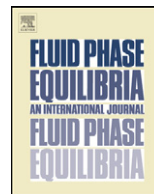




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Perfluoroalkanes and perfluoroalkylalkane surfactants in solution: Partial molar volumes in *n*-octane and hetero-SAFT-VR modelling

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ABSTRACT

Partial molar volumes at infinite dilution have been obtained for 3 perfluoroalkylalkanes (PFAA) in *n*-octane at 298.15 K from experimental apparent molal volumes. The results were interpreted estimating the contributions of the hydrogenated and perfluorinated segments to the partial molar volume. For this reason, partial molar volumes at infinite dilution for 3 perfluoroalkanes (PFA) in *n*-octane at 298.15 K have also been obtained. The results were further interpreted using the hetero-SAFT-VR equation of state, which models the perfluoroalkylalkanes as heterosegmented di-block chains. The cross interactions, both intra and intermolecular, were characterised using parameters developed in earlier studies for (alkane + perfluoroalkane) mixtures: the calculations are thus fully predictive. The theory is able to accurately predict the volumetric behaviour of the solutions of perfluoroalkylalkanes, without fitting to any experimental data.

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1. Introduction

Perfluoroalkylalkanes (PFAA, also known as semifluorinated alkanes) are very interesting molecules made of hydrogenated segments and perfluorinated segments covalently bonded to form single linear chains. Mixtures of alkanes and perfluoroalkanes, however, are well known to be highly non-ideal, in spite of their structural similarity. As a result, PFAA are amphiphilic molecules: however, unlike common hydrophilic–hydrophobic surfactants, the amphiphilicity of PFAA, and consequently their potential for self-organization, results from a subtle balance of weak and *even weaker* dispersion forces. This has led to PFAA sometimes being called *primitive surfactants*. Aggregation of PFAA in solvents selective for one of the chains [1,2], the observation of smectic liquid crystalline phases [3–5], and 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].

In addition to the interest in PFAAs because of their amphiphilic nature, PFAA have become important in a number of medical applications because of their inertness, biocompatibility and ability to solubilize high levels of respiratory gases (characteristic of fluorinated solvents). For example, PFAAs find application as components of liquid ventilation solvents and temporary blood substitute for-

mulations [12,13], as fluids used in eye surgery and in the treatment of burns [14].

This work is part of a systematic study of the thermophysical properties of PFAA, either pure or mixed with other substances, which is essential to develop reliable theoretical models for these interesting molecules. A number of properties, including vapour pressures, viscosities [15] and surface tensions as a function of temperature, liquid densities as a function of temperature and pressure [16,17], water solubility in PFAA and partial molar volumes at infinite dilution of PFAA in *n*-octane [18], have already been measured. In this work, partial molar volumes at infinite dilution for three liquid PFAAs (perfluorobutylpentane, perfluorobutylhexane and perfluorobutyloctane, in short F4H5, F4H6 and F4H8) in *n*-octane were experimentally determined. The substances were chosen so that the influence of the hydrogenated segment length could be evaluated. The new results, combined with previous work on F6H6, F6H8, F10H8 and F8H18 provide a much broader picture of the solution behaviour of these substances in *n*-alkanes. Furthermore, in previous work, we interpreted the solution results in terms of the individual contributions to the partial molar volume at infinite dilution of the fluorinated and hydrogenated segments. These were calculated from the experimentally determined partial molar volumes at infinite dilution of several PFA in *n*-octane and from the equivalent quantities for *n*-alkanes found in the literature: however, given the large uncertainties associated with the group contributions to the partial molar volume at infinite dilution of the fluorinated segments, the comparison was rather inconclusive. We have, therefore, also obtained

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new experimental data for the partial molar volumes at infinite dilution of several perfluoroalkanes (PFA) (*n*-perfluorohexane, *n*-perfluorooctane and *n*-perfluorononane, in short F6, F8 and F9) in *n*-octane, with the purpose of reducing this uncertainty. This objective could be achieved expanding the composition range of the studied solutions, while keeping them low enough to be considered dilute.

As in previous work, the results have again been interpreted using a hetero-segmented version of the SAFT-VR equation [19,20] that describes a chain molecule composed of two different types of segments, allowing the perfluoroalkylalkanes to be modelled as di-block chains. In this way, the work is similar to the group-contribution based SAFT approaches, SAFT- γ [21] and GC-SAFT-VR [22], but much simpler since only two different types of segments are considered. The parameters for the alkyl and perfluoroalkyl segments were determined in earlier work from those for the alkanes, perfluoroalkanes and their cross interactions. The approach is, thus, fully predictive. The theory is found to accurately describe the experimental results both for the solutions of perfluoroalkanes and for the solutions of perfluoroalkylalkanes, without fitting to experimental data.

2. Experimental

The perfluorobutylpentane (F4H5), perfluorobutylhexane (F4H6) and perfluorobutylheptane (F4H7) used were ultra-purified chemicals obtained from Fluoron GmbH, with a claimed purity of 100%; ^{19}F and ^1H NMR spectra of these samples were obtained in a 500 MHz Bruker spectrometer and only very small unexpected peaks were found which gave relative integrated values smaller than 1%. *n*-Perfluorohexane and *n*-perfluorooctane were supplied by Sigma–Aldrich, with 99% and 98% stated purities, respectively; *n*-perfluorononane (99%) was supplied by Apollo Scientific. The *n*-octane (*puriss p.a. grade*, $\geq 99\%$) was obtained from Sigma–Aldrich. All compounds were used as received, without further purification. Solutions were prepared by weight in 4 ml screw-cap vials, taking care to leave the minimum possible free volume in order to reduce errors in composition due to differential evaporation. The density measurements 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 the literature values was found to be less than $\pm 0.00002 \text{ g cm}^{-3}$. The density of air was verified at the beginning of each series of measurements to ensure the cleanliness of the measurement cell.

3. Model and theory

In the SAFT-VR approach molecules are modelled 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,

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

where σ_{ij} is the diameter of the interaction, λ_{ij} is the range and ε_{ij} is 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 molecules studied are given in Table 4 and discussed further in Section 4. The inter- and intra-molecular cross interactions between segments

are obtained from the modified Lorentz–Berthelot combining rules [23]

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

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

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

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

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

We will briefly present each contribution in turn for a non-associating binary mixture in which one of the components is a diblock-heteronuclear chain molecule and direct the reader to the original references for full details of the hetero-SAFT-VR approach [19,20].

The ideal contribution to the Helmholtz energy is expressed as:

$$\frac{A^{ideal}}{NkT} = \sum_{i=1}^n x_i \ln(\rho_i \Lambda_i^3) - 1 \quad (6)$$

where $\rho_i = N_i/V$ the number density, Λ_i is the thermal de Broglie wavelength of species i and x_i is the mole fraction of component i .

The monomer Helmholtz energy is given by,

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

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^M is the Helmholtz 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 [24], viz

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

where $\beta = 1/kT$, a^{HS} is the Helmholtz energy of the hard sphere reference fluid and a_1 and a_2 are the first and second perturbation terms respectively. a^{HS} is determined from the expression of Boublik [25] and Mansoori et al. [26] for multicomponent hard sphere systems, while a_1 is obtained from mean-value theorem as proposed by Gil-Villegas et al. [27], a_2 is obtained through the local compressibility approximation

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

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

$$\frac{A^{chain}}{NkT} = - \sum_{ij \text{ bonds}} \ln y_{ij}^{SW}(\sigma_{ij}) \quad (10)$$

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

$$y_{ij}^{SW}(\sigma_{ij}) = \exp(-\beta\varepsilon_{ij})g_{ij}^{SW}(\sigma_{ij}) \quad (11)$$

For the binary mixture of an alkane and a perfluoroalkylalkane as studied in this work Eq. (10) becomes,

$$\frac{A^{chain}}{NkT} = -(m_1 - 1) \ln y_{11}^{SW}(\sigma_{11}) - (m_2 - 1) \ln y_{22}^{SW}(\sigma_{22}) - \ln y_{23}^{SW}(\sigma_{23}) - (m_3 - 1) \ln y_{33}^{SW}(\sigma_{33}) \quad (12)$$

Table 1
Empirical parameters of the equation $d = A + Bc + Cc^2$, for perfluoroalkanes and perfluoroalkylalkanes in *n*-octane at 298.15 K.

Substance	A	B	C	Std ^a /g cm ⁻³	<i>d</i> (<i>n</i> -octane)/g cm ⁻³
F6	0.698785	0.124162	-0.0180691	1.3×10^{-4}	0.698807
F8	0.698736	0.169826	-0.0288533	3.1×10^{-5}	0.698810
F9	0.698845	0.189885	-0.0301154	2.2×10^{-5}	0.698808
F4H5	0.698821	0.088359	-0.0119855	3.5×10^{-6}	0.698814
F4H6	0.698788	0.091077	-0.0163804	1.9×10^{-5}	0.698818
F4H8	0.698849	0.093775	-0.0143612	7.9×10^{-6}	0.698802

^a $Std = \sqrt{\sum (d_{fit} - d_{exp})^2 / (N - 3)}$, where d_{exp} and d_{fit} are the experimental and fitted densities and N is the number of data points.

where component one refers to the alkane solvent, two to the alkyl-segments and three to the perfluoroalkyl-segments of the perfluoroalkylalkane 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:

$$g_{ij}^{SW}(\sigma_{ij}; \zeta_3) = g_{ij}^{HS}(\sigma_{ij}; \zeta_3) + \beta \varepsilon_{ij} g_1^{SW}(\sigma_{ij}) \quad (13)$$

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 and $g_1^{SW}(\sigma_{ij})$ is determined from the Clausius virial theorem and the first derivative of the Helmholtz energy with respect to the density. This model has been used to make predictions for the phase behaviour perfluoroalkylalkane surfactants and their mixtures with alkanes and perfluoroalkanes [16,28,29].

4. Results

The partial molar volume at infinite dilution of the three PFAAs (F4H5, F4H6 and F4H8) and three PFAs (F6, F8 and F9) in *n*-octane, have been measured. The experimental density for each of the studied solutions (~10 per solute) in *n*-octane, were fitted to equations of the type

$$d = A + B \cdot c + C \cdot c^2 \quad (14)$$

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 experimental densities for pure *n*-octane, $d(n\text{-octane})$, in each series of measurements.

The apparent molal volumes, V_ϕ , of the solutes in all solutions were calculated with the usual equation, which results from the definition of apparent molal volume [30],

$$V_\phi = \frac{MPd^0 - MPd}{pd^0} + \frac{M}{d} \quad (15)$$

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

The partial molar volumes at infinite dilution \bar{V}^0 of the solutes are normally obtained by linear extrapolation of V_ϕ to infinite dilution by a least squares fitting method. In this work, however, we have found that the apparent molal volumes are, within experimental uncertainty, constant over the composition range studied. The reported partial molar volumes at infinite dilution are, thus, the average value of all the determined apparent molal volumes.

The results are plotted in Fig. 1 as a function of the solute chain length, and summarized in Table 3 along with the molar volumes for the pure substances (V^0) and the excess partial molar volumes at infinite dilution, calculated as $\Delta \bar{V} = \bar{V}^0 - V^0$. As previously noted, all studied substances have positive ΔV 's. In the case of the *n*-perfluoroalkanes the increase of volume is of the order of 12.5%. In the case of perfluoroalkylalkanes the excess partial molar volumes are also positive, varying between 2.5 and 4.5%; the relative increase correlates linearly with the proportion of fluorinated carbons (Fig. 2). It is also interesting to note that this correlation, when extrapolated to a fully fluorinated molecule, reproduces the more than 10% increase found experimentally for the *n*-perfluoroalkanes.

Lepori et al. [31] have determined partial molar volumes for several perfluoroalkanes in alkanes and vice versa. The only sys-

Table 2
Apparent molal volumes in *n*-octane of the perfluoroalkanes and perfluoroalkylalkanes studied at 298.15 K.

<i>c</i> /mol kg ⁻¹	V_ϕ /cm ³ mol ⁻¹	<i>c</i> /mol kg ⁻¹	V_ϕ /cm ³ mol ⁻¹	<i>c</i> /mol kg ⁻¹	V_ϕ /cm ³ mol ⁻¹
Perfluorohexane		Perfluorononane		F4H6	
0.0880	229.4	0.0532	306.9	0.0465	249.6
0.1035	231.2	0.0565	307.0	0.0608	250.1
0.1310	229.3	0.0714	307.3	0.0703	249.8
0.1624	227.8	0.0832	306.7	0.1003	249.8
0.1833	229.2	0.1105	307.0	0.1403	249.8
0.2156	229.9	0.1219	306.2	0.1663	249.3
0.2594	227.6	0.1488	305.8	0.1689	249.2
0.2680	230.8	0.1513	306.5	0.2127	249.7
0.3040	228.8				
0.3424	228.5	0.0527	233.8	0.0685	281.6
0.3621	230.0	0.0601	233.7	0.0996	281.5
0.4051	228.8	0.0947	233.7	0.1061	281.7
Perfluorooctane		F4H5		F4H8	
		0.1337	233.7	0.1259	281.5
0.0362	282.2	0.1437	233.6	0.1271	281.7
0.0617	281.6	0.1755	233.4	0.1522	281.8
0.0923	279.8	0.1914	233.4	0.1885	281.5
0.1157	280.3	0.2141	233.4	0.2032	281.5
0.1445	279.2				
0.1585	278.6				
0.1808	278.4				
0.2115	278.8				

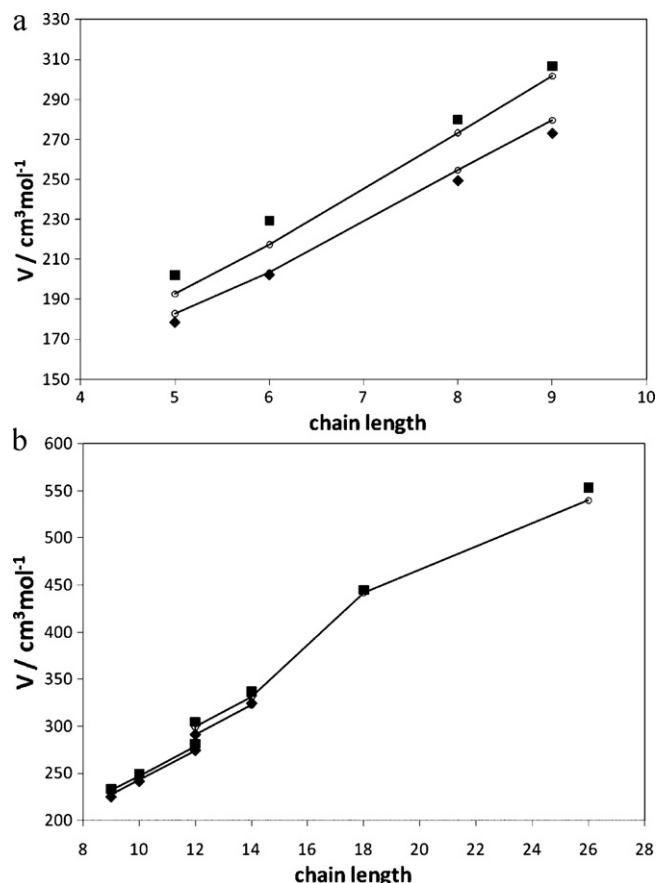


Fig. 1. Experimental and theoretical molar and partial molar volumes at infinite dilution in *n*-octane at 298.15 K of (a) perfluoroalkanes and (b) perfluoroalkylalkanes. The diamonds represent experimental molar volumes, the squares experimental partial molar volumes and the open circles, connected with lines, the SAFT-VR (a) and hetero-SAFT-VR (b) predictions.

tem in common with the present work is *n*-perfluorohexane in *n*-octane. Their reported value for the partial molar volume compares favourably with the value determined in this work.

As in the previous work [18], the contributions to the partial molar volume at infinite dilution from the CF_2 and CF_3 groups have been estimated from the linear dependence of the partial molar volume at infinite dilution with the number of carbon atoms for the studied *n*-perfluoroalkanes in *n*-octane. A least-squares regression of the form $\bar{V}^0 = a + b(n_C - 2)$, where a and b are empirical parameters and n_C is the number of carbon atoms, was made. In this form,

Table 3

Experimental molar volumes, partial molar volumes at infinite dilution and excess partial molar volumes in *n*-octane at 298.15 K.

Substance	$V^0 / \text{cm}^3 \text{mol}^{-1}$	$\bar{V}^0 / \text{cm}^3 \text{mol}^{-1}$	$\Delta \bar{V} / \text{cm}^3 \text{mol}^{-1}$
F5	178.63 ^a	202.0 ± 2.5^b	23.4
F6	202.40 ^a	229.3 ± 1.1^c	26.9
F8	249.50 ^a	279.9 ± 1.4^c	30.4
F9	273.12 ^a	306.7 ± 0.5^c	33.6
F4H5	225.47 ^a	233.6 ± 0.2^c	8.1
F4H6	241.88 ^a	249.7 ± 0.3^c	7.8
F4H8	274.80 ^a	281.6 ± 0.1^c	6.8
F6H6	291.62 ^d	304.6 ± 0.4^b	13.0
F6H8	324.83 ^d	336.8 ± 0.2^b	11.9
F8H18	n/a	553.5 ± 1.7^b	n/a
F10H8	n/a	444.7 ± 3.7^b	n/a

^a Ref. [17].

^b Calculated as the average value of all determinations from the data in Ref. [18].

^c This work.

^d Ref. [16].

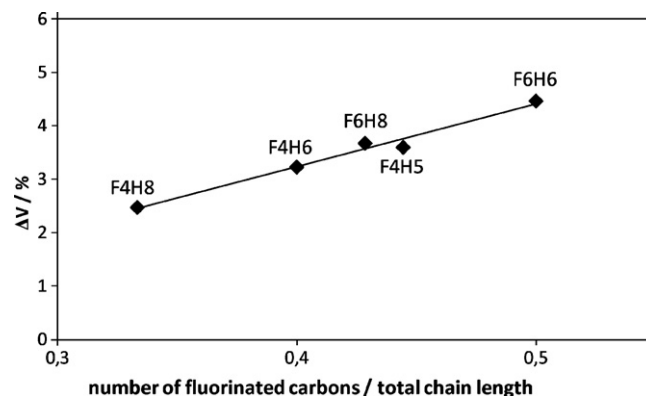


Fig. 2. Relative excess partial molar volume at infinite dilution $((\bar{V}^0 - V^0)/V^0)$ of F4H5, F4H6, F4H8, F6H6 and F6H8 in *n*-octane at 298.15 K, as a function of the fraction of the fluorinated chain.

Table 4

Contributions to the partial molar volume at infinite dilution in *n*-octane at 298.15 K.

Group	$\bar{V}^0 / \text{cm}^3 \text{mol}^{-1}$
CH_2	16.09 ± 0.01
CH_3	33.53 ± 0.04
CF_2	26.0 ± 0.3
CF_3	62.2 ± 0.7

the slope b can be interpreted as the contribution from the perfluoromethylene group (denoted $\bar{V}_{\text{CF}_2}^0$) and the intercept a as the sum of two perfluoromethyl group contributions ($\bar{V}_{\text{CF}_3}^0$). The same procedure was applied to the results of Itsuki et al. [32] for solutions of *n*-alkanes in *n*-octane and the results are reported in Table 4. As can be seen from the table, the uncertainties associated with the contributions of perfluorinated groups, although much lower than those previously reported, are still considerably larger than those for hydrogenated groups. This reflects the lower accuracy of perfluorinated results, which has been noted by other authors studying solutions involving perfluorinated compounds [33].

Using these group contributions, we have calculated the \bar{V}^0 's for the PFAAs studied in this work and of those previously investigated. It should be stressed that the deviations from ideal solution behaviour of the hydrogenated and perfluorinated segments in *n*-octane are included in the contributions, but the scheme "ignores" the existence of the $-(\text{CH}_2)-(\text{CF}_2)$ junction. Any differences between the experimental and the calculated partial molar volumes at infinite dilution, $\bar{V}_{\text{exp}}^0 - \bar{V}_{\text{calc}}^0$, should, thus, be a measure of the contribution of this junction to the partial molar volume. The results are shown in Table 5 and plotted in Fig. 3. As can be seen from the figure, the contribution of the CH_2-CF_2 junction to the partial molar volume is not significantly affected by the increase in the hydrogenated segment chain length, but decreases considerably as the perfluorinated segment chain length increases. The results distinctly divide into three groups according to the chain length of the

Table 5

Experimental and calculated partial molar volumes at infinite dilution of the perfluoroalkylalkanes studied in *n*-octane at 298.15 K.

Substance	$\bar{V}_{\text{exp}}^0 / \text{cm}^3 \text{mol}^{-1}$	$\bar{V}_{\text{calc}}^0 / \text{cm}^3 \text{mol}^{-1}$	$\bar{V}_{\text{exp}}^0 - \bar{V}_{\text{calc}}^0 / \text{cm}^3 \text{mol}^{-1}$
F4H5	233.6 ± 0.2	238.1	-4.5
F4H6	249.7 ± 0.3	254.2	-4.5
F4H8	281.6 ± 0.1	286.4	-4.8
F6H6	304.6 ± 0.4	306.2	-1.5
F6H8	336.8 ± 0.2	338.3	-1.6
F8H18	553.5 ± 1.7	551.2	2.3
F10H8	444.7 ± 3.7	442.3	2.4

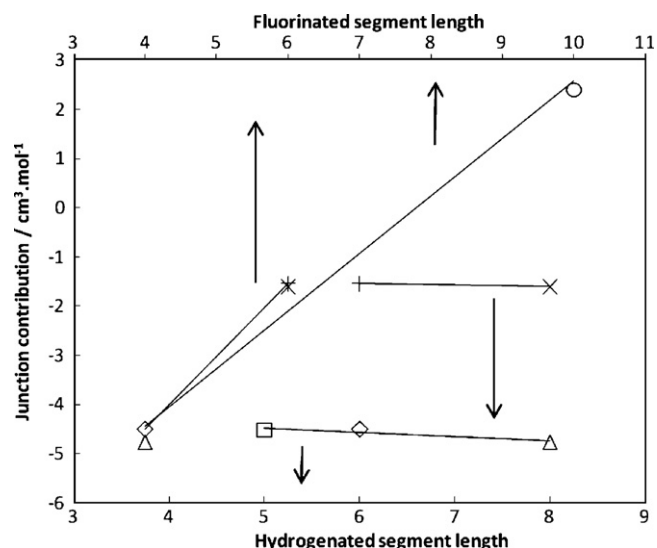


Fig. 3. Contribution of the $\text{CF}_2\text{-CH}_2$ junction to the partial molar volume at infinite dilution of PFAA in *n*-octane at 298.15 K, as a function of either segment length. The symbols are as follows: F4H5 (\square), F4H6 (\diamond), F4H8 (\triangle), F6H6 (+), F6H8 (\times), F10H8 (\circ).

fluorinated segment, F4, F6 and $F \geq 8$. The presence of the junction appears to contribute negatively to the partial molar volume in the case of F4 and F6, but positively for F8 and F10. In spite of the large experimental uncertainties involved in these calculated volumes, these conclusions seem to be well established.

5. Discussion

As previously stated, perfluoroalkylalkanes can be considered as being formed by joining together an alkyl and a perfluoroalkyl segments. The same strategy was used to model the perfluoroalkylalkanes with the hetero-SAFT-VR approach [19,20].

The number of spherical segments forming the alkyl and perfluoroalkyl chains was determined using established expressions [34] that relate the number of segments (m) in the model chain to the number of carbon atoms (C) in both the alkane ($m_A = 1 + ((C - 1)/3)$) and the perfluoroalkane ($m_{PFA} = 1 + ((C - 1) \times 0.37)$) molecules. From these relations 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 m of each type necessary to describe the perfluoroalkylalkanes studied can be calculated. In order to develop a truly predictive approach, the square-well parameters ϵ , σ and λ , for the alkyl and perfluoroalkyl chains were taken from earlier work on the alkanes and perfluoroalkanes. For example, the pentyl and octyl segments were modelled using the square-well parameters for pentane and octane, respectively, and the perfluorobutyl and perfluorohexyl segments were described using the perfluorobutane and perfluorohexane parameters. All the model parameters are summarized in Table 6.

Finally, to describe the inter- and intra-molecular interactions between hydrogenated and perfluorinated segments, it is necessary to include the binary interaction parameters ξ_{ij} and γ_{ij} in Eqs. (3) and (4), to account for deviations from the Lorentz–Berthelot combining rules. In previous work [16], values of ξ_{ij} and γ_{ij} fitted [35] to the UCST and excess volumes of (hexane + perfluorohexane) mixtures ($\xi_{ij} = 0.840$ 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 SAFT-VR predictions for the molar volumes and partial molar volumes at infinite dilution of the

Table 6

Hetero-SAFT-VR parameters for the molecules and molecular segments studied.

Substance/segment	m	λ	$\sigma/\text{\AA}$	$\epsilon/k/K$	Reference
C_5H_{11} –	2.00	1.505	3.931	265.0	[36]
C_6H_{13} –	2.33	1.552	3.920	250.4	[36]
C_8H_{18} –	3.33	1.574	3.945	250.3	[36]
C_8H_{17} –	3.00	1.574	3.945	250.3	[36]
$\text{C}_{18}\text{H}_{37}$ –	6.33	1.653	3.941	230.2	[37]
C_4F_9 –	1.80	1.406	4.462	283.3	[36]
C_5F_{12} –	2.48	1.421	4.469	282.0	[35]
C_6F_{14} –	2.85	1.432	4.456	283.0	[38]
C_6F_{13} –	2.54	1.432	4.456	283.0	[38]
C_8F_{18} –	3.59	1.462	4.472	274.0	[35]
C_8F_{17} –	3.28	1.462	4.472	274.0	[35]
C_9F_{20} –	3.96	1.461	4.486	278.6	[18]
$\text{C}_{10}\text{F}_{20}$ –	4.02	1.466	4.489	278.1	[18]

n-perfluoroalkanes studied are presented in Fig. 1a along with the corresponding experimental results. As can be seen from the figure, the theoretical results slightly over predict the experimental molar volumes and under predict the partial molar volumes at infinite dilution; however, the overall agreement can be considered quite good given that this is a purely predictive approach and the differences between the experimental and the theoretical results are less than 5% in all cases.

The hetero-SAFT-VR predictions for the molar volumes and partial molar volumes at infinite dilution of the perfluoroalkylalkanes studied in this work are plotted in Fig. 1b 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 molar volumes at infinite dilution. The differences between the experimental and the theoretical results lie between 0.1% and 1.8% (except in the case of F8H18 where the difference is slightly higher at 2.5%) and are slightly better than those found for the perfluoroalkanes. This can indeed be considered a remarkable result and 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.

6. Conclusions

New partial molar volumes at infinite dilution for three perfluoroalkanes (perfluorohexane, perfluorooctane and perfluorononane) and three perfluoroalkylalkanes (F4H5, F4H6 and F4H8) in *n*-octane have been measured at 298.15 K. The results indicate that the contribution of the $\text{CH}_2\text{-CF}_2$ junction to the partial molar volume of the PFAA is not affected by the length of the hydrogenated segments, but decreases as the length of the fluorinated segments increases. The results were interpreted using the hetero-SAFT-VR equation of state as applied to mixtures. The perfluoroalkylalkanes were modelled as heterosegmented di-block 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 predict the experimental results without fitting any parameters to experimental data.

List of symbols

U_{ij}	pair potential between component i and j
r	distance between two spherical segments
A	Helmholtz free energy
N	number of molecules or segments
k	Boltzmann's constant
T	temperature
x	mole fraction

V	volume
V_ϕ	apparent molal volume
V^0	molar volume of a pure substance
\bar{V}^0	partial molal volume at infinite dilution
M	molecular weight
m	number of segments in a molecule
P	mass of solvent
p	mass of solute
a^M	Helmholtz free energy per monomer segment
a^{HS}	Helmholtz energy of the hard sphere reference fluid
β	inverse of the temperature
a_1	first-order perturbation term
a_2	second-order perturbation term
K^{HS}	isothermal compressibility of the hard-sphere fluid
y_{ij}^{SW}	background correlation function
g_{ij}^{SW}	radial distribution function for the square-well fluid
c	concentration in molality
d	density
d^0	density of pure solvent

Greek letters

σ	hard-core segment diameter
λ	square-well potential range parameter
ε	square-well potential depth parameter
ζ	energy binary interaction parameter
γ	range binary interaction parameter
ρ	number density
Λ	thermal de Broglie wavelength
ζ	reduced density

Superscript letters

<i>ideal</i>	ideal contribution
<i>chain</i>	chain contribution
<i>mono</i>	monomer contribution
<i>assoc</i>	association contribution
<i>HS</i>	hard-sphere
<i>SW</i>	square well

Subscript letters

<i>ij</i>	type of component
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