

Surface Tension of Liquid Fluorocompounds

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This work aims at studying the surface tension of some linear, cyclic, aromatic, and α -substituted perfluorocarbons. Despite its fundamental interest, information about this property for these compounds is scarce, and the available data are old and present strong discrepancies among each other. The measurements were carried out in the temperature range (283 to 327) K with the Du Noüy ring method. The analysis of the experimental data shows that the molecular structure is an important factor in the surface behavior of the studied compounds since the aromatic fluorocompounds present the highest surface tensions, followed by the cyclic and substituted fluorocompounds. The linear *n*-perfluoroalkanes exhibit the lowest surface tension values, slightly increasing with the carbon number. The surface thermodynamic functions such as surface entropy and enthalpy were derived from surface tension values and are also reported. The experimental data were compared against the Faizullin correlation, and it is shown that this correlation describes the measured surface tensions with deviations inferior to 4 %.

Introduction

Highly fluorinated molecules such as perfluorocarbons (PFCs) and their substituted homologues are nonpolar compounds that, as a result of their strong intramolecular bonding and weak intermolecular interactions, are chemically and biochemically inert.¹ Their atypical physicochemical properties lead to interesting and valuable applications in innumerable fields such as surfactants in supercritical solvents, substitutes for chlorinated solvents, environmental probes to determine the exchanges between the atmosphere and natural waters, anticorrosive and antifriction components, flame retardants, and water repellents. It is, however, in the biomedical field that the most relevant applications are found. Fluorocarbons (FCs) can be used in tissue oxygenation fluids as blood substitutes, anti-tumoral agents, perfusates for isolated organs, gas carriers in eye surgery, diagnostic imaging agents, lubrication and cushioning for articular disorders, cell culture media, and drug delivery systems.^{2–6}

Many engineering applications in the chemical process industry, such as the mass-transfer operations such as distillation, extraction, absorption, and adsorption, require surface tension data. Taking into account that FCs can dissolve large volumes of gases such as carbon dioxide² and oxygen,^{3,4} the FCs interfacial properties are particularly important as they determine the mass-transfer enhancement in gas–liquid–liquid systems.^{7,8} Usually, the addition of FCs in a process aims at enhancing the mass transfer from the gas to the aqueous phase, and thus the interfacial properties of FCs clearly play a vital role. For example, the low surface tension of FCs is directly responsible for the excellent performance of FCs in liquid-assisted ventilation.⁹

Surface tension is equivalent to the surface free energy, and it is related to the difference between the intermolecular interaction in the bulk and at the surface, accounting for the molecular ordering and structuring of the surface. Although some surface and interfacial tension data can be found in the literature

for FC systems, the majority are old and present discrepancies among different authors.^{10–19} Due to the lack of reliable experimental information and the availability of high-purity compounds nowadays, surface tension measurements were carried out as a function of temperature for linear, cyclic, aromatic, and α -substituted FCs.

In this work, a correlation previously proposed by Faizullin²⁰ for the surface tension, using the vaporization enthalpy and liquid molar volume, was used. A deviation inferior to 4 % was found between the experimental data measured in this work and the proposed correlation.

Experimental Section

Materials. Surface tensions were measured for four *n*-perfluoroalkanes, two cyclic and two aromatic perfluorocompounds, and one α -substituted fluorooctane. The linear 1,1,1,2,2,3,3,4,4,5,5,6,6,6-tetradecafluorohexane, C₆F₁₄ [Chemical Abstracts Service Registry Number (CASRN) 355-42-0]; the 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-octadecafluorooctane, C₈F₁₈ [CASRN 307-34-6]; and the 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-eicosafluorononane, C₉F₂₀ [CASRN 375-96-2], were obtained from Fluorochem with purities verified by gas chromatography (GC) of (99.11, 98.36, and 99.18) wt %, respectively. The 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-hexadecafluoroheptane, C₇F₁₆ [CASRN 335-57-9], was from Apollo Scientific with a purity of 99.92 wt %. The cyclic 1,1,2,2,3,3,4,4,5,5,6-undecafluoro-6-(trifluoromethyl)cyclohexane, C₇F₁₄ [CASRN 355-02-2] was from Apollo Scientific with a purity of 99.98 wt %, and the 1,1,2,2,3,3,4,4,4a,5,5,6,6,7,7,8,8,8a-octadecafluorodecalin, C₁₀F₁₈ [CASRN 306-94-5], was from Flutec with a purity of 99.88 wt %. The aromatic 1,2,3,4,5,6-hexafluorobenzene, C₆F₆ [CASRN 392-56-3], was obtained from Fluorochem and the 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene, C₇F₈ [CASRN 434-64-0], was from Apollo Scientific with purities of 99.99 and 99.90 wt %, respectively. The 1-bromo-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane, C₈F₁₇Br [CASRN 423-55-2], was from Apollo Scientific presenting a purity of 99.90 wt %.

The FCs were used without any further purification, with the exception of C₁₀F₁₈, which was purified by passage through a

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Table 1. Experimental Surface Tension (γ) of Linear Perfluoroalkanes

| C ₆ F ₁₄ | | C ₇ F ₁₆ | | C ₈ F ₁₈ | | C ₉ F ₂₀ | |
|--------------------------------|-----------------------|--------------------------------|-----------------------|--------------------------------|-----------------------|--------------------------------|-----------------------|
| T | $\gamma \pm \sigma^a$ |
| K | mN·m ⁻¹ |
| 283.15 | 14.13 ± 0.06 | 289.05 | 14.46 ± 0.02 | 288.05 | 15.39 ± 0.05 | 287.15 | 16.32 ± 0.06 |
| 288.15 | 13.44 ± 0.04 | 293.25 | 14.09 ± 0.04 | 293.15 | 14.92 ± 0.04 | 292.75 | 15.82 ± 0.03 |
| 293.15 | 12.97 ± 0.06 | 298.25 | 13.55 ± 0.03 | 298.35 | 14.47 ± 0.04 | 298.25 | 15.39 ± 0.04 |
| 298.15 | 12.23 ± 0.04 | 303.45 | 13.04 ± 0.03 | 303.45 | 14.10 ± 0.12 | 303.45 | 14.91 ± 0.02 |
| 303.15 | 11.70 ± 0.06 | 308.45 | 12.62 ± 0.03 | 308.45 | 13.56 ± 0.03 | 308.75 | 14.46 ± 0.06 |
| 308.15 | 11.25 ± 0.01 | 313.45 | 12.17 ± 0.05 | 318.75 | 12.68 ± 0.03 | 313.85 | 13.96 ± 0.03 |
| | | 318.45 | 11.73 ± 0.03 | 323.85 | 12.22 ± 0.05 | 319.15 | 13.51 ± 0.04 |

^a Expanded uncertainty with an approximately 95 % level of confidence.

silica column (ca. 10 times) according to the suggestions from Gaonkar and Newman²¹ and Goebel and Lunkenheimer.²² The initial purity of this compound was 97.75 wt % and after purification was 99.88 wt %, as determined by GC.

Apparatus and Procedures. The purity of each compound was analyzed by GC with a Varian gas chromatograph CP 3800 with a flame ionization detector (FID). Chromatographic separations were accomplished with a Varian CP-Wax 52CB column with an i.d. of 0.53 mm and equipped with Coating WCot fused silica.

The surface tensions of each pure liquid fluorocompound were measured with a NIMA DST 9005 tensiometer from NIMA Technology, Ltd. with a Pt/Ir Du Nouiy ring, based on force measurements, for which it has a precision balance able to measure down to 10⁻⁹ N. The sample surface was cleaned before each measurement by aspiration to remove the surface active impurities present at the interface and to allow the formation of a new interface. The measurements were carried in the temperature range (283 to 327) K and at atmospheric pressure. The liquid under measurement was kept thermostated in a double-jacketed glass cell by means of a water bath, using an HAAKE F6 circulator equipped with a Pt100 probe, immersed in the solution, and able to control temperature within ± 0.01 K.

For each sample at least five sets of three immersion/detachment cycles each were measured, giving a minimum of at least 15 surface tension values, which allow the determination of an average surface tension value for each temperature as well as the expanded associated uncertainty.^{23,24} Further details about the equipment and method can be found elsewhere.²⁵⁻²⁷

Surface Tension versus Vaporization Enthalpy Correlation. Both vaporization and surface formation processes are related to the energy required to break down intermolecular forces existent in a liquid. This suggests that there is a relationship between the vaporization enthalpy ($\Delta_{\text{vap}}H$) and the surface tension of the pure liquid (γ). Analysis of a large amount of experimental data allowed the development of a simple and reliable empirical relationship between these properties as proposed by Faizullin.²⁰ This correlation is here compared against the measured data in this work:

$$\gamma_r = \left(\frac{\Delta_{\text{vap}}H_r}{v_{L_r}} \right)^m \quad (1)$$

where

$$T_r = \frac{T}{T_c} \quad (2)$$

$$\gamma_r = \frac{\gamma}{\gamma_{T_r=0.6}} \quad (3)$$

$$\Delta_{\text{vap}}H_r = \frac{\Delta_{\text{vap}}H}{\Delta_{\text{vap}}H_{T_r=0.6}} \quad (4)$$

$$v_{L_r} = \frac{v_L}{v_{L_{T_r=0.6}}} \quad (5)$$

where γ stands for the surface tension, $\Delta_{\text{vap}}H$ is the vaporization enthalpy, v_L is the liquid molar volume, m is a generalized constant that is equal to 2.15, and T is the temperature. The subscript r and c in eqs 1 to 5 represent the reduced and critical properties, respectively. As can be confirmed from eq 1, this relation does not require fluid-dependent correlation parameters. The only necessary target fluid information is the vaporization enthalpy, the liquid phase molar volume, and the surface tension at the reduced temperature of 0.6. These data may be experimentally available or can be easily estimated from corresponding states relationships.²⁵⁻²⁷

Results and Discussion

Surface Tension Measurements. Previous measurements have confirmed the ability of the above-described equipment to accurately measure interfacial tensions for hydrocarbons, validating the methodology and experimental procedure adopted in this work.²⁵⁻²⁷ The pure liquid densities necessary for the surface tension measurements were taken from Dias et al.^{28,29} Results for the pure, linear, cyclic, aromatic, and substituted FCs are reported in Tables 1 to 3. The measured values of n -perfluoroalkanes surface tensions show that they are strongly dependent on the temperature and only weakly dependent on the carbon number. Also, fluorocarbons present lower surface tensions than the corresponding hydrocarbons, indicating that the van der Waals interactions between fluorinated molecules are usually smaller when compared with the corresponding non-fluorinated molecules. The results obtained are in agreement with other experimental¹⁰⁻¹⁹ and theoretical evidences,¹⁶ which show their high intramolecular and low intermolecular forces and permit their application in a wide variety of fields.

The relative deviations between the experimental data obtained in this work and those reported by other authors¹⁰⁻¹⁶ are presented in Figure 1. A better agreement can be observed at the higher temperatures with the higher deviations appearing at the lower temperatures. These deviations are larger than those found previously for pure and mixed n -alkanes²⁵⁻²⁷ using the same equipment. Note also that large discrepancies exist among the available data from different authors,¹⁰⁻¹⁶ with average absolute deviations ranging from 1 up to 19 %.

As indicated in Tables 1 to 3, the measured data have a good precision, with small associated expanded uncertainties for each compound. Furthermore, the compounds used in this work are of high purity, and the surface was carefully and thoroughly

Table 2. Experimental Surface Tension (γ) of Cyclic and Substituted Fluorocompounds

| C ₇ F ₁₄ | | C ₁₀ F ₁₈ | | C ₈ F ₁₇ Br | |
|--------------------------------|-----------------------|---------------------------------|-----------------------|-----------------------------------|-----------------------|
| <i>T</i> | $\gamma \pm \sigma^a$ | <i>T</i> | $\gamma \pm \sigma^a$ | <i>T</i> | $\gamma \pm \sigma^a$ |
| K | mN·m ⁻¹ | K | mN·m ⁻¹ | K | mN·m ⁻¹ |
| 286.75 | 16.33 ± 0.06 | 288.15 | 20.34 ± 0.01 | 287.15 | 18.42 ± 0.03 |
| 293.25 | 15.65 ± 0.07 | 293.15 | 19.85 ± 0.07 | 292.75 | 17.92 ± 0.04 |
| 298.35 | 15.10 ± 0.05 | 298.15 | 19.41 ± 0.03 | 298.35 | 17.43 ± 0.07 |
| 303.35 | 14.54 ± 0.03 | 303.15 | 18.99 ± 0.03 | 303.35 | 17.01 ± 0.03 |
| 308.55 | 13.95 ± 0.05 | 308.15 | 18.53 ± 0.04 | 308.45 | 16.54 ± 0.03 |
| 313.65 | 13.38 ± 0.05 | 318.15 | 17.61 ± 0.08 | 313.45 | 16.04 ± 0.04 |
| | | 327.15 | 16.80 ± 0.05 | 318.55 | 15.66 ± 0.05 |

^a Expanded uncertainty with an approximately 95 % level of confidence.

Table 3. Experimental Surface Tension (γ) of Aromatic Perfluorocompounds

| C ₆ F ₆ | | C ₇ F ₈ | |
|-------------------------------|-----------------------|-------------------------------|-----------------------|
| <i>T</i> | $\gamma \pm \sigma^a$ | <i>T</i> | $\gamma \pm \sigma^a$ |
| K | mN·m ⁻¹ | K | mN·m ⁻¹ |
| 288.05 | 23.38 ± 0.04 | 287.15 | 23.02 ± 0.04 |
| 293.35 | 22.76 ± 0.06 | 293.15 | 22.29 ± 0.05 |
| 298.45 | 22.02 ± 0.05 | 298.25 | 21.76 ± 0.06 |
| 303.45 | 21.40 ± 0.03 | 303.35 | 21.12 ± 0.05 |
| 308.55 | 20.81 ± 0.03 | 308.55 | 20.51 ± 0.04 |
| 313.65 | 20.19 ± 0.04 | 313.75 | 19.92 ± 0.04 |
| 318.75 | 19.52 ± 0.06 | 318.85 | 19.35 ± 0.04 |

^a Expanded uncertainty with an approximately 95 % level of confidence.

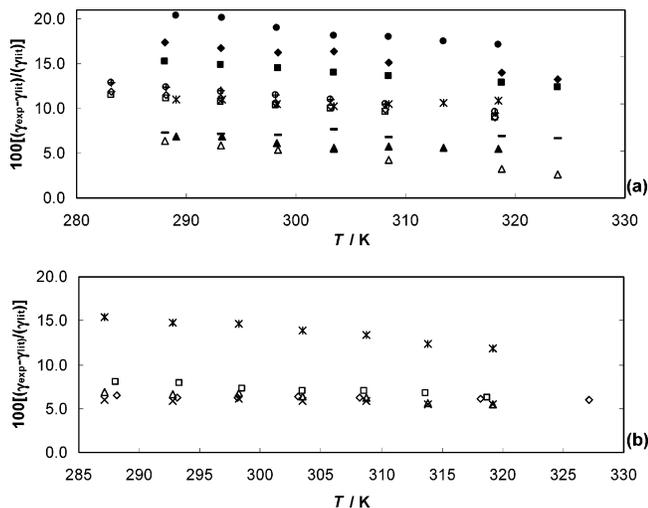


Figure 1. Relative deviations between the experimental surface tension data of this work and those reported in the literature. (a) ○, C₆F₁₄;¹⁰ ◇, C₆F₁₄;¹¹ □, C₆F₁₄;¹² +, C₆F₁₄;¹³ *, C₇F₁₆;¹¹ ●, C₇F₁₆;¹² ▲, C₇F₁₆;¹⁴ −, C₈F₁₈;¹¹ ◆, C₈F₁₈;¹² ■, C₈F₁₈;¹³ △, C₈F₁₈;¹⁵ (b) ×, C₉F₂₀;¹¹ *, C₉F₂₀;¹² △, C₉F₂₀;¹⁵ ◇, C₁₀F₁₈;¹⁵ □, C₆F₆.¹²

cleaned between each measurement allowing for a new interface formation. This procedure may explain the systematically higher results obtained in this work when compared to literature data since interfacial tensions normally decrease with the presence of impurities. Usually, higher interfacial tensions are an indication of high-purity compounds. Most of the authors who also measured surface tensions of FCs either do not report the purity of the compounds or low purity compounds were used. Haszeldine and Smith¹⁵ present no indication of the PFCs purity and used the maximum bubble pressure method. McLure et al.¹³ only considered the presence of isomers (<1 mol % for C₆F₁₄ and <10 mol % for C₈F₁₈), and Skripov and Firsov¹¹ presented no purity statement indicating, however, isomer contamination.

Table 4. Surface Thermodynamic Functions for the FCs at 298.15 K

| fluid | 10 ⁻⁵ (<i>S</i> ^γ ± σ ^a) | 10 ⁻³ (<i>H</i> ^γ ± σ ^a) |
|-----------------------------------|---|---|
| | J·m ⁻² ·K ⁻¹ | J·m ⁻² |
| C ₆ F ₁₄ | 11.6 ± 0.6 | -22.5 ± 0.2 |
| C ₇ F ₁₆ | 9.3 ± 0.3 | -14.3 ± 0.8 |
| C ₈ F ₁₈ | 8.8 ± 0.2 | -11.9 ± 0.6 |
| C ₉ F ₂₀ | 8.1 ± 0.1 | -10.9 ± 0.5 |
| C ₇ F ₁₄ | 11.0 ± 0.2 | -17.7 ± 0.5 |
| C ₁₀ F ₁₈ | 9.0 ± 0.1 | -7.5 ± 0.4 |
| C ₆ F ₆ | 12.6 ± 0.2 | -15.5 ± 0.8 |
| C ₇ F ₈ | 11.6 ± 0.2 | -12.8 ± 0.5 |
| C ₈ F ₁₇ Br | 8.9 ± 0.2 | -9.2 ± 0.5 |

^a Expanded uncertainty with an approximately 95 % level of confidence.

Another fact that has to be taken into account is that surface tension measurements require density data of the compounds under study. Previously authors either obtained these densities from empirical correlations or from experimental measurements with a pycnometer. Finally, due to their unique properties, some surface tension measurement methods are not adequate when working with PFCs. Most authors used the capillary rise method, which is not a good technique for PFCs due to their extremely high hydrophobicity and poor wetting of the hydrophilic glass capillary wall. Also, the drop weight method leads to large uncertainties for these compounds due to the difficulty in the formation of the droplet as a consequence of their large densities. These are the first data reported using the Du Noüy ring method, using compounds with high purity and accurate experimental densities.^{28,29}

Another important indication on the quality of the surface tension data available in the literature is given by the work of Sakka and Ogata,¹⁶ who evaluated the parachor assigned to fluorine atoms and concluded that the calculated surface tensions using parachors for PFCs are higher than the available literature data. This may also be an indication of the defective quality of the available data for the surface tension of PFCs.

Using the quasi-linear surface tension variation with temperature for all the FCs observed in the studied temperature range, the surface thermodynamic properties (namely, surface entropy and enthalpy) were derived. The surface entropy, *S*^γ, can be obtained from^{30,31}

$$S^\gamma = - \frac{d\gamma}{dT} \quad (6)$$

And the surface enthalpy, *H*^γ, can be obtained from the following expression:^{30,31}

$$H^\gamma = \gamma - T \left(\frac{d\gamma}{dT} \right) \quad (7)$$

where γ stands for the surface tension and *T* stands for the temperature.

The thermodynamic functions for all the studied FCs at 298.15 K and the respective expanded uncertainties, derived from the slope of the curve $\gamma = f(T)$ in combination with the law of propagation of uncertainty, are presented in Table 4.³² For the linear PFCs, the increase in chain length leads to the increase in the surface enthalpy, followed by a decrease in the surface entropy, which is a result of an increase in intermolecular interactions. The combined effect of the surface enthalpy and entropy yields a slightly increase in the surface tension with the chain length. A similar behavior is observed for the cyclic compounds, with a strong change in surface enthalpy observed

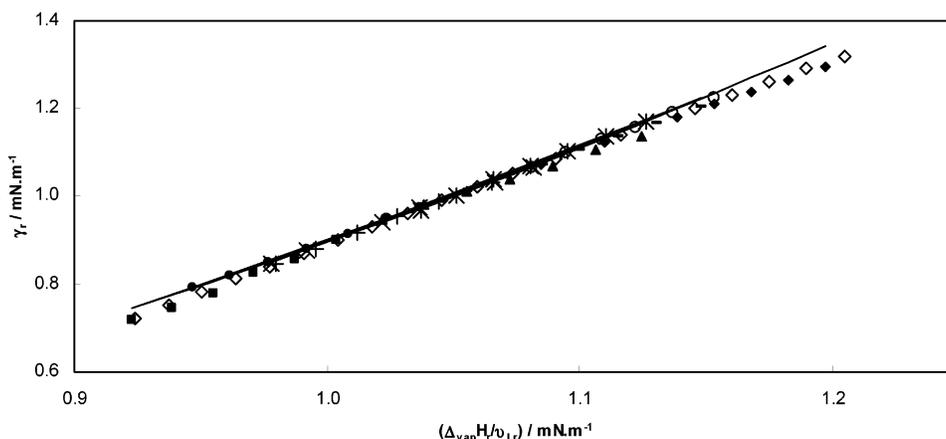


Figure 2. Surface tension vs vaporization enthalpy correlation: ■, C₆F₁₄; ●, C₇F₁₆; ×, C₈F₁₈; *, C₉F₂₀; ▲, C₆F₆; —, C₇F₈; +, C₇F₁₄; ◆, C₁₀F₁₈; ○, C₈F₁₇Br; ◇, C₈H₁₈. The solid line represents the Faizullin²⁰ correlation.

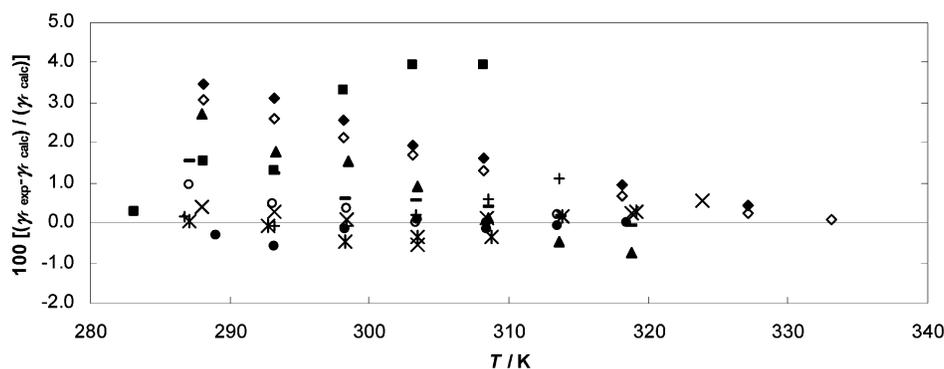


Figure 3. Relative deviations between the experimental reduced surface tensions and those calculated with the Faizullin²⁰ correlation: ■, C₆F₁₄; ●, C₇F₁₆; ×, C₈F₁₈; *, C₉F₂₀; ▲, C₆F₆; —, C₇F₈; +, C₇F₁₄; ◆, C₁₀F₁₈; ○, C₈F₁₇Br; ◇, C₈H₁₈.

for the octadecafluorodecalin that results in an important increase in the surface tension.

Comparing the surface tension of the C₈F₁₇Br (Table 2) with the respective fully fluorinated octadecafluorooctane, it can be seen that the inclusion of a less electronegative heteroatom leads to an increase in surface tension. This substituted compound presents a similar surface entropy to octadecafluorooctane but an important difference in surface enthalpy. This increase in surface tension can thus be explained by the increase in surface enthalpy value due to the stronger interactions resulting from a dipole at the heteroatom.

The aromatic PFCs show the highest surface entropy from all the compounds studied. The methyl substitution on the aromatic ring lowers the surface entropy that is compensated by a change in enthalpy, thus leading to a small variation on the surface tension, in the same line of what was observed for the *n*-perfluoroalkanes.

Surface Tension versus Vaporization Enthalpy Correlation.

The Faizullin²⁰ approach was used to calculate reduced surface tensions of fluorocarbons, and the results were compared with the reduced surface tension calculated from experimental data measured in this work, as graphically presented in Figure 2. The *n*-octane³³ was included to test and validate the procedure, and a plot showing the deviations from the Faizullin estimated behavior is presented in Figure 3. The required experimental information is summarized in Table 5. Critical temperatures were either compiled from experimental measurements or obtained from reliable correlations.^{34–47} Liquid volumes and vaporization enthalpies were obtained from Dias et al.,^{28,29} and the required surface tensions at the reduced temperature of 0.6 were obtained from correlations, as a function of temperature, of the experimental data collected for the present work.

Table 5. Properties Required for the Faizullin Correlation²⁰

| fluid | T_c K | $v_{L,T=0.6}$ $10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}$ | $\gamma_{T=0.6}$ $\text{mN} \cdot \text{m}^{-1}$ | $\Delta_{\text{vap}} H_{T=0.6}$ $\text{kJ} \cdot \text{mol}^{-1}$ |
|-----------------------------------|------------|--|---|--|
| C ₆ F ₁₄ | 449.0 | 1.92 | 15.68 | 34.20 |
| C ₇ F ₁₆ | 474.8 | 2.20 | 14.83 | 37.50 |
| C ₈ F ₁₈ | 498.0 | 2.48 | 14.44 | 40.65 |
| C ₉ F ₂₀ | 524.0 | 2.79 | 13.93 | 44.29 |
| C ₇ F ₁₄ | 485.9 | 1.94 | 15.83 | 35.11 |
| C ₁₀ F ₁₈ | 566.0 | 2.52 | 15.68 | 39.06 |
| C ₆ F ₆ | 517.0 | 1.17 | 20.59 | 35.36 |
| C ₇ F ₈ | 534.5 | 1.46 | 19.12 | 39.17 |
| C ₈ F ₁₇ Br | 541.7 | 2.70 | 15.06 | 44.02 |
| C ₈ H ₁₈ | 569.4 | 1.73 | 16.92 | 39.03 |

As shown in Figure 2, surface tension relationship with the vaporization enthalpy given by eq 1 is also valid for PFCs with the generalized correlation parameter $m = 2.15$ proposed by Faizullin,²⁰ who used different fluid families and a broad range of thermodynamic conditions for its determination. The Faizullin correlation provides a good description of the measured surface tension data with typical deviations inferior to 3 % (as shown in Figure 3). Larger deviations of 3.9 % were observed for the tetradecafluorohexane and 3.5 % for octadecafluorodecalin, which can be an indication of uncertainties in the critical properties used.

Conclusions

Experimental data for the surface tensions for C₆ to C₉ linear perfluoroalkanes, two cyclic and two aromatic fluorocompound, and one α -substituted fluorocompound in the temperature range (283 to 327) K using the Du Noüy ring method are presented. New experimental data are presented for the C₇F₁₄, C₇F₈, and C₈F₁₇Br fluorocompounds. PFCs present lower surface tensions

than their alkane homologues due to their weaker intermolecular interactions. For the same number of carbon atoms in the molecule, the surface tension increases from linear to cyclic and from cyclic to aromatic PFCs. Substitution of fluorine with bromine in the same chain molecule increases the surface tension, as intermolecular interactions increase.

A generalized correlation between measured surface tension, vaporization enthalpy, and liquid molar volume was verified for FCs. It is shown that using a fluid-independent exponent, m , the description of the reported experimental data is provided with a deviation inferior to 4 %.

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