, Fuchs;¹⁷ double dashes, Fouad;¹⁸ double line, von Solms.¹⁹ Data from Luck.³⁵

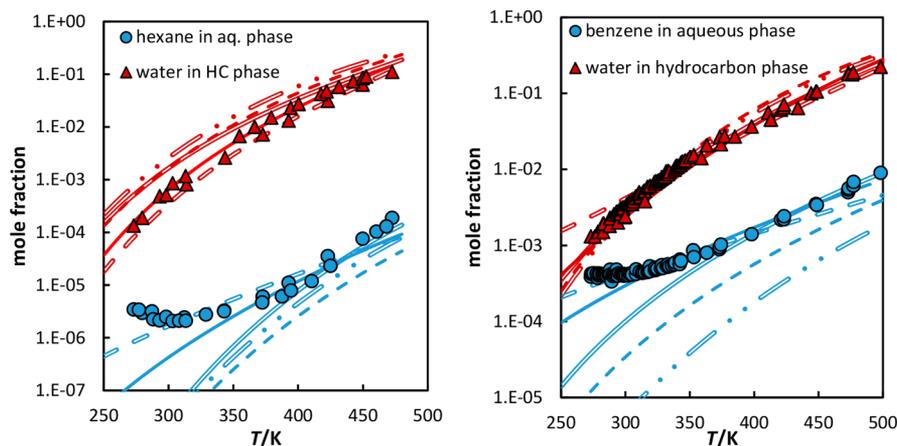


Figure 9. Results for water + hexane (left) and water + benzene (right). Full lines, volume shifted set; dashed lines, original parameters;^{11,14} double dashes and dots, Fuchs et al.;¹⁷ double dashes, Fouad;¹⁸ double lines, von Solms.¹⁹ Data taken from Góral et al.^{37,38}

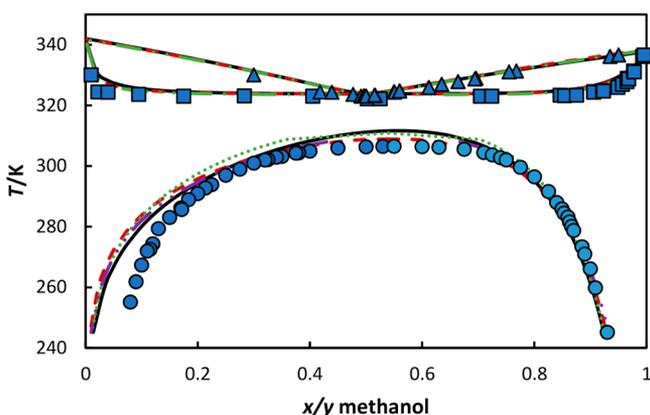


Figure 10. VLE for methanol + hexane. Full lines, volume shifted set; dashed lines, original set;^{11,14} dashes and dots, Liang;¹⁶ dots, Liang¹⁶ (MeOH universal). Data from Hradetzky and Lempe⁴² and Raal et al.⁴³

description of this property as the approach proposed by Liang et al.;¹⁶ thus the description of the speed of sound for the mixture presented in Figure 13 is slightly less accurate with the present approach. It is important to note, however, that while advantageous for the speed of sound, for most other properties and equilibria, the results are either similar or improved with

the present set. Also, the present approach is easily applicable to other EoS, such as other SAFT variants, and may be applied to fit other properties during the main parametrization routine (if these are not affected by a constant volume shift).

4. CONCLUSIONS

The use of a volume shift with PC-SAFT is proposed and analyzed in order to improve the description of the speed of sound and other derivative properties, while keeping the description of the phase equilibria. The results here reported show that it is possible to obtain simultaneously a good description of liquid density, vapor pressure, and speed of sound in liquid media in a large temperature range using a constant volume shift and reparametrizing the pure compounds by taking into account $\left(\frac{\partial P}{\partial V}\right)_T$, instead of just vapor pressure and liquid density.

The removal of liquid density from the parametrization also leads to a better description of some derivative properties not directly linked with volumetric properties. However, some care needs to be taken, as by forcing a better description of $\left(\frac{\partial P}{\partial V}\right)_T$ other derivative properties can be negatively affected.

Results for high pressure are accurate for liquid density and are improved for the speed of sound, when compared to the

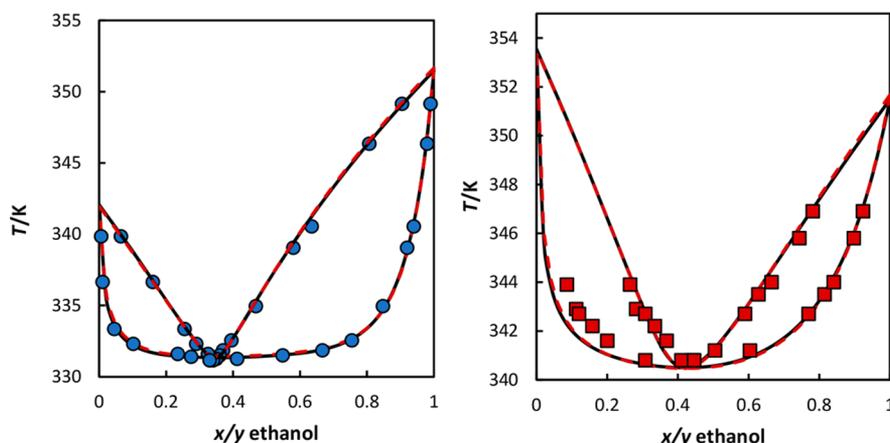


Figure 11. VLE of ethanol + hexane (left) and ethanol + benzene (right) both at 1 atm. Full lines, volume shifted set; dashed lines, original parameters.^{11,14} Data from Wehe and Coates⁴⁴ and Sinor and Weber.⁴⁵

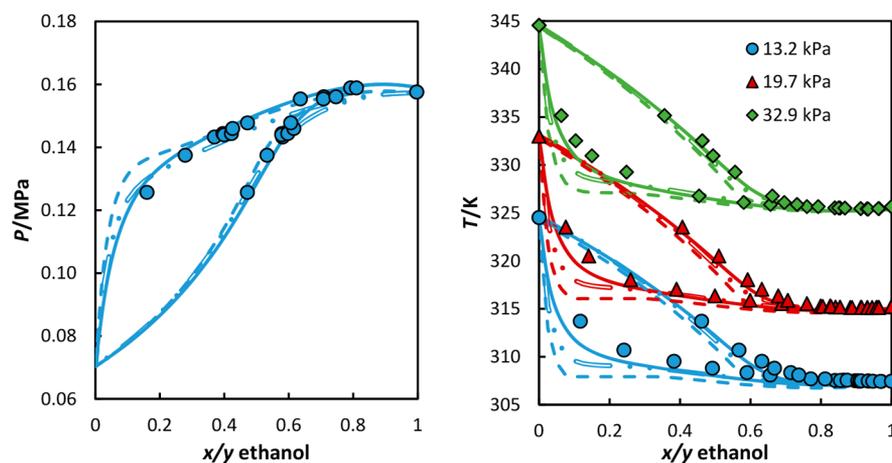


Figure 12. Description of ethanol + water, at 363 K (left) and at three different pressures (right). Full lines, volume shifted set; dashed lines, original parameters; double dashes and dots, Fuchs. (For a comparison with the remaining water sets, see the Supporting Information.) Data from Voutsas et al.⁴⁶ and Cristino et al.⁴⁷

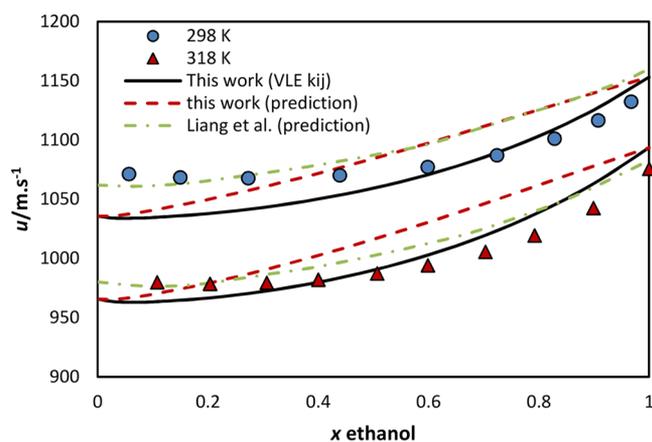


Figure 13. Description of the speed of sound for ethanol + hexane at two temperatures. Data from Orge et al.^{48,49}

original PC-SAFT parameters. However, the results for the speed of sound at high pressures are not as accurate, as a global reparametrization of the universal constants of PC-SAFT, which takes this property into account.

When comparing the results for methanol, the sets which fitted speed of sound at saturation still present a better description of this property, k_T , and α_p . To improve this, one could use a larger range of temperatures for the derivative used in the parametrization. In this work it was chosen to use this derivative only at conditions where the compound would be liquid at 1 bar.

Monomer fractions were studied as well with accurate results using the new parametrization. However, it is important to note that no experimental uncertainties are reported for this type of data, and thus one should be cautious when using them.

For the mixtures analyzed there is no noticeable decrease in accuracy by using this method, while there are some improvements for mixtures containing water, especially when comparing to the sets which use the 2B association scheme.

The presented approach is a direct application of the volume shift concept and can be extended to other EoS, namely, other SAFT variants. It is important to note, however, that the accuracy of the speed of sound results will depend greatly on the capacity of the base EoS to describe $\left(\frac{\partial P}{\partial V}\right)_{T,n}$.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b02646.

Binary interaction parameters, results for monomer fractions of methanol and ethanol, more detailed figures for some properties of water with all sets in analysis (PDF)

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Notes

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■ NOMENCLATURE

C_p = isobaric heat capacity ($\text{J mol}^{-1}\cdot\text{K}^{-1}$)

k_T = isothermal compressibility (Pa^{-1})

P = pressure (Pa)

T = temperature (K)

V_0, V_t = volume before and after translation, respectively ($\text{m}^3\cdot\text{mol}^{-1}$)

x, y = liquid, vapor mole fractions

H^{vap} = heat of vaporization (J mol^{-1})

u = speed of sound ($\text{m}\cdot\text{s}^{-1}$)

Greek Symbols

α_p = isobaric expansivity coefficient (K^{-1})
 ρ = molar density ($\text{mol}\cdot\text{m}^{-3}$)

Abbreviations

EoS = equation(s) of state
 PC-SAFT = perturbed-chain statistical associating fluid theory
 LLE = liquid–liquid equilibrium
 VLE = vapor–liquid equilibrium
 npsat = number of saturation pressure data points applied to fit PC-SAFT parameters
 nder = number of $\left(\frac{dp}{dV}\right)_{T,n}$ data points applied to fit PC-SAFT parameters

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