

## Thermophysical properties of some perfluorocompounds

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## **Abstract**

The properties of fluorocarbons are at the center of attention today due to their unique properties that may provide interesting applications in areas as environment, biomedical and material sciences. However, the behavior of these compounds and their properties are still poorly characterized. Only very limited data, and often unreliable, can be found in the open literature and company technical reports.

This work addresses some thermophysical properties of a few saturated perfluorocarbons. The vapor pressures, the densities and the surface tensions of perfluoro-n-hexane, heptane, octane, nonane and decaline are reported in the temperature range between 288 and 333 K.

## **Introduction**

Fluorinated molecules such as perfluorocarbons (PFCs) and their derivatives are a very interesting and promising class of chemicals in the physical chemistry and polymer science due to their specific and unusual properties. Perfluorochemicals are non-polar highly fluorinated compounds that are chemical and biochemical inert. The chemical structure and the weak intermolecular interactions are responsible for the specific properties of PFCs namely the low surface tensions ( $<20 \text{ mN m}^{-1}$ ), dielectric constants and refractive indices. The high densities, viscosities and gas solubilities are among the largest known for pure liquids. In spite of their interest, very limited thermophysical data is available for these compounds in the open literature.

The aim of this work is to provide new thermophysical data that will allow the development of models to describe the behavior of these compounds. For this purpose the vapor pressures, densities and surface tensions of perfluoro-n-hexane, heptane, octane, nonane and decaline were measured in the temperature range between 288 and 333 K.

## **Materials**

The Chemicals used for the measurements were perfluoro-n-hexane, perfluoro-n-heptane, perfluoro-n-octane and perfluoro-n-nonane from Aldrich with a stated purity of 99%, 85%, 98% and 97% respectively. Perfluorodecaline was a mixture of isomers obtained from ABCR with a purity of 98%. Dissolved gases and light compounds were removed by vacuum distillation.

## **Vapor pressures**

Vapor pressures were measured by the static method using the apparatus depicted in Figure 1. The pressure was determined using a calibrated Paroscientific pressure transducer model 2100A-101 with an accuracy of  $\pm 0.01\%$ . The temperature was measured with a

calibrated platinum resistance thermometer with an uncertainty of  $\pm 0.05$  K. A water bath, with a stability of  $\pm 0.1$  K, was used.

The vapor pressures for the perfluorocompounds studied are reported in Table 1 along with values calculated with the Antoine equation

$$\ln(P/kPa) = A - \frac{B}{(T/K) + C} \quad (1)$$

The Antoine constants adjusted to the experimental data are reported in Table 2. The average absolute deviations (AAD) are below 0.1%.

## Densities

The densities were measured with a vibrating tube Anton Paar DSA-48 densimeter capable of measure between 263.15 and 343.15 K at atmospheric pressure using a 2.5 ml sample. The cell used to measure the density has a U shape and is inserted in a glass jacket filled with a high thermal conductivity gas and covered with copper in order to guarantee a proper heat transfer between the thermostat and the measuring sample. The precision of the measurements is  $\pm 5.10^{-5}$  g.cm<sup>-3</sup>. Due to the limited temperature range studied the density data was correlated with a linear dependence on the temperature

$$r = A + BT \quad (2)$$

Experimental values are presented on Table 3 and compared with the values calculated from the correlation. The correlation parameters are given on Table 4.

## Surface Tensions

The surface tension was measured with a Lauda tensiometer (model TVT2). The technique used was the pending drop, which determines the equilibrium between forces that occur when a drop is pending at the end of a capillary. Due to the balance of forces between the gravity and the surface tension, the drop critical volume,  $V_d$ , can be directly related with the surface tension  $\sigma$ , and the difference in the densities of the two adjacent phases in the following way:

$$s = \frac{V\Delta r g}{2pr_{cap}f} \quad (3)$$

where  $g$  is the acceleration of gravity,  $\Delta\rho$  is the difference between the density of the liquid and the vapor phases,  $r_{cap}$  is the internal capillary's radius and  $f$  is a correction factor that is determined experimentally.

To guarantee the equilibrium between the liquid and the vapor phases, 1ml of the measuring compound is introduced in the measuring cell. The temperature in both the syringe and the measuring cell is kept constant with a recirculating water bath capable of maintain the temperature to  $\pm 0.01$  K.

In this work, a syringe of 2.5 ml and a capillary with internal radius of 1.08 mm were used. Three runs of 30 drops each were made at the same temperature and values with a standard deviation higher than  $\pm 0.05$  mNm<sup>-1</sup> were discarded. The surface tension values measured are reported on Table 5 along with the correlated values using the scaling law

$$s = A \left( 1 - \frac{T}{T_c} \right)^B \quad (23)$$

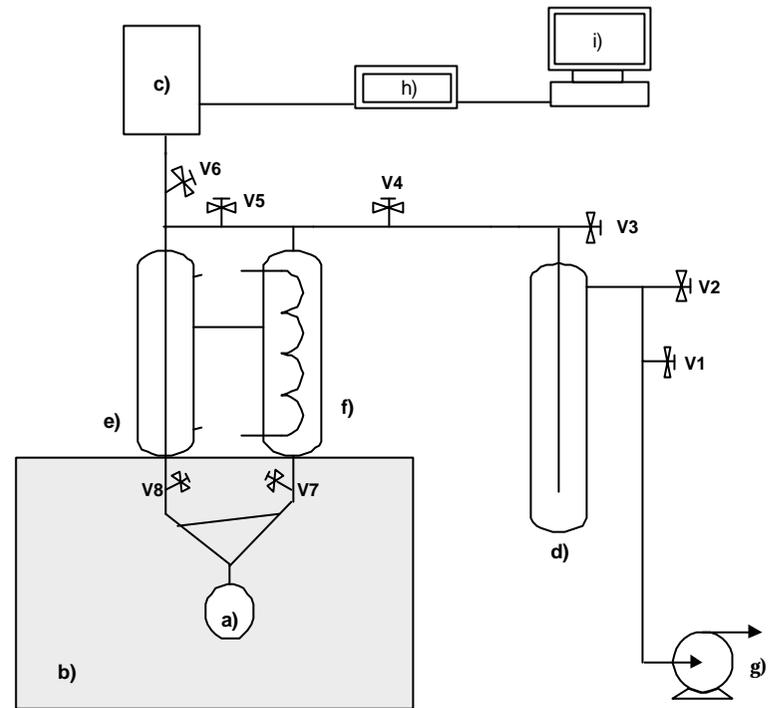
where A and B are adjustable parameters, reported on Table 6. The critical temperatures used were obtained from Vandana et al. [1].

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### **References**

- [1] V. Vandana, D. Rosenthal, A. Teja, Fluid Phase Equilibria, 99 (1994) 209



**Figure 1-** Scheme of the vapor pressure apparatus used in this work

**Table 1- Measured and calculated vapor pressures for the studied compounds**

<b>C6F14</b>			<b>C10F18</b>				
T/K	P <sub>exp</sub> /kPa	P <sub>calc</sub> /kPa	ΔP/kPa	T/K	P <sub>exp</sub> /kPa	P <sub>calc</sub> /kPa	ΔP/kPa
298.07	29.27	29.29	-0.02	303.23	1.19	1.17	0.02
303.06	36.277	36.24	0.04	308.22	1.58	1.56	0.02
303.04	36.227	36.21	0.02	313.21	2.05	2.06	-0.01
308.19	44.76	44.71	0.05	318.18	2.66	2.69	-0.03
313.21	54.46	54.47	-0.01	323.17	3.47	3.47	0.00
318.19	65.72	65.76	-0.03	328.16	4.43	4.42	0.01
323.20	78.98	78.91	0.07				
328.18	93.69	93.95	-0.26				
330.68	102.32	102.31	0.01				
333.18	111.38	111.23	0.15				

**Table 2- Antoine Constants and AAD between calculated and experimental pressures**

	<b>A</b>	<b>B</b>	<b>C</b>	<b>AAD%</b>
<b>C6F14</b>	13.82152	2503.264	-58.3954	0.088
<b>C10F18</b>	12.83547	2699.61	-90.2959	0.79

**Table 3- Measured and calculated densities for the studied compounds**

<b>C6F14</b>			<b>C7F16</b>			<b>C8F18</b>			<b>C9F20</b>			<b>C10F18</b>			
T/K	ρ <sub>exp</sub> /g/cm <sup>3</sup>	ρ <sub>calc</sub> /g/cm <sup>3</sup>	Δρ/g/cm <sup>3</sup>	ρ <sub>exp</sub> /g/cm <sup>3</sup>	ρ <sub>calc</sub> /g/cm <sup>3</sup>	Δρ/g/cm <sup>3</sup>	ρ <sub>exp</sub> /g/cm <sup>3</sup>	ρ <sub>calc</sub> /g/cm <sup>3</sup>	Δρ/g/cm <sup>3</sup>	ρ <sub>exp</sub> /g/cm <sup>3</sup>	ρ <sub>calc</sub> /g/cm <sup>3</sup>	Δρ/g/cm <sup>3</sup>	ρ <sub>exp</sub> /g/cm <sup>3</sup>	ρ <sub>calc</sub> /g/cm <sup>3</sup>	Δρ/g/cm <sup>3</sup>
288.15	1.70233	1.70476	-0.00243	1.75532	1.75545	-0.00013	1.79015	1.79034	-0.00020	1.81216	1.81222	-6E-05	1.95282	1.95286	-4E-05
293.15	1.69237	1.69039	0.00198	1.74186	1.74168	0.00019	1.77749	1.77747	0.00002	1.80008	1.79997	0.00011	1.94167	1.94161	6E-05
298.15	1.67754	1.67602	0.00152	1.72825	1.72790	0.00035	1.76475	1.76459	0.00016	1.78793	1.78772	0.00021	1.93046	1.93035	0.000106
303.15	1.66252	1.66165	0.00087	1.71448	1.71413	0.00036	1.75187	1.75172	0.00015	1.77569	1.77547	0.00022	1.91921	1.91910	0.000111
313.15	1.63172	1.63291	-0.0012	1.68649	1.68658	-0.00008	1.72579	1.72597	-0.00018	1.75093	1.75097	-4E-05	1.89656	1.89659	-2E-05

**Table 4- Constants for the densities correlations and AAD between calculated and experimental values**

	<b>A</b>	<b>B</b>	<b>AAD%</b>
<b>C6F14</b>	$-2.874 \cdot 10^{-3}$	2.532905	0.095
<b>C7F16</b>	$-2.755 \cdot 10^{-3}$	2.549303	0.013
<b>C8F18</b>	$-2.575 \cdot 10^{-3}$	2.532328	0.008
<b>C9F20</b>	$-2.450 \cdot 10^{-3}$	2.518187	0.007
<b>C10F18</b>	$-2.251 \cdot 10^{-3}$	2.60149	0.004

**Table 5- Measured and calculated surface tensions for the studied compounds**

T/K	<b>C6F14</b>			<b>C7F16</b>			<b>C8F18</b>			<b>C9F20</b>			<b>C10F18</b>		
	$\sigma_{exp}/$ mN/m	$\sigma_{clc}/$ mN/m	$\Delta\sigma/$ mN/m												
288.15	12.50	12.47	0.03	13.60	13.62	-0.02	14.48	14.49	-0.01	15.22	15.21	0.02	18.90	18.98	-0.08
293.15	11.83	11.89	-0.06	13.08	13.07	0.01	13.94	13.96	-0.03	14.74	14.71	0.04	18.60	18.46	0.14
298.15	11.36	11.33	0.03	12.58	12.53	0.05	13.54	13.44	0.09	14.14	14.21	-0.07	17.95	17.94	0.01
303.15				11.97	12.00	-0.03	12.88	12.93	-0.05	13.71	13.72	-0.02	17.33	17.43	-0.10
313.15							11.93	11.92	0.00	12.80	12.77	0.03	16.44	16.42	0.03

**Table 6- Constants for the scaling laws and AAD between calculated and experimental values**

	<b>A</b>	<b>B</b>	<b>AAD%</b>
<b>C6F14</b>	58.09436	1.508649	0.34
<b>C7F16</b>	55.96873	1.516096	0.21
<b>C8F18</b>	54.74503	1.538903	0.28
<b>C9F20</b>	52.77958	1.558716	0.24
<b>C10F18</b>	56.7999	1.540312	0.39