

# Thermodynamic and Interfacial properties of hydrogenated and fluorinated alcohols mixtures: a molecular modelling approach

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## ABSTRACT

The mutual phobicity between mixtures involving hydrogenated and fluorinated chains is, at the origin, of an unusual and interesting behaviour. For instance, mixtures of long chain hydrogenated and fluorinated alcohols form nanopatterned Langmuir films at the air-water interface, while liquid mixtures of shorter alcohols display minimum on the surface tension vs. composition curve, a rare phenomenon called aneotropy. In this work, SAFT equation of state (EoS), coupled with a Density Gradient Theory (DGT), are used to attain a robust molecular model for the pure fluorinated alcohols family and for the mixtures of these compounds with hydrogenated alcohols. The pure components model was successfully achieved. In addition, its consistency and robustness were analysed with derivative properties calculations, parameters transferability and the interfacial properties. The model obtained for the mixtures with fluorinated and hydrogenated alcohols, besides showing a good agreement regarding parameterization results, has enabled the parameters transferability to related families. Moreover, the surface tension curve of the mixtures was achieved and the aneotrope value for the correct composition was obtained. Lastly, the microscopic structure in the interface was also studied for compositions under and above the aneotrope composition and for aneotrope composition itself.

## 1. Introduction

One of the most pressing challenges for the past few years is in finding a way of getting accurate predictions for a wide range of physical property data. The need of keeping up with new industry processes demands the development of models that are capable of describing a wide range of thermodynamic properties; as a result of such need, numerous works are continuously published in this field.

The importance of fluorine compounds is increasing day by day. The fluorochemical industry has never stop growing, partly because of the discovery of these compounds' applications and how to synthesize them safely. This is explained by the large numbers of fluorine compounds that are already known and the wide range of applications that they have [1]. Some of those applications are in firefighting foams, batteries, refrigerants (CFC's), plastics (polymers), pharmaceutical reactants, to name but a few. [1-4].

The compounds of interest in this work (fluorinated alcohols) represent only a fraction of the big fluorine compounds' family. These molecules, also known as *fluorinated* surfactants or *fluorotelomer alcohols*, are composed by a semi organic fluorinated chain and have a hydroxyl (*OH*) group, as a terminal group. Fluorinated alcohols can be described by the general formula  $CF_3(CF_2)_n(CH_2)_mOH$ , with:  $m \geq 1$ . In contrast with hydrogenated alcohols, fluorinated alcohols are rigid molecules and have their amphiphilic behaviour enhanced. Both properties are due to the existence of the fluorotelomer, which reduces significantly the translational and rotational movement of the molecules and increases their hydrophobic behaviour. In addition, these molecules have a higher dipole as a result of the electronegativity difference felt in the opposite side of the molecule [5]. Consequently, the electronic cloud is pulled to the fluorine telomer side, turning the hydrogen of the *OH* group more acid. The study addressed in this work will focus on the fluorinated alcohols with only one hydrogenated carbon, *i.e.*  $m = 1$ .

The importance of the fluorine surfactants has also been raising in the last years. Fluorine surfactants have been widely used in industrial processes as; solvents, reaction promoters, refrigerants, pharmaceutical reactants and others [6-12]. The newest and the most substantial applications for these compounds belongs to the biomedical field. These compounds were tested with success as blood substitutes in oxygen transportation and as bioactive materials (Drugs) deliverers in the respiratory system [13-14].

Several models are being used to study these kind of molecules such as empirical correlations, coefficients' models and cubic equations of state (EOS). However, most of these models are unable to capture the effects of the chemical structure and key intermolecular interactions on the properties of fluorine surfactants. Consequently, the application of these models is often limited to a range of conditions and properties, requiring a large number of model parameters for an accurate description of the phase behaviour and properties of fluorine surfactants. Moreover, the extension of these models to other thermodynamic conditions and properties may lead to erroneous calculations due to the lack of physical basis in the inception of the models. A more rigorous approach consists on using a molecular-based EoS for describing the properties and phase behaviour of these systems. In this context, the Statistical Associating Fluid Theory (SAFT) stands as a powerful and robust model capable of accounting for the effects of the molecular structure and functional groups integrating the molecules. In particular, highly directional attractive forces such as hydrogen bonding interactions, which play a key role in the phase non-idealities, can be explicitly accounted for as specific interactions between association sites placed in the molecular models. Furthermore, the spectrum of properties which can be calculated with SAFT-type EoSs can be easily extended by coupling with other theories. For instance, as shown in literature [15][16][17] the capabilities of the SAFT-type models can be extended to the calculation of interfacial properties by coupling with either the Density functional Theory (DFT) or the Density Gradient Theory (DGT). Furthermore, compared to molecular simulations, SAFT-type EoSs constitute a class of thermodynamic tools capable of providing reliable properties estimations with a much lower computational effort. Furthermore, molecular simulations can also be taken into account when predicting properties. However, despite being a good tool to increase the precision in the results, the time that needs to be spent on it when compared to the amount of results is not suitable for what is pretended with this work.

In the last years, a number of works addressing the study of the thermodynamic properties of these kind of molecules were published. This include experimental works, EoS modelling and molecular simulations. For the pure components, most of works are centred in the study of TFE, including VLE properties [18-21], liquid and gas densities [22], enthalpies of vaporization [23-24], diffusion coefficients [25], viscosities [26] and derivative

properties[21][27-30]. This happens because, as described by Shuklov I.A. *et al.*[6], this molecule is relatively cheap to produce and have the widest range of applications when compared to the rest of the family of compounds. Nevertheless, experimental studies for other pure fluorine surfactants have also been reported, and include vapour pressures[18][31][32] liquid densities[31], enthalpies of vaporization and derivative properties[24][31-33]. The experimental studies of mixtures, as happened for pure components, are largely focused on the study of mixtures containing TFE, for the same reasons. There are included VLE diagrams at constant pressure or constant temperature[34-36], excess properties[37-42], solid-liquid equilibrium[23], derivative properties[33], diffusion coefficients[25] and interfacial

properties[43]. In terms of works addressing the molecular modelling of these systems with SAFT-type EoSs, a literature review shows that they are quite scarce. In fact, to the best of our knowledge, the work of Silva *et al.*[31] is the first and only work in literature describing the use of SAFT for these systems. In their work, in addition to reporting new experimental, the authors investigated the capabilities of GC-SAFT-VR and molecular simulations for describing the properties of pure fluorinated alcohols.

In spite of all the data that are already known and that are available, there are some fields that remain poorly studied, specially interfacial properties. In previous work, Teixeira *et al.*[43] measured the interfacial tension of mixtures containing TFE and hydrogenated alcohols at 293 K. However, the study of the interfacial properties of pure fluorine surfactants has only recently been reported experimentally[44] and the molecular modelling still unexplored..

This work will be focused in the thermodynamic modelling of fluorinated surfactants compounds using the soft SAFT EoS coupled with DGT. This thesis commences with a brief description of the fundamental concepts of relevance for the present work, followed by a description of the thermodynamic models (soft-SAFT and DGT). Subsequently, the molecular models of fluorinated surfactants are proposed and the molecular parameters obtained from pure property data. The robustness of the proposed models is tested by assessing their capabilities for predicting derivative and interfacial property data. The molecular models are then transferred for the study of the VLE and interfacial properties of hydrogenated and fluorinated alcohol mixtures. As it will be shown, the model can accurately capture the complex phase behaviour and the appearance of an azeotrope in the interfacial tension of these mixtures. These results were interpreted by studying the microstructure of the interface, through the density profiles, and thereby showcasing the feasibility of the present modelling strategy as a tool for understanding the appearance of an azeotrope in these systems.

## 2. Theory

### 2.1. Soft-SAFT

The Statistical Association Fluid Theory (SAFT) has been one of the most studied Equations of State (EoS) for the past few years. Its framework is based on a microscopic model that is capable of predicting the macroscopic properties of a given fluid. Based on the Wertheim's thermodynamic perturbation theory of first order (TPT1), SAFT is described by the residual Helmholtz free energy,  $A^{res}$ . For a system of associative chains, the residual Helmholtz free energy can be described by the equation 1[45].

$$A^{res} = A^{total} - A^{ideal} = A^{ref} + A^{chain} + A^{assoc} \quad (1)$$

where  $A^{ref}$ ,  $A^{chain}$  and  $A^{assoc}$  stands for the monomer reference fluid term, the formation of the monomers chain term and the association contribution term, respectively.

Different versions of SAFT EoS have been developed throughout the past years. As in all of them, the ideal term ( $A^{ideal}$ ) is calculated as the free energy of an ideal gas. Due to this, the main difference between them is the reference term ( $A^{ref}$ ). In soft-SAFT it is used a spherical Lennard-Jones (LJ) fluid as reference that takes into account the repulsive and attractive interactions between the monomers that constitute the chain. To calculate the free energy and derived properties of the LJ spheres it was used the accurate Johnson EoS *et al.* The chain term,  $A^{chain}$ , derives from the first-order Wertheim's perturbation theory for associating spherical molecules. In contrast with the reference term, this term is practically the same among all the SAFT versions. The LJ spheres connected by association sites right positioned results in a chain with spheres bonded covalently. This term is given by equation 2.

$$A^{chain} = k_b T \sum_i x_i (1 - m_i) \ln g_{ii}^{LJ}(\sigma_{ii}) \quad (2)$$

where  $k_b$  is the Boltzmann constant,  $T$  is the temperature and  $g_{ii}^{LJ}(\sigma_{ii})$  is the pair radial distribution function of the spherical segments  $i$ , to a bond length of  $\sigma_{ii}$ . The association contribution comes, as the chain one, from the first-order perturbation theory of Wertheim. As this term depends on the number of associative sites, the cumulative contribution of those were taken into account, as described in equation 3:

$$A^{assoc} = k_b T \left[ \sum_i x_i \sum_a \left( \ln X_i^a - \frac{X_i^a}{2} \right) + \frac{M_i}{2} \right] \quad (3)$$

Where  $M_i$  gives the number of the association sites and  $X_i^a$  the fraction on non-bonded sites of molecule  $i$ . where  $M_i$  stands for the number of association sites and  $X_i^a$  the fraction of non-bonded sites of a molecule  $i$ . As a consequence,  $X_i^a$  can be described by:

$$X_i^a = \frac{1}{1 + \rho \sum_j x_j \sum_\beta X_j^\beta \Delta_{AB}^{ij}} \quad (4)$$

where  $\Delta_{AB}^{(ij)}$  is related to the association bond strength between two sites, following the square-well potential, and is written by:

$$\Delta_{AB}^{ij} = \left( \exp \left[ \frac{\varepsilon_{A_i B_j}^{HB}}{k_B T} \right] - 1 \right) \kappa_{A_i B_j}^{HB} g_{ii}^{LJ} \quad (5)$$

where  $\varepsilon_{A_i B_j}^{HB}$  is the energy of association between sites of two molecules and  $\kappa_{A_i B_j}^{HB}$  is the association volume between two sites of two molecules.

The second order derivative properties are calculated analytically by the soft SAFT, by making use of the direct derivation of the Helmholtz free energy and of the pressure implemented in the code.

$$k_T^{-1} = \rho \left( \frac{\partial P}{\partial \rho} \right)_T \quad (6)$$

$$\alpha = k_T \left( \frac{\partial P}{\partial T} \right)_\rho \quad (7)$$

$$c_v = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_v \quad (8)$$

**Table 1. Molecular parameters and influence parameter for the fluorinated alcohols family and Average Absolute Deviation (AAD(%)) from Vapour Pressure and Density parameterization**

Molecule	$m$	$\sigma$ (Å)	$\varepsilon/k_B(K)$	$\varepsilon^{HB}/k_B(K)$	$\kappa^{HB}(\text{Å}^3)$	AAD_P(%)	AAD_D(%)	$c$ (J.m5.mol <sup>-2</sup> )
TFE	1.774	3.84	214.0	3424	2882	1.94%	0.11%	9.58E-20
PFP	1.979	4.13	225.1	3450	2250	6.77%	0.15%	1.46E-19
HFB	2.210	4.32	239.0	3450	2250	17.21%	0.72%	2.34E-19
NFP	2.445	4.46	250.0	3450	2250	6.35%	0.54%	3.41E-19
UFH	2.690	4.56	259.6	3450	2250	5.50%	0.15%	4.76E-19
TRFH	2.956	4.64	266.0	3450	2250	4.87%	0.26%	6.62E-19

$$C_p = C_v - \frac{T\alpha^2}{k_T\rho} \quad (9)$$

Soft-SAFT calculations are extended to mixtures by applying the van der Waals one-fluid theory (vdW-1f), and the required the crossed size ( $\sigma_{ij}$ ) and energy ( $\varepsilon_{ij}$ ) parameters are calculated through the generalized Lorentz-Berthelot (LB) mixing rules as follows [46] the equations 10 and 11:

$$\sigma_{ij} = \eta_{ij} \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (10)$$

$$\varepsilon_{ij} = \xi_{ij} \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (11)$$

where  $\eta_{ij}$  and  $\xi_{ij}$  are binary adjustable parameters between substances  $i$  and  $j$ . When these parameters are set equal to 1, the EoS is used in a fully predictive manner. The volume and association parameters characterizing the interactions between different association sites belonging to different types of molecules are calculated by mixing rules in an analogous manner to that followed for  $\sigma_{ij}$  and  $\varepsilon_{ij}$ , and given from equations 12 and 13:

$$\varepsilon_{ij}^{HB} = \alpha_{ij}^{HB} \sqrt{\varepsilon_{ii}^{HB} \varepsilon_{jj}^{HB}} \quad (12)$$

$$\kappa_{ij}^{HB} = \left( \frac{\kappa_{ii}^{HB(1/3)} + \kappa_{jj}^{HB(1/3)}}{2} \right)^3 \quad (13)$$

where  $\alpha_{ij}^{HB}$  is a binary adjustable parameter which can be used to correct for possible deviations of the cross-association energy to that calculated by the geometric mean.

The fluids enthalpy is also calculated by soft SAFT. This property results from the direct application of the equation 14 in the code:

$$H = U + \frac{P}{\rho} \quad (14)$$

where  $H$  and  $U$  corresponds to enthalpy and internal energy, respectively. The vaporization enthalpy ( $\Delta H_{vap}$ ) can be obtained by the difference between the enthalpies of the gaseous ( $H_g$ ) and the liquid ( $H_l$ ) saturated phases, from equation 15:

$$\Delta H_{vap} = H_g - H_l \quad (15)$$

## 2.2. Density Gradient Theory (DGT)

Formulated by Cahn and Hilliard, the density gradient theory (DGT) is a robust approach for computing interfacial properties. Originally based on the van der Waals gradient theory, this theory consists in the expansion of the Helmholtz free energy density,  $a_0(\rho)$ , into a Taylor series at a local composition, near the interface[47]:

$$\tilde{A} = \int \left[ a_0(\rho) + \sum_i \sum_j \frac{1}{2} c_{ij} \nabla \rho_i \nabla \rho_j \right] d^3r \quad (16)$$

where  $\nabla \rho_i$  and  $\nabla \rho_j$  are the local density gradient of compounds  $i$  and  $j$  and  $c_{ij}$  is a coefficient, generally called of the influence parameter.

This coefficient is related to the square-gradient term and, even though its value can be derived from theoretical expressions[48][49][50]. For convenience it is usually fitted to pure surface tension data. For mixtures, the cross-influence parameter ( $\beta$ ) is related with the pures' influence parameter and it can be obtained following the combination rule:

$$c_{ij} = \beta_{ij} \sqrt{c_{ii}c_{jj}} \quad (17)$$

where  $\beta_{ij}$  is a binary adjustable parameter which can be used to correct possible deviations in the description of the interfacial tension of binary mixtures.

Then, it is possible to calculate the interfacial tension ( $\gamma$ ) by minimizing the free energy, given by Equation 18, attaining to the interface equilibrium[17].

$$\gamma = \sum_i \sum_j \int c_{ij} \frac{\partial \rho_i}{\partial z} \frac{\partial \rho_j}{\partial z} dz \quad (18)$$

$$\gamma = 2 \int_{-\infty}^{+\infty} \left[ a_0(\rho) - \sum_i \rho_i \mu_{oi} - p_0 \right] dz \quad (19)$$

where  $\mu_{oi}$  and  $p_0$  are the equilibrium chemical potential and pressure and  $z$  is the perpendicular direction to the interface. In this work the influence parameter was fitted to the available experimental surface tension data.

Density profiles are also calculated through the concept of transformation from location space to density space, by integration:

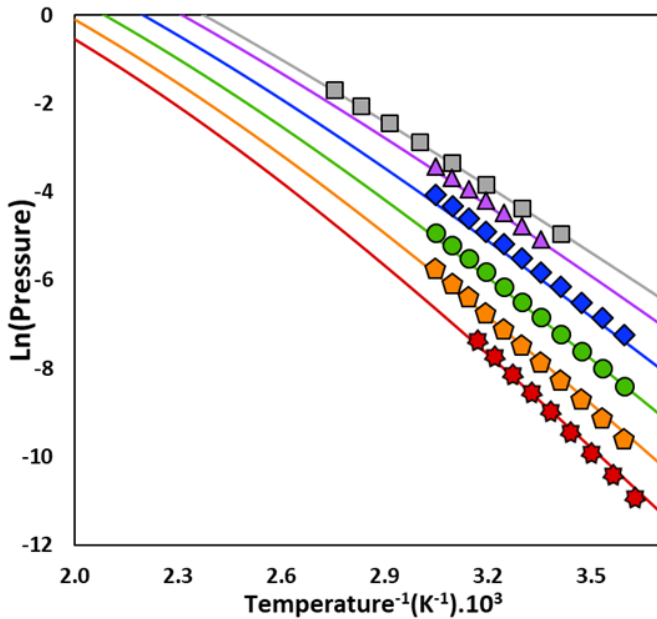


Figure 1. Vapour pressure for the fluorinated alcohols family. Squares (■) and grey colour – TFE; Triangles (▲) and purple – PFP, Diamonds (◆) and blue – HFB, Circles (●) and green – NFP; Pentagons (⬠) and orange – UFH; Stars (★) and red – TRFH. Solid lines represent soft SAFT results and full symbols the experimental data

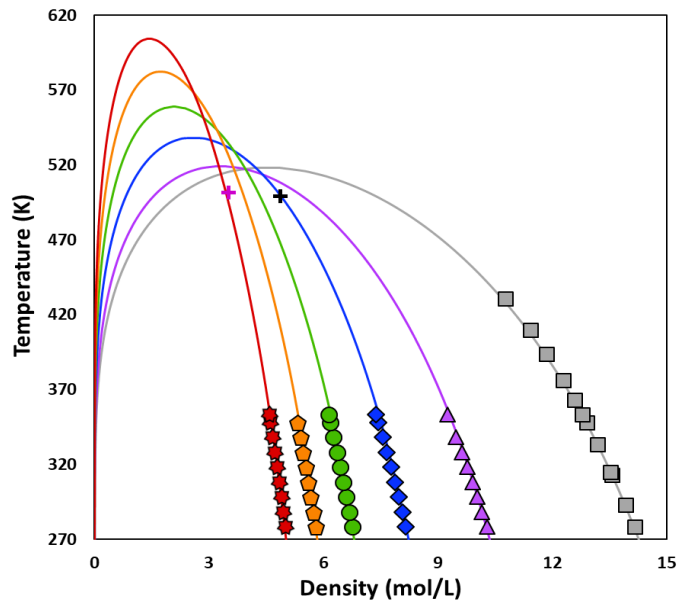


Figure 1. Saturated Densities curves of the fluorinated alcohols family. Squares (■) and grey colour – TFE; Triangles (▲) and purple – PFP, Diamonds (◆) and blue – HFB, Circles (●) and green – NFP; Pentagons (⬠) and orange – UFH; Stars (★) and red – TRFH. Plus symbols (⊕) (⊕) are related with critical temperatures for TFE and PFP, respectively. Solid lines represent soft SAFT results and full symbols the experimental data.

$$z = z_0 + \int_{\rho_j(z_0)}^{\rho_j(z)} \sqrt{\frac{c'}{\Delta\Omega(\rho_i, \rho_j)}} d\rho_j \quad (20)$$

Where  $z_0$  corresponds to the origin,  $\Delta\Omega(\rho_i, \rho_j)$  the reduced grand thermodynamic potential and  $c'$  represents a regression that depends of influence parameters values.

### 3. Results and Discussion

#### 3.1. Pure components Parameterization

Fluorinated alcohols are considered to be composed by chains of spherical homonuclear segments. In each molecule, the chain by an  $m$  number of segments (with a  $\sigma$  diameter) that interact with each other according to the dispersive energy  $\varepsilon/k_B$ . Taking into account the composition of the molecule, the existence of a hydroxyl group activates the association term of the model. Moreover, it was defined that each chain has 2 different associative sites, a positive and a negative one. The positive one stands for the hydrogen of the functional group and the negative one for the two existing pairs of free electrons of the functional group. Despite having 2 different pairs of electrons, it was assumed that the pairs would only correspond to one negative site, due to the size and the stereochemistry of these kind of molecules. To reinforce this, some simulations were carried out in order to calculate the average number of hydrogen bonds made per molecule, for pure compositions. The obtained results in this simulations are in line with the assumption taken[51]. The valid association scheme for this model was only the O-H (hydrogen bond) bond, hindering the O-O and the H-H associative bonds.

Since the association doesn't depend on the size of the chain, the associative energy ( $\varepsilon^{HB}$ ) and volume ( $\kappa^{HB}$ ) were set as constants, apart from the smallest compound in study, the TFE. Its size gives him an enhanced interactivity, due to its improved stereochemistry and associative availability to interact. Then, the association energy ( $\varepsilon^{HB}/k_B$ ) was fixed in 3450 K and the associative volume were fixed in 2250 Å.

The parameterization of fluorinated alcohols was executed under the forms explained above for the first 6 compounds of the family, starting with TFE and ending with TRFH. As experimental data they were used the VLE properties, most precisely vapour pressure and saturated liquid densities[31][20][21]. It is possible to find in the literature different sources of TFE VLE experimental data. Chaudhari *et al.*[20] was considered to take data on vapour pressure and Sauermann *et al.*[21] to gather data on saturated densities. This choice was based on the need of using experimental data in a specific range of temperatures that is consistent with the remaining

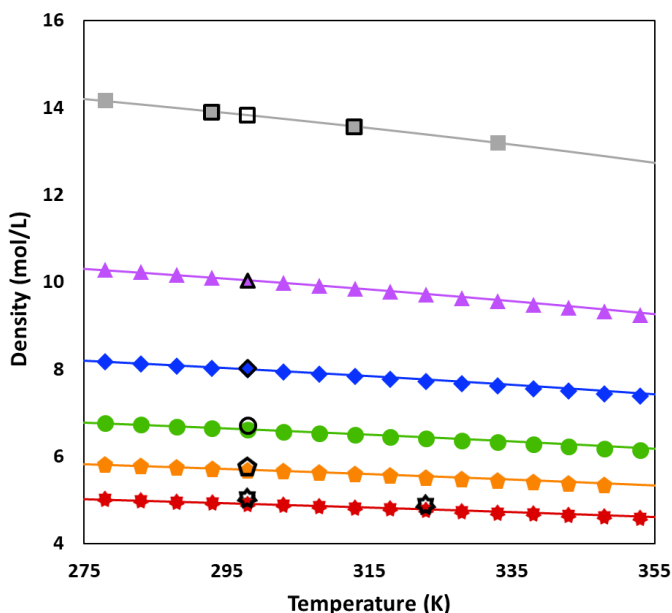


Figure 3. Comparison of the liquid densities at 0.1MPa for all the family of compounds. Squares (■) and grey colour – TFE; Triangles (▲) and purple – PFP, Diamonds (◆) and blue – HFB, Circles (●) and green – NFP; Pentagons (⬠) and orange – UFH; Stars (★) and red – TRFH. Solid lines represent soft SAFT results, full symbols the experimental data[22][32][45] and the open symbols the molecular simulations[30][32][45].

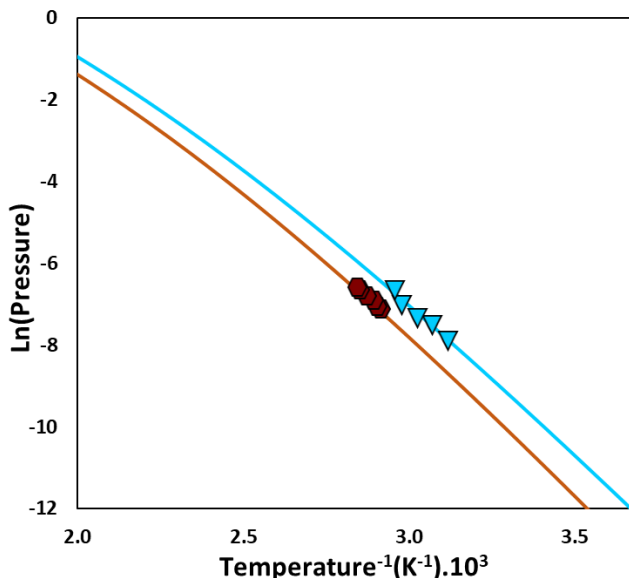


Figure 4. Comparison between soft SAFT pure prediction results and experimental data for vapour pressures of PDFO and HDFN. Inverted triangles (▼) and light blue – PDFO; Hexagons (●) and brown – HDFN. Solid line represents soft SAFT and full symbols the experimental values

compounds of the family. For the rest of the molecules the vapour pressure and the saturated liquid density were obtained from Silva G. M. *et al.*[31][44], except the vapour pressure for TRFH[32]. Here, the single-phase density, at 0.1MPa, was considered as a saturated liquid density. This happened because the density of a liquid does not have a considerable change with the pressure, at these ranges. Because of the lack of data, the saturated gaseous density was not taken into account. For the same reason, the subsequent compounds of TRFH were not modelled, since there only exists vapour pressure data for them[52]. The proposed parameters are presented in Table 1.

The obtained correlations for the segment number, the molecule volume and the molecule energy are described by the following equation 34, 35 and 36:

$$m = 0.0048 \times M_w + 1.28 \quad (34)$$

$$m\sigma^3(\text{Å}^3) = 0.78 \times M_w + 22.28 \quad (35)$$

$$m\varepsilon(K) = 1.64 \times M_w + 205.41 \quad (36)$$

The VLE results are exposed in Figure 1 and Figure 2, for vapour pressure and liquid saturated density, respectively. In those results it was attached the critical temperatures available in the literature for TFE and PFP[21][24]. The results fit quite well the experimental data and their average absolute deviation (AAD%) values are 7.44% and 0.32%, respectively. Regarding the vapour pressure, the HFB is the greatest contributor for the AAD (%) of this property (without it the AAD% would decrease to 5.48%). The observed proportionality in the vapour pressure results was only possible by forcing it to happen. This was done maintain the patterns observed in the results. Because of this, the HFB parameterization was manipulated with intention to obtain consistent results. Despite the parameter manipulation, its result for the saturated liquid density is well described. Regarding the critical temperature, the estimated result by Soft SAFT is overestimated, as expected. This was expected because no EoS takes into account the existing fluctuations in this zone due to the critical behaviour, namely in density. Moreover, it is possible to fit the critical zone with Soft SAFT+Crossover if there is VLE data near this region [53][54]. This can be an interesting procedure, for future works, because the critical temperatures for TFE and PFP are close to one another, leading to some possible interesting results and behaviours of the components.

#### 3.2. Model Validation

Liquid densities at 0.1MPa were compared for all of the parameterized fluorinated alcohols [51][29][44]. These results enforce the choice of the proposed parameters, once they are consistent not only with experimental, but also with simulation data. As said previously, it was assumed the densities at 0.1MPa and saturated temperatures, because of the lack of data. The results presented in Figure 3 came to support the assumption

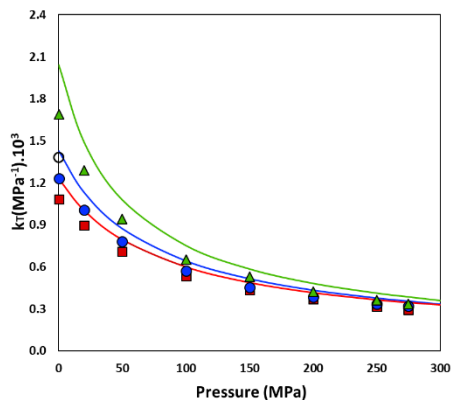


Figure 5. Isothermal compressibility for TFE at different constant temperatures. Squares (■) and red colour – 278.15K; Circles (●) and blue – 298.15K; Triangles (▲) and green – 338.15K. Solid lines represent soft SAFT results, full symbols the experimental data[31] and open symbols the molecular simulations[30].

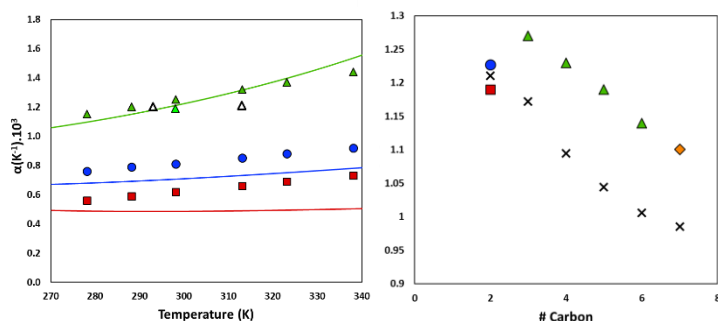


Figure 6. a) Thermal expansion coefficient for TFE at different constant pressures. Triangles (▲) and green – 338.15K; Circles (●) and blue – 298.15K; Squares (■) and red colour – 278.15K. Solid lines represent soft SAFT results, full symbols the experimental data[30][31] and open symbols the molecular simulations[30]. b) Thermal expansion coefficient for the fluorinated alcohols family, at 0.1MPa and 298.15K. Different symbols are related to different literatures: Squares (■) are from Fioroni M. et al.[29]; Circles (●) from Malhotra R. et al.[30]; Triangles (▲) from Silva G. M. C. et al.[31]; Diamonds (◆) from unpublished results[44]. Soft SAFT are represented by crosses (X).

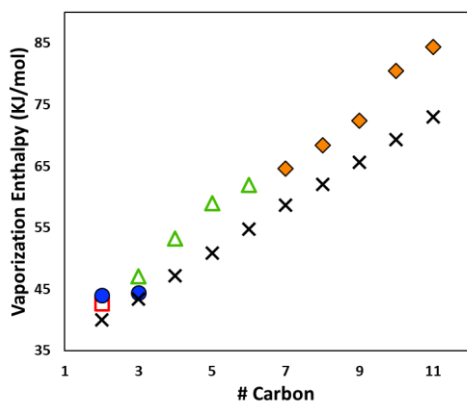


Figure 7. Vaporization enthalpy for the fluorinated alcohols family, at 298.15K. Different symbols are related to different literatures: Squares (■) results are from Fioroni M. et al[30]; Circles (●) from Rochester C. H. et al.[25]; Triangles (▲) from Silva G. M. C. et al.[32]; Diamonds (◆) from Costa J. C. S. et al.[33]. Soft SAFT are represented by crosses (X). Full symbols represent experimental data and open symbols represents molecular simulations.

taken, since the soft SAFT results for 0.1MPa are in line with the experimental, used in fitting as saturated densities.

With the aim to complement the study for the obtained parameters and their consistency, for PDFO and HDFN (non-modelled molecules), the molecular parameters were obtained from equations 34, 35 and 36. The parameter values obtained from correlations are: 3.179 and 3.420 for the number of segments, 4.721Å and 4.781Å for the size parameter and 272.8 K and 278.2K for the dispersive energy parameter, respectively. The results are compared to vapour pressure experimental data in Figure 4[32]. As these

parameters were obtained by pure prediction, the results only fulfil the proposed goal by extrapolation, providing, this way, consistent results

For the final test, the reliability of the proposed parameters and the soft SAFT performance, obtained from the VLE data, the derivative properties were estimated using Soft SAFT. The studied properties were: the isothermal compressibility ( $k_T$ ), the thermal expansion coefficient ( $\alpha$ ), the vaporization enthalpy ( $\Delta H_{vap}$ ) and the isobaric heat capacity ( $C_p$ ). In Figure 5, Figure 6 and Figure 7 there are exposed the results for the isothermal compressibility of TFE at three different constant pressures, the results for the thermal expansion coefficient for TFE at three different constant temperatures and the results for the family of fluorinated alcohols, at 0.1MPa and 298.15K and the results for the vaporization enthalpy of the family of compounds, at 298.15K. These results show a good agreement, not only for the values obtained, but also for the trends described by soft SAFT. As the properties conditions gets far from the parametrization conditions, the soft SAFT calculations tend to deviate from the experimental and molecular simulation data. This is clearly observed in the figures 5 and 6 a). Regarding the trend of the values with respect to the family of compounds, in Figure 6b) and Figure 7, soft SAFT apparently tend to underestimate those values. However, it is important to be said that, for the range chosen to the y plots, the values are very close to the experimental and molecular simulation data.

### 3.3. Interfacial properties

In addition to the study of the VLE properties it was done a study related with the surface tension. The combination between soft SAFT and DGT enables a good description of this property. However, for this to occur it is necessary to fit the influence parameter,  $c$  ( $J.m^2/mol^2$ ). The compounds were parameterized from TFE to TRFH to a temperature of 310K, using the available experimental data in the literature[44]. As the parameterization of surface tensions is made using only one parameter, mathematically is useless to fit that to a range of parameters[47]. The obtained parameter values, and their average absolute deviation, as the molecular parameters, are exposed in Table 1 and the results are plotted in Figure 8. The influence parameter was described by a 2<sup>nd</sup> grade correlation:

$$c(J.m^2.mol^{-2}) = 6.19.10^{-24}M_w^2 - 5.44.10^{-22}M_w + 8.92.10^{-20} \quad (37)$$

The obtained results from parameterization are concordant with the experimental data. As DGT depends on a good description of the molecular models, because it is highly dependent on the density, the good agreement observed would not only be obtained with a well-chosen influence parameter. This reinforces the molecular parameter values chosen for the molecular model.

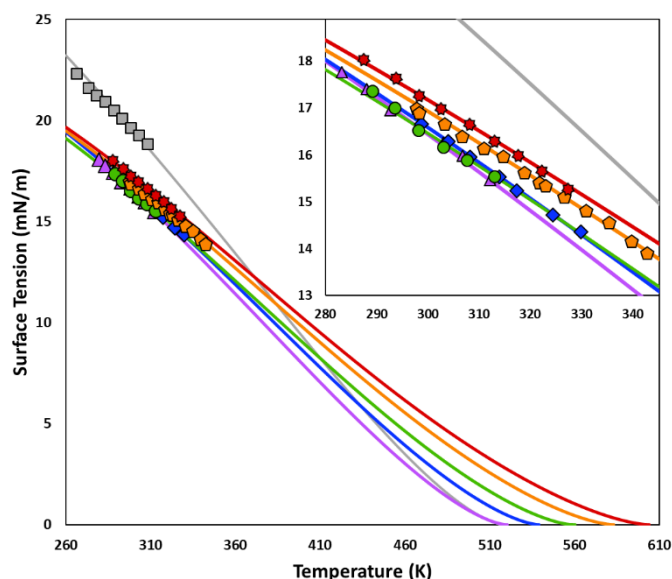


Figure 8. Surface tension for family of fluorinated alcohols in function of the temperature. Squares (■) and grey colour – TFE; Triangles (▲) and purple – PFP; Diamonds (◆) and blue – HFB; Circles (●) and green – NFP; Pentagons (⬠) and orange – UFH; Stars (★) and red – TRFH. Solid lines represent soft SAFT+DGT results and full symbols the experimental data.

### 3.4. Mixtures: Description and Considerations

Once finished the pure components study, the following step is, indeed, a study of the mixtures of compounds involving these molecules. This work appears as an important tool into the improvement and extension of the study regarding these systems. As said in the introduction chapter, for mixtures between fluorinated and hydrogenated alcohols it can be observed an interesting phenomena: the azeotropy. Because of this, the main aim of this mixture's chapter is to study the azeotrope and its capture.

For this, initially, it is important to introduce the hydrogenated alcohols. These molecules are similar to the fluorinated alcohols in respect of their structure. The main difference lies in the fact that for hydrogenated alcohols there is a saturated hydrogenated chain of carbons, instead of a semi fluorinated chain. Because of that, some properties change significantly between these two families. To enforce that, and as a small exercise, some saturation properties can be compared between both families for molecules with an equivalent number of carbons [55][56][20][51]. In this work it was only studied the family of alcohols with the hydroxyl (OH) as terminal group.

As it was studied, the dispersive energy between hydrogenated and fluorinated chains is unfavoured[16][57]. So, to achieve the main objective, the mixtures were modelled using soft SAFT+DGT. For this it was necessary to set binary parameters in order activate the cross interactions. These cross interactions comprise: the cross dispersive energy( $\xi$ ), the cross volume( $\eta$ ) and the cross-association energy( $\alpha$ ).

The studied and modelled mixtures in this work have in common the same fluorinated alcohol molecule, the TFE. Then, the studied mixtures are a mix of TFE with some different hydrogenated alcohols, such as: Methanol (MetOH), Ethanol (EtOH), Propanol (PrOH), Butanol (ButOH), Pentanol (PentOH), Hexanol (HexOH) and Heptanol (HeptOH). As it was said in the

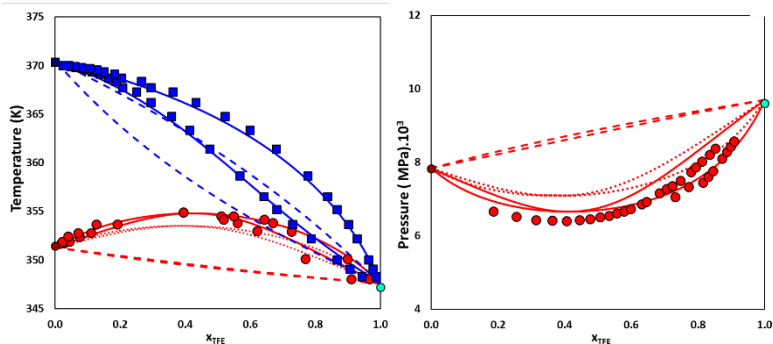


Figure 9. Isobaric a) and isothermal a) VLE diagrams parameterization results for TFE mixtures with hydrogenated alcohols at 0.1MPa or 298K, respectively. Red colour and circles (●) - TFE+EtOH mixture; Blue and squares (■) - TFE+PrOH mixture. The pure alcohols properties are represented with the respective family symbols, EtOH (●), PrOH (■) and TFE (○). Dashed lines (---) represent soft SAFT pure prediction results, dotted line (.....) the soft SAFT results for  $\alpha^{HB} = 1.035$ , solid line (—) the soft SAFT results for  $\alpha^{HB} = 1.045$  and full symbols represent experimental results[35][34][36].

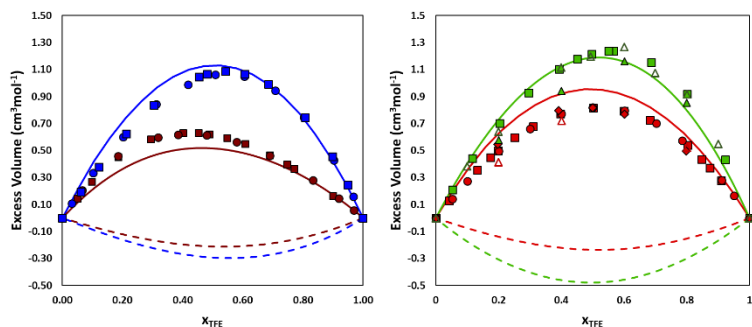


Figure 10. Excess volume parameterization results for TFE mixtures with MetOH and PrOH in plot a) and EtOH and ButOH in plot b), at 0.1MPa and 298K. Different symbols represent different literatures: circles (○) - Minamihonoki et al.; squares (□) - Sassi et al.; triangles (△) - Morgado et al.; diamonds (◇) - Duarte et al.. Brown lines (—) - TFE+MetOH mixture; Red lines (—) - TFE+EtOH mixture; Blue lines (—) - TFE+PrOH mixture; Green lines (—) the TFE+ButOH mixture. Dashed lines (---) represent soft SAFT pure prediction results, solid line (—) the soft SAFT results for  $\eta = 1.012$ , full symbols represent experimental results and open symbols the simulation data.

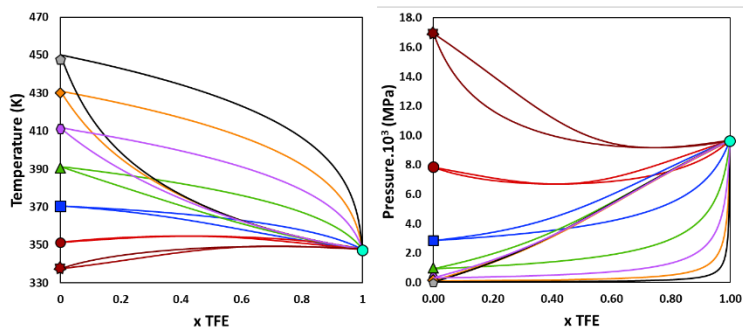


Figure 11. Isobaric and isothermal VLE curves obtained with soft SAFT for binary mixtures composed by TFE and hydrogenated alcohols, between MetOH and HeptOH, at 0.1MPa or 298K. The parameters used were:  $\alpha^{HB} = 1.045$  and  $\eta = 1.012$  for MetOH and EtOH mixtures and  $\alpha^{HB} = 1.035$  and  $\eta = 1.012$  for the rest of the mixtures. Brown colour and stars (★) - MetOH mixture; Red and circles (●) - EtOH mixture; Blue and squares (■) - PrOH mixture; Green and triangles (▲) - ButOH mixture, Purple and Hexagons (⬡) - PentOH mixture; Orange and diamonds (◆) - HexOH mixture; Grey and pentagons (⬠) - HeptOH mixture. Solid line represents soft SAFT results, full symbols the pure fluids experimental data, where TFE pure properties are represented with a light blue circle (○).

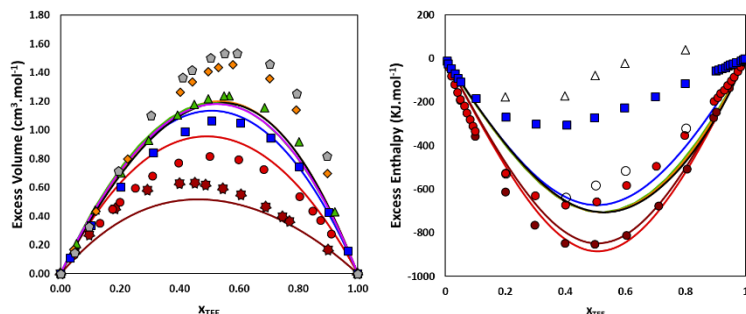


Figure 12. Excess volume a) and excess enthalpy b) results obtained for binary mixtures between TFE and hydrogenated alcohols, between MetOH and HeptOH, 0.1MPa and 298K. The parameters used were:  $\alpha^{HB} = 1.045$  and  $\eta = 1.012$  for MetOH and EtOH mixtures and  $\alpha^{HB} = 1.035$  and  $\eta = 1.012$  for the rest of the mixtures. Brown colour and stars (★) - MetOH mixture; Red and circles (●) - EtOH mixture; Blue and squares (■) - PrOH mixture; Green and triangles (▲) - ButOH mixture; Purple and Hexagons (⬡) - PentOH mixture; Orange and diamonds (◆) - HexOH mixture; Grey and pentagons (⬠) the HeptOH mixture. Solid line represents soft SAFT results, full symbols the experimental data and the open symbols the molecular simulation data.

introduction, the available data is not vast, however, it appears to be enough to proceed with this work. For MetOH, EtOH, PrOH and ButOH molecules, there are isothermal and isobaric VLE curves (except for MetOH and ButOH)[35][34][36], excess properties, such as excess enthalpy[40][38] and excess volume[39][42], and interfacial tensions[43]. For HexOH and HeptOH there is only available excess volumes data[39]. About PentOH, there was not found any data regarding it.

### 3.5. Mixtures Parameterization

In order to correct this non-ideality observed in this kind of mixtures, the parametrization was made due to the manipulation of the binary parameters with the objective to describe correctly the available properties. These binary parameters affect directly the cross parameters values and, consequently, influence the mixture properties. By the analysis of the Figure 9, for the VLE diagrams, the negative deviation to the Raoult's law should be corrected and captured. For the excess properties, the correct sign for the excess volume and excess enthalpy should be at least caught. For that, it was used two different parameters. The binary parameters chosen for the manipulation were the cross association binary parameter ( $\alpha_{ij}^{HB}$ ) and the size binary parameter ( $\eta_{ij}$ ). The first one was manipulated in order to adjust properties related to the interactions energy, such as the VLE diagrams and the excess enthalpy. The second one was manipulated specifically to obtain the excess volume curve. Some authors argue that only one parameter should be manipulated for mixtures, since the use of more than one increases the degrees of freedom, decreasing the physical meaning of those parameters. However, for this work the two parameters were necessary. Since the  $\alpha_{ij}^{HB}$  only affects VLE and excess enthalpy curves, the excess volume was not corrected with it. Then, as it can be observed in Figure 10, for mixtures of fluorinated and hydrogenated alcohols the excess volume is very high. In addition, even the correct sign for

this mixture property is not captured. Because of these two factors the  $\eta_{ij}$  was considered. The cross association binary parameter ( $\alpha_{ij}^{HB}$ ) was chosen instead of the cross dispersive binary parameter ( $\xi_{ij}$ ). For these,  $\alpha_{ij}$  appears as the most efficient parameter. This happens because a small change in this parameter value has a higher impact in the VLE and excess enthalpy values than a change in  $\xi_{ij}$ . Some authors, such as Morgado *et al.*[38] and Duarte *et al.*[37] have studied the cross association interactions between these molecules and they have concluded that, in fact, the cross association energy increases for these mixtures.

For the parametrization some considerations were taken. It was intended to obtain a pair of binary parameters ( $\alpha_{ij}^{HB}$  and  $\eta_{ij}$ ) that could be transferable for all of the family mixtures (TFE with Hydrogenated alcohols). In order to obtain these,  $\alpha_{ij}^{HB}$  was manipulated to obtain the VLE isobaric diagrams for TFE mixtures with EtOH and PrOH. During the parametrization it was observed that the  $\alpha_{ij}^{HB}$  value that captures the azeotrope for the mixture with EtOH is higher than the same parameter for PrOH mixture. The improved stereochemistry of the ethanol, when compared with propanol, enhances its associative interaction energy and justifies the higher parameter required. The obtained cross association energy binary parameters were: 1.045 for EtOH mixture ( $\alpha_{ij}^{HB} = 1.045$ ) and 1.035 for PrOH mixture ( $\alpha_{ij}^{HB} = 1.035$ ). For the mixtures' excess volume, only one parameter was necessary to correct it, as meant. Its parametrization was focused not only in the EtOH and PrOH mixtures but also in the MeOH and ButOH mixture was considered with the intention to test the chosen parameter robustness. Its value is: 1.012 ( $\eta_{ij} = 1.012$ ). The results of the VLE diagrams parametrization are exposed in Figure 9. The excess volume parametrization is exposed in Figure 10.

As it can be observed, the parametrization fits quite well for the VLE graphics, especially for the isobaric diagram, from Figure 9. Theoretically, both the isobaric and the isothermal curves should be captured equally. This is not happening for the mixture with EtOH, where the azeotrope in the isobaric diagram is captured, but in the isothermal it is not. Since VLE binary experimental results came from different literatures, it is expected that this gap is related with some possible deviations on the experimental results. So, it was given preference to the isobaric data as it was considered to be more trustworthy, because those results took a further and deeper analyses by some authors. This means that those results are better described when comparing to the ones for the isothermal curve.

Regarding the excess properties, for the excess volume parametrization results the chosen parameter makes the results to be in line with the literature data for this property. Besides that, the curves' tendencies are fully captured.

The binary parameters chosen for the mixtures could be transferred for others from the same family with heavier hydrogenated alcohols. In line with this, the cross-association energy binary parameter ( $\alpha_{ij}^{HB} = 1.035$ ) from the PrOH mixture and the chosen cross volume binary parameter ( $\eta_{ij} = 1.012$ )

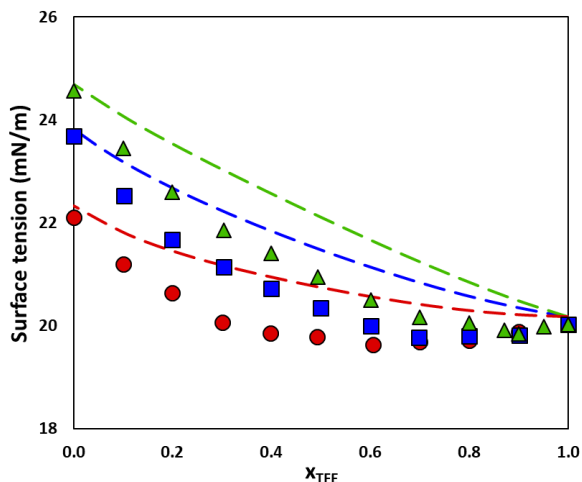


Figure 13. Surface tension results for SAFT+DGT pure prediction for cross influence parameter ( $\beta=1$ ), for mixtures with TFE and hydrogenated alcohols, such as: EtOH, PrOH and ButOH. Red and circles (●) - EtOH mixture; Blue and squares (■) - PrOH mixture; Green and triangles (▲) - ButOH mixture

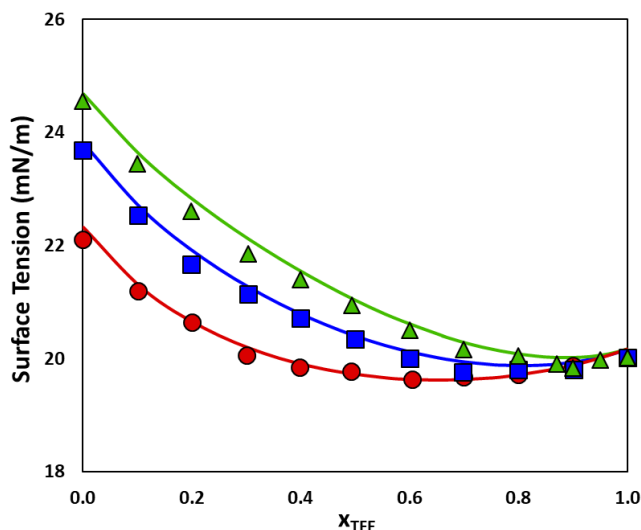


Figure 14. Surface tension obtained from parametrization of mixture composed by TFE and hydrogenated alcohols, such as: EtOH, PrOH and ButOH. Red and circles (●) - EtOH mixture; Blue and squares (■) - PrOH mixture; Green and triangles (▲) - ButOH mixture. Solid lines represent the soft SAFT+DGT results and full symbols the experimental data.

were transferred for heavier mixtures, until the HeptOH. The VLE results from these parameters transferability are shown for VLE in Figure 11 and for the excess volume and excess enthalpy in Figure 12.

As it is possible to conclude, as hydrogenated alcohols get heavier, the azeotrope disappears. The excess volume requires a more detailed analysis. In Figure 12, the mixture with MeOH, EtOH, PrOH and ButOH is well captured, but the same does not happen for HexOH and HeptOH (no data for PentOH). Soft SAFT predicts that because the PentOH excess volume practically does not change. Since MeOH to HeptOH the mixtures excess volume increases proportionally, as in the experimental and molecular simulation results. However, HexOH and HeptOH does not look like to follow that observed proportion, being the values overestimated. Otherwise, soft SAFT is not capable of capturing the excess volume for higher molecules. To conclude, more experimental data is required. For the excess enthalpy the soft SAFT prediction is moved away from the experimental and molecular simulation data. Not only the curve shape was not captured, but also the family trend was not obtained.

### 3.6. Mixtures: Interfacial Properties

Once obtained the molecular parameters for the pure components and mixtures and the influence parameters for all the studied molecules, it was proceeded to the surface tension calculation for mixtures. As referred before, experimental data on surface tensions is only available for mixtures with EtOH, PrOH and ButOH. It was tested to obtain the surface tension curve with the cross-influence parameter ( $c_{12}$ ) equal to the geometric average of the pure influence parameters, as reported in equation 17, and for the cross-influence binary parameter ( $\beta$ ) equal to 1. The Figure 13 shows the results at 293.15K.

To fix this, the parameterization of cross-influence parameter ( $\beta$ ) was required. This way, the surface tension curve for mixtures with EtOH, PrOH and ButOH is obtained for a cross influence binary parameter ( $\beta$ ) of 0.8. In Figure 14 those results are exposed.

As represented in figure 14, the soft SAFT accoupled with the DGT can obtain the surface tension curve for the mixtures well, and it is capable to catch the azeotrope values. These results support the parameters chosen before, not only for the pure components, but also for the mixtures, namely the binary parameters. As explained in the Fundamentals chapter, the azeotropy came from the unfavoured interactions between molecules present at the surface. In order to take further conclusions about it, it is important to analyse the density profiles. For this, it was calculated the the density profiles in the azeotrope composition, exposed in Figure 15 respectively.

From Figure 15 it is possible to conclude about what is happening in the interface at azeotrope composition. It's important to refer that soft SAFT predictions for that compositions are close to the experimental values.

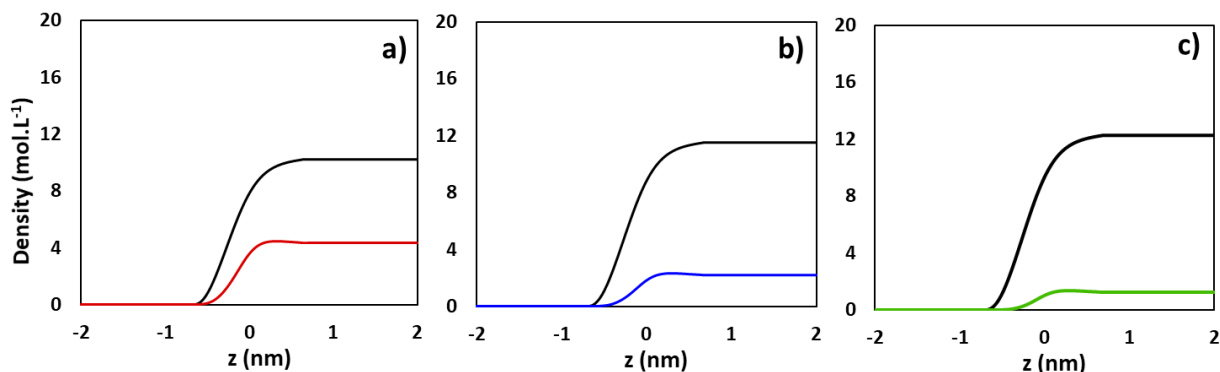


Figure 2. Density profiles for TFE+EtOH a), TFE+PrOH b) and TFE+ButOH c) mixtures at aneutrope composition. Red line (—) - EtOH, Blue line (—) - PrOH, Green line (—) - ButOH; Dark line (—) the TFE.

However, the apparent fluctuations in the experimental results show that the soft SAFT aneutrope composition prediction is, apparently, more precise than the experimental results. For that compositions, soft SAFT density profiles show that the hydrogenated alcohols are slightly absorbed to the interface. This induces that the aneutrope is the composition in where the relative absorption inverts from one to another component, increasing the surface tension.

#### 4. Conclusions

The parameters for the 1H-1H-perfluorinated alcohols family were modelled to the experimental data (from TFE to TRFH), obtaining a good agreement between them. The obtained parameters proved to be consistent not only with the other related family parameters values but also with the expected tendencies (alkanes, alcohols and perfluoro alkanes). In addition, despite the short range of available experimental data, the model was capable of describing well the VLE curves for distant ranges from critical zone.

The robustness of the proposed parameters was tested by applying the transferability of the parameters concept. The parameters for PDFO and HDFN were obtained from the number of segments, molecular volume and energy correlations (pure prediction – non-modelled molecules). The results from the model fit with the experimental vapour pressure experimental data available for these two molecules.

Derivative Properties were also calculated using the soft SAFT framework and compared with the experimental or simulated data with the aim to test how accurate the model could be by predicting these properties when modelling with the VLE data. Having this premise in mind, the results from the model have captured nicely, in most of the cases, the values and the trends of the literature data. The global balance is positive when referring to the accuracy of the derivative properties on this terms.

To enhance the study of this family of molecules, the influence parameter for each compound was modelled using experimental data. The expected trend for this was achieved and the model results are in line with the experimental ones.

Regarding the binary mixtures between TFE and hydrogenated alcohols, VLE diagrams were obtained, for experimental data available. In addition, for both excess properties studied (excess volume and excess enthalpy) the results were more complex. The excess volume was fully captured for mixtures with shorter hydrogenated alcohols molecules, but not for longer molecules. However, the experimental data available for mixtures with longer hydrogenated alcohols molecules inhibit further and precise conclusions. For excess enthalpy, neither the values nor the tendencies were captured. Since it's a sensitive variable, only a parametrization made specially to that property would fix it.

Finally, the interfacial properties of the binary mixtures with TFE and hydrogenated alcohols were successfully captured. The successful parameterization of molecular parameters for pure components, mixtures and for influence parameters for pure components allows the attainment of the surface tension of the binary mixtures. This way, the robustness and consistency of all the models used and created in this work are supported by the fact that it was only necessary one constant parameter for the capture of all

the curves. Otherwise, the curve trends and aneutrope composition would not be greatly obtained as it is in this work.

#### Acknowledgments

This work wouldn't have been possible without the availability, support and collaboration from Dr. Lourdes Vega and Dr. Eduardo Filipe. The support given by their both scientific groups (in Khalifa University and in Instituto Superior Técnico) was essential in the development of the results and in results analysis. A special thank to Dr. Luis Pereira for his care in all phases of this work.

#### Nomenclature

##### Symbols

$A$	- Helmholtz energy
$k_b$	- Boltzman's Constant
$m$	- Chain Length
$\sigma$	- Segment diameter
$\epsilon/k_b$	- Dispersive energy
$\epsilon^{HB}/k_b$	- Association Energy
$\kappa^{HB}$	- Association Volume
$X_i^a$	- Non-Bonded sites fraction
$\Delta_{AB}^{ij}$	- Association Bond Strength Between Two Associative Sites
$g_{ii}^{LJ}$	- Pair Radial Distribution Function
$M_i$	- Number of Association Sites
$k_T$	- Isothermal Compressibility
$\alpha$	- Thermal Expansion Coefficient
$C_V$	- Isochoric Heat Capacity
$C_P$	- Isobaric Heat Capacity
$\eta$	- Size Binary Parameter
$\xi$	- Dispersive Energy Binary Parameter
$\alpha^{HB}$	- Association Energy Binary Parameter
$\Delta H_{VAP}$	- Vaporization Enthalpy
$\bar{A}$	- Helmholtz free Energy Density of the Homogeneous Fluid.
$a_0$	- Helmholtz free Energy Density of the Homogeneous Fluid.
$\nabla\rho$	- Density Gradient
$\beta$	- Binary Influence Parameter
$\gamma$	- Surface Tension
$\Delta\Omega$	- Reduced Grand Thermodynamic Coefficient

##### Acronyms

TFE	- 1H-1H-Trifluoroethanol
PFP	- 1H-1H-Pentafluoropropanol
HFB	- 1H-1H-Heptafluorobutanol
NFP	- 1H-1H-Nonafluoropentanol
UFH	- 1H-1H-Undecafluorohexanol
TRFH	- 1H-1H-Tridecafluoroheptanol
PDFO	- 1H-1H-Pentadecafluoroctanol
HDFN	- 1H-1H-Heptadecafluorononanol
SAFT	- Statistical Association Fluid Theory
EoS	- Equation of State
TPT1	- Thermodynamic Perturbation Theory of First Order
DGT	- Density Gradient Theory
LJ	- Lennard-Jones
VLE	- Vapour-Liquid Equilibrium



## References

- [1] T. OKAZOE, "Overview on the history of organofluorine chemistry from the viewpoint of material industry," *Proc. Japan Acad. Ser. B*, vol. 85, no. 8, pp. 276–289, 2009.
- [2] M. Pabon and J. M. Corpart, "Fluorinated surfactants: Synthesis, properties, effluent treatment," *J. Fluor. Chem.*, vol. 114, no. 2, pp. 149–156, 2002.
- [3] K. Kanamura, "Fluorine Compounds in Battery Applications," *Adv. Inorg. Fluorides*, pp. 521–554, Jan. 2000.
- [4] B. J. Finlayson-Pitts and J. N. Pitts, "Homogeneous and Heterogeneous Chemistry in the Stratosphere," in *Chemistry of the Upper and Lower Atmosphere*, Elsevier, 2000, pp. 657–726.
- [5] M. Paluch and P. Dynarowicz, "Electrical properties of the mixed films of 2,2,2-trifluoroethanol—ethanol at the water/air interface," *J. Colloid Interface Sci.*, vol. 98, no. 1, pp. 131–137, Mar. 1984.
- [6] I. A. Shuklov, N. V. Dubrovina, and A. Börner, "Fluorinated alcohols as solvents, cosolvents and additives in homogeneous catalysis," *Synthesis (Stuttg.)*, no. 19, pp. 2925–2943, 2007.
- [7] P. Trillo, A. Baeza, and C. Nájera, "Fluorinated Alcohols As Promoters for the Metal-Free Direct Substitution Reaction of Allylic Alcohols with Nitrogenated, Silylated, and Carbon Nucleophiles," *J. Org. Chem.*, vol. 77, no. 17, pp. 7344–7354, Sep. 2012.
- [8] J.-P. Bégué, D. Bonnet-Delpon, and B. Crousse, "Fluorinated Alcohols: A New Medium for Selective and Clean Reaction," *Synlett*, no. 1, pp. 18–29, 2004.
- [9] M. O. Ratnikov, V. V. Tumanov, and W. A. Smit, "Lewis Acid Catalyst Free Electrophilic Alkylation of Silicon-Capped  $\pi$  Donors in 1,1,1,3,3,3-Hexafluoro-2-propanol," *Angew. Chemie Int. Ed.*, vol. 47, no. 50, pp. 9739–9742, Dec. 2008.
- [10] S. Khaksar, "Fluorinated alcohols: A magic medium for the synthesis of heterocyclic compounds," *J. Fluor. Chem.*, vol. 172, pp. 51–61, 2015.
- [11] William Andrew Publishing, "Pharmaceutical Manufacturing Encyclopedia," vol. F, pp. 1691–1693, 2007.
- [12] A. N. Merchant, "Binary azeotropic compositions of 1,1,1,2,3,3-hexafluoro-3-methoxypropane and 2,2,3,3,3-pentafluoropropanol-1," US5023009A, 1991.
- [13] H. M. Courrier, T. F. Vandamme, and M. P. Krafft, "Reverse water-in-fluorocarbon emulsions and microemulsions obtained with a fluorinated surfactant," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 244, no. 1–3, pp. 141–148, Sep. 2004.
- [14] S. Rossi, C. Szijjártó, F. Gerber, G. Waton, and M. P. Krafft, "Fluorinated materials in microbubble engineering science and technology—Design and development of new bubble preparation and sizing technologies," *J. Fluor. Chem.*, vol. 132, no. 12, pp. 1102–1109, Dec. 2011.
- [15] J. Gross, "A density functional theory for vapor-liquid interfaces using the PCP-SAFT equation of state," *J. Chem. Phys.*, vol. 131, no. 20, p. 204705, Nov. 2009.
- [16] J. Pàmies Corominas, "Bulk and interfacial properties of chain fluids: a molecular modelling approach," *Thesis*, 2004.
- [17] L. E. Urlic, L. J. Florusse, E. J. M. Straver, S. Degrange, and C. J. Peters, "Phase and Interfacial Tension Behavior of Certain Model Gas Condensates: Measurements and Modeling," *Transp. Porous Media*, vol. 52, no. 2, pp. 141–157, 2003.
- [18] A. C. Meeks and I. J. Goldfarb, "Vapor Pressure Of Fluoroalcohols," *J. Chem. Eng. Data*, vol. 12, no. 2, p. 196, 1967.
- [19] Y. Kabata, S. Yamaguchi, M. Takada, and M. Uematsu, "Densities of 2,2,2-trifluoroethanol in the temperature range from 310 K to 420 K II. Compressed-liquid densities at pressures up to 200 MPa," *J. Chem. Thermodyn.*, vol. 24, no. 8, pp. 785–796, 1992.
- [20] S. K. Chaudhari, K. R. Patil, J. Allepús, and A. Coronas, "Measurement of the vapor pressure of 2,2,2-trifluoroethanol and tetraethylene glycol dimethyl ether by static method," *Fluid Phase Equilib.*, vol. 108, no. 1–2, pp. 159–165, Jul. 1995.
- [21] P. Sauermann, K. Holzapfel, J. Oprzynski, J. Nixdorf, and F. Kohler, "Thermodynamic properties of saturated and compressed liquid 2,2,2-trifluoroethanol," *Fluid Phase Equilib.*, vol. 84, pp. 165–182, Apr. 1993.
- [22] H. D. Baehr, "Vapor Pressure and Liquid and Gas Densities of 2, 2, 2-Trifluoroethanol," *Int. J. Thermophys.*, vol. 10, no. 3, pp. 577–589, 1989.
- [23] A. Cooney and K. W. Morcom, "Thermodynamic behaviour of mixtures containing fluoroalcohols II. (2,2,2-trifluoroethanol + benzene)," *J. Chem. Thermodyn.*, vol. 20, no. 12, pp. 1469–1476, 1988.
- [24] C. H. Rochester and J. R. Symonds, "Thermodynamic studies of fluoroalcohols. Part I.—Vapour pressures and enthalpies of vaporization," *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases*, vol. 69, no. 0, p. 1267, 1973.
- [25] L. F. Martins, L. A. Pereira, G. M. Silva, J. R. Ascenso, P. Morgado, J. P. Prates Ramalho, and E. J. Filipe, "Fluorinated surfactants in solution: Diffusion coefficients of fluorinated alcohols in water," *Fluid Phase Equilib.*, vol. 407, pp. 322–333, 2016.
- [26] CH. Wohlfarth, *Landolt-Börnstein, Group IV, Volume 25, Supplement to IV/18*. Springer, 2009.
- [27] J. Hu, K. Tamura, and S. Murakami, "Excess thermodynamic properties of binary mixtures of ethyl formate with benzene, ethanol, and 2,2,2-trifluoroethanol-1-ol at 298.15 K," *Fluid Phase Equilib.*, vol. 131, no. 1–2, pp. 197–212, May 1997.
- [28] S. Miyanaga, K. Tamura, and S. Murakami, "Excess enthalpies and excess isobaric heat capacities of (2,2,2-trifluoroethanol-1-ol + benzene), (benzene + dimethylsulfoxide), and (2,2,2-trifluoroethanol-1-ol + dimethylsulfoxide), at the temperature 298.15 K," *J. Chem. Thermodyn.*, vol. 24, no. 3, pp. 291–296, 1992.
- [29] M. Fioroni, K. Burger, A. E. Mark, and D. Roccatano, "A New 2, 2, 2-Trifluoroethanol Model for Molecular Dynamics Simulations," *Society*, pp. 12347–12354, 2000.
- [30] R. Malhotra and L. A. Woolf, "Thermodynamic properties of 2,2,2-trifluoroethanol," *Int. J. Thermophys.*, vol. 12, no. 2, pp. 397–407, Mar. 1991.
- [31] G. M. C. Silva, P. Morgado, J. D. Haley, V. M. T. Montoya, C. McCabe, L. F. G. Martins, and E. J. M. Filipe, "Vapor pressure and liquid density of fluorinated alcohols: Experimental, simulation and GC-SAFT-VR predictions," *Fluid Phase Equilib.*, vol. 425, pp. 297–304, 2016.
- [32] J. C. S. Costa, M. Fulem, B. Schröder, J. A. P. Coutinho, M. J. S. Monte, and L. M. N. B. F. Santos, "Evidence of an odd-even effect on the thermodynamic parameters of odd fluorotelomer alcohols," *J. Chem. Thermodyn.*, vol. 54, pp. 171–178, Nov. 2012.
- [33] M. Alexandre, P. Costa, E. Jorge, M. Filipe, and E. J. Fonseca, "Property Data and Phase Equilibria for the Design of Chemical Processes involving Carbon Dioxide," no. October, 2017.
- [34] L. M. Mukherjee and E. Grunwald, "Physical properties and hydrogen bonding in the system ethanol-2,2,2-trifluoroethanol," *J. Phys. Chem.*, vol. 62, no. 10, pp. 1311–1314, 1958.
- [35] R. Jadot and M. Fraiha, "Isobaric vapor-liquid equilibrium of 2,2,2-Trifluoroethanol with water and 1-Propanol binary systems," *J. Chem. Eng. Data*, vol. 33, no. 3, pp. 237–240, 1988.
- [36] L. S. Smith, E. E. Tucker, and S. D. Christian, "Vapor-density and liquid-vapor equilibrium data for binary mixtures of 2,2,2-trifluoroethanol with water, methanol, ethanol, and 2-butanol," *J. Phys. Chem.*, vol. 85, no. 9, pp. 1120–1126, 1981.
- [37] P. Duarte, M. Silva, D. Rodrigues, P. Morgado, L. F. G. Martins, and E. J. M. Filipe, "Liquid Mixtures Involving Hydrogenated and Fluorinated Chains: ( $p, p, T, x$ ) Surface of (Ethanol + 2,2,2-Trifluoroethanol), Experimental and Simulation," *J. Phys. Chem. B*, vol. 117, no. 33, pp. 9709–9717, Aug. 2013.
- [38] P. Morgado, A. R. Garcia, L. M. Ilharco, J. Marcos, M. Anastácio, L. F. G. Martins, and E. J. M. Filipe, "Liquid Mixtures Involving Hydrogenated and Fluorinated Alcohols: Thermodynamics, Spectroscopy, and Simulation," *J. Phys. Chem. B*, vol. 120, no. 38, pp. 10091–10105, Sep. 2016.
- [39] M. Sassi and Z. Atik, "Excess molar volumes of binary mixtures of 2,2,2-trifluoroethanol with water, or acetone, or 1,4-difluorobenzene, or 4-fluorotoluene, or  $\alpha, \alpha, \alpha$ -trifluorotoluene or 1-alcohols at a temperature of 298.15 K and pressure of 101 kPa," *J. Chem. Thermodyn.*, vol. 35, no. 7, pp. 1161–1169, Jul. 2003.
- [40] T. Minamihonoki, H. Ogawa, H. Nomura, and S. Murakami, "Thermodynamic properties of binary mixtures of 2,2,2-trifluoroethanol with water or alkanols at T = 298.15 K," *Thermochim. Acta*, vol. 459, no. 1–2, pp. 80–86, Jul. 2007.
- [41] C. Wohlfarth, *Landolt-Börnstein: Volume 24 - Surface Tension of Pure Liquids and Binary Liquid Mixtures*. Springer.
- [42] Z. Atik, "Densities and excess molar volumes of binary and ternary mixtures of aqueous solutions of 2,2,2-trifluoroethanol with acetone and alcohols at the temperature of 298.15 K and Pressure of 101 kPa," *J. Solution Chem.*, vol. 33, no. 11, pp. 1447–1466, 2004.
- [43] M. C. Teixeira, "Complex Interfacial Behaviour of Mixtures of Fluorinated and Hydrogenated Alcohols," pp. 1–10, 2014.
- [44] L. V. and E. J. M. F. Gonçalves M. C. Silva, José Justino, João Afonso, Mariana Leitão, Miguel Teixeira, Luís M. C. Pereira, Pedro Morgado, "Surface tension of highly fluorinated alcohols: experimental, simulation and soft-SAFT-DGT modeling," *unpublished*, 2018.
- [45] F. J. Blas and L. F. Vega, "Associating Fluid Theory ( SAFT ) Equation of State," vol. 5885, no. 1996, pp. 660–674, 1998.
- [46] F. J. B. L. Vega, "Thermodynamic behaviour of homonuclear and heteronuclear Lennard-Jones chains with association sites from simulation and theory," *Mol. Phys.*, vol. 92, no. 1, pp. 136–150, 1997.
- [47] B. Breure and C. J. Peters, "Modeling of the surface tension of pure components and mixtures using the density gradient theory combined with a theoretically derived influence parameter correlation," *Fluid Phase Equilib.*, vol. 334, pp. 189–196, Nov. 2012.
- [48] A. J. M. Yang, P. D. Fleming, and J. H. Gibbs, "Molecular theory of surface tension," *J. Chem. Phys.*, vol. 64, no. 9, pp. 3732–3747, May 1976.
- [49] V. Bongiorno, L. Scriven, and H. Davis, "Molecular theory of fluid interfaces," *J. Colloid Interface Sci.*, vol. 57, no. 3, pp. 462–475, Dec. 1976.
- [50] V. Bongiorno and H. T. Davis, "Modified Van der Waals theory of fluid interfaces," *Phys. Rev. A*, vol. 12, no. 5, pp. 2213–2224, Nov. 1975.
- [51] G. M. C. Silva, P. Morgado, J. D. Haley, V. M. T. Montoya, C. McCabe, L. F. G. Martins, and E. J. M. Filipe, "Vapor pressure and liquid density of fluorinated alcohols: Experimental, simulation and GC-SAFT-VR predictions," *Fluid Phase Equilib.*, vol. 425, pp. 297–304, Oct. 2016.
- [52] J. C. S. Costa, M. Fulem, B. Schröder, J. A. P. Coutinho, M. J. S. Monte, and L. M. N. B. F. Santos, "Evidence of an odd-even effect on the thermodynamic parameters of odd fluorotelomer alcohols," *J. Chem. Thermodyn.*, vol. 54, pp. 171–178, 2012.
- [53] F. Llovel, J. C. Pàmies, and L. F. Vega, "Thermodynamic properties of Lennard-Jones chain molecules: Renormalization-group corrections to a modified statistical associating fluid theory," *J. Chem. Phys.*, vol. 121, no. 21, pp. 10715–10724, Dec. 2004.
- [54] A. M. A. Dias, F. Llovel, J. A. P. Coutinho, I. M. Marrucho, and L. F. Vega, "Thermodynamic characterization of pure perfluoroalkanes, including interfacial and second order derivative properties, using the crossover soft-SAFT EoS," *Fluid Phase Equilib.*, vol. 286, no. 2, pp. 134–143, 2009.
- [55] Karamat Nasirzadeh, Denys Zimin, and Roland Neueder, and W. Kunz\*, "Vapor-Pressure Measurements of Liquid Solutions at Different Temperatures: Apparatus for Use over an Extended Temperature Range and Some New Data," 2004.
- [56] †, ‡ Karamat Nasirzadeh, † and Roland Neueder, and † Werner Kunz\*, "Vapor Pressure Determination of the Aliphatic C5 to C8 1-Alcohols," 2005.
- [57] V. Alexandra, "SAFT Modelling of Fluorinated Substances and their Mixtures using SAFT- $\gamma$  Mie EoS approach November / December 2016," no. December, 2016.