Solution Behavior of Perfluoroalkanes and Perfluoroalkylalkane Surfactants in *n*-Octane[†]

Pedro Morgado,[‡] Rogério Tomás,[‡] Honggang Zhao,[£] M. Carolina dos Ramos,[£,§] Felipe J. Blas,[§] Clare McCabe,[£] and Eduardo J. M. Filipe*,[‡]

Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal, Department of Chemical Engineering, Vanderbilt University, Nashville, Tennessee 37235-1604, and Departamento de Física Aplicada, Facultad de Ciencias Experimentales, Universidad de Huelva, 21071 Huelva, Spain

Received: May 15, 2007; In Final Form: August 18, 2007

Apparent molal volumes of a number of *n*-perfluoroalkanes (PA) and perfluoroalkylalkanes (PFAA) in *n*-octane have been measured at 298.15 K as a function of composition. The corresponding partial molal volumes at infinite dilution have been obtained by extrapolating the apparent molal volumes to zero composition. The results were interpreted using the hetero-SAFT-VR equation of state. The perfluoroalkylalkanes were modeled as heterosegmented diblock chains, and the cross interactions, both intra- and intermolecular, were characterized using parameters developed in earlier studies of alkane + perfluoroalkane mixtures. Through this strategy, a fully predictive approach has been developed that is able to accurately predict the volumetric behavior of the solutions of perfluoroalkylalkanes studied, without fitting to any experimental data for perfluoroalkylalkanes.

Introduction

Perfluoroalkylalkanes (PFAA, also known as semifluorinated alkanes) are molecules made up of a hydrogenated segment and a perfluorinated segment covalently bonded to form a single linear chain. Perfluoroalkyl and alkyl chains, however, have been amply demonstrated to be "mutually phobic". Perfluoroalkylalkanes thus gather the requisites to combine the "dual character" of amphiphilic molecules and the physics of orientational ordering of smectogenic liquid crystals. Accordingly, aggregation in solvents selective for one of the chains,[1,2] the observation of smectic liquid crystalline phases,[3–5] and recently, the formation of nanoscale patterns in molecular films of either pure[6] or mixed perfluoroalkylalkanes have all been reported.[7] Organization in the solid state into layered structures has also been described.[8–11]

As a result of their unique properties, which include inertness, biocompatibility, and the ability to solubilize high levels of respiratory gases characteristic of fluorinated solvents, perfluoroalkylalkanes have become important for a number of medical applications, for example, as components of liquid ventilation solvents and temporary blood substitute formulations,[12,13] as fluids in eye surgery, and in the treatment of burns.[14]

Given the structural similarity between the alkane and perfluoroalkane molecules, one could expect that mixtures of such species would behave almost ideally. However, mixtures of alkanes and perfluoroalkanes show large regions of liquid–liquid immiscibility, as first observed in the early 1950s.[15] Since then, a considerable amount of work has been devoted to understanding why these mixtures exhibit this particular type of "antipathy". Although most of these studies imply the existence of an unusually weak hydrocarbon–fluorocarbon interaction, a satisfactory explanation still awaits.[16] This implies that, unlike common hydrophilic–hydrophobic surfactants, the amphiphilicity of perfluoroalkylalkanes, and consequently their potential for self-organization, results from a subtle balance of

weak and even weaker dispersion forces and has led to perfluoroalkylalkanes sometimes being called primitive surfactants. Investigating the solution behavior of these substances in selected solvents, that is, assessing the effect of both the absolute and relative chain length of the constituent chains, is an important contribution to understand the behavior of complex liquids in the absence of strong directional intermolecular forces.

Despite their interesting behavior and potential, very little work has been done experimentally to characterize the thermodynamic behavior of perfluoroalkylalkanes in the liquid state, either pure or mixed, with other substances. De Loos and co-workers[17] determined the phase envelope of binary and quasi-binary mixtures of the simplest semifluorinated alkane, CF_3CH_3, with the linear alkanes undecane, dodecane, tridecane, and their binary mixtures. The behavior of CF_3CH_3, 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. Tochigi et al.[18] have measured the vapor–liquid equilibria of liquid mixtures of perfluorobutylethane and octane at 101.3 kPa. More recently, we have reported the liquid densities of two PFAAs, perfluorohexylhexane (F6H6) and perfluorohexyloctane (F6H8) as a function of temperature and pressure.[19] As far as we are aware, this was the first example of a systematic study of the thermophysical properties of pure semifluorinated alkanes which are essential to develop reliable theoretical models.

From a theoretical point of view, a major step in our understanding of liquids and liquid mixtures has been the development of molecular-based equations of state (EOS) such as the SAFT equation.[20–22] SAFT, 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. In this work, we focus on hetero-SAFT-VR, a version of SAFT-VR which describes chain molecules as hard-core monomers of different size and/ or energy of interaction. In comparison, in the SAFT-VR approach, molecules are modeled as homonuclear chains that interact through attractive potentials of variable range, typically a square well,[23,24] and has been successfully used to describe

Solution Behavior of PA and PFAA in *n*-Octane

J. Phys. Chem. C, Vol. 111, No. 43, 2007 **15963**

the phase equilibria of a wide range of industrially important systems (see reference 25 and the references therein).

Of particular relevance is the study of alkane + perfluoroalkane binary mixtures. McCabe et al. [26] 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 more recent work,[27] the behavior of alkane + perfluoroalkane binary mixtures with chain lengths between five and eight carbon atoms 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 based on the reproduction of the UCST and excess volumes for the *n*-hexane + *n*-perfluorohexane system and used to correctly describe the phase behavior of the other systems studied without any additional fitting to experimental data. As discussed above, in closely related work,[19] the liquid density of two semifluorinated alkanes (F6H6, F6H8) has been reported as a function of temperature and pressure, and a theoretical approach was proposed to describe the behavior of these pure PFAAs based on the hetero-SAFT-VR equation;[28,29] the perfluoroalkylalkanes chains were modeled as heterosegmented diblock chains, with the alkyl and perfluoroalkyl segments described using parameters developed in earlier work and the cross interactions, both intra- and intermolecular, described using parameters developed in earlier studies of alkane + perfluoroalkane mixtures. The approach is, thus, fully predictive. The theory has been shown to describe the experimental results well, without fitting to any experimental data.

In this work, partial molal volumes at infinite dilution for a number of *n*-perfluoroalkanes and perfluoroalkylalkanes in *n*-octane have been obtained at 298.15 K. The volumetric behavior of solutes has proven to be a powerful tool to understand interactions in solution. In particular, partial molar volumes at infinite dilution, where solvent−solvent and solute−solvent but not solute−solute interactions are present, can make an important contribution to the understanding of liquid solutions. These results therefore provide useful information about the volumetric behavior of fluorinated and partially fluorinated chains in *n*-octane in the absence of solute−solute interactions. As before, the results were interpreted using the hetero-SAFT-VR equation, and the theory was found to accurately predict the experimental results both for the solutions of perfluoroalkanes and solutions of perfluoroalkylalkanes studied.

Experimental Section

n-Perfluoropentane was supplied by Apollo Scientific, with a claimed purity of 90%, *n*-perfluorohexane by Sigma-Aldrich, with 99% purity, and *n*-perfluorooctane and *n*-perfluorononane by ABCR GmbH & Co. KG., with 98% claimed purities. The *n*-octane was supplied by Acros Organics and Merck, both with purities of 99+%. All compounds were used without further purification. The perfluorohexylhexane (F6H6), perfluorohexyloctane (F6H8), and perfluorodecyloctane (F10H8) used were ultrapurified chemicals obtained from Fluoron GMBH, with a claimed purity of 100%, and were used without further purification. The perfluorooctyloctadecane (F8H18) was synthesized in our laboratory according to the procedure described in reference 30; the product was submitted to elemental analysis, ^{1}H and ^{19}F NMR spectroscopy, and gas chromatography, and no evidence for impurities was found.

Solutions were prepared by weight in 5 or 10 mL flasks, taking care to leave the minimum possible free volume in order to reduce evaporation. Design to prevent evaporation was introduced into the flasks. In the case of solutions of *n*-perfluoropentane in octane, because of high volatility of the fluorinated compound, it was necessary to add the solute while the solvent was frozen in liquid nitrogen. The mixture was then allowed to reach ambient temperature before weighing.

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 Mili-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.

Model and Theory

In the hetero-SAFT-VR approach, 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

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

where σ_{ij} is the diameter of the interaction, λ_{ij} the range, and ϵ_{ij} the well depth of the SW potential. The parameters used in this work to model octane, the perfluoroalkanes, and the alkyl and perfluoroalkyl segments of each perfluoroalkylalkane molecule studied are given in Table 4 and discussed further in the Results section. The inter- and intramolecular cross interactions between segments are obtained from the modified Lorentz−Berthelot combining rules[31]

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

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

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

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 a binary mixture within the hetero-SAFT-VR approach, with particular emphasis on the case of binary mixtures in which one of the components is a diblock−heteronuclear chain molecule. 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

$$\frac{A^{\text{ideal}}}{NkT} = \sum_{k=1}^{n} x_k \ln(\rho_k \Lambda_k^3) - 1 \quad (6)$$

where $\rho_k = N_k/V$ is the number density, Λ_k the thermal de Broglie wavelength of species k, and x_k the mole fraction of component k.

The monomer free energy is given by

$$\frac{A^{\text{mono}}}{NkT} = \left(\sum_{i=1}^{n} m_i x_i\right)\frac{A^{\text{M}}}{N_s kT} = \left(\sum_{i=1}^{n} m_i x_i\right)a^{\text{M}} \quad (7)$$

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 of type i m_i. The 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,[32] namely

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

where $\beta = 1/kT$, a^{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^{HS} is determined from the expression of Boublik[33] and Mansoori and co-workers[34] for multicomponent hard-sphere systems, namely

$$a^{\text{HS}} = \frac{6}{\pi\rho_s}\left[\left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right)\ln(1 - \zeta_3) + \frac{3\zeta_1\zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2}\right] \quad (9)$$

where ρ_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 ζ_l is the reduced density given by a sum over all segments i

$$\zeta_l = \frac{\pi}{6}\rho_s\left[\sum_{i=1}^{n} x_{s,i}(\sigma_i)^l\right] \quad (10)$$

where σ_i is diameter of segments of type i and $x_{s,i}$ is the mole fraction of segments of type i.

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

$$a_1 = \sum_{i=1}^{n}\sum_{j=1}^{n} x_{s,i}x_{s,j}(a_1)_{ij} \quad (11)$$

where $(a_1)_{ij}$ is obtained from the mean-value theorem as proposed by Gil-Villegas et al.[23]

$$(a_1)_{ij} = -2\pi\rho_s\epsilon_{ij}\int_{\sigma_{ij}}^{\infty} r_{ij}^2 g_{ij}^{\text{HS}}(r_{ij})dr_{ij}$$
$$= -\rho_s\alpha_{ij}^{\text{VDW}}g_{ij}^{\text{HS}}(\sigma_{ij};\zeta_3^{\text{eff}}) \quad (12)$$

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 $g_{ij}^{\text{HS}}(\sigma_{ij};\zeta_3^{\text{eff}})$ is approximated by that for a pure fluid; hence, eq 12 becomes

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

where $g_0^{\text{HS}}(\sigma_x;\zeta_x^{\text{eff}})$ is obtained from the Carnahan and Starling equation of state[35]

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

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

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

where

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2.25855 & -1.50349 & 0.249434 \\ -0.669270 & 1.40049 & -0.827739 \\ 10.1576 & -15.0427 & 5.30827 \end{pmatrix}\begin{pmatrix} 1 \\ \lambda_{ij} \\ \lambda_{ij}^2 \end{pmatrix} \quad (17)$$

and

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

with

$$\sigma_x^3 = \sum_{i=1}^{n}\sum_{j=1}^{n} x_{s,i}x_{s,j}\sigma_{ij}^3 \quad (19)$$

This corresponds to mixing rule MX1b in the original SAFT-VR approach for mixtures.[24] In previous work,[29] we compared the results obtained from this formulation with the MX3b mixing rule, in which the actual packing fraction of the system is used to obtain ζ_3^{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

$$a_2 = \sum_{i=1}^{n}\sum_{j=1}^{n} x_{s,i}x_{s,j}(a_2)_{ij} \quad (20)$$

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^{HS} is the Percus−Yevick expression for the hard-sphere isothermal compressibility

$$K^{\text{HS}} = \frac{\zeta_0(1 - \zeta_3)^4}{\zeta_0(1 - \zeta_3)^2 + 6\zeta_1\zeta_2(1 - \zeta_3) + 9\zeta_2^3} \quad (22)$$

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

$$\frac{A^{\text{chain}}}{NkT} = -\sum_{k=1}^{n} x_k \sum_{ij \text{ bonds}} \ln y_{ij}^{\text{SW}}(\sigma_{ij}) \quad (23)$$

where the first sum is over the components k of the mixture and the second sum is over all bonds in the chain molecule

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

For the binary mixture of an alkane and a perfluroalkylalkane,

TABLE 1: Empirical Parameters of the Equation $d = A + Bc + Cc^2$ for *n*-Perfluoroalkanes and Perfluoroalkylalkanes in *n*-Octane at 298.15 K; std is the Standard Deviation of the Fit

substance	A	B	C	std/g·cm^{-3}	d(*n*-octane)/g·cm^{-3}
F5	0.698346	0.107262	−0.03054395	2.0×10^{-4}	0.698619
F6	0.698919	0.126086	0.00429291	8.2×10^{-6}	0.698914
F8	0.698896	0.174568	−0.07321119	1.3×10^{-5}	0.698914
F9	0.698908	0.195172	−0.10396014	1.6×10^{-5}	0.698914
F6H6	0.698615	0.133195	−0.01987915	4.2×10^{-6}	0.698610
F6H8	0.698614	0.137599	−0.030071485	3.0×10^{-6}	0.698617
F10H8	0.698635	0.225415	−0.108804994	3.2×10^{-6}	0.698638
F8H18	0.698926	0.195859	0.113459986	6.6×10^{-6}	0.698914

as studied in this work, eq 23 becomes

$$\frac{A^{chain}}{NkT} = -x_1(m_1 - 1)\ln y_{11}^{SW}(\sigma_{11}) - x_2(m_2 - 1)\ln y_{22}^{SW}(\sigma_{22}) - \\ x_2\ln y_{23}^{SW}(\sigma_{23}) - x_2(m_3 - 1)\ln y_{33}^{SW}(\sigma_{33}) \quad (25)$$

where the subscript 1 refers to the alkane solvent, 2 to the alkyl segments, and 3 the perfluoroalkyl segments of the perfluroalkylalkane solute. The radial distribution function for the square-well monomers $g_{ij}^{SW}(\sigma_{ij})$ is approximated by a first-order high-temperature perturbation expansion

$$g_{ij}^{SW}(\sigma_{ij};\zeta_3) = g_{ij}^{HS}(\sigma_{ij};\zeta_3) + \beta\epsilon_{ij}g_1^{SW}(\sigma_{ij}) \quad (26)$$

where the contact value of the radial distribution function $g_{ij}^{HS}(\sigma_{ij};\zeta_3)$ at the actual packing fraction ζ_3 is obtained from the expression of Boublik[33]

$$g_{ij}^{HS}(\sigma_{ij};\zeta_3) = \frac{1}{1 - \zeta_3} + 3\frac{D_{ij}\zeta_3}{(1 - \zeta_3)^2} + 2\frac{(D_{ij}\zeta_3)^2}{(1 - \zeta_3)^3} \quad (27)$$

where

$$D_{ij} = \frac{\sigma_{ii}\sigma_{jj}\sum_{i=1}^{n} x_{s,i}\sigma_{ii}^2}{(\sigma_{ii} + \sigma_{jj})\sum_{i=1}^{n} x_{s,i}\sigma_{ii}^3} \quad (28)$$

and $g_1^{SW}(\sigma_{ij})$ is determined by using the Clausius virial theorem and the first derivative of the free energy with respect to the density,[23] giving

$$g_1^{SW}(\sigma_{ij}) = \frac{1}{2\pi\epsilon_{ij}\sigma_{ij}^3}\left[3\left(\frac{\partial(a_1)_{ij}}{\partial\rho_s}\right) - \frac{\lambda_{ij}}{\rho_s}\frac{\partial(a_1)_{ij}}{\partial\lambda_{ij}}\right] \quad (29)$$

Results

The measured experimental densities for the studied *n*-perfluoroalkane and perfluoroalkylalkane solutions in *n*-octane were fitted to equations of the type

$$d = A + B\cdot c + C\cdot c^2 \quad (30)$$

where d is the density of the solution, A, B, and C are empirical fitting coefficients, shown in Table 1, and c is the concentration, expressed in molality. It can be seen that the values obtained for A are in good agreement with the obtained densities for the pure *n*-octane, d(*n*-octane), in each series of measurements. In the case of the perfluoropentane solutions, the agreement is poorer, and the standard deviation (std) of the fitting is also larger than that in other systems; we believe that this is due to

its high volatility, which can induce significant errors in the determination of composition.

The apparent molal volumes, V_Φ, of the solutes in all solutions were calculated with the usual equation

$$V_\Phi = \frac{MPd^0 - MPd}{pdd^0} + \frac{M}{d} \quad (31)$$

where M is the molecular weight of the solute, P and p are the masses of the solvent and solute, and d^0 and d are the densities of the pure solvent and solution, respectively. The V_Φ values for the range of molalities studied are given in Table 2.

The partial molal volumes at infinite dilution $\bar{V}^0$ of the solutes were obtained by linear extrapolation of the V_Φ's to infinite dilution by a least-squares fitting method. The results are summarized in Table 3, along with the molar volumes of the pure substances V^0 and the excess partial molal volumes at infinite dilution, calculated as $\Delta\bar{V} = \bar{V}^0 - V^0$. As can be seen, all studied substances have positive $\Delta\bar{V}$'s. In the case of the *n*-perfluoroalkanes, the increase of volume is on the order of 10%! Literally, when a perfluoroalkane molecule is dissolved in *n*-octane, a cavity forms around the solute molecule. Lepori et al.[36] determined partial molal volumes of several perfluoroalkanes in several alkanes and vice versa. The only system in common is that of *n*-perfluorohexane in *n*-octane. Its value for the partial molar volume compares favorably with the value determined in this work.

In the case of perfluoroalkylalkanes, the excess partial molar volumes are also positive but on the order of 5%. It was previously found[37,38] that, for a homologous series of alkanes or alkyl compounds, a linear dependence between the partial molar volume at infinite dilution in a certain solvent and the number of carbon atoms is observed. This linearity was also found in our measurements on the homologous series of *n*-perfluoroalkanes in *n*-octane. In order to obtain a set of group contributions for the $\bar{V}^0$'s of perfluoroalkanes in *n*-octane, a least-squares regression of the form $\bar{V}^0 = a + b\cdot(n_C - 2)$, where a and b are the empirical regression parameters and n_C is the number of carbon atoms, was made. With the linear regression in this form, the slope b could be interpreted as the perfluoromethylene group contribution $\bar{V}_{CF_2}^0$ and the intercept a as the sum of two perfluoromethyl group contributions $\bar{V}_{CF_3}^0$. The following group contributions were obtained: $\bar{V}_{CF_2}^0 = 25.4 \pm 0.9$ cm^3·mol^{-1} and $\bar{V}_{CF_3}^0 = 61.8 \pm 2.4$ cm^3·mol^{-1}. Applying the same form of linear regression to the results of Itsuki et al.[37] for solutions of *n*-alkanes in *n*-octane, the contributions $\bar{V}_{CH_2}^0 = 16.087 \pm 0.008$ cm^3·mol^{-1} and $\bar{V}_{CH_3}^0 = 33.53 \pm 0.04$ cm^3·mol^{-1} are obtained.

Using these group contributions, we have calculated the $\bar{V}^0$'s of the four perfluoroalkylalkanes studied. Since this calculation does not include the effect of the $-(CH_2)-(CF_2)-$ junction, the differences between the experimental and the calculated partial molal volumes at infinite dilution $\bar{V}_{exp}^0 - \bar{V}_{calc}^0$ should be

TABLE 2: Apparent Molal Volumes of the Studied Substances in *n*-Octane at 298.15 K

$c/$ (mol·kg^{-1})	$V_\Phi/$ (cm^{-3}·mol^{-1})	$c/$ (mol·kg^{-1})	$V_\Phi/$ (cm^{-3}·mol^{-1})	$c/$ (mol·kg^{-1})	$V_\Phi/$ (cm^{-3}·mol^{-1})
Perfluoropentane		Perfluorononane		F10H8	
0.0793	199.4	0.00626	300.2	0.00105	438.8
0.0832	199.3	0.01096	300.0	0.00191	450.8
0.0956	205.5	0.01700	302.0	0.00219	441.8
0.1018	202.0	0.02155	303.6	0.00267	443.8
0.1145	203.8	0.02614	302.2	0.00344	450.0
0.1452	198.7	0.02620	303.3	0.00452	444.1
0.1560	202.4	0.03304	304.1	0.00573	445.8
0.2122	201.8	0.04070	303.0	0.00702	443.1
0.2586	201.3	0.04643	304.4	0.00838	442.5
0.2615	205.8	0.05264	306.6	0.00998	446.6
Perfluorohexane		F6H6		F8H18	
0.00357	222.4	0.01565	304.4	0.00217	550.7
0.01034	225.3	0.02885	305.3	0.00416	553.6
0.01270	222.9	0.03228	304.9	0.00577	555.5
0.02324	224.9	0.04397	304.5	0.00767	553.0
0.02341	223.2	0.05318	304.5	0.00985	555.8
0.03651	223.5	0.08199	304.2	0.01247	553.5
0.04655	223.0			0.01517	554.1
				0.01777	554.1
				0.02044	551.5
Perfluorooctane		F6H8			
0.00333	280.7	0.05916	336.6		
0.00706	273.1	0.01839	336.7		
0.01091	277.0	0.02626	337.1		
0.01338	274.6	0.04791	336.8		
0.01533	270.9	0.08538	336.6		
0.01689	273.0				
0.01734	271.8				
0.02068	273.8				

TABLE 3: Experimental Molar Volumes and Partial Molal Volumes at Infinite Dilution in *n*-Octane at 298.15 K

substance	$V^0/$(cm^{-3}·mol^{-1})	$\bar{V}^0/$ (cm^{-3}·mol^{-1})	$\Delta\bar{V}/$ (cm^{-3}·mol^{-1})
F5	178.97[a]	200.4 ± 2.0	21.4
F6	201.64[a]	223.7 ± 0.8	22.1
F8	248.83[a]	279.4 ± 2.3	30.6
F9	272.98[b]	299.7 ± 0.6	26.7
F6H6	291.62[c]	305.0 ± 0.3	13.4
F6H8	324.83[c]	337.0 ± 0.2	12.1
F10H8	n/a	444.4 ± 2.4	n/a
F8H18	n/a	553.5 ± 1.2	n/a

[a] Ref 36. [b] Ref 40. [c] Ref 19.

a measure of the contribution of this junction to the partial molal volume. The values for $\bar{V}^0_{exp} - \bar{V}^0_{calc}$ are found to be as follows: 2.1 cm^3·mol^{-1} for F6H6, 1.9 cm^3·mol^{-1} for F6H8, 7.6 cm^3·mol^{-1} for F10H8, and 6.7 cm^3·mol^{-1} for F8H18. The experimental partial molal volumes of all studied perfluororalkylalkanes are thus larger than the calculated ones, that is, the CH$_2$−CF$_2$ junction seems to contribute positively to the partial molal volume. Although these values should be regarded with some caution, given the experimental uncertainties involved, these contributions are not constant and seem to correlate with the length of the perfluoroalkyl segment.

Discussion

As previously stated, perfluoroalkylalkanes can be considered as being formed by joining together two alkyl and perfluoroalkyl segments. The same strategy was used to model the perfluoroalkylalkanes with the hetero-SAFT-VR 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 ($m_A = 1 + ((C - 1)/3)$)[39] and perfluoroalkanes ($m_{PFA} = 1 + ((C - 1)*0.37)$),[39]

TABLE 4: Hetero-SAFT-VR Parameters for the Molecules and Molecular Segments Studied

substance/segment	m	λ	σ /Å	ϵ/k /K	reference
C$_6$H$_{13}$−	2.33	1.552	3.920	250.4	26
C$_8$H$_{18}$	3.33	1.574	3.945	250.3	26
C$_8$H$_{17}$−	3.00	1.574	3.945	250.3	26
C$_{18}$H$_{37}$−	6.33	1.653	3.941	230.2	41
C$_5$F$_{12}$	2.48	1.421	4.469	282.0	27
C$_6$F$_{14}$	2.85	1.432	4.456	283.0	42
C$_6$F$_{13}$−	2.54	1.432	4.456	283.0	42
C$_8$F$_{18}$	3.59	1.462	4.472	274.0	27
C$_8$F$_{17}$−	3.28	1.462	4.472	274.0	27
C$_9$F$_{20}$	3.96	1.461	4.486	278.6	this work[a]
C$_{10}$F$_{20}$−	4.02	1.466	4.489	278.1	this work[a]

[a] Extrapolated according to the procedure described in ref 41, using the parameters for perfluoroalkanes available in the references cited in the table.

it can be easily demonstrated that $m(CH_3) = 0.665$, $m(CH_2) = 0.333$, $m(CF_3) = 0.685$, and $m(CF_2) = 0.370$. From these contributions, the number of segments m of each type necessary to build up all of the studied perfluoroalkylalkanes were calculated. In order to develop a truly predictive approach, the remaining potential model parameters (ϵ, σ, and λ) for the alkyl and perfluoroalkyl chains were taken from earlier work on the alkanes and perfluoroalkanes. For example, the hexyl and octadecyl segments were modeled using the square-well parameters for hexane and octadecane, respectively, and the perfluorohexyl and perfluorodecyl segments were described using the perfluorohexane and perfluorodecane parameters. All of the model parameters are summarized in Table 4.

Finally, to describe the inter- and intramolecular interactions between hydrogenated and perfluorinated segments, it is necessary to include the binary interaction parameters ξ_{ij} and γ_{ij} given in eqs 3 and 4 to account for deviations from the Lorentz−Berthelot combining rules. In previous work,[19] values of ξ_{ij} and γ_{ij} fitted to the UCST and excess volumes of hexane +

Solution Behavior of PA and PFAA in *n*-Octane

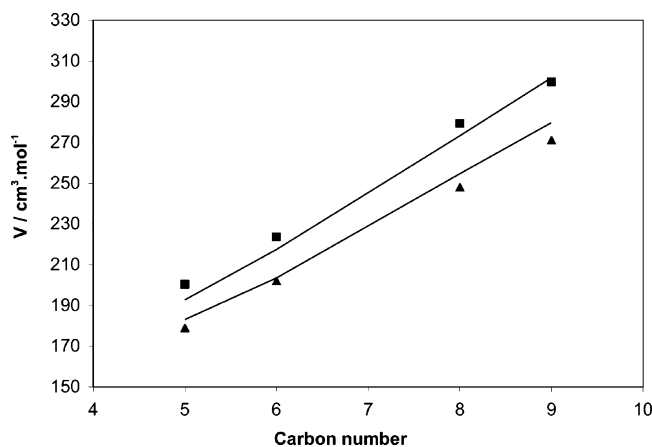*J. Phys. Chem. C, Vol. 111, No. 43, 2007* **15967**

Figure 1. Experimental and theoretical molar and partial molal volumes at infinite dilution (in *n*-octane at 25 °C) of the studied perfluoroalkanes. The triangles represent experimental molar volumes, the squares experimental partial molal volumes, and the lines the hetero-SAFT-VR predictions.
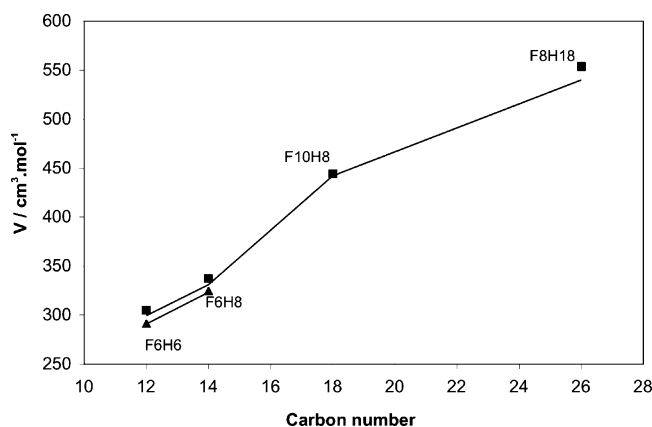

Figure 2. Experimental and theoretical molar and partial molal volumes at infinite dilution (in *n*-octane at 25 °C) of the studied perfluoroalkylalkanes. The triangles represent experimental molar volumes, the squares experimental partial molal volumes, and the lines the hetero-SAFT-VR predictions.

perfluorohexane mixtures[27] ($\xi_{ij} = 0.840$ and $\gamma_{ij} = 1.0451$) were used to successfully predict the liquid density of pure perfluoroalkylalkanes as a function of temperature and pressure. The same binary interaction parameters were used in this work.

The results of the hetero-SAFT-VR predictions for the molar volumes and partial molal volumes at infinite dilution of the *n*-perfluoroalkanes studied are plotted in Figure 1 along with the corresponding experimental results. As can be seen, the theoretical results slightly over predict the experimental molar volumes and under predict the partial molal volumes at infinite dilution, but the overall agreement can be considered quite good. The differences between the experimental and the theoretical results are less than 3% in all cases.

The hetero-SAFT-VR predictions for the molar volumes and partial molal volumes at infinite dilution of the perfluoroalkylalkanes studied in this work are plotted in Figure 2 along with the corresponding experimental results. As can be seen from the figure, the theoretical results almost quantitatively predict both the experimental molar volumes (of the perfluoroalkylalkanes that are liquid at 298 K) and the partial molal volumes at infinite dilution. The differences between the experimental and the theoretical results lie between 0.3 and 1.8%, except in the case of F8H18 where this difference is 2.5%. This can indeed be considered a remarkable result. It should again be emphasized that the theoretical results are true predictions. No parameters

were fitted to experimental data for the pure fluids or mixtures being studied.

Conclusions

Partial molar volumes at infinite dilution of four perfluoroalkanes (perfluoropentane, perfluorohexane, perfluorooctane, and perfluorononane) and four perfluoroalkylalkanes (F6H6, F6H8, F8H18, and F10H8) in *n*-octane have been measured at 298.15 K. The results indicate that the contribution of the CH_2-CF_2 junction to the partial molal volume is positive and becomes larger as the length of the fluorinated segment increases. The results were interpreted using the hetero-SAFT-VR equation of state as applied to mixtures. The perfluoroalkylalkanes were modeled as heterosegmented diblock chains, and the model parameters for the alkyl and perfluoroalkyl segments, as well as the unlike binary interaction parameters, were taken from earlier work. The theory is able to accurately predict the experimental results without fitting any parameters to experimental data.

References and Notes

(1) Turberg, M. P.; Brady, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 7797.
(2) Binks, B. P.; Fletcher, P. D. I.; Kotsev, S. N.; Thompson, R. L. *Langmuir* **1997**, *13*, 6669.
(3) Mahler, W.; Guillon, D.; Skoulios, A. *Mol. Cryst. Liq. Cryst. Lett.* **1985**, *2*, 111.
(4) Viney, C.; Russell, T. P.; Depero, L. E.; Twieg, R. J. *Mol. Cryst. Liq. Cryst.* **1989**, *168*, 63.
(5) Viney, C.; Twieg, R. J.; Russell, T. P.; Depero, L. E. *Liq. Cryst.* **1989**, *5*, 1783.
(6) Maaloum, M.; Muller, P.; Krafft, M. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 4331.
(7) Simões Gamboa, A. L.; Filipe, E. J. M.; Brogueira, P. *Nano Lett.* **2002**, *2*, 1083.
(8) Rabolt, J. F.; Russell, T. P.; Twieg, R. J. *Macromolecules* **1984**, *17*, 2786.
(9) Russell, T. P.; Rabolt, J. F.; Twieg, R. J.; Siemens, R. L.; Farmer, B. L. *Macromolecules* **1986**, *19*, 1135.
(10) Höpken, J.; Möller, M. *Macromolecules* **1992**, *25*, 2482.
(11) Marczuk, P.; Lang, P. *Macromolecules* **1998**, *31*, 9013.
(12) Krafft, M. *Adv. Drug Delivery Rev.* **2001**, *47*, 209.
(13) Reiss J. G. *Fluorine Chemistry at the New Millenium-Fascinated by Fluorine*; Banks, R. E., Ed.; Elsevier: Amsterdam, The Netherlands, 2000; pp 385−431.
(14) May, G. *Chem. Br.* **1997**, *33*, 34.
(15) Scott, R. L. *J. Phys. Chem.* **1958**, *62*, 136.
(16) Song, W.; Rossky, P. J.; Maroncelli, M. *J. Chem. Phys.* **2003**, *119*, 9145.
(17) de Loos, T. W.; Poot, W. *Int. J. Thermophys.* **1998**, *19*, 637.
(18) Tochigi, K.; Satou, T.; Kurihara, K.; Ochi, K.; Yamamoto, H.; Mochizuki, Y.; Sako, T. *J. Chem. Eng. Data* **2001**, *46*, 913.
(19) Morgado, P.; Zhao, H.; Blas, F. J.; McCabe, C.; Rebelo, L. P. N.; Filipe, E. J. M. *J. Phys. Chem. B* **2007**, *111*, 2856.

(20) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. *Fluid Phase Equilib.* **1989,** *52,* 31.

(21) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709.

(22) Economou, I. G. *Ind. Eng. Chem. Res.* **2002**, *41*, 953.

(23) Gil-Villegas, A.; Galindo, A.; Whitehead, P. J.; Mills, S. J.; Jackson, G.; Burgess, A. N. *J. Chem. Phys.* **1997**, *106*, 4168.

(24) Galindo, A.; Davies, L. A.; Gil-Villegas, A.; Jackson, G. *Mol. Phys.* **1998**, *93*, 241.

(25) Zhao, H.; McCabe, C. *J. Chem. Phys.* **2006**, *125*, 4504.

(26) McCabe, C.; Galindo, A.; Gil-Villegas, A.; Jackson, G. *J. Phys. Chem. B* **1998**, *102*, 8060.

(27) Morgado, P.; McCabe, C.; Filipe, E. J. M. *Fluid Phase Equilib.* **2005**, *228*, 389.

(28) McCabe, C.; Gil-Villegas, A.; Jackson, G.; Del Rio, F. *Mol. Phys.* **1999**, *97*, 551.

(29) Peng, Y.; Zhao, H.; McCabe, C. *Mol. Phys.* **2006**, *104*, 571.

(30) Rabolt, J. F.; Russell, T. P.; Twieg, R. J. *Macromolecules* **1984**, *17*, 2786.

(31) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*, 3rd ed.; Butterworth Scientific: London, 1982.

(32) Leonard, P. J.; Henderson, D.; Barker, J. A. *Trans. Faraday Soc.* **1970**, *66*, 2439.

(33) Boublik, T. *J. Chem. Phys.* **1970**, *53*, 471.

(34) Mansoori, G. A.; Carnahan, N. F.; Starling, K. E.; Leland, T. W. *J. Chem. Phys.* **1971**, *54*, 1523.

(35) Carnahan, N. F.; Starling, K. E. *J. Chem. Phys.* **1969**, *51*, 635.

(36) Lepori, L.; Matteoli, E.; Spanedda, A.; Duce, C; Tiné, M. R. *Fluid Phase Equilib.* **2002**, *201*, 119.

(37) Itsuki, H.; Terasawa, S.; Shinohara, K.; Ikezawa, H. *J. Chem. Thermodyn.* **1987**, *19*, 555.

(38) Barbosa, E. F. G.; Lampreia, I. M. S. *Can. J. Chem.* **1986**, *64*, 387.

(39) Archer, A. L.; Amos, M. D.; Jackson, G.; McLure, I. A. *Int. J. Thermophys*. **1996**, *17*, 201.

(40) Dias, A. M. A.; Gonçalves, C. M. B.; Caço, A. I.; Santos, L. M. N. B. F.; Piñeiro, M. M.; Vega, L. F.; Coutinho, J. A. P.; Marrucho, I. M. *J. Chem. Eng. Data* **2005**, *50*, 1328.

(41) McCabe, C.; Jackson, G. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2057.

(42) Bonifácio, R. P.; Filipe, E. J. M.; McCabe, C.; Gomes, M. F. C.; Padua, A. A. H. *Mol. Phys.* **2002**, *100*, 2547.