Liquid Phase Behavior of Perfluoroalkylalkane Surfactants

Pedro Morgado, Honggang Zhao, Felipe J. Blas, Clare McCabe, Luis Paulo N. Rebello, and Eduardo J. M. Filipe

Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal, Department of Chemical Engineering, Vanderbilt University, Nashville, Tennessee 37235, Departamento de Física Aplicada, Faculdade de Ciências Experimentais, Universidade de Huelva, 21071 Huelva, Spain, and Instituto de Tecnologia Química e Biológica, ITQB2, Universidade Nova de Lisboa, Avenida República, Apartado 127, 2780-901 Oeiras, Portugal

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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 perfluorohexyl-octane (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 all 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, as fluids in eye surgery, and in the treatment of burns. 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, the observation of smectic liquid crystalline phases, and the formation of nanoscale patterns in molecular films of either pure or mixed perfluoroalkylalkanes have been reported. Organization in the solid state into layered structures has also been described.

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”. The unusual affinity of perfluorinated chains toward supercritical CO2 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. For example, Iezzi et al. studied the formation of microdispersions by semifluorinated alkanes in dense carbon dioxide, and mixed-tail dichain surfactants, such as (C3F15)(C4H8)CHSO4Na7, have been shown to form stable reverse micelles in carbon dioxide.

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. 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.

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 determined the phase envelope of binary and quasi-binary mixtures of the simplest semifluorinated alkane, CF3CH3, with the linear alkanes, undecane, dodecane and tridecane and their binary mixtures. The behavior of CF3CH3, 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. 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 perfluor-
rocarbon—hydrocarbon diblocks,26 their aggregation,27 and liquid crystalline behavior28 have been reported. Simulations have also been performed to study Langmuir monolayers of amphiphiles, such as C2F5C2H4COOH.29,30 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,31 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 perfluorooctylethylene 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 perfluorooctylethylene again prevents this molecule from being a good model for perfluoroalkylkanes.

In subsequent work32 the solubility of oxygen, carbon dioxide, and water in perfluorooctylethylene, perfluorohexylethene, and perfluorohexylethane 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,33,34 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.35 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.36,37 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,38–43 and their binary mixtures,39,44–51 perfluoroalkanes,52,53,65 hydrogen fluoride,34 boron trifluoride,55 water,42,56 refrigerant systems,57 carbon dioxide,42,49,58–61 and electrolyte solutions62–64 have all been studied.

Of particular relevance is the study of alkane + perfluoroalkane binary mixtures,52,60,61 McCabe et al.52 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 (\(\xi_n = 0.9206\)) 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 \(\xi_{bb} = 0.8948\) for the binary mixture involving n-heptane. In more recent work,58 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 perfluoroalkylkanes. In particular, the liquid density of two semifluorinated alkanes, perfluorohexylhexane (F6H6) and perfluorohexylexoctane (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 approach66 was recently tested against extensive Monte Carlo simulation data and shown to accurately capture the effect of chain molecular architecture on phase behavior.67

**Experimental**

The perfluorohexylexoctane (F6H6) and perfluorohexylexoctane (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 ±0.00002 g cm⁻³. 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 Anton Paar DMA 512P vibrating-tube densimeter, in which temperature is controlled to ±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.
The expression of Boublik and Mansoori and co-workers for the reference fluid; and 
the modified Lorentz–Berthelot combining rules, 69

where \( \sigma_j \) 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 perfluoroalkyalkane 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, 69

\[
\sigma_j = \frac{\sigma_u + \sigma_v}{2} 
\]

(2)

\[
\epsilon_{ij} = \zeta_{ij} \sqrt{\epsilon_u \epsilon_v} 
\]

(3)

\[
\lambda_{ij} = \gamma_{ij} \frac{\lambda_u \sigma_u + \lambda_v \sigma_v}{\sigma_u + \sigma_v} 
\]

(4)

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

\[
\frac{A}{NkT} = \frac{A^\text{ideal}}{NkT} + \frac{A^\text{mono}}{NkT} + \frac{A^\text{chain}}{NkT} + \frac{A^\text{assoc}}{NkT} 
\]

(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

\[
\frac{A^\text{ideal}}{NkT} = \ln(\rho N^3) - 1 
\]

(6)

where \( N \) is the total number of molecules; \( k \), Boltzmann’s 
constant; \( \rho \), the number density of chain molecules; and \( A \), the 
thermal de Broglie wavelength.

The monomer free energy is given by

\[
\frac{A^\text{mono}}{NkT} = m \frac{A^M}{NkT} = ma^M 
\]

(7)

where \( N_c \) is the total number of segments, determined from the 
product of the total number of molecules, \( N \), and the number 
of segments per molecule, \( m \). \( a^M \) 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, 70 namely,

\[
a^M = a^{\text{HS}} + \beta a_1 + \beta^2 a_2 
\]

(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 and Mansoori and co-workers 72 for 
multicomponent hard sphere systems, namely,

\[
a^{\text{HS}} = 6 \rho \left[ \left( \frac{\xi^3}{s_3} - \xi_0 \right) \ln(1 - \xi_0) + \frac{3 \xi_0}{1 - \xi_0} + \frac{\xi^3}{s_3(1 - \xi_0)^2} \right] 
\]

(9)

where \( \rho \) is the number density of segments, which is defined as 
\( N_c/V \), the total number of segments divided by the total 
volume; and \( \xi_0 \) is the reduced density given by a sum over all 
segments, \( i \),

\[
\xi_0 = \sum_i \frac{\pi}{6} \rho_i [x_{i1}(\sigma_{i1})^3 + x_{i2}(\sigma_{i2})^3] 
\]

(10)

where \( \sigma_i \) is the diameter of segments of type \( i \), and \( x_{i1} \) is 
the mole fraction of segments of type \( i \). Note that \( \xi_0 \) 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

\[
a_1 = x_{i1}^a (a_{11})_{i1} + 2 x_{i1} x_{i2} (a_{12})_{i12} + x_{i2}^a (a_{12})_{i2} 
\]

(11)

where \( (a_{1i})_{ij} \) is obtained from the mean-value theorem as 
presented by Gil-Vallegas et al. 36

\[
(a_{1i})_{ij} = -2 \pi \rho \epsilon_{ij} \int_{r_{ij}}^{\infty} r_{ij}^2 g_{ij}^{\text{HS}}(r_{ij}) \, dr_{ij} = -\rho \alpha_{ij}^{\text{VDW}} g_{ij}^{\text{HS}}(\sigma_{ij}^v \xi^\text{eff}) 
\]

(12)

where

\[
\alpha_{ij}^{\text{VDW}} = \frac{2 \pi}{3} \sigma_{ij}^v \epsilon_{ij} (\lambda_{ij}^v - 1) 
\]

(13)

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

\[
(a_{1i})_{ij} = -\rho \alpha_{ij}^{\text{VDW}} g_0^{\text{HS}}[\sigma_{ij}^v \xi^\text{eff}(\lambda_{ij})] 
\]

(14)

where \( g_0^{\text{HS}}(\sigma_{ij}^v \xi^\text{eff}) \) is obtained from the Carahnan and Starling 
equation of state, 73

\[
\lambda_{ij}^{\text{HS}}[\sigma_{ij}^v \xi^\text{eff}(\lambda_{ij})] = \frac{1}{1 - \xi^\text{eff} \left[ \frac{2}{(1 - \xi^\text{eff})^2} \right]} 
\]

(15)

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

\[
\xi_{im}(\xi_m, \lambda_{ij}) = c_1(\lambda_{ij})_x^v \xi_{im}^v + c_2(\lambda_{ij})_x^v \xi_{im}^v + c_3(\lambda_{ij})_x^v \xi_{im}^v 
\]

(16)

where

\[
\xi_{im}(\xi_m, \lambda_{ij}) = c_1(\lambda_{ij})_x^v \xi_{im}^v + c_2(\lambda_{ij})_x^v \xi_{im}^v + c_3(\lambda_{ij})_x^v \xi_{im}^v 
\]

(16)

and

\[
\xi_s = \frac{\pi}{6} \rho \sigma_s^3 
\]

(18)

with

\[
\sigma_s^3 = x_{i1}^2 \sigma_{11}^3 + 2 x_{i1} x_{i2} \sigma_{12}^3 + x_{i2}^2 \sigma_{22}^3 
\]

(19)

This corresponds to mixing rule MX1b in the original SAFT- 
VR approach for mixtures. 37 In previous work, 65 we compared 
the results obtained from this formulation with the MX3b mixing 
rule, 37 in which the actual packing fraction of the system is used to 
obtain \( \xi^\text{eff} \) 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
\[
a_2 = x_{ij}^2 (a_{ij})_{11} + 2 x_{ij} x_{jk} (a_{ij})_{12} + x_{jk}^2 (a_{jk})_{22}
\]
where \((a_{ij})_{ij}\) is obtained through the local compressibility approximation,
\[
(a_{ij})_{ij} = \frac{1}{2} K^{HS} \frac{\partial (a_{ij})_{ij}}{\partial \rho_s}\n\]
and \(K^{HS}\) is the Percus–Yevick expression for the hard-sphere isothermal compressibility,
\[
K^{HS} = \frac{\zeta_0 (1 - \zeta_3)^2}{\zeta_0 (1 - \zeta_3) + 6 \zeta_1 \zeta_2 (1 - \zeta_3) + 9 \zeta_2^3}
\]
Finally, the contribution due to chain formation from the monomer segments is given in terms of the background correlation function \(y_{ij}^{SW}\),
\[
\frac{A^{chain}}{NkT} = -(m_1 - 1) \ln y_{ij}^{SW} (\sigma_{ij}) - \ln y_{ij}^{SW} (\sigma_{ij}) - (m_2 - 1) \ln y_{ij}^{SW} (\sigma_{ij})
\]
where the sum is over all bonds in the chain molecule,
\[
y_{ij}^{SW} (\sigma_{ij}) = \exp (-\beta g_{ij}^{SW} (\sigma_{ij}))
\]
The radial distribution function for the square well monomers, \(g_{ij}^{SW} (\sigma_{ij})\), is approximated by a first-order high-temperature perturbation expansion,
\[
g_{ij}^{SW} (\sigma_{ij}; \zeta_3) = g_{ij}^{HS} (\sigma_{ij}; \zeta_3) + \beta \varepsilon g_{ij}^{SW} (\sigma_{ij})
\]
where the contact value of the radial distribution function, \(g_{ij}^{HS} (\sigma_{ij}; \zeta_3)\), at the actual packing fraction, \(\zeta_3\), is obtained from the expression of Boublik,
\[
g_{ij}^{HS} (\sigma_{ij}; \zeta_3) = \frac{1}{1 - \zeta_3} + \frac{3}{(1 - \zeta_3)^2} + \frac{2 (D_y \zeta_3)^2}{(1 - \zeta_3)^3}
\]
where
\[
D_y = \sum_{i,j} \frac{x_{ij}^2 \sigma_{ij}^2}{(\sigma_i + \sigma_j) \sum_j x_{ij} \sigma_{ij}^3}
\]
and \(g_{ij}^{SW} (\sigma_{ij})\) is determined by using the Clausius virial theorem and the first derivative of the free energy with respect to the density,
\[
g_{ij}^{SW} (\sigma_{ij}) = \frac{1}{2 \pi \varepsilon g_{ij}^{SW} \zeta_3} \left[ \frac{\partial (a_{ij})_{ij}}{\partial \rho_s} - \frac{\rho_s \partial (a_{ij})_{ij}}{\partial \rho_s} \right]
\]

Results
The densities and molar volumes of the studied semifluorinated alkanes at atmospheric pressure and as a function of temperature, are presented in Table 1. For convenience, the isobaric densities were used to fit a simple polynomial of the form
\[
d = \sum_{i=0}^{3} a_i (T - 100 \text{ K})^i
\]
where \(d\) is the density and \(T\) the absolute temperature; the coefficients obtained were \(a_0 = 1.949672, a_1 = -0.257571\), \(a_2 = 3.643006 \times 10^{-3}\), and \(a_3 = -4.507740 \times 10^{-3}\) for F6H6 and \(a_0 = 1.906376, a_1 = -0.285170\), \(a_2 = 4.627201 \times 10^{-3}\), and \(a_3 = -5.158583 \times 10^{-3}\) 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 \((V_m (C_6H_{13}))\) and perfluorohexyl \((V_m (C_6F_{13}))\) segments, the excess volume of a hypothetical equimolar (hexyl + perfluorohexyl) mixture \((V^E_m (C_6H_{13} + C_6F_{13}))\), and the volume change resulting from the formation of the hexyl-perfluoro- hexyl 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.

\[
V_m (F6H6) = V_m (C_6H_{13}) + V_m (C_6F_{13}) + V^E_m (C_6H_{13} + C_6F_{13}) + \Delta V
\]
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 + perfluoroalkyl) can be estimated as 11 cm$^3$ 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 perfluoroalkyl 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$^3$ mol$^{-1}$. This contribution opposes the excess volume expansion by ~45%. A similar procedure applied to F6H8 leads to $\Delta V = -2$ cm$^3$ mol$^{-1}$.

### Table 2: Experimental Density as a Function of Pressure for Perfluorohexane (F6H6)

<table>
<thead>
<tr>
<th>T/K</th>
<th>P, bar</th>
<th>d, g cm$^{-3}$</th>
<th>d, g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>1.0</td>
<td>1.388 18</td>
<td>1.371 54</td>
</tr>
<tr>
<td>308.15</td>
<td>1.0</td>
<td>1.388 18</td>
<td>1.371 54</td>
</tr>
<tr>
<td>318.15</td>
<td>1.0</td>
<td>1.354 93</td>
<td>1.309 28</td>
</tr>
<tr>
<td>328.15</td>
<td>1.0</td>
<td>1.393 28</td>
<td>1.359 73</td>
</tr>
</tbody>
</table>

### Table 3: Experimental Density as a Function of Pressure for Perfluorohexylcotane (F6H8)

<table>
<thead>
<tr>
<th>T/K</th>
<th>P, bar</th>
<th>d, g cm$^{-3}$</th>
<th>d, g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>1.0</td>
<td>1.354 18</td>
<td>1.318 28</td>
</tr>
<tr>
<td>308.15</td>
<td>1.0</td>
<td>1.354 18</td>
<td>1.318 28</td>
</tr>
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<td>318.15</td>
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<td>1.354 93</td>
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</tr>
<tr>
<td>328.15</td>
<td>1.0</td>
<td>1.393 28</td>
<td>1.359 73</td>
</tr>
</tbody>
</table>

### Table 4: Coefficients Used in Eq 30 for F6H6 and F6H8

<table>
<thead>
<tr>
<th>compd</th>
<th>T/K</th>
<th>d$\alpha$, g cm$^{-3}$</th>
<th>A $\times 10^3$, cm$^3$ g$^{-1}$</th>
<th>B, bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>F6H6</td>
<td>298.15</td>
<td>1.388 18</td>
<td>5.954 42</td>
<td>622.71</td>
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<tr>
<td></td>
<td>308.15</td>
<td>1.354 18</td>
<td>6.065 02</td>
<td>573.03</td>
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<tr>
<td></td>
<td>318.15</td>
<td>1.354 93</td>
<td>6.084 24</td>
<td>519.18</td>
</tr>
<tr>
<td>F6H8</td>
<td>298.15</td>
<td>1.332 54</td>
<td>6.303 58</td>
<td>696.82</td>
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<tr>
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<td></td>
<td>318.15</td>
<td>1.302 46</td>
<td>6.460 05</td>
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</tr>
<tr>
<td></td>
<td>328.15</td>
<td>1.288 30</td>
<td>6.581 69</td>
<td>558.00</td>
</tr>
</tbody>
</table>

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,

$$1/d = 1/d^s + A \ln((B + p^s)/(B + p))$$

where $d$ is the density; $p$, the pressure; and $d^s$, the density at the reference pressure, $p^s$. This equation was used to fit the experimental data, using 1 bar as the reference pressure, $p^s$. The fitting residuals for the obtained equations are always smaller than 0.03%; the coefficients $A$, $B$, and $d^s$ 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

<table>
<thead>
<tr>
<th>segment</th>
<th>( m )</th>
<th>( \lambda )</th>
<th>( \sigma, \text{Å} )</th>
<th>( \epsilon/k, \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_3\text{H}_7 )</td>
<td>0.998</td>
<td>1.449</td>
<td>3.788</td>
<td>241.8</td>
</tr>
<tr>
<td>( \text{C}<em>4\text{H}</em>{11} )</td>
<td>2.332</td>
<td>1.552</td>
<td>3.920</td>
<td>250.4</td>
</tr>
<tr>
<td>( \text{C}<em>5\text{H}</em>{12} )</td>
<td>2.998</td>
<td>1.574</td>
<td>3.945</td>
<td>250.3</td>
</tr>
<tr>
<td>( \text{C}<em>6\text{F}</em>{13} )</td>
<td>2.535</td>
<td>1.432</td>
<td>4.456</td>
<td>283.1</td>
</tr>
<tr>
<td>( \text{C}<em>6\text{H}</em>{13} )</td>
<td>3.275</td>
<td>1.462</td>
<td>4.472</td>
<td>274.0</td>
</tr>
</tbody>
</table>

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 \( (m_{PF,x} = 1 + ((C - 1) \times 0.37)) \) \(^{79} \), 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. \(^{40,53,65} \) 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, \(^{65} \) \( \xi_{ij} \) 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, \(^{80} \) 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.

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, perfluoroheptylhexane (F6H6) and perfluoroheptyloctane (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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References and Notes