

## Liquid Phase Behavior of Perfluoroalkylalkane Surfactants

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We have performed a combined experimental and theoretical study of the thermodynamic properties of semifluorinated alkanes. In particular, the liquid density of perfluorohexylhexane (F6H6) and perfluorohexyloctane (F6H8) has been measured as a function of temperature from 273.15 to 353.15 K and at four temperatures as a function of pressure up to 600 bar. The results were interpreted using the SAFT-VR equation of state. The perfluoroalkylalkanes were modeled as heterosegmented diblock chains using parameters for the alkyl and perfluoroalkyl segments developed in earlier work. Through this simple approach, we are able to predict the thermodynamic behavior of the perfluoroalkylalkanes studied without fitting to any experimental data for the systems being studied.

### Introduction

Semifluorinated alkanes (SFA, also known as perfluoroalkylalkanes) have received growing attention in recent years due to their unique properties, which ally the inertness, biocompatibility, and ability to solubilize high levels of respiratory gases characteristic of fluorinated solvents with a marked amphiphilic character, as revealed by their tendency to auto-organize in different media and interfaces. The former make perfluoroalkylalkanes potentially interesting for medical applications, such as components of liquid ventilation solvents and temporary blood substitutes formulations,<sup>1,2</sup> as fluids in eye surgery, and in the treatment of burns.<sup>3</sup> The fact that perfluoroalkane chains and hydrocarbon chains are mutually phobic gives rise to innumerable possibilities for the use of semifluorinated molecules as surface-active agents. Accordingly, aggregation in solvents selective for one of the blocks;<sup>4,5</sup> the observation of smectic liquid crystalline phases;<sup>6–8</sup> and recently, the formation of nanoscale patterns in molecular films of either pure<sup>9</sup> or mixed perfluoroalkylalkanes have been reported.<sup>10</sup> Organization in the solid state into layered structures has also been described.<sup>11–14</sup>

Other major applications of semifluorinated species include their use as solvents or additives for biphasic synthesis and catalysis, a rapidly developing field currently known as “fluorous chemistry”.<sup>15,16</sup> The unusual affinity of perfluorinated chains toward supercritical CO<sub>2</sub> has motivated a considerable number of studies in which fluorinated compounds are used as a means to improve the solubility of chemicals in supercritical reaction or extraction media.<sup>17,18</sup> For example, Iezzi et al.<sup>19</sup> studied the formation of microdispersions by semifluorinated alkanes in dense carbon dioxide, and mixed-tail dichain surfactants, such as (C<sub>7</sub>F<sub>15</sub>)(C<sub>7</sub>H<sub>15</sub>)CHSO<sub>4</sub>Na<sup>+</sup>, have been shown to form stable reverse micelles in carbon dioxide.<sup>20,21</sup>

As previously stated, the unique properties of semifluorinated alkanes result from the combined presence of alkyl and perfluoroalkyl chains, which are mutually phobic. Given the structural similarity between the alkane and perfluoroalkane molecules, one could expect that mixtures of such species would behave almost ideally and be miscible in all proportions. However, mixtures of alkanes and perfluoroalkanes show large gaps of liquid–liquid immiscibility, as first observed in the early 1950s.<sup>22</sup> Since then, considerable effort has been devoted to understanding why these mixtures exhibit this particular type of “antipathy”. Most of these studies concluded that the usual combining rules (i.e., Lorentz–Berthelot) for the crossed intermolecular potential parameters fail to give satisfactory results because of an unusually weak hydrocarbon–fluorocarbon interaction. The subject has been recently reviewed.<sup>23</sup>

Despite their interesting behavior and enormous potential, very little work has been done experimentally to characterize the thermodynamic behavior of semifluorinated alkanes in the liquid state, either pure or mixed with other substances. De Loos and co-workers<sup>24</sup> determined the phase envelope of binary and quasi-binary mixtures of the simplest semifluorinated alkane, CF<sub>3</sub>CH<sub>3</sub>, with the linear alkanes, undecane, dodecane and tridecane and their binary mixtures. The behavior of CF<sub>3</sub>CH<sub>3</sub>, however, is probably heavily influenced by the presence of the dipole, given the small size of this molecule, and less by the combined presence of the alkyl and perfluoroalkyl chains. More recently, Tochigi et al.<sup>25</sup> measured the vapor–liquid equilibria of liquid mixtures of perfluorobutylethane and octane at 101.3 kPa. As far as we are aware, no systematic studies have been published on the density, vapor pressure or other thermophysical properties of pure semifluorinated alkanes, all of which are essential to develop reliable theoretical models.

Perfluoroalkylalkanes have also been the subject of several simulation studies in an effort to gain molecular level insight into the behavior of these molecules. For example, simulation studies of the structure of the liquid interface of pure perfluoro-

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rocarbon–hydrocarbon diblocks,<sup>26</sup> their aggregation,<sup>27</sup> and liquid crystalline behavior<sup>28</sup> have been reported. Simulations have also been performed to study Langmuir monolayers of amphiphiles, such as C<sub>7</sub>F<sub>15</sub>C<sub>4</sub>H<sub>8</sub>COOH.<sup>29,30</sup> In general, although the simulation studies confirm the ability of SFA to self-organize, in many cases, the results did not quantitatively agree with the experimental data. However, typically, the force fields used were not specifically developed for the systems studied, and so the discrepancies could be due to inadequacies in the potential model. This problem has been at least partially addressed in more recent work,<sup>31</sup> in which force field parameters for describing the torsional potential between the fluorocarbon and hydrocarbon moieties was presented. All-atom molecular dynamics simulations of liquid perfluorooctylethane were performed using the new torsional term in conjunction with the all-atom OPLS force field for the remaining parameters; however, the force field could only be tested against experimental data for a single value of the density. Moreover, the short alkyl chain in perfluorooctylethane again prevents this molecule from being a good model for perfluoroalkylalkanes. In subsequent work<sup>32</sup> the solubility of oxygen, carbon dioxide, and water in perfluorooctylethane, perfluorohexylethane, and perfluorohexylhexane was studied, again using the modified OPLS force field. However, no experimental data is available for these systems, and so the calculations were predictions whose validity is based on obtaining good results for the solubility of the same substances in perfluorooctylbromide. It should be noted, however, that in the later case, alkyl segments are absent, and so the perfluoroalkylalkane force field has yet to be truly validated.

From a theoretical point of view, a major step in our understanding of liquids and liquid mixtures has been the development of molecularly based equations of state. A particularly successful example is the SAFT equation of state,<sup>33,34</sup> which unlike typical engineering or cubic equations of state, explicitly takes into account the contribution of molecular details, such as nonsphericity (molecular shape), polarity, and association on the thermodynamics and phase behavior of fluids. The many different versions of SAFT essentially correspond to different choices for the monomer fluid, and different theoretical approaches to the calculation of the monomer free energy and structure. For an overview, the reader is directed to a recent review.<sup>35</sup> In this work, we focus on SAFT-VR, which describes chain molecules formed from hard-core monomers that interact through attractive potentials of variable range, typically a square well.<sup>36,37</sup> The SAFT-VR equation has been successfully used to describe the phase equilibria of a wide range of industrially important systems; for example, alkanes of low molecular weight through to simple polymers,<sup>38–43</sup> and their binary mixtures,<sup>39,44–51</sup> perfluoroalkanes,<sup>52,53,65</sup> hydrogen fluoride,<sup>54</sup> boron trifluoride,<sup>55</sup> water,<sup>42,56</sup> refrigerant systems,<sup>57</sup> carbon dioxide,<sup>42,49,58–61</sup> and electrolyte solutions<sup>62–64</sup> have all been studied.

Of particular relevance is the study of alkane + perfluoroalkane binary mixtures.<sup>52,60,61</sup> McCabe et al.<sup>52</sup> studied the phase behavior of *n*-alkane + *n*-perfluoroalkane binary mixtures, focusing on the high-pressure phase behavior and critical lines for binary mixtures of perfluoromethane + *n*-alkanes (from methane to octane) and for symmetric systems of the light *n*-alkanes + *n*-perfluoroalkanes (from methane to butane). In this study, a single binary interaction parameter ( $\xi_{ij} = 0.9206$ ) was determined from a fit to the high-pressure critical line for the perfluoromethane + *n*-butane system and then successfully transferred to the other perfluoromethane + *n*-alkane mixtures

studied. Using this parameter, it was then possible to capture the transition from the type II phase behavior exhibited by the perfluoromethane + ethane and propane binary mixtures to the type III phase behavior displayed by the perfluoromethane + *n*-butane and higher binary mixtures. However, it was observed that as the chain length of the *n*-alkane component increased, deviations between the theoretical predictions and experimental data occurred. As a result, an additional  $\xi_{12}$  was determined ( $\xi_{12} = 0.8948$ ) for the binary mixture involving *n*-heptane. In more recent work,<sup>65</sup> the behavior of alkane + perfluoroalkane binary mixtures with chain lengths between 5 and 8 carbon atoms for both components was studied. Here, the focus was on the liquid–liquid immiscibility found close to ambient temperatures, rather than the high-pressure phase behavior. Transferable binary interaction parameters were proposed on the basis of the reproduction of the UCST and excess volumes for the *n*-hexane + *n*-perfluorohexane system and were again used in a transferable fashion to correctly predict the phase behavior of the other systems studied without any additional fitting to experimental data.

In this work, we have performed a combined experimental and theoretical study of perfluoroalkylalkanes. In particular, the liquid density of two semifluorinated alkanes, perfluorohexylhexane (F6H6) and perfluorohexyloctane (F6H8) has been measured as a function of temperature from 273.15 to 353.15 K and at four temperatures as a function of pressure up to 600 bar. Building on the prior success for alkane and perfluorinated systems, the results were again interpreted using the SAFT-VR equation. The perfluoroalkylalkane chains are modeled as heterosegmented diblock chains using the alkane and perfluoroalkane parameters developed in earlier work. The hetero-SAFT-VR approach<sup>66</sup> was recently tested against extensive Monte Carlo simulation data and shown to accurately capture the effect of chain molecular architecture on phase behavior.<sup>67</sup>

## Experimental

The perfluorohexylhexane (F6H6) and perfluorohexyloctane (F6H8) used were ultrapurified chemicals obtained from Fluoron GMBH, with a claimed purity of 100%, and were used without further purification.

The density measurements at ambient pressure were made in an Anton Paar DMA 5000 vibrating-tube densimeter. The instrument was calibrated with water (distilled, purified with a Milli-Q 185 Plus water purification system and freshly boiled) and air at 20.000 °C taking into account atmospheric pressure. The calibration was checked with water over the whole range of operating temperatures, and the maximum deviation from literature values was found to be less than  $\pm 0.00002$  g cm<sup>-3</sup>. The density of air was verified at the beginning of each series of measurements to ensure the cleanliness of the measurement cell.

The densities at high pressure were measured using a previously calibrated<sup>68</sup> Anton Paar DMA 512P vibrating-tube densimeter, in which temperature is controlled to  $\pm 0.01$  K and pressure accuracy and precision are better than 0.05%. The overall density precision is typically 0.002%, and its estimated uncertainty (judging by the residuals of the overall fit in comparison with literature data for the calibrating liquids) is 0.02%.

**Model and Theory.** Perfluoroalkylalkane molecules are modeled as chains of tangentially bonded hard-spherical segments that interact through an attractive potential of variable range. Specifically, each segment interacts through a square well (SW) potential,

$$U_{ij}(r) = \begin{cases} +\infty & \text{if } r < \sigma_{ij} \\ -\epsilon_{ij} & \text{if } \sigma_{ij} \leq r < \lambda_{ij}\sigma_{ij} \\ 0 & \text{if } r \geq \lambda_{ij}\sigma_{ij} \end{cases} \quad (1)$$

where  $\sigma_{ij}$  is the diameter of the interaction;  $\lambda_{ij}$ , the range; and  $\epsilon_{ij}$ , the well depth of the SW potential. The parameters used in this work to model the alkyl and perfluoroalkyl segments of each perfluoroalkylalkane molecule are given in Table 5 and discussed further in the results section. The inter- and intramolecular cross interactions between segments are obtained from the modified Lorentz–Berthelot combining rules,<sup>69</sup>

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

$$\epsilon_{ij} = \xi_{ij} \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (3)$$

$$\lambda_{ij} = \gamma_{ij} \frac{\lambda_{ii}\sigma_{ii} + \lambda_{jj}\sigma_{jj}}{\sigma_{ii} + \sigma_{jj}} \quad (4)$$

The general form of the Helmholtz free energy,  $A$ , within the SAFT framework is given by

$$\frac{A}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{mono}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{assoc}}}{NkT} \quad (5)$$

We will present each contribution in turn for the treatment of pure fluids composed of diblock–heteronuclear chain molecules. We do not give details of the association term, since the chain fluids considered in this work are nonassociating.

The ideal contribution to the free energy is expressed as

$$\frac{A^{\text{ideal}}}{NkT} = \ln(\rho\Lambda^3) - 1 \quad (6)$$

where  $N$  is the total number of molecules;  $k$ , Boltzmann's constant;  $\rho$ , the number density of chain molecules; and  $\Lambda$ , the thermal de Broglie wavelength.

The monomer free energy is given by

$$\frac{A^{\text{mono}}}{NkT} = m \frac{A^{\text{M}}}{N_s kT} = ma^{\text{M}} \quad (7)$$

where  $N_s$  is the total number of segments, determined from the product of the total number of molecules,  $N$ , and the number of segments per molecule,  $m$ .  $a^{\text{M}}$  is the free energy per monomer segment and in the SAFT-VR equation is approximated by a second-order, high-temperature expansion using Barker and Henderson perturbation theory for mixtures,<sup>70</sup> namely,

$$a^{\text{M}} = a^{\text{HS}} + \beta a_1 + \beta^2 a_2 \quad (8)$$

where  $\beta = 1/kT$ ;  $a^{\text{HS}}$  is the free energy of the hard sphere reference fluid; and  $a_1$  and  $a_2$  are the first and second perturbation terms, respectively.

The hard sphere reference term,  $a^{\text{HS}}$ , is determined from the expression of Boublik<sup>71</sup> and Mansoori and co-workers<sup>72</sup> for multicomponent hard sphere systems, namely,

$$a^{\text{HS}} = \frac{6}{\pi\rho_s} \left[ \left( \frac{\xi_2^3}{\xi_3^2} - \xi_0 \right) \ln(1 - \xi_3) + \frac{3\xi_1\xi_2}{1 - \xi_3} + \frac{\xi_2^3}{\xi_3(1 - \xi_3)^2} \right] \quad (9)$$

where  $\rho_s$  is the number density of segments, which is defined as  $N_s/V$ , the total number of segments divided by the total

volume; and  $\xi_l$  is the reduced density given by a sum over all segments,  $i$ ,

$$\xi_l = \frac{\pi}{6} \rho_s [x_{s,1}(\sigma_1)^l + x_{s,2}(\sigma_2)^l] \quad (10)$$

where  $\sigma_i$  is the diameter of segments of type  $i$ , and  $x_{s,i}$  is the mole fraction of segments of type  $i$ . Note that  $\xi_3$  is the volume fraction occupied by the molecules and is generally denoted  $\eta$ .

The first perturbation term,  $a_1$ , describing the mean-attractive energy is obtained from the sum of all pair interactions

$$a_1 = x_{s,1}^2(a_1)_{11} + 2x_{s,1}x_{s,2}(a_1)_{12} + x_{s,2}^2(a_1)_{22} \quad (11)$$

where  $(a_1)_{ij}$  is obtained from the mean-value theorem as proposed by Gil-Villegas et al.<sup>36</sup>

$$(a_1)_{ij} = -2\pi\rho_s\epsilon_{ij} \int_{\sigma_{ij}}^{\infty} r_{ij}^2 g_{ij}^{\text{HS}}(r_{ij}) dr_{ij} = -\rho_s \alpha_{ij}^{\text{VDW}} g_{ij}^{\text{HS}}(\sigma_{ij}; \xi_3^{\text{eff}}) \quad (12)$$

where

$$\alpha_{ij}^{\text{VDW}} = \frac{2\pi}{3} \sigma_{ij}^3 \epsilon_{ij} (\lambda_{ij}^3 - 1) \quad (13)$$

Within the van der Waals, one fluid theory, the radial distribution function  $g_{ij}^{\text{HS}}(\sigma_{ij}; \xi_3^{\text{eff}})$ , is approximated by that for a pure fluid; hence, eq 12 becomes

$$(a_1)_{ij} = -\rho_s \alpha_{ij}^{\text{VDW}} g_0^{\text{HS}}[\sigma_x; \xi_x^{\text{eff}}(\lambda_{ij})] \quad (14)$$

where  $g_0^{\text{HS}}(\sigma_x; \xi_x^{\text{eff}})$  is obtained from the Carnahan and Starling equation of state,<sup>73</sup>

$$g_0^{\text{HS}}[\sigma_x; \xi_x^{\text{eff}}(\lambda_{ij})] = \frac{1 - \xi_x^{\text{eff}}/2}{(1 - \xi_x^{\text{eff}})^3} \quad (15)$$

The effective packing fraction  $\xi_x^{\text{eff}}(\lambda_{ij})$  is obtained within the van der Waals one-fluid theory from the corresponding packing fraction of the mixture,  $\xi_x$ , given by

$$\xi_x^{\text{eff}}(\xi_x, \lambda_{ij}) = c_1(\lambda_{ij})\xi_x + c_2(\lambda_{ij})\xi_x^2 + c_3(\lambda_{ij})\xi_x^3 \quad (16)$$

where

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2.258\ 55 & -1.503\ 49 & 0.249\ 434 \\ -0.669\ 270 & 1.400\ 49 & -0.827\ 739 \\ 10.157\ 6 & -15.042\ 7 & 5.308\ 27 \end{pmatrix} \begin{pmatrix} 1 \\ \lambda_{ij} \\ \lambda_{ij}^2 \end{pmatrix} \quad (17)$$

and

$$\xi_x = \frac{\pi}{6} \rho_s \sigma_x^3 \quad (18)$$

with

$$\sigma_x^3 = x_{s,1}^2\sigma_{11}^3 + 2x_{s,1}x_{s,2}\sigma_{12}^3 + x_{s,2}^2\sigma_{22}^3 \quad (19)$$

This corresponds to mixing rule MX1b in the original SAFT-VR approach for mixtures.<sup>37</sup> In previous work,<sup>67</sup> we compared the results obtained from this formulation with the MX3b mixing rule,<sup>37</sup> in which the actual packing fraction of the system is used to obtain  $\xi_3^{\text{eff}}$  and found that the difference between the two was negligible in most cases.

The second-order perturbation term for the monomer excess free energy  $a_2$  is expressed as

$$a_2 = x_{s,1}^2(a_2)_{11} + 2x_{s,1}x_{s,2}(a_2)_{12} + x_{s,2}^2(a_2)_{22} \quad (20)$$

where  $(a_2)_{ij}$  is obtained through the local compressibility approximation,

$$(a_2)_{ij} = \frac{1}{2} K^{\text{HS}} \epsilon_{ij} \rho_s \frac{\partial(a_1)_{ij}}{\partial \rho_s} \quad (21)$$

and  $K^{\text{HS}}$  is the Percus–Yevick expression for the hard-sphere isothermal compressibility,

$$K^{\text{HS}} = \frac{\xi_0(1 - \xi_3)^4}{\xi_0(1 - \xi_3)^2 + 6\xi_1\xi_2(1 - \xi_3) + 9\xi_2^3} \quad (22)$$

Finally, the contribution due to chain formation from the monomer segments is given in terms of the background correlation function  $y_{ij}^{\text{SW}}$ ,

$$\frac{A^{\text{chain}}}{NkT} = -(m_1 - 1) \ln y_{11}^{\text{SW}}(\sigma_{11}) - \ln y_{12}^{\text{SW}}(\sigma_{12}) - (m_2 - 1) \ln y_{22}^{\text{SW}}(\sigma_{22}) \quad (23)$$

where the sum is over all bonds in the chain molecule,

$$y_{ij}^{\text{SW}}(\sigma_{ij}) = \exp(-\beta \epsilon_{ij}) g_{ij}^{\text{SW}}(\sigma_{ij}) \quad (24)$$

The radial distribution function for the square well monomers,  $g_{ij}^{\text{SW}}(\sigma_{ij})$ , is approximated by a first-order high-temperature perturbation expansion,

$$g_{ij}^{\text{SW}}(\sigma_{ij}; \xi_3) = g_{ij}^{\text{HS}}(\sigma_{ij}; \xi_3) + \beta \epsilon_{ij} g_{11}^{\text{SW}}(\sigma_{ij}) \quad (25)$$

where the contact value of the radial distribution function,  $g_{ij}^{\text{HS}}(\sigma_{ij}; \xi_3)$ , at the actual packing fraction,  $\xi_3$ , is obtained from the expression of Boublík,<sup>71</sup>

$$g_{ij}^{\text{HS}}(\sigma_{ij}; \xi_3) = \frac{1}{1 - \xi_3} + 3 \frac{D_{ij}\xi_3}{(1 - \xi_3)^2} + 2 \frac{(D_{ij}\xi_3)^2}{(1 - \xi_3)^3} \quad (26)$$

where

$$D_{ij} = \frac{\sigma_{ii}\sigma_{jj} \sum_{i=1}^n x_{s,i}\sigma_{ii}^2}{(\sigma_{ii} + \sigma_{jj}) \sum_{i=1}^n x_{s,i}\sigma_{ii}^3} = \frac{\sigma_{ii}\sigma_{jj}(x_{s,1}\sigma_{11}^2 + x_{s,2}\sigma_{22}^2)}{(\sigma_{ii} + \sigma_{jj})(x_{s,1}\sigma_{11}^3 + x_{s,2}\sigma_{22}^3)} \quad (27)$$

and  $g_{11}^{\text{SW}}(\sigma_{ij})$  is determined by using the Clausius virial theorem and the first derivative of the free energy with respect to the density,<sup>36</sup> giving

$$g_{11}^{\text{SW}}(\sigma_{ij}) = \frac{1}{2\pi\epsilon_{ij}\sigma_{ij}^3} \left[ 3 \left( \frac{\partial(a_1)_{ij}}{\partial \rho_s} \right) - \frac{\lambda_{ij}}{\rho_s} \frac{\partial(a_1)_{ij}}{\partial \lambda_{ij}} \right] \quad (28)$$

## Results

The densities and molar volumes of the studied semifluorinated alkanes at atmospheric pressure and as a function of

**TABLE 1: Experimental Densities and Molar Volumes as a Function of Temperature for Perfluorohexylhexane (F6H6) and Perfluorohexyloctane (F6H8)**

T, K	F6H6		F6H8	
	d, g cm <sup>-3</sup>	V <sub>m</sub> , cm <sup>3</sup> mol <sup>-1</sup>	d, g cm <sup>-3</sup>	V <sub>m</sub> , cm <sup>3</sup> mol <sup>-1</sup>
273.15	1.426 061	283.446	1.367 554	316.086
278.15	1.418 079	285.041	1.360 150	317.806
283.15	1.410 096	286.655	1.352 779	319.538
288.15	1.402 110	288.288	1.345 427	321.284
293.15	1.394 108	289.942	1.338 083	323.047
298.15	1.386 091	291.619	1.330 747	324.828
303.15	1.378 054	293.320	1.323 410	326.629
308.15	1.369 995	295.046	1.316 066	328.452
313.15	1.361 908	296.797	1.308 717	330.296
318.15	1.353 790	298.577	1.301 353	332.165
323.15	1.345 641	300.385	1.293 970	334.060
328.15	1.337 451	302.225	1.286 570	335.982
333.15	1.329 224	304.095	1.279 148	337.931
338.15	1.320 958	305.998	1.271 701	339.910
343.15	1.312 642	307.937	1.264 227	341.920
348.15	1.304 281	309.911	1.256 722	343.962
353.15	1.295 862	311.924	1.249 186	346.037

temperature, are presented in Table 1. For convenience, the isobaric densities were used to fit a simple polynomial of the form

$$\frac{d}{\text{g cm}^{-3}} = \sum_{i=0}^3 a_i(T, 100 \text{ K})^i$$

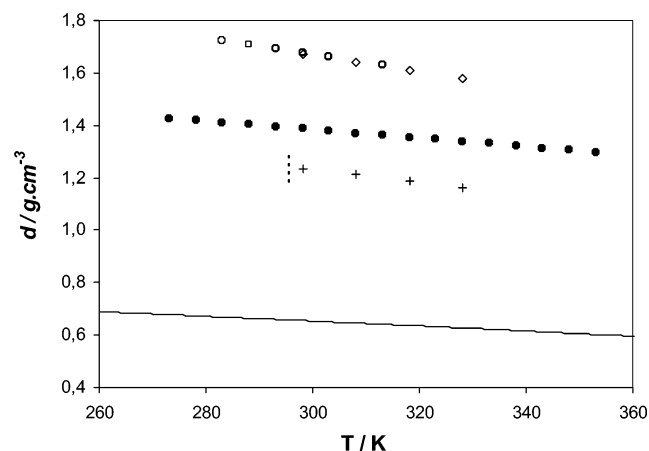
where  $d$  is the density and  $T$ , the absolute temperature; the coefficients obtained were  $a_0 = 1.949\,672$ ,  $a_1 = -0.257\,571\,5$ ,  $a_2 = 3.643\,006 \times 10^{-2}$ , and  $a_3 = -4.507\,740 \times 10^{-3}$  for F6H6 and  $a_0 = 1.906\,376$ ,  $a_1 = -0.285\,170\,9$ ,  $a_2 = 4.627\,201 \times 10^{-2}$ ,  $a_3 = -5.158\,583 \times 10^{-3}$  for F6H8. These coefficients allow the reproduction of the experimental data within the reproducibility of the measurements. It should be noted, however, that the equation used lacks any physical meaning and should not be used for extrapolation. The densities of F6H6 are plotted in Figure 1 as a function of temperature, along with the densities of hexane, perfluorohexane, and of the equimolar mixture of hexane and perfluorohexane for comparison. As can be seen, the semifluorinated substance has a density between the alkane and perfluoroalkane and is 10% denser than the equimolar mixture of hexane and perfluorohexane.

An attempt was made to decompose the molar volume of F6H6 at 298.15 K into the sum of the molar volumes of the hexyl ( $V_m(\text{C}_6\text{H}_{13})$ ) and perfluorohexyl ( $V_m(\text{C}_6\text{F}_{13})$ ) segments, the excess volume of a hypothetical equimolar (hexyl + perfluorohexyl) mixture ( $V_m^E(\text{C}_6\text{H}_{13} + \text{C}_6\text{F}_{13})$ ), and the volume change resulting from the formation of the hexyl–perfluorohexyl bond ( $\Delta V$ ). This later term should include contributions of several effects, such as the formation of the dipole at the  $\text{CH}_2\text{--CF}_2$  junction and the reorganization of the liquid, resulting from the impossibility of the two segments to separate and the building up of amphiphilic character.

$$V_m(\text{F6H6}) = V_m(\text{C}_6\text{H}_{13}) + V_m(\text{C}_6\text{F}_{13}) + V_m^E(\text{C}_6\text{H}_{13} + \text{C}_6\text{F}_{13}) + \Delta V \quad (29)$$

The molar volumes of the hexyl and perfluorohexyl segments can be estimated from literature data for the molar volumes of alkanes<sup>74</sup> and perfluoroalkanes<sup>75–77</sup> as a function of the chain length at 298.15 K. A simple numerical procedure leads to  $V_m(\text{C}_6\text{H}_{13}) = 113.8 \text{ cm}^3 \text{ mol}^{-1}$  and  $V_m(\text{C}_6\text{F}_{13}) = 171.8 \text{ cm}^3 \text{ mol}^{-1}$ . In a recent paper, Lepori et al.<sup>78</sup> reported excess molar volumes





**Figure 1.** Densities at atmospheric pressure for F6H6 (this work) (●); perfluorohexane (○),<sup>81</sup> (□),<sup>75</sup> (◇);<sup>82</sup> hexane (continuous line)<sup>74</sup>; and the equimolar mixture of hexane and perfluorohexane (+).<sup>82</sup> The vertical dashed line marks the UCST for the hexane + perfluorohexane mixture.

**TABLE 2: Experimental Density as a Function of Pressure for Perfluorohexylhexane (F6H6)**

298.15 K		308.15 K		318.15 K		328.15 K	
<i>P</i> , bar	<i>d</i> , g cm <sup>-3</sup>	<i>P</i> , bar	<i>d</i> , g cm <sup>-3</sup>	<i>P</i> , bar	<i>d</i> , g cm <sup>-3</sup>	<i>P</i> , bar	<i>d</i> , g cm <sup>-3</sup>
1.0	1.388 18	1.0	1.371 54	1.0	1.354 93	1.0	1.339 28
11.0	1.389 84	14.7	1.373 93	21.9	1.359 16	22.1	1.343 84
26.7	1.392 69	15.8	1.374 10	37.8	1.362 51	39.1	1.347 59
47.7	1.396 43	37.6	1.378 45	46.6	1.364 31	46.1	1.349 13
72.6	1.400 78	63.0	1.383 20	72.7	1.369 50	72.6	1.354 68
93.3	1.404 21	73.8	1.385 22	98.4	1.374 43	98.7	1.359 99
102.2	1.405 66	95.1	1.389 07	110.9	1.376 75	110.9	1.362 32
119.1	1.408 42	110.0	1.391 68	124.6	1.379 25	123.3	1.364 72
144.0	1.412 34	118.8	1.393 17	148.5	1.383 49	147.3	1.369 21
169.8	1.416 27	123.7	1.394 05	172.3	1.387 58	169.4	1.373 19
186.6	1.418 78	147.4	1.397 99	197.2	1.391 70	196.9	1.377 97
198.4	1.420 48	172.3	1.402 07	213.0	1.394 24	216.3	1.381 17
210.9	1.422 34	197.2	1.405 99	222.7	1.395 84	221.8	1.382 18
241.0	1.426 62	215.7	1.408 84	246.4	1.399 55	246.1	1.386 18
265.9	1.430 03	221.8	1.409 78	271.4	1.403 37	272.6	1.390 36
292.8	1.433 65	246.1	1.413 41	295.7	1.406 96	295.7	1.393 96
297.2	1.434 18	272.0	1.417 16	307.2	1.408 61	312.4	1.396 40
318.2	1.437 01	295.4	1.420 45	319.9	1.410 49	319.8	1.397 58
342.5	1.440 13	311.1	1.422 63	345.5	1.414 11	345.3	1.401 34
369.8	1.443 59	319.7	1.423 83	369.9	1.417 52	375.0	1.405 61
392.9	1.446 44	344.3	1.427 18	392.6	1.420 60	394.1	1.408 33
396.1	1.446 75	368.6	1.430 43	412.4	1.423 21	409.1	1.410 36
418.0	1.449 48	393.8	1.433 70	418.3	1.424 03	419.3	1.411 81
441.1	1.452 24	407.6	1.435 45	444.6	1.427 46	443.4	1.415 08
465.6	1.455 13	418.8	1.436 89	468.3	1.430 48	466.9	1.418 24
490.5	1.458 01	442.5	1.439 85	492.0	1.433 46	492.7	1.421 63
498.1	1.458 80	467.5	1.442 92	506.1	1.435 20	506.4	1.423 36
512.4	1.460 45	491.1	1.445 76	519.1	1.436 79	515.4	1.424 55
538.2	1.463 34	505.7	1.447 48	539.4	1.439 25	541.9	1.427 95
565.3	1.466 32	517.9	1.448 91	564.4	1.442 27	566.2	1.430 96
589.6	1.468 98	540.6	1.451 57	589.6	1.445 23	590.4	1.433 99
		565.0	1.454 33				
		589.6	1.457 13				

for a number of alkane + perfluoroalkane mixtures at 298.15 K as a function of the chain length of both alkanes and perfluoroalkanes. From this data, the excess volume of a hypothetical equimolar mixture of (hexyl + perfluorohexyl) can be estimated as 11 cm<sup>3</sup> per mole of mixture. This should be very close to twice the excess volume of an equimolar (pentane + perfluoropentane) binary mixture, since the molar volumes of the hexyl and perfluorohexyl segments are very similar to the molar volumes of pentane and perfluoropentane, respectively. The volume change,  $\Delta V$ , should then be negative and on the order of 5 cm<sup>3</sup> mol<sup>-1</sup>. This contribution opposes the excess volume expansion by ~45%. A similar procedure applied to F6H8 leads to  $\Delta V = -2$  cm<sup>3</sup> mol<sup>-1</sup>.

**TABLE 3: Experimental Density as a Function of Pressure for Perfluorohexyloctane (F6H8)**

298.15 K		308.15 K		318.15 K		328.15 K	
<i>P</i> , bar	<i>d</i> , g cm <sup>-3</sup>	<i>P</i> , bar	<i>d</i> , g cm <sup>-3</sup>	<i>P</i> , bar	<i>d</i> , g cm <sup>-3</sup>	<i>P</i> , bar	<i>d</i> , g cm <sup>-3</sup>
1.0	1.332 56	1.0	1.317 23	1.0	1.302 46	1.0	1.288 30
14.8	1.334 56	7.5	1.318 14	17.6	1.305 19	13.0	1.290 33
26.4	1.336 39	20.6	1.320 42	24.7	1.306 47	29.1	1.293 48
39.5	1.338 46	36.7	1.323 22	36.1	1.308 54	40.4	1.295 71
49.8	1.340 05	49.5	1.325 29	50.1	1.311 06	50.6	1.297 55
74.1	1.343 78	74.1	1.329 31	75.3	1.315 52	75.6	1.302 12
97.5	1.347 24	100.9	1.333 54	98.7	1.319 38	100.2	1.306 43
106.0	1.348 45	114.8	1.335 72	112.7	1.321 62	120.9	1.309 98
110.4	1.349 08	123.9	1.337 06	123.4	1.323 36	124.9	1.310 60
122.7	1.350 85	149.0	1.340 79	147.7	1.327 18	148.2	1.314 45
138.9	1.353 11	173.8	1.344 36	173.8	1.331 13	171.8	1.318 20
148.3	1.354 39	197.5	1.347 72	197.2	1.334 61	198.1	1.322 28
172.3	1.357 65	210.6	1.349 50	210.6	1.336 47	211.5	1.324 23
195.7	1.360 75	223.7	1.351 29	223.0	1.338 29	221.5	1.325 72
217.6	1.363 54	247.9	1.354 50	247.3	1.341 68	248.0	1.329 61
217.9	1.363 60	271.7	1.357 59	272.1	1.345 06	271.1	1.332 85
244.9	1.367 03	295.7	1.360 65	296.2	1.348 25	296.3	1.336 35
272.9	1.370 46	308.4	1.362 20	311.5	1.350 21	310.0	1.338 18
297.2	1.373 37	322.1	1.363 94	320.6	1.351 46	320.0	1.339 52
314.4	1.375 39	345.1	1.366 72	344.3	1.354 44	344.0	1.342 72
320.0	1.376 04	374.1	1.370 18	371.1	1.357 78	370.4	1.346 13
343.7	1.378 82	394.4	1.372 55	394.4	1.360 64	392.6	1.348 97
371.3	1.381 94	404.8	1.373 76	410.9	1.362 57	409.0	1.350 99
394.4	1.384 51	419.3	1.375 43	418.0	1.363 45	417.8	1.352 09
410.0	1.386 23	444.0	1.378 23	442.2	1.366 30	444.7	1.355 39
420.0	1.387 32	468.3	1.380 89	468.0	1.369 27	468.0	1.358 18
443.1	1.389 82	492.8	1.383 56	492.9	1.372 09	492.9	1.361 13
467.4	1.392 39	507.0	1.385 08	505.4	1.373 50	503.7	1.362 35
491.7	1.394 93	516.3	1.386 06	518.4	1.374 96	516.6	1.363 88
506.8	1.396 49	540.7	1.388 66	541.8	1.377 50	541.6	1.366 75
517.6	1.397 60	566.5	1.391 33	568.3	1.380 38	565.5	1.369 45
540.7	1.399 93	590.2	1.393 77	590.8	1.382 77	589.6	1.372 16
567.1	1.402 60						
589.3	1.404 79						

**TABLE 4: Coefficients Used in Eq 30 for F6H6 and F6H8**

compd	<i>T</i> , K	<i>d</i> <sup>*</sup> , g cm <sup>-3</sup>	<i>A</i> × 10 <sup>2</sup> , cm <sup>3</sup> g <sup>-1</sup>	<i>B</i> , bar
F6H6	298.15	1.388 18	5.954 42	622.71
	308.15	1.371 54	6.065 02	573.03
	318.15	1.354 93	6.084 24	519.18
	328.15	1.339 28	6.266 29	493.41
F6H8	298.15	1.332 56	6.303 58	696.82
	308.15	1.317 23	6.293 80	626.87
	318.15	1.302 46	6.460 05	592.82
	328.15	1.288 30	6.581 69	558.00

The densities of the two liquid semifluorinated compounds were also measured as a function of pressure at four different temperatures between 1 and 600 bar; the density results as a function of both temperature and pressure are reported in Tables 2 and 3. The isothermal pressure dependence of density can be correctly described by the Tait equation,

$$1/d = 1/d^* + A \ln((B + p^*)/(B + p)) \quad (30)$$

where *d* is the density; *p*, the pressure; and *d*<sup>\*</sup>, the density at the reference pressure, *p*<sup>\*</sup>. This equation was used to fit the experimental data, using 1 bar as the reference pressure, *p*<sup>\*</sup>. The fitting residuals for the obtained equations are always smaller than 0.03%; the coefficients *A*, *B*, and *d*<sup>\*</sup> for each isotherm are given in Table 4.

## Discussion

As previously discussed, perfluoroalkylalkanes can be considered as being formed by joining an alkyl segment to a perfluoroalkyl segment. This same approach was used to model

**TABLE 5: Optimized SAFT-VR Parameters for the Segments of the Molecules Studied**

segment	$m$	$\lambda$	$\sigma, \text{\AA}$	$\epsilon/k, \text{K}$
C <sub>2</sub> H <sub>5</sub> <sup>-</sup>	0.998	1.449	3.788	241.8
C <sub>6</sub> H <sub>13</sub> <sup>-</sup>	2.332	1.552	3.920	250.4
C <sub>8</sub> H <sub>17</sub> <sup>-</sup>	2.998	1.574	3.945	250.3
C <sub>6</sub> F <sub>13</sub> <sup>-</sup>	2.535	1.432	4.456	283.1
C <sub>8</sub> F <sub>17</sub> <sup>-</sup>	3.275	1.462	4.472	274.0

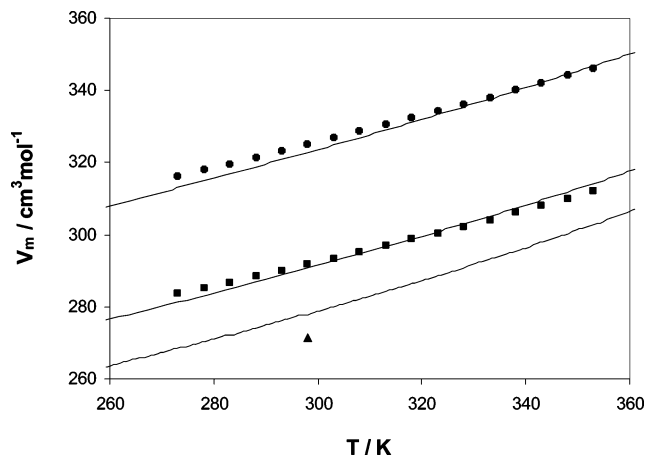
F6H6 and F6H8 using the hetero-SAFT-VR approach and enables a totally predictive approach.

The number of spherical segments forming the alkyl and perfluoroalkyl chains was determined as follows: From the established expressions relating the number of segments ( $m$ ) to the number of carbon atoms ( $C$ ) in alkanes ( $m_A = 1 + ((C - 1)/3)^{79}$ ) and perfluoroalkanes ( $m_{PFA} = 1 + ((C - 1) \times 0.37)^{79}$ ), it can be easily demonstrated that  $m(\text{CH}_3) = 0.665$ ,  $m(\text{CH}_2) = 0.333$ ,  $m(\text{CF}_3) = 0.685$ , and  $m(\text{CF}_2) = 0.370$ . From these contributions, the number of segments in the hexyl, octyl, and perfluorohexyl groups is 2.332, 2.998, and 2.535, respectively. To develop a truly predictive approach, the square-well parameters  $\epsilon$ ,  $\sigma$ , and  $\lambda$ , for the alkyl and perfluoroalkyl chains are taken from earlier work on the alkanes and perfluoroalkanes.<sup>40,53,65</sup> Therefore, the hexyl and octyl segments were modeled using the square-well parameters for hexane and octane, respectively, and the perfluorohexyl segment was described using the perfluorohexane parameters. All the model parameters used in this work are summarized in Table 5.

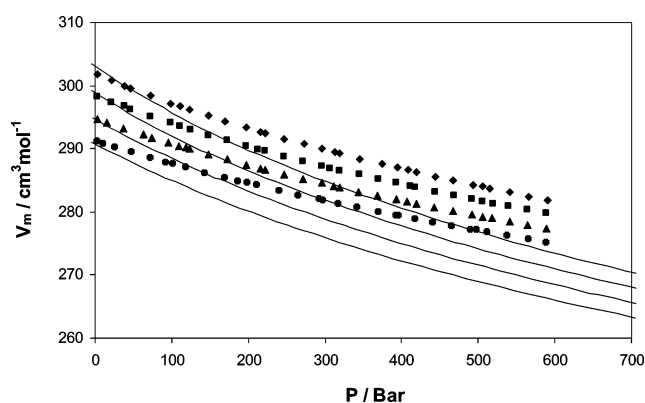
Finally, to describe the inter- and intramolecular interactions between alkyl and perfluoroalkyl segments, it is necessary to include the binary interaction parameters,  $\xi_{ij}$  and  $\gamma_{ij}$  given in eqs 3 and 4, to account for deviations from the Lorentz–Berthelot rules. In previous work,<sup>65</sup>  $\xi_{ij}$  and  $\gamma_{ij}$  were fitted to the UCST and excess volumes of hexane + perfluorohexane mixtures. It was shown that the obtained values ( $\xi_{ij} = 0.840$  and  $\gamma_{ij} = 1.0451$ ) can be used transferably to predict the phase equilibria and excess volumes of other alkane + perfluoroalkane systems. We therefore decided to use the same parameters in the description of the perfluoroalkylalkanes studied in this work.

The results of the SAFT-VR predictions for the molar volumes of both semifluorinated compounds at a pressure of 1 atm are presented in Figure 2, along with the corresponding experimental results. It can be seen that, although the expansivity is over predicted by the theory, the error in the molar volumes compared to the experimental data is always less than 1%. This agreement is remarkable, especially considering that the theoretical results are true predictions, since no parameters were fitted to experimental data for the fluids being studied.

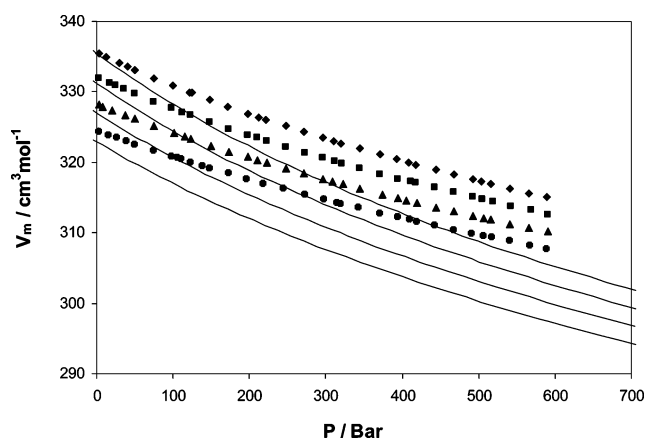
The molar volumes of perfluorooctylethane (F8H2), for which only one density point at a single temperature is available in the literature,<sup>80</sup> have also been calculated and are included in Figure 2. The agreement can again be considered quite good, given the simplicity of our approach, although the deviation from the experimental result appears to be slightly larger than that observed for the other two PFAAs studied. This is probably due to the very short hydrogenated segment of the F8H2 molecule and the fact that the dipole at the junction between the two segments is likely to contribute more significantly to the thermodynamic properties and is not addressed in our approach. Furthermore, the binary interaction parameters used in the calculations are expected to work better for systems that are comparable to those studied in earlier work, that is, chains of five to eight carbon atoms in the alkane and perfluoroalkane segments.



**Figure 2.** Experimental molar volumes at atmospheric pressure as a function of temperature for F6H6 (■), F6H8 (●) and F8H2 (▲). The lines correspond to the hetero-SAFT-VR predictions.



**Figure 3.** Experimental molar volumes as a function of pressure for F6H6 at 298.15 (●), 308.15 (▲), 318.15 (■), and 328.15 K (◆). The lines represent the hetero-SAFT-VR predictions.



**Figure 4.** Experimental molar volumes as a function of pressure for F6H8 at 298.15 (●), 308.15 (▲), 318.15 (■), and 328.15 K (◆). The lines represent the hetero-SAFT-VR predictions.

SAFT-VR calculations were also performed to determine the molar volumes of F6H6 and F6H8 as a function of pressure. The results are presented in Figures 3 and 4, along with the experimental data. From the Figure, it can be seen that the theory overpredicts the compressibility, since the slope of the theoretical curves is considerably larger than that of the experimental results; however, if a comparison is made directly between the predicted molar volumes and the experimental data, the error is smaller than 3.5%, even to 600 bar.

## Conclusions

The liquid density of two semifluorinated alkanes, perfluorohexylhexane (F6H6) and perfluorohexyloctane (F6H8), has been measured at atmospheric pressure as a function of temperature from 273.15 to 353.15 K and at four temperatures as a function of pressure up to 600 bar. The results were interpreted using the SAFT-VR equation of state by modeling the perfluoroalkylalkanes as heterosegmented diblock chains. The parameters for the alkyl and perfluoroalkyl segments, as well as the unlike binary interaction parameters, were developed in earlier work. With this simple and fully predictive approach, we were able to reproduce the experimental densities at atmospheric pressure within 1% and the densities at high pressure within 3.5%.

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