

SAFT Modelling of fluorinated substances and their mixtures using SAFT- γ Mie EoS approach

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Perfluoroalkanes are becoming more important, due to their applications on the pharmaceutical, medical and petrochemical industry. It is then important to have the capacity of predicting the thermodynamic properties of these compounds. Using a *heteronuclear* approach of the Statistical Associating Fluid Theory (SAFT), the SAFT- γ Mie EoS, parameters that allow to calculate thermodynamic properties of the perfluoroalkanes were obtained. Good results were obtained when calculating the vapour pressure, P_v , saturated liquid density, $\rho_{sat,liq}$, and the single phase density, ρ_{liq} , for some perfluoroalkanes, verified with the calculation of the percentage average absolute deviation (%AAD), that showed values lower than 3% for the majority of the compounds.

Because alkanes are also a part of this work, mixtures of alkanes and ethers were studied, with parameters obtained on a recently published paper. From this study, it was found that, although the parameters describe well the behaviour of alkanes, that doesn't happen with ethers, what indicates that new parameters should be obtained, on a future work, only to ethers.

With the parameters obtained from the perfluoroalkanes and the parameters taken from the published paper for alkanes, this work is concluded by obtaining the dispersion energy (unlike interactions) parameters between the groups that compose the perfluoroalkanes (CF_2 , CF_3 e CF_4) and the groups that compose the alkanes (CH_2 , CH_3 and CH_4) because only with these parameters is possible to calculate the thermodynamic properties of these mixtures. Having the parameters, thermodynamic properties of the mixtures were calculated for a few different mixtures: the Vapour-Liquid Equilibrium, the Liquid-Liquid Equilibrium, Excess Enthalpy and Excess Volume.

Concordant results with the experimental data were obtained, after the decrease of the unlike interaction, specially the repulsive unlike interactions, parameter that influences a lot the excess volume, the property with the worst results on a first approach

Introduction

Thermodynamic models have a very important role in the design and optimization of processes with different applications, being employed for the calculation and prediction of thermodynamic properties of pure or multicomponent compounds and being decisive in the design, cost and, in some cases, the feasibility of a given unit operation. Group contribution (GC) is a method on which molecules are modelled in terms of each functional group that they contain, allowing complex systems to be broken down into small fragments. Each functional group is characterised by a set of parameters, usually determined by regression to large sets of experimental data, that are able to determine thermodynamic properties of pure components and mixtures. In recent years, the GC concept has been applied within the framework of SAFT. The statistical Association Fluid Theory (SAFT) is

an advanced molecular-based equation of state (EoS) in which molecules are modelled as chain of tangentially bonded spherical segments, interacting via an attractive potential with short-ranged sites placed on the segments to mediate aggregate formation as occurs in hydrogen bonding and polar fluids.

The equation is written as a perturbation theory, where the Helmholtz energy is calculated considering that the effects of molecular shape and interactions on the thermodynamic properties can be separated and quantified, given specific contributions to the total free energy. The SAFT equation of state is, then, written in terms of the Helmholtz free energy of the system as a sum of different contributions:

$$\frac{A}{N k_B T} = \frac{A^{IDEAL}}{N k_B T} + \frac{A^{MONO}}{N k_B T} + \frac{A^{CHAIN}}{N k_B T} + \frac{A^{ASSOC}}{N k_B T} \quad (1)$$

There's an ideal term A_{IDEAL} that represents the ideal free energy, a term to account for the attractive and dispersion interactions between

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attractive segments (monomers) forming the molecules, A_{MONO} , a term for the energy change due to the formation of chain of monomers, A_{CHAIN} , and for the effect of association there's the term A_{ASSOC} . N is the total number of molecules in the mixture, T is the absolute temperature and k_B is the Boltzmann constant. Many approaches of SAFT EoS have been applied to describe the phase behaviour of different systems: The *homonuclear* approaches are based on the original molecular description proposed by Chapman *et al.*,^[1,2] in which molecules are represented as identically sized spheres and therefore all parameters are identical. It is a limited approach as it doesn't consider the variety of groups present in one compound. This approaches are typically limited to the prediction of the properties of pure compounds, once no information on the nature of the unlike interactions between groups and/or molecules can be extracted from the pure-component data that are used to characterize the functional groups. As an alternative to the *homonuclear* approaches, a *heteronuclear* molecular model has been implemented. This model allows more detail about a compound's molecular structure, since different types of monomeric segments are used to describe the different chemical functional groups of the molecule and the molecules are represented as chains of segments not necessarily identical.

SAFT- γ Mie

SAFT- γ Mie equation of state^[3] is an approach where an *heteronuclear* model is implemented and a Mie (generalized Lennard-Jonesium) potential of variable repulsive and attractive ranges is used to represent the segment-segment interactions.

In this approach, molecules are represented as comprising distinct functional chemical groups and it has allowed to predict fluid-phase behaviour (vapour-liquid and liquid-liquid equilibria) and excess thermodynamic properties of a variety of binary mixtures where has been observed very good agreement with the experimental data.

As happens with other group contribution approaches, the determination of molecular properties with the SAFT- γ Mie EoS is done by subdividing the molecules into distinct functional groups, with appropriate summations over the contributions of each functional group. The representation of the pair interaction energy between two segments k and l as a form of intersegment distance r_{kl} is given by:

$$\Phi_{kl}^{\text{Mie}}(r_{kl}) = C_{kl}\epsilon_{kl} \left[\left(\frac{\sigma_{kl}}{r_{kl}} \right)^{\lambda_{kl}^r} - \left(\frac{\sigma_{kl}}{r_{kl}} \right)^{\lambda_{kl}^a} \right] \quad (2)$$

Where r_{kl} is the distance between the centers of the segments, σ_{kl} the segment diameter, ϵ_{kl} the depth of the potential well, and λ_{kl}^r and λ_{kl}^a the repulsive and attractive exponent of the segment-segment interactions, respectively. The prefactor C_{kl} is a function of these exponents and ensures that the minimum of the interaction is $-\epsilon_{kl}$:

$$C_{kl} = \frac{\lambda_{kl}^r}{\lambda_{kl}^r - \lambda_{kl}^a} \left(\frac{\lambda_{kl}^r}{\lambda_{kl}^a} \right)^{\frac{\lambda_{kl}^a}{\lambda_{kl}^r - \lambda_{kl}^a}} \quad (3)$$

As happens in other SAFT approaches, hydrogen bonding or strongly polar interactions can be treated through the incorporation of a number of additional short-range square-well association site, which are placed on any given segments as required. The association interaction between two square-well association site of type a in segment k and b in segment l is given by:

$$\Phi_{kl,ab}^{\text{HB}}(r_{kl,ab}) = \begin{cases} -\epsilon_{kl,ab}^{\text{HB}} & \text{if } r_{kl,ab} \leq r_{kl,ab}^c \\ 0 & \text{if } r_{kl,ab} \geq r_{kl,ab}^c \end{cases} \quad (4)$$

Where $r_{kl,ab}$ is the centre-centre distance between sites a and b , $-\epsilon_{kl,ab}^{\text{HB}}$ is the associating energy, and $r_{kl,ab}^c$ the cut-off range of the interaction between sites a and b on groups k and l , respectively.

So, a (non-associating) functional group k is fully described by six parameters: the number v_k^* of identical spherical segments forming the group, the shape factor of the segments S_k , the diameters of the segments σ_{kk} , the segment energy of interaction ϵ_{kk} , and the exponents of the Mie potential λ_{kk}^r and λ_{kk}^a . The interactions between groups of different types k and l are characterized by the unlike parameters σ_{kl} , ϵ_{kl} , λ_{kl}^r , λ_{kl}^a , $\epsilon_{kl,ab}^{\text{HB}}$ and $K_{kl,ab}$.

Combining Rules

The unlike intermolecular parameters are calculated through combining rules, commonly employed within equations of state to facilitate the study of binary and multicomponent systems. When required, the values obtained for each parameter with the combining rules are refined by experimental data.

The unlike segment diameter σ_{kl} is obtained using the Lorentz-like arithmetic mean of the like diameters

$$\sigma_{kl} = \frac{\sigma_{kk} + \sigma_{ll}}{2} \quad (5)$$

The same combining rule is applied for the calculation of the unlike effective hard-sphere diameter

$$d_{kl} = \frac{d_{kk} + d_{ll}}{2} \quad (6)$$

The unlike dispersion energy ϵ_{kl} between groups k and l , can be obtained by applying an augmented geometric mean rule, which also accounts for the asymmetry in size:

$$\epsilon_{kl} = \frac{\sqrt{\sigma_{kk}^3 \sigma_{ll}^3}}{\sigma_{kl}^3} \sqrt{\epsilon_{kk} \epsilon_{ll}} \quad (7)$$

The exponents of the unlike segment-segment interaction, λ_{kl}^r and λ_{kl}^a are obtained as

$$\lambda_{kl} = 3 + \sqrt{(\lambda_{kk} - 3)(\lambda_{ll} - 3)} \quad (8)$$

The unlike value of the association energy can be obtained by means of a simple geometric rule

$$\epsilon_{kl,ab}^{HB} = \sqrt{\epsilon_{kl,aa}^{HB} \epsilon_{kl,bb}^{HB}} \quad (9)$$

while the unlike bonding volume $K_{kl,ab}$ is obtained as

$$K_{kl,ab} = \left(\frac{\sqrt[3]{K_{kk,aa}} + \sqrt[3]{K_{ll,bb}}}{2} \right)^3 \quad (10)$$

Although these combining rules provide a good first estimate of the values of the required unlike group parameters, it's always better to use experimental data when available to estimate these parameters, especially in the case of unlike attractive interactions.

Perfluoroalkanes

The study of perfluoroalkanes is becoming more and more important nowadays due to the fact that fluorinated pharmaceutical compounds are becoming increasingly popular, with a growing need to determine their thermodynamic properties. Therefore, the study of simpler compounds such as n-perfluoroalkanes (PFAs) is a good start in that matter.

Therefore, two phases divide the study: the parameter estimation, using *gSAFTmm*, and thermodynamic properties calculation, using *gPROMS ModelBuilder*®, with the previously estimated parameters.

Parameter estimation

A previous work was done in this matter, by Wong and Lu^[4], where parameters that describe the groups CF₂ and CF₃ were obtained, using experimental as input for vapour pressure, P_v and saturated liquid density, $\rho_{Sat,liq}$, taken from correlations from NIST^[5].

In this work, parameters for those groups were estimated an extra property as experimental data, the single phase liquid density, ρ_{liq} , for a few of the studied compounds.

The optimized parameters obtained can be observed below, in table 1.

Table 1. Optimised like and unlike group parameters for CF₂ and CF₃ groups using the SAFT- γ Mie Group contribution approach on *gSAFT Materials Modeller*

| Group | v_k^* | S_k | λ_{kk}^r | λ_{kk}^a | σ_{kk} /Å | $(\frac{\epsilon_{kk}}{k_B})/K$ | $(\frac{\epsilon_{kl}}{k_B})/K$ |
|-------------------|---------|-------|------------------|------------------|---------------------|---------------------------------|---------------------------------|
| CF ₃ | 1 | 0.55 | 28.90 | 6.00 | 4.93 | 325.0 | - |
| CF ₂ | 1 | 0.28 | 33.96 | 6.00 | 5.20 | 459.9 | - |
| CF ₃ - | - | - | - | - | - | - | 390.0 |
| CF ₂ | - | - | - | - | - | - | - |

Thermodynamic Properties of the components

Having the final parameters, from table 1, thermodynamic properties for each component were calculated, as well as graphical comparisons between the predicted results and experimental data/correlated calculations for components C₃F₈ to C₉F₂₀. Since there are several components and properties, only two components were presented in this article.

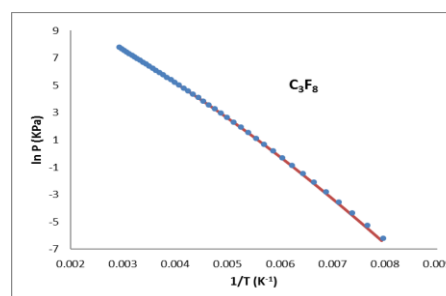


Figure 1. SAFT- γ Mie prediction of the vapour pressure of the component C₃F₈ in a Clausius-Clapyron representation. The circles are data from NIST^[5] correlations

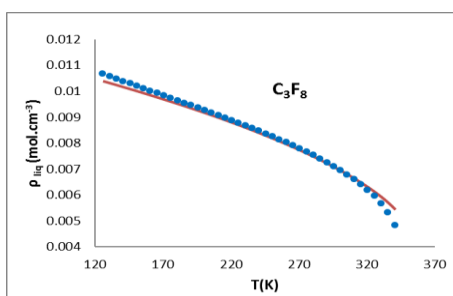


Figure 2. SAFT- γ Mie prediction of saturated liquid density of the component C_3F_8 . The circles are data from NIST^[5] correlations

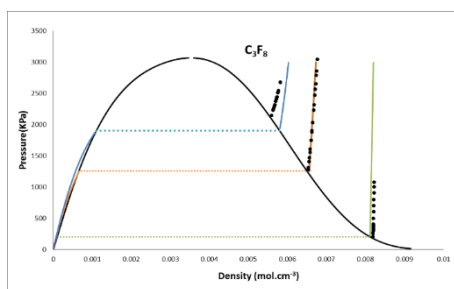


Figure 3. SAFT- γ Mie prediction of pressure-density envelope for C_3F_8 at 253.18 K (green), 313.16 K (orange) and 333.17 K (blue). The circles are experimental data for reference [6].

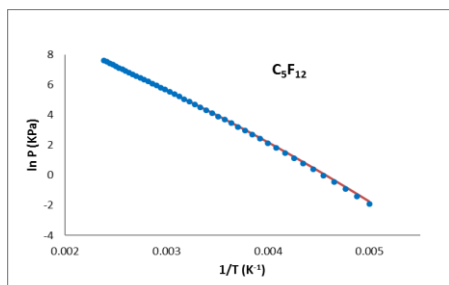


Figure 4. SAFT- γ Mie prediction of the vapour pressure of the component C_5F_{12} in a Clausius-Clayprn representation. The circles are data from NIST^[5] correlations.

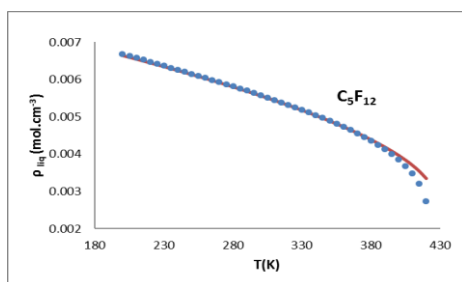


Figure 5. SAFT- γ Mie prediction of saturated liquid density of the component C_5F_{12} . The circles are data from NIST^[5] correlations

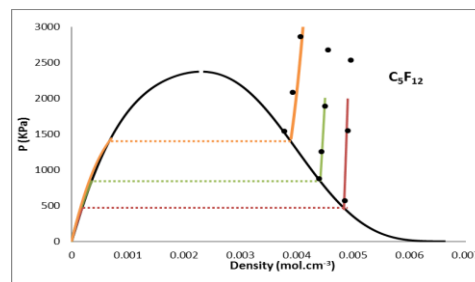


Figure 6. SAFT- γ Mie prediction of pressure-density envelope for C_5F_{12} at 353.18 K (red), 378.31 K (green) and 403 K (orange). The circles are experimental data from ref. [7].

Table 2. Percentage Absolute Average Deviations (%AAD) for the vapour pressure, P_v , and saturated liquid densities, $\rho_{liq,sat}$, for the selected n-perfluoroalkane

| n | T (K) | Component | % AAD | |
|----|---------|-------------|-------|------------------|
| | | | P_v | $\rho_{sat,liq}$ |
| 44 | 126-341 | C_3F_8 | 3.31 | 1.76 |
| 39 | 189-379 | C_4F_{10} | 3.30 | 1.46 |
| 45 | 200-420 | C_5F_{12} | 4.42 | 1.39 |
| 49 | 200-440 | C_6F_{14} | 3.23 | 0.89 |
| 49 | 230-470 | C_7F_{16} | 1.38 | 1.13 |
| 43 | 290-500 | C_8F_{18} | 2.14 | 0.97 |
| 15 | 288-454 | C_9F_{20} | 7.33 | 1.29 |

Table 3. Percentage Absolute Average Deviations (%AAD) for single phase liquid density, for the selected n-perfluoroalkanes

| n | T (K) | Component | % AAD ρ_{liq} |
|----|--------|-------------|--------------------|
| 18 | 353.18 | C_3F_8 | 0.52 |
| 18 | 313.16 | | 0.27 |
| 16 | 333.17 | | 3.7 |
| 5 | 353.17 | C_5F_{12} | 0.54 |
| 6 | 378.31 | | 0.37 |
| 3 | 403.0 | | 1.98 |
| 4 | 303.15 | C_6F_{14} | 0.47 |

From figures 1 to 6 above, it's possible to conclude that the final parameters are capable of predicting all the studied properties for the selected compounds very accurately.

Tables 2 and 3 show very small %AAD for both thermodynamic properties, with ranges on 1-7% for P_v and less than 2% for $\rho_{sat,liq}$. This prediction shows that the SAFT- γ Mie is a good approach, with great accuracy, even when looking at properties not so usually observed, as the single phase liquid density.

Mixtures of alkanes and Perfluoroalkanes

Having parameters to study the thermodynamic properties of alkanes (Jakob *et al.*,2015) and having the parameters to study the properties and behaviour of alkanes, from previous chapter, it would be of interest to find out how a mixture of alkanes and perfluoroalkanes behaviour.

Mixture of Methane and Tetrafluoromethane

The mixture of CH₄ and CF₄ is an interesting study since it's a simple mixture but where previous studies have found it hard to obtain an excess volume that is consilient with the experimental data existent for the mixture.

To study this mixture is necessary to obtain first the parameters necessary to describe each component individually. The parameters that describe the methane, were previously calculated and taken from *Burger et al.*^[8] and can be observed below in table 4 . Since there are no parameters that describe the tetrafluoromethane, the parameters were calculated using experimental data for the properties saturated liquid density, saturated vapour density and vapour pressure. The optimal parameters obtained can be observed below, in table 4.

Table 4. The Like Group interactions for Use with the SAFT- γ Mie GC EoS

| Group k | v_k^* | S_k | λ_{kk}^r | λ_{kk}^a | $\sigma_{kk} / \text{\AA}$ | $(\frac{\epsilon_{kk}}{k_B}) / \text{K}$ |
|-----------------|---------|-------|------------------|------------------|----------------------------|--|
| CH ₄ | 1 | 1.00 | 12.50 | 6.00 | 3.74 | 152.28 |
| CF ₄ | 1 | 1.00 | 28.41 | 6.00 | 4.34 | 255.76 |

To describe the behaviour of a mixture is necessary to calculate the parameters that

describe the unlike interactions between the CH₄ and the CF₄, i.e., the ϵ_{kl} and the λ_{kl} . Obtaining these parameters through parameter estimation didn't give good results, giving a excess volume negative while it should be positive, a LLE with a UCST above of what is was supposed to be, so some changes were made the parameters: as the excess volume should be positive and it only varies with the repulsive interactions, the λ_{kl}^r was decreased until the excess volume was positive and with good values. However, for such low values, the critical temperature (or UCST) is very low and, although there is good curve for the excess volume, the LLE was very poor. So, in a method of "try and error", it was found the parameters that described the better the four properties, below in table 5.

Table 5. Unlike parameters modified to allow better curves

| Property | Value |
|------------------------|-------|
| $\lambda_{CH_4-CF_4}$ | 15.5 |
| $\epsilon_{CH_4-CF_4}$ | 180.1 |

With these parameters, the following curves were obtained:

Table 6. Percentage Absolute Average Deviations (%AAD) for the studied properties for the selected mixtures

| Property | T | n | %AAD |
|--------------|--------|----|-------|
| P_v | 159.61 | 9 | 4.57 |
| | 173.9 | 9 | 6.07 |
| LLE | 88-95 | 18 | 41.81 |
| ΔH^E | 98.06 | 7 | 40.00 |
| ΔV^E | 106.7 | 9 | 8.01 |

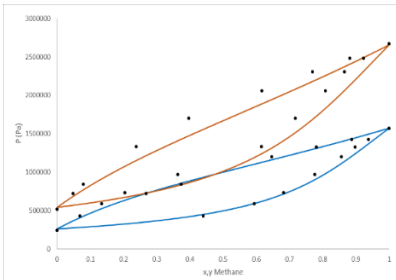


Figure 7. Vapour-liquid equilibrium of the mixture at 159.61K (blue) and 173.9K (red) calculated through the SAFT- γ Mie EoS. The circles represent the experimental data^[9]

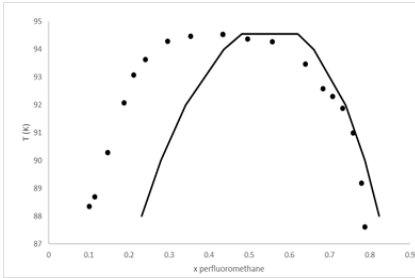


Figure 8. Liquid-Liquid Equilibrium of the mixture at atmospheric pressure. The circles represent the experimental data^[10].

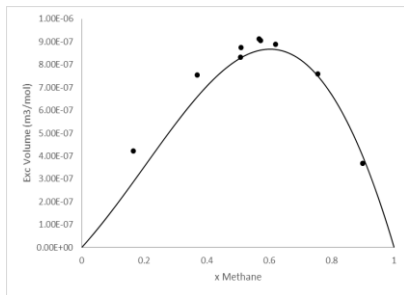


Figure 9. Excess Volume of the mixture calculated with SAFT- γ Mie EoS at 106.7K. The circles represent the experimental data^[10].

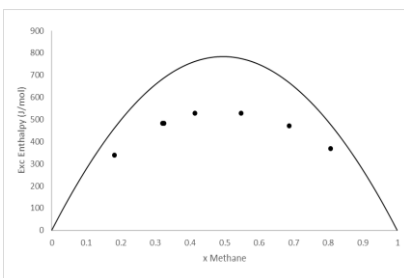


Figure 10. Excess Enthalpy of the mixture calculated with the SAFT- γ Mie EoS at 98K. The circles represent the experimental data^[11].

To obtain a positive and good excess volume's curve, it was needed to decrease the repulsive interaction to a value very low, below the expected according to the combining rules. Having a decrease in the epsilon, allowed to find a liquid-liquid equilibrium that would have a UCST as expected according to the experimental

data, for a low lambda repulsive. The vapour-liquid equilibrium is not as good as was with the first parameters used, but is acceptable. The excess enthalpy is around 40% higher than the experimental data. However, with these parameters it was impossible to find better values for this property because it was observed that the excess enthalpy decreases with the increase of the epsilon and the increase of the lambda repulse. Well, if there's an increase of the λ_{kl}^r , the excess volume values decrease which is not desirable, but if the epsilon increases, the UCST in the Liquid-liquid equilibrium increases which is also not desirable.

Mixtures with CF₂ and CF₃

On a mixture of alkanes and perfluoroalkanes there are several parameters to be considered. Individually, on the alkanes, there are the like and unlike interactions of the CH₂ and CH₃ groups and on the perfluoroalkanes there are the like and unlike interactions of the CF₂ and CF₃ groups. All these parameters have been obtained before and are on tables 7 and 8:

Table 7. The Like Group interactions for the alkanes with the SAFT- γ Mie GC EoS

| Group k | v_k^* | S_k | $\sigma_{kk}(\text{\AA})$ | λ_{kk}^a | λ_{kk}^r | (ϵ_{kk}/k_B) (K) |
|----------------------------------|---------|-------|---------------------------|------------------|------------------|---------------------------|
| CH ₃ | 1 | 0.58 | 4.08 | 6.00 | 15.05 | 256.77 |
| CH ₂ | 1 | 0.23 | 4.88 | 6.00 | 19.87 | 473.39 |
| CH ₃ -CH ₂ | - | - | - | - | - | 350.77 |

Table 8. The Like Group interactions for the perfluoroalkanes with the SAFT- γ Mie GC EoS

| Group k | v_k^* | S_k | λ_{kk}^r | λ_{kk}^a | $\sigma_{kk}/\text{\AA}$ | $(\epsilon_{kk}/k_B)/K$ | $(\epsilon_{kl}/k_B)/K$ |
|----------------------------------|---------|-------|------------------|------------------|--------------------------|-------------------------|-------------------------|
| CF ₃ | 1 | 0.55 | 28.90 | 6.00 | 4.93 | 325.0 | - |
| CF ₂ | 1 | 0.28 | 33.96 | 6.00 | 5.20 | 459.9 | - |
| CF ₃ -CF ₂ | - | - | - | - | - | - | 390.0 |

Once again, with the unlike interactions obtained through parameter estimation, the results were not good enough with the mixture hexane and perfluorohexane. So, in order to get better results, the parameters were changed to obtain better results with this mixture. As in the mixture of methane with tetrafluoromethane the decrease of the unlike interactions allowed good results, the same procedure was tried in this mixture. Decreasing both parameters in the same proportion that was decreased in the mixture methane and tetrafluoromethane, comparatively with the combining rules an increase in the values of the excess volume was observed but still with a curve that shows phase separation. As the excess volume changes with the repulsive lambda but is not very affected by the epsilon, the values of the epsilon were fixed in the values obtained by the decrease but not the repulsive interactions, with the objective of getting excess properties close to the experimental values.

With that decrease, the epsilon values changed to the values seen below:

Table 9. The Unlike Group interactions for the mixtures with the SAFT-γ Mie GC EoS

| ϵ_{kl} | CH_3 | CH_2 |
|-----------------|--------|--------|
| CF_3 | 263.1 | 362.3 |
| CF_2 | 310.7 | 430.5 |

Having these values fixed, the objective was to decrease or increase the values of the λ_{kl}^r parameters in the same proportion in order to obtain a liquid-liquid curve with a critical temperature coinciding with the one from the experimental data and excess properties that don't show phase separation. Some things were taken in account doing this change in the parameters: the λ_{kl}^r can't be too low or the critical temperature of the mixture will be below of what is supposed to be but can't be too high or the excess volume of the mixture will be too low. Having this in consideration, the final parameters obtain to the repulsive interactions are below in table 10.

Table 10. The Unlike Group repulsions for the mixtures with the SAFT-γ Mie GC EoS

| λ_{kl}^r | CH_3 | CH_2 |
|------------------|--------|--------|
| CF_3 | 18.37 | 21.25 |
| CF_2 | 19.84 | 28.99 |

With these parameters, the thermodynamic properties of the mixture hexane and perfluorohexane can be observed below

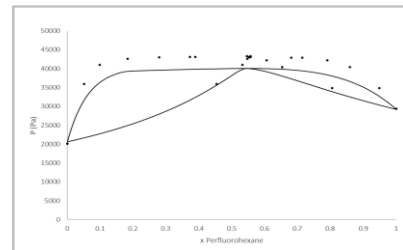


Figure 11. Vapour-liquid equilibrium of the binary mixture at 298.15K.. The circles represent the experimental data^[12]. The curves represent the calculation with the SAFT-γ Mie EoS approach

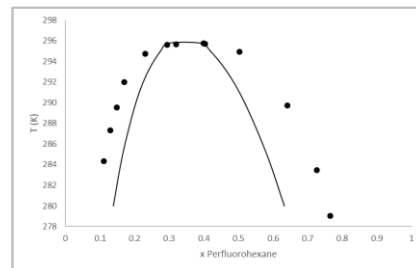


Figure 12. . T-x curve for the system at atmospheric pressure. The circles represent the experimental data^[13]. The curves represent the calculation with the SAFT-γ Mie EoS approach.

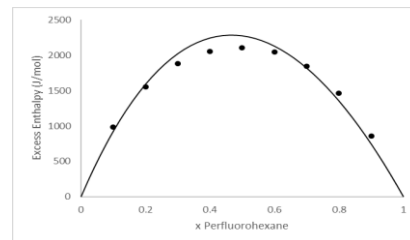


Figure 13. . Excess Enthalpy of the binary mixture at 298.15 K The circles represent the experimental data^[14,15]. The curve represents the calculation with the SAFT-γ Mie EoS approach

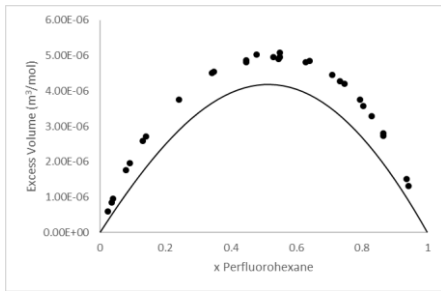


Figure 14. . Excess Volume of the binary mixture at 298.15 K. The circles represent the experimental data^[16]. The curve represents the calculation with the SAFT- γ Mie EoS approach.

As can be observed, the results obtained with these parameters are very close to the experimental ones. With such good results, the same parameters were used to calculate the thermodynamic properties of other different mixtures of alkanes and perfluoroalkanes.

Butane and Perfluorobutane

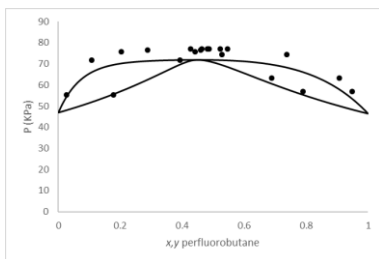


Figure 15. Vapour-liquid equilibrium of the binary mixture. The curves represent the calculation with the SAFT- γ Mie EoS approach.

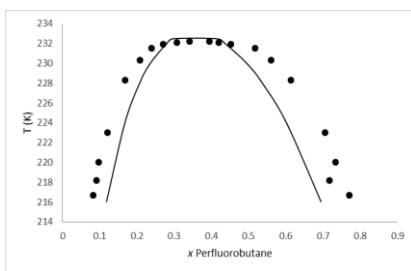


Figure 16. T-x curves for the system at atmospheric pressure. The squares represent the experimental data^[17]. The curve represents the calculation with the SAFT- γ Mie EoS approach.

Pentane and Perfluoropentane

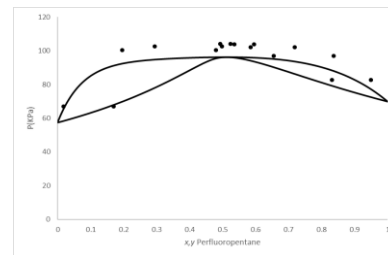


Figure 17. Vapour-liquid equilibrium of the binary mixture at 293 K. The circles represent the experimental data^[18]. The curves represent the calculation with the SAFT- γ Mie EoS approach.

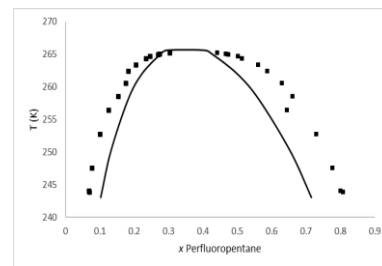


Figure 18. T-x curves for the system at atmospheric pressure. The squares represent the experimental data^[18]. The curves represent the calculation with the SAFT- γ Mie EoS approach.

Perfluoropentane and Hexane

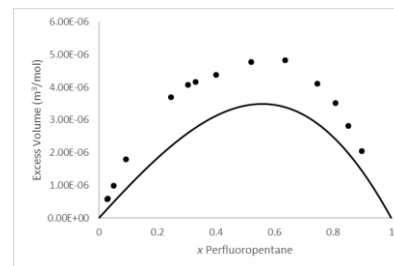


Figure 19. Excess Volume of the binary mixture at 298.15 K. The circles represent the experimental data^[19]. The curve represents the calculation with the SAFT- γ Mie EoS approach..

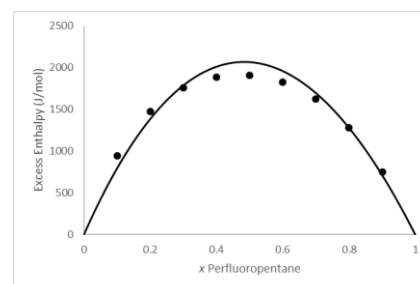


Figure 20. Excess Enthalpy of the binary mixture at 293.15 K. The circles represent the experimental data^[20]. The curve represents the calculation with the SAFT- γ Mie EoS approach.

Different mixture's UCSTs

Although there isn't much more experimental data for mixtures of alkanes and perfluoroalkanes that was show above, there are experimental values of the UCST (Upper Critical Solution Temperature), or critical temperature as is commonly said, for some more mixtures.

Table 11. UCST calculated values for different mixtures

| | C ₅ H ₁₂ | C ₆ H ₁₄ | C ₇ H ₁₆ | C ₈ H ₁₈ |
|--------------------------------|--------------------------------|------------------------------------|--------------------------------|--------------------------------|
| C ₅ F ₁₂ | 266 ^b | 288 ^b | | |
| | 266 ^a | 284 ^a | | |
| C ₆ F ₁₄ | 273 ^b | 294 ^d /296 ^b | 315/316 ^b | 335 ^b |
| | 278 ^a | 296 ^a | 313 ^a | 329 ^a |
| C ₇ F ₁₆ | 282 ^b | 303 ^b | 323 ^b | 343 ^b |
| | 288 ^a | 306 ^a | 324 ^a | 340 ^a |
| C ₈ F ₁₈ | 288 ^c | 299 ^c | 320 ^c | 349 ^b |
| | 297 ^a | 315 ^a | 333 ^a | 350 ^a |

^a Theoretical values

^b Experimental values from ref.[21]

^c Experimental values from ref.[22]

^d Experimental values from ref.[20]

From the table 11 containing the UCST values for different mixtures is possible to observe that the parameters give good results when the mixtures have the same number of Carbons but give results with some difference in the remaining mixtures.

Conclusions

On the calculation of parameters that describe the behaviour of perfluoroalkanes, it was possible to conclude that the parameters obtained in this work are good, showing low %AAD for all the properties studied. The fact that the %AAD of this work is so low is very satisfactory because, with the addition of a new type of experimental data, the single phase density, ρ_{liq} , as an input to the parameter estimation, it would be expected worse %AAD on the vapour pressure, P_v , and saturated liquid density, $\rho_{sat,liq}$, calculations, what didn't happen.

Relatively to mixtures of alkanes and perfluoroalkanes, it was found that the λ_{kl}^r influences a lot the results, with lower values on

this parameter allowing better results regarding the excess volume in different mixtures. It was also found that it's possible, but not easy to obtain good results in the VLE, LLE, excess volume and excess enthalpy at the same time: the diminution of the λ_{kl}^r allows better excess volume but gives a worse LLE and the increase of the ϵ_{kl} allows a better excess enthalpy but, to have a LLE with a correct UCST, forces the λ_{kl}^r to increase it's value and so, giving a worse excess volume. Good results were, overall, accomplished with these mixtures. However, on a future work better like parameters should be studied for the tetrafluoromethane, since the thermodynamic calculations of the mixture between this compound and the methane weren't as good as the thermodynamic calculations between the mixture hexane and the perfluorohexane: on the mixture of hexane and perfluorohexane were accomplished good results on the four properties studied, while on the mixture of methane and tetrafluoromethane there were good results in all the properties with exception for the excess enthalpy, with a deviation of 40% comparatively with the experimental data. This shows that it's possible to obtain parameters that allow to have good results in all these studied properties, as was proved with the mixture of hexane with perfluorohexane. Although it wasn't possible to accomplish that with the mixture of tetrafluoromethane and methane, it's probably possible to accomplish that with better parameters describing the CF₄.

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