

MODELING THE SURFACE TENSION OF PURE ALKANES AND PERFLUOROALKANES USING THE soft-SAFT EoS COUPLED WITH THE GRADIENT THEORY EXTENDED TO THE CRITICAL REGION

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The type and magnitude of the molecular interactions that occur at interfaces are responsible for many of the phenomena that are observed in nature as, for example, the formation of micelles by amphiphilic surfactant molecules in aqueous solutions (like soaps and cosmetics), the nature of the lipid bilayers that form cell membranes, the stability of colloids in emulsions (such as milk and paintings), etc. The low surface tensions that characterize the perfluoroalkane's family associated with a set of other interesting properties that these compounds present, can find applications in many areas including the biomedical, as is the case of liquid ventilation applications. However, literature data regarding the modelling of surface tensions of perfluoroalkanes is almost inexistent.

In this work, the soft-SAFT equation is incorporated within the Cahn-Hilliard DGT approach together with the renormalization group (RG) theory, for the quantitative prediction of vapour-liquid interfacial tensions of *n*-alkanes and *n*-perfluoroalkanes from C1 to C9. Accurate predictions far and close to the critical region are presented, enhancing the potentialities of the model.

INTRODUCTION

In the last years, highly fluorinated molecules have aroused the curiosity of many researchers not only because of the large number of applications that these compounds have in different research fields, but also because of the valuable information that they can give about bulk and interfacial intermolecular interactions.

Surface tension is a macroscopic thermodynamic property that is intimately related with the microscopic structuring of molecules in the vapour-liquid interface. It is related to the difference between the intermolecular interaction in the bulk and at the surface, and also related to molecular ordering and structuring.

It is widely accepted that the van der Waals interaction between polyfluorinated molecules is usually very small compared with corresponding non-fluorinated molecules. Therefore, the difference in an absolute measure between the free energy of polyfluorinated molecules at the surface and in the bulk is also small thus justifying the low surface tensions of perfluoroalkanes when compared with their corresponding alkanes and partially fluorinated compounds. This was recently confirmed by the study of Sakka and Ogata [1] which reported the parachor for different highly and partially fluorinated compounds, concluding that the former presented lower and constant parachors suggesting a systematic stabilization due to the structuring of the molecules.

In spite of the importance of these studies, the number of published work dedicated to the prediction of the surface tension of fluorinated compounds is reduced. Moreover, molecular dynamics studies on the surface structure and surface properties of fluorinated alkanes showed that the surface tension was not quantitatively reproduced [2].

In this work it is proposed to predict the surface tension of pure perfluoroalkanes and alkanes in a broad temperature range including the critical region. For that purpose, the soft-SAFT EoS was

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coupled with the density gradient theory. An advantage of this approach is that simple analytical expressions for the density profiles and surface tension can be obtained. More importantly, the approach is straightforwardly applicable to any equation of state making it useful for engineering applications [3]. Finally, in order to extend the approach to the critical region, a crossover approach based on Wilson's RG theory was considered in order to account for the long-wavelength density fluctuations that characterize the near-critical region [4].

MODEL

The density gradient theory, based on van der Waals work [5], and widespread by Cahn and Hilliard [6], relates an equation of state to interfacial properties. The theory explicitly considers the local free energy density within the interface, hence providing a route to obtain density profiles across the interface and the interfacial thickness, which cannot be calculated by empirical methods [7]. Several authors have applied the DGT to different equation of state models, mostly the Peng-Robinson and SAFT equations [8-11]. Chapman first suggested the use of Wertheim's TPT within a density functional approach [12] and meanwhile the theory has been incorporated to the soft-SAFT approach by Duque et al. [13]. According to the model, the computation of interfacial properties requires, apart from the traditional molecular parameters for the pure compounds, the specification of the influence parameter which is treated in an empirical way due to the difficulty and some times even impossibility to calculate it.

Several temperature-dependent expressions for the influence parameter are usually presented to improve the accuracy of the interfacial tensions, particularly near the critical point. In the present approach, it is assumed that the temperature dependence of the influence parameter is negligible, hence avoiding the need of additional parameters.

Density functional theories start by expressing the Helmholtz free energy of the system, a , as a functional of the density profile $\rho(\mathbf{r})$. Within the DGT, it is expanded around its bulk value [5]:

$$A[\rho(r)] = \int dr \left\{ a(\rho(r)) + \frac{c}{2} [\nabla \rho(r)]^2 \right\} \quad (1)$$

where a is the Helmholtz free energy density of the bulk phases, $\rho(\mathbf{r})$ is the molecular density profile, and c includes the direct correlation function among the molecules, although, as already stated, it is treated as an adjustable parameter, the so-called influence parameter. For a planar interface, functional minimization of Equation 1 for phase coexistence conditions lead to the following expression for the surface tension [6]:

$$\gamma = \int_{\rho_v}^{\rho_l} d\rho \sqrt{2c\Delta\omega(\rho)} \quad (2)$$

where the integration takes place from the vapour bulk densities to the liquid one and $\Delta\omega$ is the excess grand free energy density:

$$\Delta\omega(\rho) = a(\rho) - \mu\rho + p/k_B T \quad (3)$$

where p and μ are the equilibrium pressure and chemical potential, k_B is Boltzmann's constant, and T is the temperature.

The success of the description will depend on the underlying theory for the bulk. In this work, the statistical associated fluid theory molecular based soft-SAFT EoS was employed. In this version, the reference fluid is a LJ monomer fluid, which accounts for both the repulsive and attractive interactions of the monomers forming the chain. In its simpler structure, the Helmholtz free energy density of these systems is given as the sum of three terms,

$$a_0 = a^{id} + a^{ref} + a^{chain} \quad (4)$$

where a^{id} states for the ideal term, a^{ref} is the Helmholtz free energy density of the reference LJ fluid and a^{chain} is the chain term that comes from the TPT1 approximation of Wertheim's theory. Further details regarding the theory and its implementation can be found in the open literature [14].

To correctly describe the long range fluctuations actuating on the properties of the fluid near the critical point, a crossover contribution was also accounted in this work. The treatment, based on White's work [15], is done by incorporating the scaling laws governing the asymptotic behavior close to the critical point, while reducing to the original equation of state far from the critical region. The crossover term is expressed mathematically as a set of recursive equations that incorporate the fluctuations in a progressive way, being the value of a_{n-1} correspondent to the original soft-SAFT value:

$$a = \sum_{n=1}^{\infty} (a_{n-1} + a_n^{cross}) \quad (5)$$

where a^{cross} represents the crossover contribution to the model.

RESULTS

Linear perfluoroalkanes and alkanes are modeled as homonuclear chainlike molecules, composed by m Lennard-Jones segments of equal diameter σ , and the same dispersive energy ε , bonded tangentially to form the chain, plus the crossover parameters L and ϕ to include the long-range fluctuations in the critical region. In order to minimize the number of adjusted calculations, and considering the analogy of the series in study, the L parameter was fixed to the same value in both cases. Linear relations were obtained between the molecular parameters and the number of carbons (NC), as shown in Figure 1, being the parameters optimized in order to describe each compound densities and vapor pressures with the lowest deviation from experimental data [16,17].

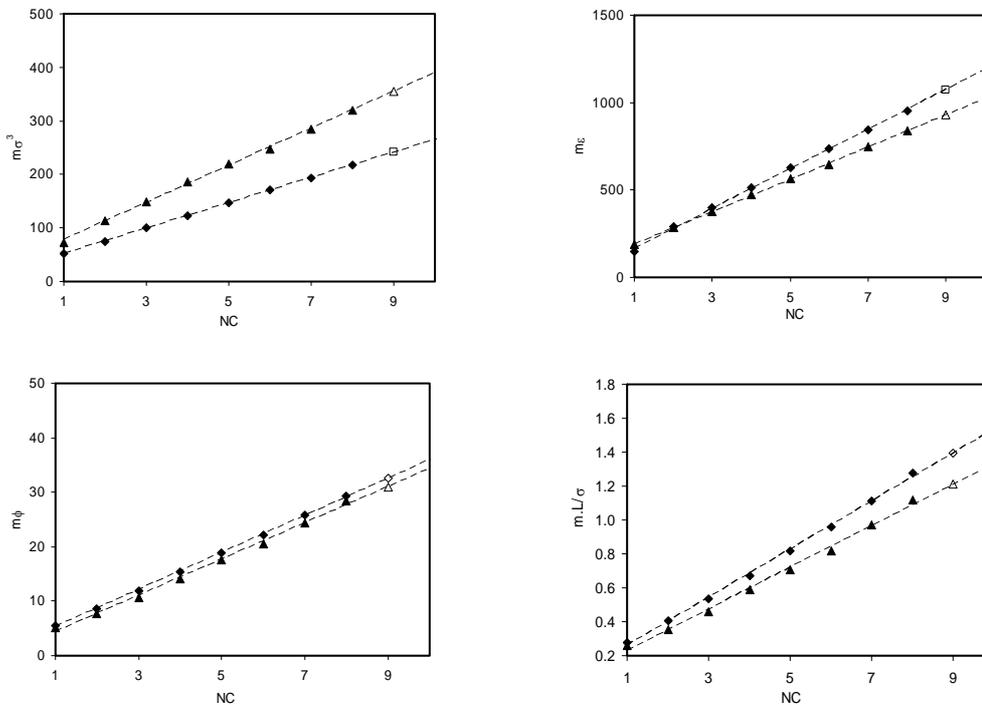


Figure 1. Linear relations obtained between the molecular parameters and the number of carbons in the linear molecule (CN). Symbols are explained in the text.

In the figure, the diamonds represent the alkane series while the triangles represent the perfluoroalkane series. The open symbols represent the extrapolation of the relations to obtain the molecular parameters for n-nonane and n-perfluoro-nonane using no experimental density or vapor pressure data to adjust the parameters. As expected the diameter, σ , of the Lennard Jones spheres representing the perfluoroalkanes is higher than the ones obtained for alkanes, simulating the larger size of the fluorine atom when compared to the hydrogen atom. Moreover, the energy parameter, ϵ , is slightly lower in the case of perfluoroalkanes simulating the lower interactions that are reported in the literature for these compounds due to strong repulsive forces originated by the large electron density involving the fluorine atom. Finally, the crossover ϕ parameter, is slightly smaller in the case of perfluoroalkanes when compared with the corresponding alkanes. It is believed that this is the way the model finds to account for the higher density and low compressibility that perfluoroalkanes exhibit in the critical region.

Once the molecular parameters are available, the influence parameter are optimized for each pure compound using experimental interfacial tension data including data measured near to the critical region. The fitted values are shown in Figure 2.

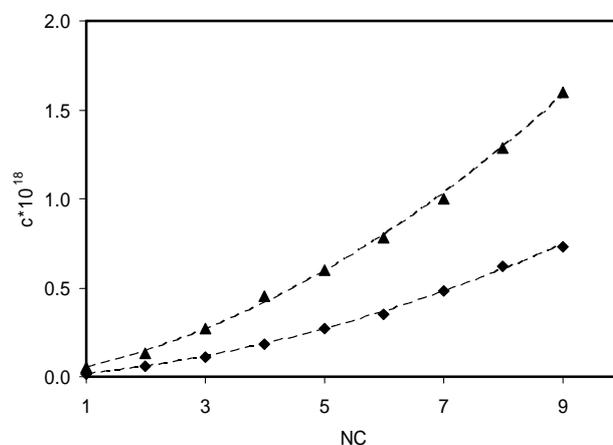


Figure 2. Optimized influence parameter for the *n*-alkane (diamonds) and *n*-perfluoroalkane (triangles) series versus the carbon number.

The trends of the influence parameter for the *n*-alkane and *n*-perfluoroalkane series with respect to the carbon number of the chain can be correlated by the following parabolic functions:

$$c_{alkane} = 6.932 \times 10^{-20} CN^2 + 2.143 \times 10^{-20} CN - 1.333 \times 10^{-20} \quad (6)$$

$$c_{perfluoroalkane} = 1.403 \times 10^{-20} CN^2 + 5.064 \times 10^{-20} CN - 1.295 \times 10^{-20} \quad (7)$$

The results obtained when using the soft-SAFT + DGT + Crossover approach to describe the surface tensions of linear series of perfluoroalkanes and alkanes are given in Figure 3 (a) and (b) respectively. The results are fairly good even for perfluoroalkanes where the literature data dispersion could lead to some confusion. However, when taking into account the sequence along the NC, it is possible to conclude that the results given by the model are in accordance with what is expected. Notice that the parameters used to model n-nonane and n-perfluoro-nonane were obtained from the correlations presented in Figure 1 and 2 without any further adjustment to experimental data. This result confirms the predictive potentiality of the model and gives confidence on the optimized parameters. The surface tension of n-alkanes had already been modelled with the soft-SAFT + DGT approach [7]. However, in that work, recalled molecular parameters were used to extend the model to the critical region. The approach here presented, with the crossover treatment considered, present clear advantages being the

most important, the fact that it permits to describe a given compound for an extended thermodynamic range with the same set of parameters and straightforwardly extend the study to mixtures once the physical meaning of the parameters is assured.

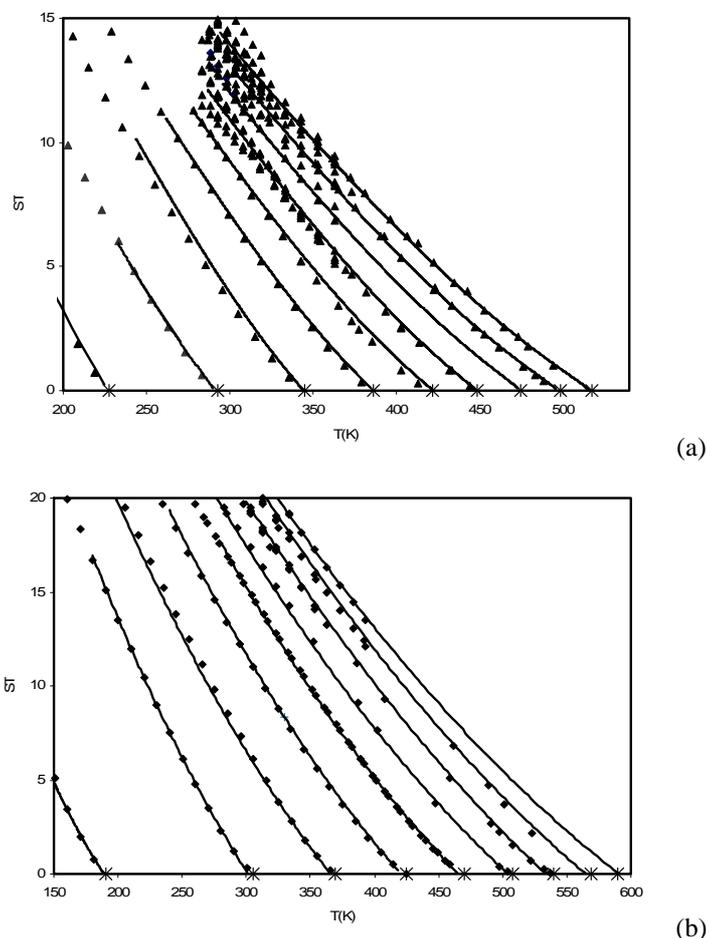


Figure 3. Vapour-liquid interfacial tensions (ST expressed in $\text{mN}\cdot\text{m}^{-1}$) of n -alkanes (a) and n -perfluoroalkanes (b) from C1 to C9. Symbols represent experimental data and lines correspond to the soft-SAFT + DGT + Crossover approach. The asterisk represents the critical temperature of the pure compounds. Experimental data was taken from NIST Chemistry WebBook and from the work of Freire et al. [18].

CONCLUSIONS

The application of the crossover-DGT-soft-SAFT equation of state to real systems has proved to be a successful predictive method. It was shown that, within this approach, the use of a constant influence parameter and crossover parameters adjusted to density and vapour pressure data, provides accurate interfacial properties for pure systems in the whole thermodynamic range. The influence parameter for the n -alkane and n -perfluoroalkane series has shown to have the same tendency with a parabolic dependence of the carbon number of the chain.

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