

# New Procedure for Enhancing the Transferability of Statistical Associating Fluid Theory (SAFT) Molecular Parameters: The Role of Derivative Properties

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## Supporting Information

**ABSTRACT:** Here, we present a simple method for optimizing the fitting of molecular parameters involving vapor–liquid equilibria (VLE) and selected second-order thermodynamic properties and experimental data. The procedure is applied, as an example to the soft Statistical Associating Fluid Theory (soft-SAFT) equation of state. The method involves the introduction and testing of coupling factors ranging from 0 (only one selected derivative property) to 1 (only VLE), to change the weight of one set of properties over the other in the fitting procedure; this allows one to assess the role of derivative properties in the robustness of the parameters and molecular model. The technique is illustrated by calculating a large number of thermodynamic properties of different compounds: the *n*-alkanes, *n*-perfluoroalkanes, and 1-alkanols families, and water, as representative of different types of molecular interactions, and in a wide range of thermodynamic conditions. The most relevant thermodynamic properties to be included in the parameters fitting, the weight they should have in the regression procedure, and the influence of association are discussed in detail. It has been found that the use of just VLE data in the fitting procedure for regular nonassociating compounds, such as *n*-alkanes or perfluoroalkanes, is enough to provide good predictions of derivative properties. The use of derivative properties helped in identifying the best fitting strategy for the perfluoroalkanes family, as some limitations of the original parameters showed up when used for estimating the derivative properties. In contrast, association plays a major role in derivative properties of associating compounds such as alkanols and water. A coupling factor of 0.5 (equal weight of derivative property coupled with VLE data to fit the molecular parameters) is required to regress robust pure compound parameters that are able to simultaneously describe vapor pressures, phase densities, and derivative properties for 1-alkanols and water. The method presented here is robust, simple, and straightforward to implement; since it is not equation-dependent, it can be transferred to any other equation, providing robust molecular parameters for global equations.



## 1. INTRODUCTION

The design and optimization of industrial processes, involving the correct selection of suitable solvents, the most advantageous unit operations, and an adequate separation sequence, relies upon the accurate prediction of the behavior at different thermodynamic conditions of the relevant systems. Besides the phase equilibria description, knowledge of derivative properties, such as heats of vaporization, isochoric and isobaric heat capacities, isothermal compressibility, and thermal expansion coefficients, are essential to fulfill the conditions of an optimized industrial process<sup>1</sup> or product.

A quick literature survey clearly shows that most modeling efforts have been devoted to the description of standard phase equilibria without taking into account the correlation/prediction of other properties of the mixtures, such as derivative properties.<sup>2</sup> However, it has been shown that second order derivatives are more sensitive to quantitative deviations than the first-order derivatives of the thermodynamic function.<sup>3</sup> In this manner, any minor deviation on the estimation of a first

derivative thermodynamic property will have a major impact when describing a second-order derivative property. Consequently, a correct description of first-order derivatives, such as phase equilibria calculations, does not ensure an accurate prediction of second-order derivatives of the same thermodynamic function (heat capacities, speed of sound, etc.) for the same compound or mixture. These derivative fluid properties present a complex behavior with different minima and maxima, not only close to critical conditions but also in other fluid range regions.<sup>4</sup> Because of this complexity, the accurate description of the second-order thermodynamic derivative properties poses a stringent test for any equation of state (EoS). In fact, most EoSs, with parameters regressed from pure compounds and mixtures phase equilibria, fail in describing them (see

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discussions in refs 3–7). Empirical corrections using a larger number of parameters, which are often dependent on temperature and/or density, have been proposed,<sup>4</sup> at the expense of reducing the predictive ability and theoretical basis of the models, reducing them to semiempirical correlations of data.

Improvements are expected with molecular-based EoSs, because they are able to retain fundamental relationships between intermolecular and intramolecular forces and the macroscopic behavior of fluids. Consequently, results must be independent of the particular properties under study and the range of thermodynamic conditions.<sup>3,8</sup> In the last three decades, several molecular-based EoSs have been proposed in the literature. Among them, the Statistical Associating Fluid Theory (SAFT)<sup>9</sup> and its refined versions, are among the most successful molecular EoSs applied to the description of the phase equilibria of a large number of compounds and their mixtures, in wide ranges of thermodynamic conditions. Nevertheless, SAFT-type EoSs have been applied to a much lesser extent to second-order derivative properties. The first SAFT approach used to calculate these derivative properties was performed by Colina et al.,<sup>6</sup> using the soft-SAFT equation<sup>10–12</sup> to predict the Joule–Thomson inversion curves of CO<sub>2</sub> and the *n*-alkanes family. Soft-SAFT was able to predict the general trend of the inversion curves, even for extreme conditions, with reduced pressures up to 40, and reduced temperatures of ~5. A strong dependence of the inversion curve on the set of molecular parameters used in the calculations was found, especially near the inversion point and in the high-temperature region. Later, Llovel and Vega<sup>13</sup> applied soft-SAFT to the calculation of other second-order derivative properties, including heat capacities, reduced bulk modulus, Joule–Thomson coefficients, and speeds of sound of two main chemical families: the *n*-alkanes and the 1-alkanols. Calculations were done in a predictive manner, with the molecular parameters of the equation obtained from previous fitting to vapor–liquid equilibrium (VLE) data of the same compounds. Taking advantage of the molecular nature of the equation, a thorough study was conducted to separate and quantify the different contributions (reference fluid, chain, and association) to the total value of the derivative properties. It was found that association plays a predominant role in energetic properties, such as the heat capacities, while there is a competition between association and dispersion forces as the chain length of the compound increases for volumetric properties, such as the isothermal compressibility. The same approach was used to calculate the derivative properties of selected mixtures<sup>3</sup> and other families of compounds.<sup>14–17</sup> In all these studies, some derivative properties (especially, the speed of sound and the isobaric heats capacity) were accurately predicted from VLE parameters, while the calculation of isochoric heats capacities and some other derivative properties pointed out on the possibility of using other approaches to quantitatively capture the behavior of all derivative properties. In a very recent contribution, Llovel et al.<sup>18</sup> proposed a methodology for modifying the original soft-SAFT EoS to take into account the anomalies of some properties at the critical region due to critical fluctuations, such as the divergence of the isochoric heat capacity. They demonstrated that adding a kernel term, whose presence is predicted by the renormalization-group theory of critical phenomena, yields a significant improvement for the representation of the anomalous behavior of the isochoric heat capacity in the critical region. Derivative

properties were predicted from VLE fitting. They also highlighted some possible procedures for further improvements.

Some other SAFT versions have also been used to calculate derivative properties, with different degrees of success. PC-SAFT<sup>19</sup> and different versions of SAFT-VR<sup>7,20</sup> were applied to the description of *n*-alkanes derivative properties. The CR-SAFT EoS, developed by Kiselev et al.<sup>21</sup> for the description of 1-propanol derivative properties, included a specific treatment for the critical region, in order to describe the weak divergence of the isochoric heat capacity, but just focused on one compound and one property. Diamantonis et al.<sup>22</sup> used SAFT and PC-SAFT for the description of CO<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, and CH<sub>4</sub> derivative properties for applications in carbon dioxide capture and sequestration processes. A very comprehensive work has been recently published by Villiers et al.,<sup>23</sup> where the ability of the PC-SAFT, SAFT and CPA equations of state in the prediction of selected derivative properties for *n*-alkanes and *n*-alcohols using pure compound molecular parameters regressed only from vapor pressure and liquid density data (as previously done with soft-SAFT) was evaluated. They concluded that none of the selected equations are able to properly describe, at the same time, all the derivative properties for both families; unfortunately, the soft-SAFT performance was not included in their comparative study.

In summary, until now, all works published in this area have indicated the need of a procedure for a robust, yet practical, description of derivative properties with these types of equations. Given the sensitivity of second-order derivative properties to inaccuracies of the models or the equations, they are an appropriate framework to perform tight tests to refine equations, search for ways to improve them, or assess the molecular model to be used.

The objective of this work is to propose, and extensively test, a new method for enhancing the transferability of the molecular parameters in SAFT by coupling vapor–liquid equilibrium (VLE) data with derivative properties in the fitting procedure. Isothermal compressibilities, thermal expansion coefficients, and isochoric and isobaric heat capacities were selected as derivative properties to be included in the fitting (one by one), while compounds from the *n*-alkanes, *n*-perfluoroalkanes (PFCs), 1-alkanols families, and water were used as case studies. The obtained optimized parameters sets were then evaluated by predicting the remaining derivative properties not included in the fitting procedure, such as the speed of sound and other additional data, including surface tensions and high-pressure densities.

## 2. THE SOFT-SAFT EOS

Wertheim's first-order thermodynamic perturbation theory,<sup>24–26</sup> is the origin of several different types of SAFT EoSs, providing the chain and association term in these equations. The soft-SAFT EoS, which is a variant of the original SAFT equation,<sup>9</sup> considering a Lennard-Jones (LJ) fluid as the reference term, was proposed by Blas and Vega<sup>10,11</sup> and further refined by Pàmies and Vega.<sup>12</sup> As performed with all other versions of SAFT, the equation is expressed as a sum of contributions to the total Helmholtz energy of the system:<sup>27,28</sup>

$$a^{\text{res}} = a - a^{\text{id}} = a^{\text{ref}} + a^{\text{chain}} + a^{\text{assoc}} \quad (1)$$

where  $a^{\text{res}}$  is the residual Helmholtz energy and  $a^{\text{id}}$  is the ideal contribution;  $a^{\text{ref}}$ ,  $a^{\text{chain}}$ , and  $a^{\text{assoc}}$  represent the reference term (also called monomer or segment term), the chain formation,

and the association, respectively. Additional terms, such as polar terms, can be added, depending on the system under consideration.

The LJ spherical fluid takes into account the repulsive and attractive interactions of the monomers forming the chain. It includes two molecular parameters, i.e., the segment diameter ( $\sigma_{ii}$ ) and the dispersive energy between segments ( $\epsilon_{ii}/k_B$ ). The equation of Johnson et al.<sup>29</sup> is used to compute the reference term in this work.

The chain and association term are derived from Wertheim's theory<sup>24</sup> as

$$a^{\text{chain}} = \rho k_B T \sum_i x_i (1 - m_i) \ln g_{LJ} \quad (2)$$

$$a^{\text{assoc}} = \rho k_B T \sum_i x_i \sum_\alpha \left( \ln X_i^\alpha - \frac{X_i^\alpha}{2} \right) + \frac{M_i}{2} \quad (3)$$

where  $\rho$  is the molecular density,  $T$  the temperature,  $m$  the chain length,  $x_i$  the molar fraction of component  $i$ ,  $k_B$  the Boltzmann constant, and  $g_{LJ}$  the radial distribution function at density  $\rho = m\rho_{\text{monomer}}$  of a LJ spheres fluid, taken from the work of Johnson et al.<sup>30</sup> The reader is referred to previous works for details on the implementation of each term.<sup>8,10,12,27,28</sup>

Within the soft-SAFT framework, nonassociating molecules, such as  $n$ -alkanes and  $n$ -perfluoroalkanes, are defined by three molecular parameters: the chain length ( $m_i$ ), the segment diameter ( $\sigma_{ii}$ ), and the dispersive energy between segments ( $\epsilon_{ii}/k_B$ ). For associating molecules, such as alcohols and water, associating sites are mimicked by square well spheres embedded into the core of the LJ segments.<sup>27</sup> Two more parameters are needed to model the associating interactions: the site–site association energy of the embedded square well sites ( $\epsilon_{\alpha\beta,ij}^{\text{HB}}/k_B = \epsilon^{\text{HB}}/k_B$  and a parameter related to the site–site bonding-volume of association,  $\kappa_{\alpha\beta,ij} = \kappa^{\text{HB}}$ ).

The derivative properties of a thermodynamic potential function can be obtained in different manners, with one of them being the mathematical derivation of the expression for the Helmholtz energy and the pressure. These are direct calculations from the soft-SAFT equation.<sup>13</sup> The expressions for the main derivative properties calculated in this work are

$$C_v = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_V \quad (4)$$

$$k_T^{-1} = 2P + \rho^3 \left( \frac{\partial^2 A}{\partial \rho^2} \right)_T = \rho \left( \frac{\partial P}{\partial \rho} \right)_T \quad (5)$$

$$\alpha_p = k_T \rho^2 \left( \frac{\partial^2 A}{\partial P \partial T} \right)_V = k_T \left( \frac{\partial P}{\partial T} \right)_V \quad (6)$$

$$C_p = C_v + \frac{T \alpha_p^2}{k_T \rho} \quad (7)$$

$$\omega = \sqrt{\frac{C_p}{C_v} \left( \frac{\partial P}{\partial \rho} \right)_T} \quad (8)$$

where  $C_v$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) is the isochoric heat capacity,  $k_T$  ( $\text{MPa}^{-1}$ ) is the isothermal compressibility,  $\alpha_p$  ( $\text{K}^{-1}$ ) is the thermal expansion coefficient,  $C_p$  is the isobaric heat capacity ( $\text{J mol}^{-1} \text{K}^{-1}$ ), and  $\omega$  the speed of sound ( $\text{m/s}$ ).

In this work, we evaluate the possible advantages of incorporating derivative properties, along with the standard VLE data in the parameter regression procedure. A coupling procedure to consider either one set of properties or both has been designed, testing coupling factors ( $\delta$ ) ranging from 0, using only derivative property data to fit molecular parameters and use them to predict VLE, to 1, where only VLE properties are used to fit the molecular parameters and are used to predict derivative properties, as previously done in other works.<sup>13,14</sup> A value of  $\delta = 0.5$  gives equal weight to a derivative property coupled with VLE data to fit the molecular parameters.

The following objective function (OF) is used:

$$\text{OF} = \frac{1}{M} \left\{ \frac{\delta}{N} \left[ 0.80 \sum_{i=1}^n \left( \frac{\rho_{\text{cal}} - \rho_{\text{exp}}}{\rho_{\text{exp}}} \right) + 0.20 \sum_{i=1}^n \left( \frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}} \right) \right] + (1 - \delta) \sum_{i=1}^n \left( \frac{X_{\text{cal}} - X_{\text{exp}}}{X_{\text{exp}}} \right) \right\} \quad (9)$$

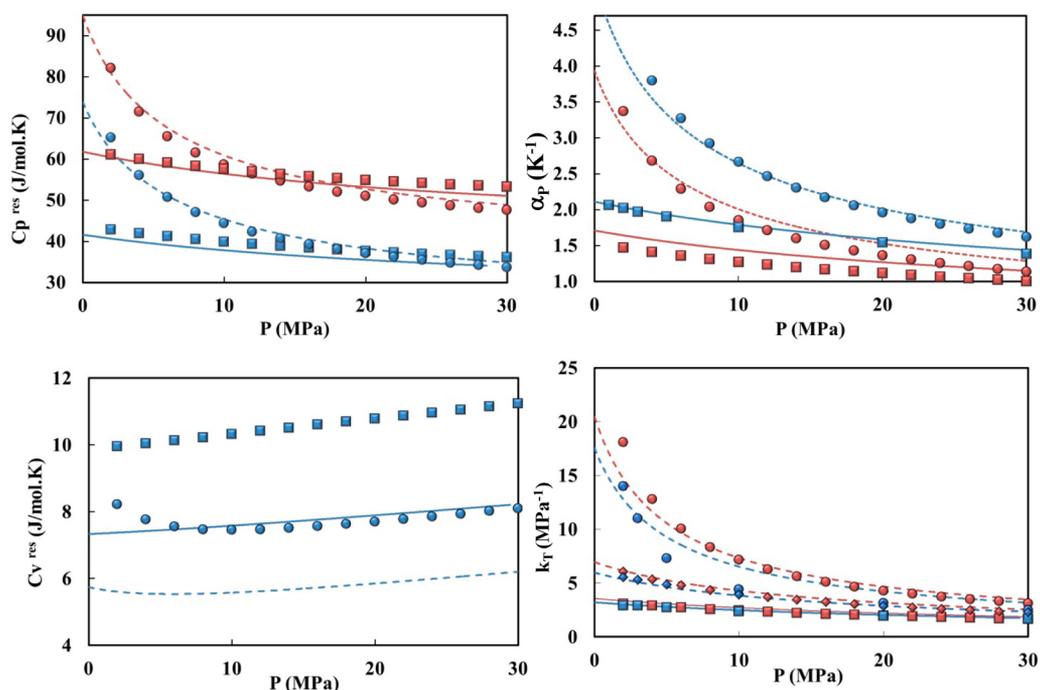
where  $\delta$  is the coupling factor,  $N$  and  $M$  represent the number of experimental phase equilibrium and derivative property data points, respectively, and  $X$  represents the chosen derivative property used in the fitting procedure. The numbers 0.80 and 0.20 correspond to the weight given in the fitting to the density and vapor pressure, respectively, within the phase equilibrium data, and are taken from previous contributions, since they were found to provide the most balanced and optimal results.<sup>8,12</sup>

### 3. RESULTS AND DISCUSSION

**3.1. Molecular Models.** Following previous works,  $n$ -alkanes<sup>3</sup> and  $n$ -perfluoroalkanes<sup>31</sup> are modeled as nonassociating homonuclear chain molecules. Alkanols are described as having two associating sites representing the hydroxyl group<sup>8</sup> and water is described as a LJ fluid with four associating sites (two sites of type e, corresponding to the lone pairs of electrons, and two of type H, corresponding to the hydrogen atoms; only e–H bonding is allowed).

**3.2.  $n$ -Alkanes.** The first studied family was the  $n$ -alkanes, as a benchmark for testing the procedure, given that it is the simplest, regular, and most studied family with any EoS. Since there is not any association, it is straightforward to quantify whether the reference and the chain terms used in soft-SAFT, and the corresponding molecular parameters, are able to properly take into account dispersive and repulsive interactions affecting the derivative properties.

Butane, hexane, and octane were selected as representative compounds of the family. The soft-SAFT molecular parameters of these compounds, fitted to liquid density and vapor pressure data (hence,  $\delta = 1$ ), were taken from the published work.<sup>12</sup>  $C_p$ ,  $C_v$ ,  $\alpha_p$ , and  $k_T$  data from the *NIST Chemistry Webbook*<sup>32</sup> at three different temperatures,  $0.7T_c$ ,  $0.8T_c$ , and  $0.9T_c$ , were gathered in order to evaluate the accuracy of the published molecular parameters to properly describe the derivative properties in the selected temperature range. This test was previously performed near to and above the critical point for methane, propane, hexane, and heptane by Llovel and Vega.<sup>13</sup> It was shown that soft-SAFT was able to capture the behavior of these properties. In the present work, the test is extended to the above-mentioned compounds in a wider pressure range, up to 30 MPa. Soft-SAFT results for the selected derivative properties for butane and octane, at two temperatures, are depicted in **Figure 1**. The remaining modeling results for the other alkanes



**Figure 1.** Derivative properties predictions for *n*-butane (blue) and *n*-octane (red) at selected temperatures with the soft-SAFT EoS with  $\delta = 1$ . Symbols are used for experimental data:<sup>32</sup> (squares, ■)  $0.7T_c$  and (circles, ●)  $0.9T_c$ . Lines are used to represent soft-SAFT results: (solid line, —)  $0.7T_c$  and (dashed line, ---)  $0.9T_c$ .

and temperatures are similar and are reported in Table S1 in the Supporting Information.

As previously observed,<sup>13</sup> the derivative properties are predicted in very good agreement with the experimental data using the molecular parameters sets regressed using only VLE data (coupling factor of  $\delta = 1$ ), with the exception of  $C_v$ . A slightly poorer prediction is observed for the lowest and highest temperatures for  $C_p$  and for  $k_T$ , respectively, still with global average deviations smaller than 3% for the three alkanes selected. These results show that the available molecular parameters for *n*-alkanes, obtained only from VLE data, are suitable for predicting, at the same time, different derivative properties in wide temperature and pressure ranges.

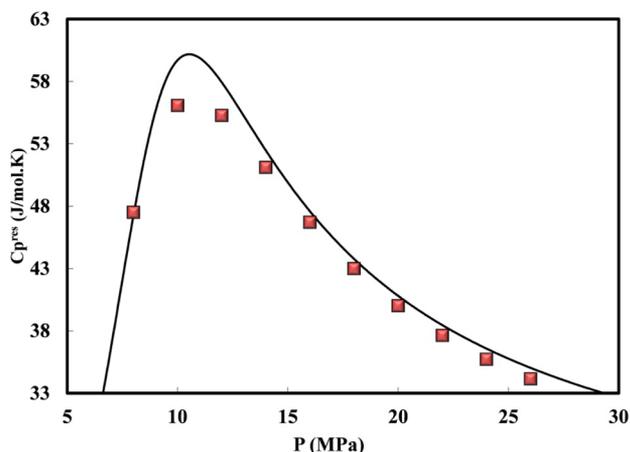
Even though the results using only VLE data were quite successful, different coupling factors  $\delta$  were further tested for the *n*-alkanes family in order to check the effect of derivative properties on the optimization of molecular parameters. Two different set of tests were carried out in a systematic manner. In the first set of tests, each derivative property ( $C_v$ ,  $C_p$ ,  $k_T$ , and  $\alpha_p$ ) was used individually in the regression in order to select the most appropriate property to be used, along with VLE data in the molecular parameters regression. In the second case, four coupling factors of  $\delta = 0, 0.1, 0.5$ , and  $0.9$  were also used in the regression tests, with  $C_p$  being the chosen derivative property. To limit the variability of the parameters, it was decided to keep  $m$  and  $\varepsilon/k_B$  equal to the previous gathered values, allowing only  $\sigma$  to vary. Correlated NIST data at the three subcritical temperatures ( $0.7T_c$ ,  $0.8T_c$ , and  $0.9T_c$ ) were used in the parameter regression. The results are all quite similar to those obtained by using a coupling factor equal to 1 (only VLE data), with regard to parameter values and the description of derivative properties; no significant improvements in the derivative properties results were obtained when using the new sets of parameters. Regarding the best choice of derivative property to be used, together with the VLE data in the

molecular parameters regression, the performance of the method with the different derivative properties was very similar; hence, for the sake of brevity, we omit their presentation. However, we have observed that the residual  $C_p$  seems to provide slightly better results than the others in some of the cases, while also being widely available for most of the compounds. Table S1 in the Supporting Information summarizes the new molecular parameters obtained for the selected alkanes using different coupling factors, as well as their performance for the selected properties. For instance, for hexane, comparing the results with coupling factors of 1 and of 0.5, the  $C_p$  description has deviations from experimental data of 3.23% and 3.20%, densities of 0.67% and 1.05%, and vapor pressures of 1.91% and 2.36%, respectively. Using another alkane (*n*-octane) as an example,  $\alpha_p$  and  $k_T$  are predicted with global average deviations inferior to 12% and 9%, respectively, for a temperature of  $0.8T_c$ .

Summarizing the results of these tests for *n*-alkanes, both the original parameters and the parameter sets regressed using  $C_p$  data describe this derivative property with deviations of <3% from the available experimental data (see Table S1), independent of the coupling factor used.

A further corroboration of the good performance of the parameters obtained using a coupling factor  $\delta = 1$  was made, to see how they perform in predicting a supercritical  $C_p$  isotherm for *n*-butane. A reduced temperature ( $T/T_c$ ) of 1.25 was chosen, and results are depicted in Figure 2, showing very good agreement with the experimental correlated  $C_p$  data.<sup>32</sup>

Therefore, it can be concluded that, for *n*-alkanes, repulsive and dispersive interactions are correctly taken into account with the current soft-SAFT EoS model parametrization, using only VLE information or only derivative properties data. Consistent physically sound molecular parameters, regressed with a coupling factor of  $\delta = 1$ , are able to simultaneously predict isothermal compressibility coefficients, isobaric expansion



**Figure 2.** Butane isobaric residual heat capacity predictions at a reduced temperature of  $T/T_c = 1.25$  with soft-SAFT with  $\delta = 1$  (symbols represent experimental data;<sup>32</sup> lines represent soft-SAFT results).

coefficients, and isobaric heat capacities in large temperature and pressure ranges. Hence, there is no need to add other properties to the fitting process to improve the capabilities of the soft-SAFT equation for these compounds.

**3.3. *n*-Perfluoroalkanes.** The perfluoroalkanes (PFCs) family was investigated following the same approach as for *n*-alkanes, in order to confirm the behavior previously observed for nonassociating compounds. Octafluoropropane ( $C_3F_8$ ), decafluorobutane ( $C_4F_{10}$ ), and dodecafluoropentane ( $C_5F_{12}$ ) were chosen as case studies.

We first evaluated the parameters proposed in a previous work,<sup>31</sup> obtained using only VLE data (coupling factor of  $\delta = 1$ ), by calculating the PFCs derivative properties. The goal was to assess if improvements over previous predictions could be achieved by using additional data. VLE data and  $C_p$  data, at temperatures of  $0.7T_c$ ,  $0.8T_c$ , and  $0.9T_c$  and at pressures up to 20 MPa were obtained from the NIST databank<sup>32</sup> and used for comparison. The results clearly show that the previously existing parameters fail in describing the PFCs derivative properties. (See Figures S1–S3 and Table S2 in the Supporting Information.)

However, it is important to note that the original parameters<sup>31</sup> were established by fixing the values of the segment chain ( $m$ ) equal to that of the correspondent *n*-alkane. This assumption, based on experimental studies, indicates that

the C–C bond lengths for crystalline poly(tetrafluoroethylene) and polyethylene are equivalent, provided an acceptable description of the VLE data, and allowed the transferability of one parameter between families. However, the current study on the derivative property predictions reveals that this constraint might be too restrictive. Consequently, before proceeding to include derivative properties in the fitting, the molecular parameters for these three PFCs were reoptimized, removing the constraint to the value of  $m$  and keeping  $\delta = 1$ . The new parameters obtained in this work are presented in Table 1, and the corresponding derivative properties and phase equilibria description are depicted in Figure 3 for  $C_3F_8$  and in Figures S1–S3 for the other PFCs. In addition to the VLE description improvement, the derivative properties are also well-predicted with the soft-SAFT EoS, with the global average deviation being reduced from a maximum of 38% to only 6%. For  $C_4F_{10}$ ,  $C_p$  data from the NIST databank<sup>32</sup> were also considered (Figure S2), obtaining a similar quality description previously observed for alkanes. The parameters obtained with this procedure are somehow consistent with the PC-SAFT results for octafluoropropane and decafluorobutane,<sup>33</sup> where  $m$  was also fitted.

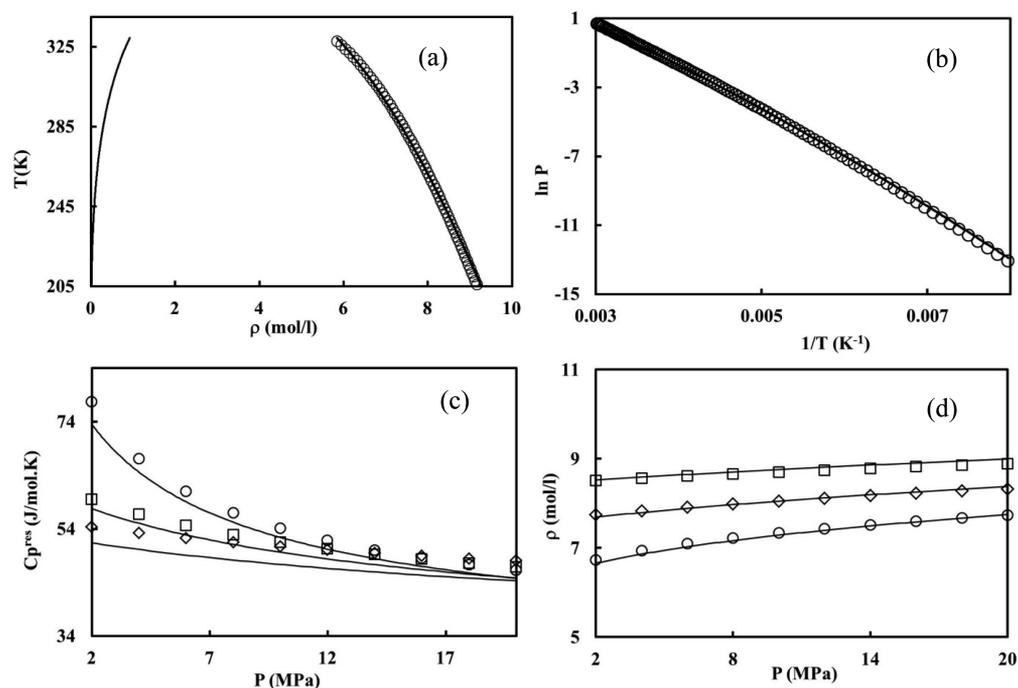
Additional calculations were performed using two different coupling factors:  $\delta = 0.5$  and  $\delta = 0$ . Parameters values and modeling results are presented in Table S2 in the Supporting Information. No significant improvement was observed in the derivative properties and VLE description by adding heat capacity data to the VLE data in the parameter regression, confirming that, for nonassociative compounds, no further data needs to be added for the parameter regression. Unexpectedly, when only heat capacity data is used ( $\delta = 0$ ), the vapor-pressure description is negatively affected. As a consequence of these calculations, it is deduced that, for PFCs, VLE data are sufficient to provide parameter sets with accurate predictive character, unlike to what happens when exclusively using derivative properties information. The quality of the description using both properties ( $\delta = 0.5$ ) is similar to that using only VLE data.

The applicability of the new parameter sets was assessed by successfully predicting high-pressure density data, up to 20 MPa. Results for these calculations are included in Figure 3 and Figures S1–S3. These new parameters follow linear dependencies with the PFC molecular weight, as depicted in Figure S4 in the Supporting Information. Correlations can therefore be proposed as previously done for the same PFCs or other organic families such as alkanes,<sup>10,11</sup> alcohols,<sup>8,12</sup> hydro-

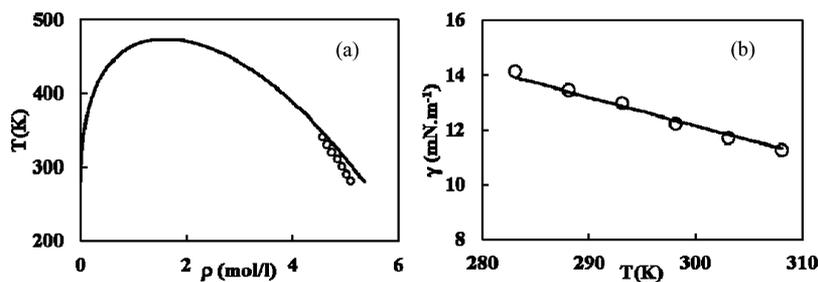
**Table 1. Optimized Molecular Parameters Sets Established in This Work for PFC and 1-Alkanols and Average Absolute Deviations (AADs) Obtained from the Soft-SAFT Calculations**

compound	$\delta^a$	$m$	$\sigma$ (Å)	$\epsilon/k_B$ (K)	$\epsilon^{HB}/k_B$ (K)	$\kappa^{HB}$ (Å <sup>3</sup> )	AAD		
							$P^v$ (%)	$\rho$ (%)	$C_p$ (%)
$C_3F_8$	1	2.886	3.646	170.9			2.710	0.510	4.770
$C_4F_{10}$	1	3.476	3.663	178.2			2.100	1.590	3.190
$C_5F_{12}$	1	4.063	3.666	184.3			2.550	1.080	6.210
methanol	0.5 and b)	1.425	3.434	220.4	3212.0	5231.9	2.435	0.183	1.967
ethanol	0.5 and b)	1.831	3.567	234.8	3387.0	2215.0	3.214	0.542	3.940
1-butanol	0.5 and b)	2.455	3.785	269.2	3450.0	1339.0	3.880	0.991	4.830
1-hexanol	0.5 and b)	2.974	3.925	291.6	3450.0	1023.8	1.572	1.625	5.381
1-octanol	0.5 and b)	3.421	4.071	305.8	3450.0	842.4	3.384	0.807	4.184

<sup>a</sup> $\delta$  is the coupling factor, while b) is the fitting strategy followed when the energy-related parameters  $\epsilon/k_B$  and  $\epsilon^{HB}/k_B$  are kept equal to their original values, while the remaining three parameters are refitted ( $m$ ,  $\sigma$ , and  $\kappa^{HB}$ ).



**Figure 3.** Modeling results for  $C_3F_8$ : (a and b) VLE, (c) residual heat capacity at selected temperatures, and (d) high-pressure density at different temperatures. Symbols represent experimental data:  $\square$  ( $\square$ )  $0.7T_c$ ; ( $\diamond$ ,  $\diamond$ )  $0.8T_c$ ; ( $\circ$ ,  $\circ$ )  $0.9T_c$ . Lines represent soft-SAFT results with a coupling factor of 1 (parameters from this work).



**Figure 4.** Saturation densities and surface tension predictions with soft-SAFT for  $C_6F_{14}$ . Symbols are experimental data<sup>38,39</sup> and lines soft-SAFT results ( $10^{19}c = 6.84 \text{ J m}^5 \text{ mol}^{-2}$ ).

fluorocarbons,<sup>34</sup> ionic liquids,<sup>16,35,36</sup> and esters<sup>37</sup> with soft-SAFT:

$$m = 0.0118M_w + 0.674 \quad (10)$$

$$m(\sigma)^3(\text{\AA}^3) = 1.658M_w - 44.347 \quad (11)$$

$$m\left(\frac{\varepsilon}{k_B}\right)(\text{K}) = 2.556M_w + 12.19 \quad (12)$$

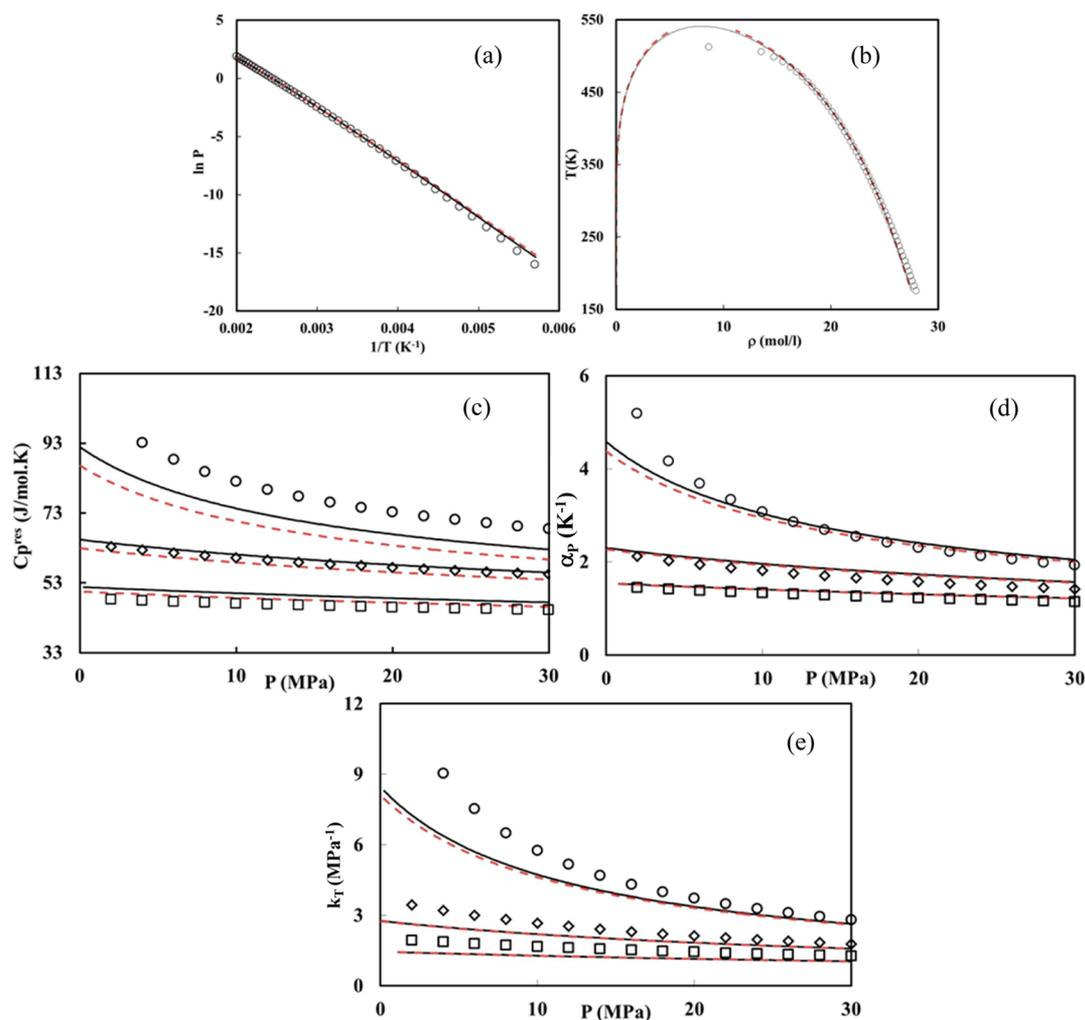
As an additional test to the predictive ability of the new proposed parameters, phase densities and interfacial tension data<sup>38,39</sup> using the density gradient theory<sup>8,40</sup> were successfully predicted for  $C_6F_{14}$ , as depicted in Figure 4, with parameters computed using the above linear relations with the molecular weight (eqs 10–12).

The results presented for *n*-alkanes and PFCs confirm that, for nonassociating compounds, accurate VLE data are sufficient for an adequate approach for the molecular parameter regression. The set of parameters obtained with this procedure is reliable for accurately describing VLE and predicting a large number of derivative properties, including their behavior with pressure and temperature. Although not needed for the fitting

procedure, an advantage of using derivative properties in this case was the guidance in identifying the best set of molecular parameters and molecular model to be used, providing robustness to them.

**3.4. 1-Alkanols.** The 1-alkanols family was studied in order to assess the influence of the association parameters in the derivative properties description, as well as the influence of the chain length. Seven compounds were selected for this purpose: methanol, ethanol, 1-propanol, 1-butanol, 1-hexanol, 1-heptanol, and 1-octanol. Contrary to what happens with *n*-alkanes, much less data are available for alcohols.

**3.4.1. Methanol.** VLE and derivative properties data were obtained from the NIST database<sup>32</sup> at  $0.7T_c$ ,  $0.8T_c$ , and  $0.9T_c$  and pressures up to 30 MPa. Following the same procedure as for the previous compounds, the first approach was to evaluate how the parameter sets obtained only fitting to VLE data ( $\delta = 1$ )<sup>8</sup> behave in predicting the isobaric heat capacity, the isothermal compressibility, and the thermal expansion coefficient. As illustrated in Figure 5 it was found that the available set of parameters provides a satisfactory prediction of the selected derivative properties, particularly for  $\alpha_p$ . This is consistent with the work of Llovel and Vega,<sup>13</sup> where it was



**Figure 5.** Methanol results: (a and b) VLE, (c–e) derivative properties at selected temperatures. Symbols represent experimental data:<sup>32</sup> (squares,  $\square$ )  $0.7T_c$ , (diamonds,  $\diamond$ )  $0.8T_c$ , and (circles,  $\circ$ )  $0.9T_c$ . Lines represent soft-SAFT results: (solid line, —)  $\delta = 1$  and (red dashed line, - - -)  $\delta = 0.5$  and parameters approach a). See text for details.

shown that the soft-SAFT original molecular parameters provided good predictions of the heat capacity data at reduced temperatures of 1.10 and 1.20.

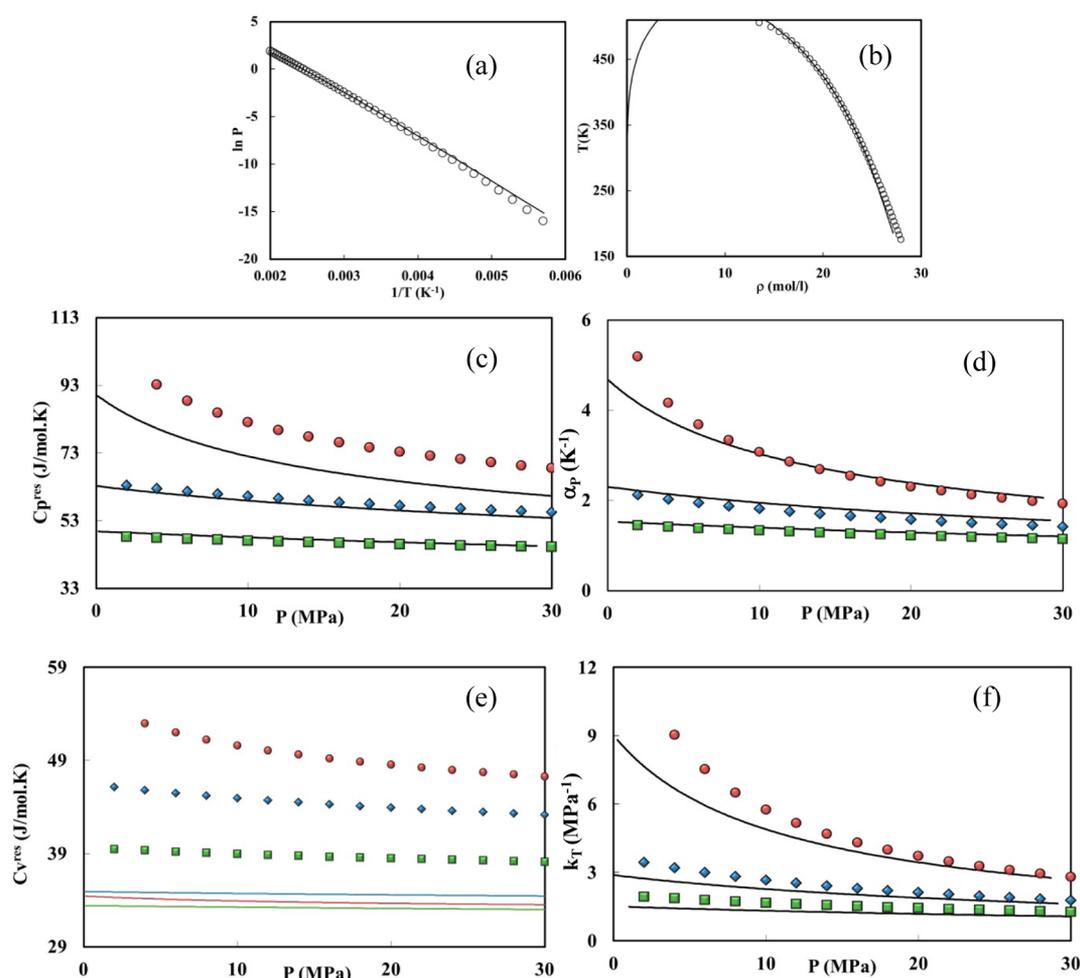
The next step consisted of fitting a set of parameters introducing derivative properties data.  $C_p$  was the selected property, and different coupling factors were used ( $\delta = 0.1$ ,  $\delta = 0.5$ , and  $\delta = 0.9$ ). All available data at the selected temperatures were included in the parameters regression.

Two parameters fitting approaches were considered: (a) only the association parameters were fitted using the available data, while keeping the original values for the other three parameters ( $m$ ,  $\sigma$ , and  $\epsilon$ ); (b) the energy-related parameters  $\epsilon/k_B$  and  $e^{HB}/k_B$  were kept equal to their original values, while the remaining three parameters were refitted ( $m$ ,  $\sigma$ , and  $\kappa^{HB}$ ). Interestingly, the results obtained with these two approaches show no major improvements, compared to the results from the original parameters (Table 1, as well as Tables S3 and S4 in the Supporting Information). Slight improvements were obtained when equal weight was given to both type of properties in the fitting procedure ( $\delta = 0.5$ ), providing good results for the description of both, the VLE and derivative properties, as observed in Figure 5 (approach a)) and Figure 6 (approach b)). Nevertheless, these improvements resulted in a reduction of the

global average deviation from 4% to 2%. The description of  $C_p$  data from the NIST databank<sup>32</sup> for methanol are also depicted in Figure 6, showing higher deviations than the rest of the properties, as observed for all fluids. This is an intrinsic limitation of the approach, as already stressed in a previous work.<sup>18</sup>

**3.4.2. Ethanol.** Greater deviations were observed for ethanol when using the original molecular parameters regressed only with VLE data ( $\delta = 1$ ).<sup>8</sup> Predictions of the available heat capacity data at 4.9 MPa<sup>41</sup> had a relative deviation of  $\sim 6\%$ , as shown in Figure 7 (see also Tables S5 and S6 in the Supporting Information). Similar deviations have been previously observed when using these parameters to predict ethanol residual heat capacity at 0.1 MPa.<sup>13</sup>

The isobaric heat capacity data was introduced in the parameters regression, following the same two approaches previously established for methanol. Both methods provide improvements in the heat capacity description, as observed in Table 1 and Tables S5 and S6 in the Supporting Information. A coupling factor  $\delta = 0.1$ , while providing an excellent heat capacity description, results in a very poor description of the vapor pressure (less weighted with this coupling factor value). In contrast, the  $\delta = 0.9$  coupling factor gives a good VLE



**Figure 6.** Methanol results: (a and b) VLE, (c) isobaric residual heat capacity, (d) thermal expansion coefficient, (e) isochoric residual heat capacity, and (f) isothermal compressibility. Symbols represent experimental data:<sup>32</sup> (squares,  $\square$ )  $0.7T_c$ , (diamonds,  $\diamond$ )  $0.8T_c$ , and (circles,  $\circ$ )  $0.9T_c$ . Lines represent soft-SAFT results with  $\delta = 0.5$  and parameters approach b).

description but fails to provide an acceptable derivative property description. In contrast, a coupling factor of  $\delta = 0.5$  is able to afford a simultaneous good description of the VLE and heat capacity data, particularly with the approach b) being considered for the molecular parameters regression, giving global average deviations of 1.6% for the vapor pressure, 0.3% for the liquid density, and 4.7% for the residual heat capacity (Table 1). Results for these calculations are provided in Figure 7.

In summary, contrary to that observed for methanol, ethanol results show that using only VLE data ( $\delta = 1$ ) is not a good strategy to provide parameter sets that are able to predict derivative properties. Significant improvements can be achieved when using a coupling factor of  $\delta = 0.5$  in the parameters regression, i.e., equally weighting VLE and one derivative property data.

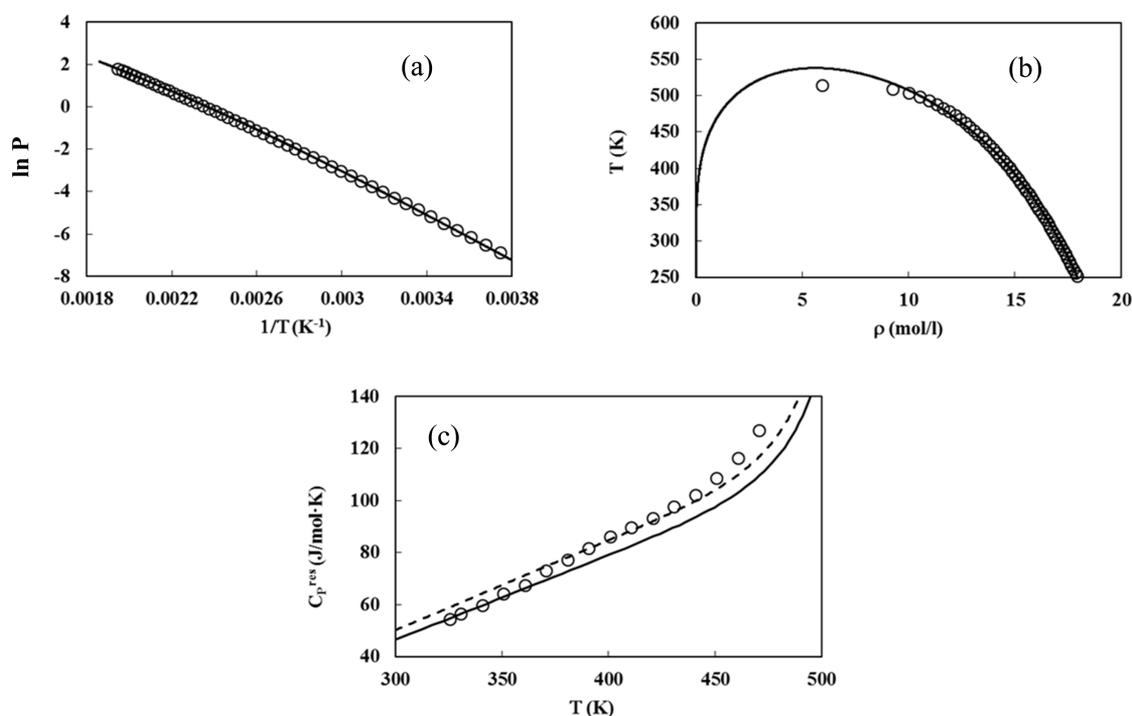
**3.4.3. 1-Butanol.** Data for the isobaric heat capacity of 1-butanol were available at 6.4 MPa.<sup>42</sup> It is observed that an increase in the alcohol chain length leads to a degradation of the soft-SAFT heat capacity description using the molecular parameters obtained from only VLE data (coupling factor of  $\delta = 1$ );<sup>8</sup> a deviation of 11.5% was found for 1-butanol (see Tables S7 and S8 and Figure S5 in the Supporting Information), pinpointing the need for using additional properties to obtain a better set of parameters. As done with the previous compounds

from the same chemical family, we have introduced derivative property data along with VLE information, in the parameters regression. Approaches a) and b), which have been described in section 3.4.1, were adopted.

Parameter values and properties deviations are presented in the Supporting Information (Tables S7 and S8). The results obtained show the same pattern observed for ethanol, regarding the coupling factors and regression approaches used (as depicted in Table 1 and Tables S7 and S8). In summary, regression approach b) (where the volume-related parameters are optimized and a coupling factor  $\delta = 0.5$  is used) can significantly improve the heat capacity description, leading to a global average deviation of 4.8%, while preserving a good VLE description, as depicted in Figure S5 in the Supporting Information.

**3.4.4. 1-Hexanol and 1-Octanol.** The discussion for these two compounds is presented in the same subsection, because of the similarity between the results obtained for them.

Heat capacity data are available at 10 MPa<sup>41</sup> for 1-hexanol, 1-heptanol, and 1-octanol. The inability of the soft-SAFT parameters regressed only from VLE information<sup>8</sup> to predict heat capacity data is again patent for these compounds. It is interesting to observe that this inadequacy has a tendency to stabilize for the longer alcohols at a deviation of  $\sim 13\%$  (see Tables S9–S14 and Figures S6 and S7 in the Supporting



**Figure 7.** Modeling results for ethanol: (a and b) VLE. (In panels (a) and (b), symbols represent experimental data.<sup>45</sup>) (c) Residual heat capacity at 4.9 MPa. Symbols represent experimental data;<sup>41</sup> solid line represents soft-SAFT results with  $\delta = 1$ , and dashed line represents soft-SAFT results with  $\delta = 0.5$  and parameters approach b). See text for details.

Information), as previously shown by Llovel and Vega for 1-hexanol and 1-heptanol.<sup>13</sup> Results for 1-heptanol are very similar and are not presented here.

Results obtained when introducing heat capacity data for the parameter regression approaches previously used, and for different coupling factors, are presented at Table 1, as well as Tables S9–S12 in the Supporting Information. As expected, the previous conclusions about the use of the coupling factor also apply to these compounds descriptions: a coupling factor of  $\delta = 0.5$  provides the best balance between heat capacity and VLE description, with global average deviations for the three alcohols of <5% for the residual heat capacity, <3% for the vapor pressure, and <2% for the liquid density.

The main difference obtained for these longer alkanols is that the approach a) now fails to provide a good parameter regression, leading to high deviations for the vapor pressure and the heat capacity. The approach b) with a coupling factor of  $\delta = 0.5$  provides sets of parameters that are able to simultaneously describe isobaric heat capacity and VLE data with accuracy, as depicted in Figures S6 and S7 in the Supporting Information. This highlights the importance of the volumetric parameters (chain length, volume of the segments, and volume of association) to provide a good description of the derivative properties for longer alkanols.

In fact, a different behavior is observed when dealing with short and longer alcohols. For methanol, the strong association interactions through hydrogen bonding described by molecular parameters fitted using only VLE data ( $\delta = 1$ ) are accurate enough to adequately describe second-order derivative properties. This ability is lost as the alcohol chain length is increased and the van der Waals interactions begin to compete with association interactions for longer alcohols. These results confirm that association and van der Waals interactions both play a decisive role in capturing the behavior of derivative

properties of associating compounds, as observed by Llovel and Vega,<sup>13</sup> with the influence of association decreasing as the chain length of the alkanol increases. For long-chain alcohols, molecular parameters based only in VLE data are not able to take into account the competition between hydrogen bonding and van der Waals interactions present in these molecules. An equal weight of derivative properties data and VLE data (coupling factor of  $\delta = 0.5$ ) is thus necessary to be included in the parameters regression in order to achieve good results. Nevertheless, it must be stressed that only information for one derivative property ( $C_p$ ) was used and, in addition, these set of parameters clearly follow trends with the molecular weight of 1-alkanols, as observed in Figure S8 in the Supporting Information, with the association energy being kept constant except for the two first compounds of the series.<sup>8</sup> This allows predicting molecular parameter values for other members of the chemical family when no VLE or heat capacity data are available, using the following equations:

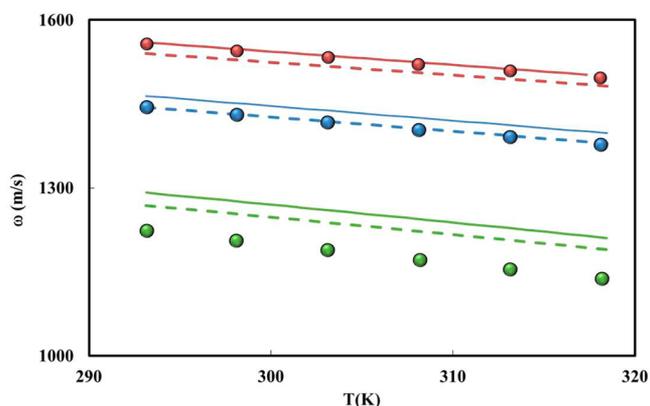
$$m = 0.0201M_w + 0.858 \quad (13)$$

$$m(\sigma^3) (\text{\AA}^3) = 1.759M_w + 1.832 \quad (14)$$

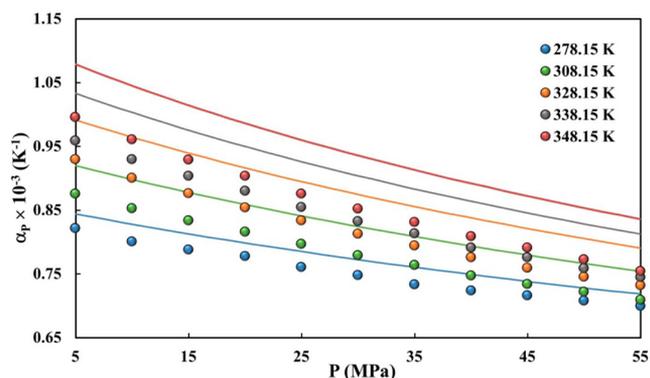
$$m\left(\frac{\epsilon}{k_B}\right) (\text{K}) = 5.714M_w + 78.967 \quad (15)$$

Note that the  $\epsilon/k_B$  value is transferred from the previous work of Pàmies,<sup>8</sup> while  $m$  and  $\sigma$  were fitted following approach b).

The predictive character of the proposed parameters sets was checked by calculating some other properties, based on the availability of experimental data. In particular, the speed of sound of 1-propanol and the thermal expansion coefficient of 1-hexanol, as a function of temperature and pressure, were calculated and compared with literature data,<sup>43,44</sup> as depicted in Figures 8 and 9, respectively. A slight improvement in the 1-



**Figure 8.** Speed of sound in 1-propanol, as a function of temperature and pressure. Symbols represent experimental data;<sup>43</sup> lines represent the soft-SAFT predictions (solid lines denote  $\delta = 1$  data (original parameters from ref 13), dashed lines denote  $\delta = 0.5$  data and the parameters approach b).



**Figure 9.** Thermal expansion coefficient of 1-hexanol, as a function of temperature and pressure. Symbols represent experimental data;<sup>44</sup> lines represent soft-SAFT predictions, with the molecular parameters provided in Table 1.

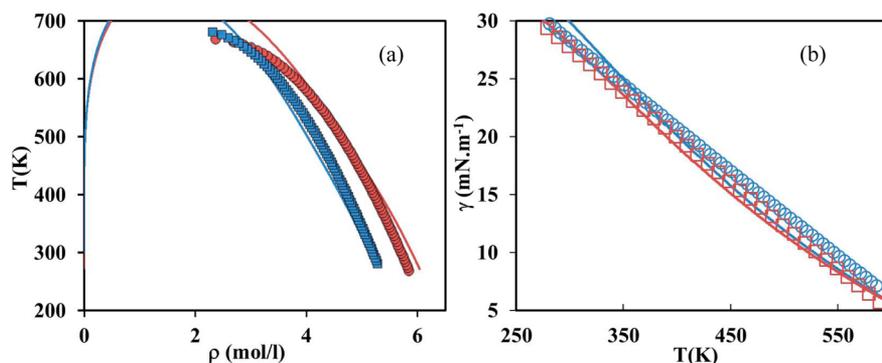
propanol speed of sound description was observed using the parameters sets obtained in this work with a coupling factor of  $\delta = 0.5$ , compared with results from the parameter sets obtained using a coupling factor of  $\delta = 1$ .<sup>13</sup> The thermal expansion coefficient of 1-hexanol is predicted with a maximum absolute average deviation of 9.76%, found for the highest temperature for which data were available: 348.15 K. In addition, the correlations with the molecular weight (eqs

13–15) were tested in the prediction of the saturation densities and surface tensions of 1-nonanol and 1-decanol available in the DIPPR database.<sup>45</sup> The results (see Figure 10) clearly show that the correlations proposed can be used to predict, with confidence, the thermodynamic properties of other compounds from the same family when no data are made available.

**3.5. Water.** The procedure presented in this work has also been tested with water. The highly directional associating interactions of water (with highly anisotropic hydrogen bonding) play a subtle role, combined with van der Waals forces under near ambient temperature conditions<sup>17,46</sup> and they are also responsible for the highly nonideal behavior of water. Because of the presence of these forces, the description of the thermophysical properties of aqueous mixtures is a stringent test to any modeling approach; hence, they provide an excellent case study to the fitting procedure presented in this work.

In a similar manner as done for the other compounds, we first checked the accuracy of the original published parameters for water,<sup>46</sup> fitted with only VLE data, for predicting selected second-order derivative properties. Results for the isobaric residual heat capacity, the thermal expansion coefficient, the isochoric residual heat capacity, and the isothermal compressibility are presented in Figure S9 in the Supporting Information, at three different temperatures (300, 400, and 500 K). Although the residual isobaric heat capacity at high temperatures is well-predicted, in most of the cases, the original parameters give a poor description of the second-order derivative properties, even though they were optimized in this range of temperature.

A new set of parameters was obtained when introducing the isobaric heat capacity in the fitting. As a first approach, the  $m$  parameter was kept equal to 1, while the rest of the parameters were optimized with a coupling factor of  $\delta = 0.5$  (equal weight to VLE and the heat capacity). Results for a constant pressure of  $P = 0.1$  MPa and the new set of parameters (see Table 2) are depicted in Figure 11, together with the corresponding experimental data. The experimental data for these properties were retrieved from the *NIST Chemistry WebBook*.<sup>32</sup> Contrary to what happens with 1-alkanols, there is a large amount of derivative properties data available for water. We have decided to use the isochoric and isobaric heat capacities, thermal expansion coefficient, and isothermal compressibility for consistency with the alkanols results presented in the previous section. As shown in Table 2, deviations of 5.17% in pressure, 1.63% in density, and 5.82% in isobaric heat capacity were obtained when the isobaric heat capacity was coupled with the

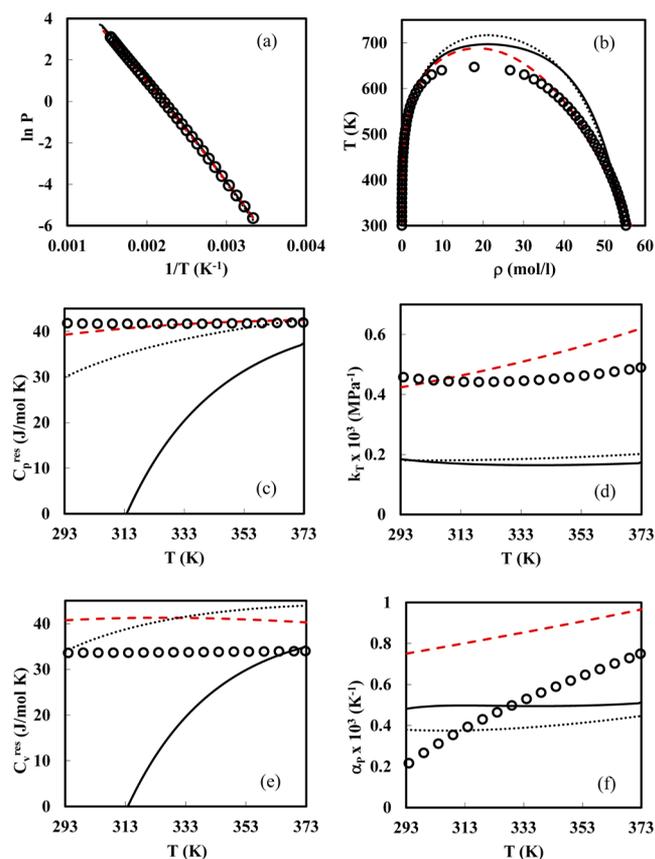


**Figure 10.** Saturation densities and surface tension predictions with soft-SAFT for 1-nonanol (red) and 1-decanol (blue). Symbols represent experimental data<sup>45</sup> and lines represent soft-SAFT results (for 1-nonanol,  $10^{19}c = 5.87 \text{ J m}^5 \text{ mol}^{-2}$ ; for 1-decanol,  $10^{18}c = 1.00 \text{ J m}^5 \text{ mol}^{-2}$ ).

**Table 2. Molecular Parameters for Water and Average Absolute Deviations (AADs) Obtained from the Soft-SAFT Calculations of This Work<sup>a</sup>**

compound	coupling factor, $\delta$	$m$	$\sigma$ (Å)	$\epsilon/k_B$ (K)	$\epsilon^{HB}/k_B$ (K)	$\kappa^{HB}$ (Å <sup>3</sup> )	AAD		
							$P^r$ (%)	$\rho$ (%)	$C_p$ (%)
water	1	1.0	3.154	365.0	2388.0	2932.0	6.93	1.33	47.8
water	0.5	1.0	3.163	259.5	2515.0	3034.0	5.17	1.63	5.82
water	0.5	1.389	2.681	120.6	2587.0	2384.0	2.01	0.97	1.2

<sup>a</sup>The original parameters, optimized in the temperature range of 300–500 K, taken from ref 46 are also included. See text for details.



**Figure 11.** Water results: (a and b) VLE, (c–e) derivative properties at constant pressure  $P = 0.1$  MPa (residual isobaric heat capacity (panel (c)), thermal expansion coefficient (panel (d)), residual isochoric heat capacity (panel (e)), and isothermal compressibility (panel (f))). Symbols represent experimental data.<sup>32</sup> The solid line corresponds to the results predicted from the original fitting ( $\delta = 1$ ); the dotted line is the result with  $\delta = 0.5$  and keeping  $m = 1$ ; and the red dashed line represents results with  $\delta = 0.5$  and  $m = 1.389$ .

VLE data in the parameters regression procedure using a coupling factor of  $\delta = 0.5$ . Note that the vapor pressures, densities, and residual isobaric heat capacities were included in the parameters regression, while the residual isochoric heat capacity, the thermal expansion coefficient, and the isothermal compressibility were predicted from this set of parameters. As observed in the figure, although the description of the second-order derivative properties improves, with respect to the original parameters, there is still room for further improvements.

Guided by the results obtained for perfluoroalkanes when describing derivative properties, we decided to relax the condition of  $m = 1$  and fitted all parameters using VLE and heat capacities in the regression. Note that some other authors have also used values of  $m$  that were different than 1 for water

(see, for instance, refs 46 and 47). In fact, since  $m$  and  $\sigma$  are both related to the volume of the molecule, a higher value of  $m$  should necessarily imply a lower value of  $\sigma$ . We would like to emphasize, however, that there is one more parameter fitted than in the previous case. The parameters obtained with this approach ( $\delta = 0.5$  and  $m$  being allowed to vary) are presented in Table 2. In this case, deviations are reduced, with respect to the previous case (2.01% in pressure, 0.97% in density, and 1.2% in heat capacity). The fact that the constraint of  $m = 1$  was relieved leads to a value of  $m > 1$  (1.389), implying lower values for the segment parameters ( $\sigma$  and  $\epsilon$ ), with respect to the other two cases.<sup>12</sup> While the value of  $\sigma$  is within most of the segment values published for water by different authors,<sup>17</sup> the value obtained for  $\epsilon$  is in the lower range. As inferred from Figure 11, the new set of parameters improves the description of the derivative properties not included in the fitting procedure.

Figure 12 shows the prediction of selected derivative properties of water at three constant temperatures (300, 400, and 500 K) with the two sets of parameters including heat capacity data in the regression procedure. Again, the particular properties and conditions were chosen for similarity with the alkanols study. Both sets of parameters provide more accurate results than the original ones (see also Figure S9), with the set of parameters with  $m = 1.389$  being considered the most accurate one.

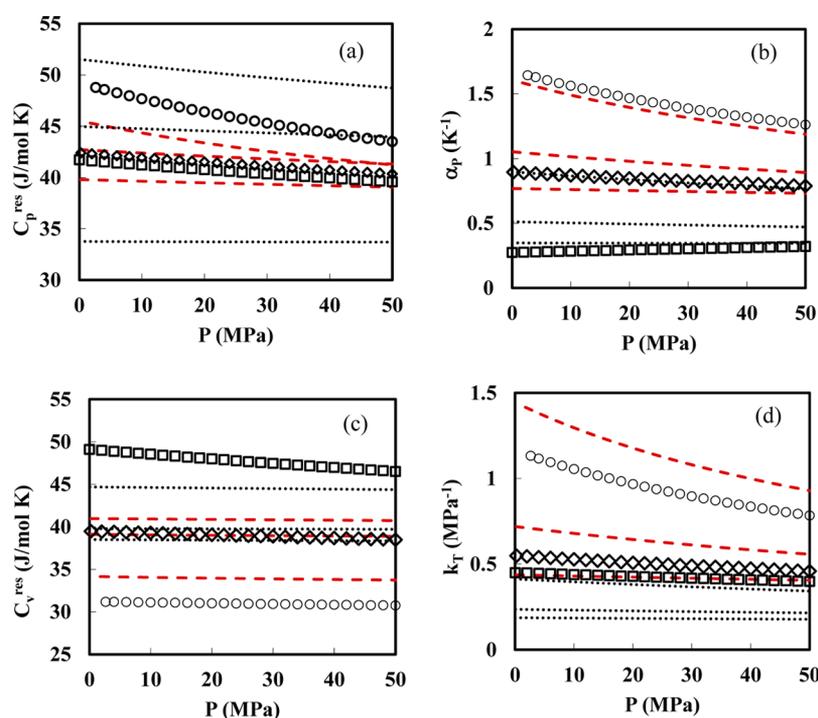
Results obtained for water are consistent with those obtained for alkanols. The challenging behavior of water and the good results obtained here act in favor of including derivative properties as part of the regression process for obtaining molecular parameters. However, extensive tests and even the inclusion of other properties, which are beyond the scope of the present work, should be done before claiming the water parameters proposed in this work are the best parameters to be used for water with the soft-SAFT approach.

## 4. CONCLUSIONS

In this contribution, we have proposed a simple, yet accurate, method to optimize the molecular parameters of a SAFT equation by adding derivative properties data in the molecular parameters regression weighted with VLE data, according to a coupling factor. The method is general and can be applied to any molecular-based equation of state. The soft-SAFT EoS has been used to illustrate the procedure, with coupling factors ranging from 0 (only derivative properties) to 1 (only VLE).

The technique has been tested for predicting isothermal compressibilities, thermal expansion coefficients, and isochoric and isobaric heat capacities data gathered in wide temperatures and pressures ranges for selected members of the  $n$ -alkanes,  $n$ -perfluoroalkanes, and 1-alkanols families, as well as for water.

For the nonassociating families,  $n$ -alkanes and PFCs, molecular parameters regressed using a coupling factor of  $\delta = 1$  (only VLE data) were able to successfully describe isothermal



**Figure 12.** Water predictions of derivative properties at a constant temperature of (squares,  $\square$ )  $T = 300$  K, (diamonds,  $\diamond$ )  $T = 400$  K, and (circles,  $\circ$ )  $T = 500$  K: (a) residual isobaric heat capacity, (b) thermal expansion coefficient, (c) isochoric heat capacity, and (d) isothermal compressibility. Symbols represent experimental data,<sup>32</sup> and lines represent soft-SAFT results (red dashed line denotes data with  $\delta = 0.5$  and  $m = 1.389$ , dotted line denotes data with  $\delta = 0.5$  and  $m = 1$ ).

compressibility, thermal expansion coefficients and isobaric heat capacities, with no need to re-estimate any molecular parameter using additional properties. In summary, for nonassociating families, accurate vapor liquid equilibria are sufficient to obtain transferable parameters for other properties, provided that care has been taken in the fitting procedure and the physical meaning of them.

A different conclusion is obtained for the associating compounds. The ability of the VLE regressed molecular parameters to predict derivative properties data is lost for alcohols heavier than ethanol, further degrading with the chain length increase. The situation is even more acute for water. Different procedures were tested to improve these descriptions. In the case of 1-alkanols, it has been observed that just coupling residual  $C_p$  data with phase equilibria data to regress molecular pure compound parameters provides the simultaneous description of phase equilibria and of a large number of second-order derivative properties, in very good agreement with available experimental data. An equal weight for the derivative properties and VLE data regression was appropriate, highlighting the competitive role that van der Waals and association forces play in the description of derivative properties. In the case of water, predictions are greatly improved when the residual isobaric heat capacity is included in the parameters regression with a weighting factor of  $\delta = 0.5$ , especially when all five molecular parameters are simultaneously optimized.

The use of just  $C_p$  as a derivative property to be included is not a limitation of the approach, as any other derivative property can be used, but a convenient procedure, as  $C_p$  is more readily available than other derivative properties. An additional advantage of using derivative properties is that it allows

checking the accuracy of the molecular model or the fitting procedure, as it happens in this work for the PFCs and water.

These results emphasize the robustness of soft-SAFT and the underlying model for accurately describing a wide range of thermodynamic properties of different compounds, while providing an additional tool to be used for the accurate description of highly nonideal systems. The simultaneous regression of VLE and derivative properties presented here can be used for other compounds or for other types of properties and other molecular-based equations, depending on the needs and the predictive capability of the equation.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b02205.

The set of soft-SAFT parameters for  $n$ -alkanes,  $n$ -perfluoroalkanes, and 1-alkanols, as well as deviations from the experimental data for the different approaches considered in this work (Tables S1–S12); modeling results for perfluoroalkanes  $C_3F_8$ ,  $C_4F_{10}$ , and  $C_5F_{12}$  (Figures S1–S3), alcohols 1-butanol, 1-hexanol and 1-octanol (Figures S5–S7), and water (Figure S9). Trends of the new parameters sets proposed for perfluoroalkanes (Figure S4) and 1-alkanols (Figure S8) (PDF)

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### Notes

The authors declare no competing financial interest.

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