Densities and Vapor Pressures of Highly Fluorinated Compounds

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Vapor pressures and liquid densities of highly fluorinated compounds were measured in this work. Vapor pressures were measured in the temperature range between 288 K and 333 K with an apparatus based on the static method. Liquid densities were measured with a vibrating tube densimeter in the temperature range between 288 K and 313 K. Experimental data was fitted with appropriate equations and compared with literature data when possible. Vapor pressures and densities were also correlated with the soft-SAFT equation of state, and the fitted parameters for the studied fluids are presented. The boiling points, enthalpies of vaporization, and thermal expansion coefficients, derived from vapor pressure and density data, are also reported.

Introduction

The current interest in fluorinated compounds arises from their unusual properties, which give them a variety of uses ranging from artificial blood to lubricants. The increasing number of applications of fluorinated compounds in medicine, the environment, and industry requires a wide knowledge of the thermophysical properties of these substances. Despite their many applications, literature data relating these compounds is in some cases old and many times discrepant; in other cases, only one set of results can be found, and for some compounds with current application, experimental data is completely nonexistent. It is therefore of both practical and theoretical interest to measure the thermophysical properties of these compounds to create a wide and reliable experimental database to use in understanding their different behavior and to be able to predict it accurately.

The aim of this work is to collect and compare vapor pressure and density data for different saturated and nonsaturated fluorinated compounds that are being studied for different applications.[1−3] When literature data is available, comparison is made between the different methods and samples used. For perfluoro-*n*-nonane, perfluorodecalin, 1Br-perfluorooctane, and 1H-perfluorooctane, new experimental and correlated data are presented in this work. Experimental vapor pressure and density data are correlated using appropriate equations for the temperature ranges studied. The soft-SAFT equation of state (EoS)[4,5] is also used to correlate experimental data. A main advantage of using this approach versus more traditional ones is that this equation uses parameters with physical meaning that are independent of the thermodynamic conditions. The molecular parameters are adjusted for the pure compounds in a given temperature range, and data can be predicted for different thermodynamic conditions with the same molecular parameters, using the equation as a reliable predictive tool.

The boiling points, enthalpies of vaporization, and thermal expansion coefficients derived from vapor pressure and density data are also reported in this article.

Experimental Section

Materials. Chemicals used for the measurements were perfluoro-*n*-hexane, (purity 99%) from Aldrich, perfluoro-*n*-nonane (purity 99%) from Apollo Scientific, perfluorodecalin (purity 99%) from ABCR, 1Br-perfluoro-*n*-octane (purity 99%) from ABCR, 1H-perfluoro-*n*-octane (purity 99%) from Interchim, perfluorotoluene (purity 99%) from Apollo Scientific, and perfluorobenzene (purity 99%) from Fluorochem. The purities of the compounds studied were confirmed through gas chromatographic analyses.

Vapor Pressure Measurement System. Vapor pressures were measured using the apparatus based on the static method, depicted in Figure 1. It consists mainly of a glass sample cell (A), a thermostatic bath (B), a temperature measurement system, a pressure measurement system (C), and a temperature-controlled glass vacuum line connecting the sample cell to the degassing system and to the pressure sensor.

For the temperature range studied, water was used as the thermostatic bath fluid. The temperature in the bath was controlled with a digitally controlled immersion thermostat (Digiterm 100 (J)). For temperatures below 298 K, a refrigerated immersion cooling coil was used. The stability and uniformity of the temperature in the working area of the thermostatic bath was better than ±0.01 K.

The temperature of the glass sample cell was measured with a calibrated Pt100 temperature sensor (class 1/10 (L)) using a 6$^1/_2$ digit data-logger system (H) (Agilent model 34401A) for continuous data acquisition with an uncertainty of ±0.05 K. In accordance with the International Temperature Scale of 1990, IST-90, this sensor was cali-

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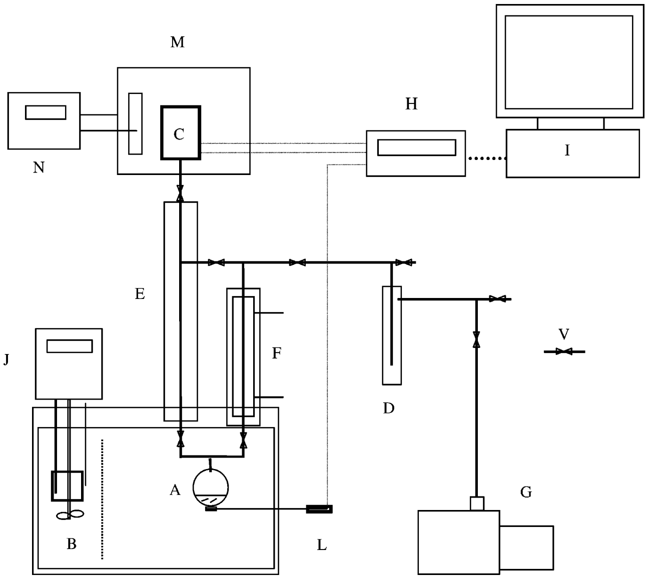

Figure 1. Scheme of the vapor pressure apparatus: A, cell; B, water bath; C, pressure transducer; D, liquid-nitrogen trap; E, hot-water-jacket-protected tube; F, condenser; G, vacuum pump; H, data logger; I, computer; J, temperature controller; L, cell-temperature sensor (Pt100); M, hot-block box for the pressure sensor; N, PID temperature controller; V, high-vacuum Teflon valves.

brated against an SPRT (25 Ω ; Tinsley, 5187A) temperature probe by using an ASL bridge (model F26).

For pressure measurements, a high-precision, temperature-compensated quartz pressure tranducer (C) (Paroscientific, Inc., model 2100A-101) was used. The accuracy of the pressure transducer is ±0.01% in the working range of (0 to 1.38) MPa. Two output frequency signs (corresponding to the sensor temperature and the quartz pressure sensor) were registered in the 6$^1/_2$ digit data-logger system (Agilent model 34401A), and the corresponding pressure was calculated using the calibration function that includes temperature compensation.

In the glass vacuum line, all glass connections were assembled with greaseless spherical joints, Teflon O-rings, and high-vacuum Teflon valves. The vacuum line is connected to the rotatory vacuum pump (G) (BOC Edwards, model RV5) through a glass cold trap (D) filled with liquid nitrogen.

The apparatus was designed to permit degassing of the solvent using the condenser (F). The solvent is refluxed into the sample cell (A) while noncondensable gases are pumped out. Previous experience[6] with the degassing of fluorinated compounds showed that they could be efficaciously and quickly degassed through successive melting/freezing cycles while vacuum pumping noncondensable gases, and that was the procedure used in this work. The sample cell with a volume of 10 cm^3 containing the degassed solvent is then immersed in the thermostatic water bath. When the equilibrium temperature is reached, the apparatus is isolated from the vacuum source, and the sample cell valve is opened to connect the sample container to the closed line and the quartz pressure sensor. After pressure stabilization, the pressure and time experimental data are recorded.

To avoid condensation, the apparatus from the sample cell to the pressure transducer is maintained at a higher temperature than the sample cell. This heating system includes a hot-water-jacket-protected tube (E) and a hot-block box (M) for the pressure transducer.

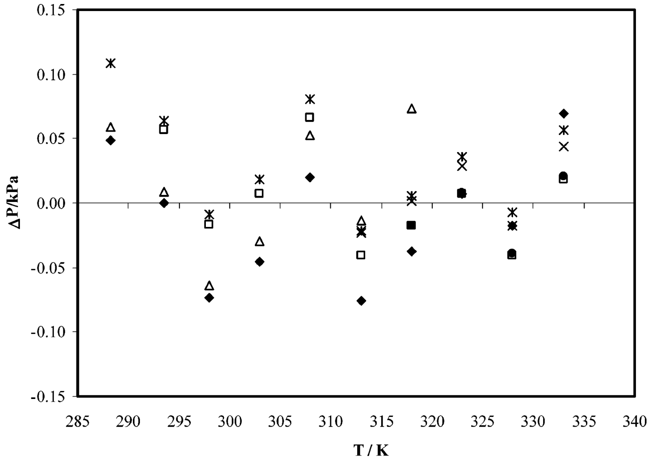

Figure 2. Comparison between correlated experimental and literature vapor-pressure data of perfluoroperfluorobenzene: ◆, this work; □, Ambrose;[10] △, Findlay et al.;[12] ×, Counsell et al.;[8] *, Douslin et al.[9] $\Delta P = P_{\text{exptl}} - P_{\text{calcd}}$.

Table 1. Comparison between Experimental and Literature Vapor Pressures of Perfluorobenzene

T/K	P_{exptl}/kPa	$P_{\text{lit}}{}^{8}$/kPa	$P_{\text{lit}}{}^{9}$/kPa	$P_{\text{lit}}{}^{10}$/kPa	$P_{\text{lit}}{}^{11}$/kPa	$P_{\text{lit}}{}^{12}$/kPa
288.23	6.90		6.79			6.84
293.51	9.00		8.94	8.94		8.99
297.98	11.16		11.17	11.18		11.22
302.96	14.20		14.18	14.19		14.23
307.96	17.93		17.85	17.87		17.88
312.96	22.25	22.28	22.27	22.29		22.27
317.96	27.56	27.56	27.55	27.58	27.58	27.49
322.96	33.85	33.82	33.81	33.84	33.84	
327.95	41.16	41.18	41.17	41.20	41.20	
333.01	49.95	49.91	49.89	49.93	49.93	

Density. The density was measured with an Antón Paar DMA 4500 vibrating tube densimeter between 288.15 K and 313.15 K at atmospheric pressure. The measuring principle is based on the calculation of the frequency of resonance of a mechanic oscillator with a given mass and volume, which is excited to be in resonance. The cell used to measure the density has a U shape and is inserted into a glass jacket filled with a high-thermal-conductivity gas and covered with copper to guarantee proper heat transfer between the thermostat and the measuring sample.The uncertainty of the measurements is $\pm 5 \times 10^{-5}$ g·cm^{-3} with an accuracy of $\pm 1 \times 10^{-5}$ g·cm^{-3}.

Results and Discussion

Vapor Pressures. To evaluate the accuracy and estimate the precision of the experimental apparatus, the vapor pressure of perfluorobenzene was measured. Perfluorobenzene was chosen as the reference fluid once the vapor pressures of the compounds studied in this work were of the same order of magnitude as those of perfluorobenzene in the temperature range studied. Also, perfluorobenzene is a compound included in the IUPAC recommendations of reference materials for pressure−volume−temperature relations[7] because agreement between the normal boiling temperatures of perfluorobenzene measured by Counsell et al.,[8] Douslin et al.,[9] and Ambrose[10] were within a range of 0.005 K. More recently, Ambrose et al.[11] remeasured the vapor pressure of perfluorobenzene using the same technique with an absolute deviation from the previous results that was lower than 0.015 kPa. All of the measurements were made using comparative ebulliometric apparatus. Findlay et al.[12] also measured the vapor pressure of perfluorobenzene but used a static method as in the case of this work.

A comparison between the experimental data measured in this work and literature data is presented in Table 1.

Table 2. Experimental and Calculated Vapor Pressures of the Studied Compounds

		Antoine's equation		soft-SAFT EoS				Antoine's equation		soft-SAFT EoS	
T/K	P_{exptl}/kPa	P_{calcd}/kPa	ΔP^{a}/kPa	P_{calcd}/kPa	ΔP^{a}/kPa	T/K	P_{exptl}/kPa	P_{calcd}/kPa	ΔP^{a}/kPa	P_{calcd}/kPa	ΔP^{a}/kPa
					C_6F_{14} − Perfluoro-*n*-hexane						
288.31	18.78	18.76	0.02	20.40	−1.62	313.17	54.56	54.54	0.02	53.34	1.22
293.22	23.58	23.59	−0.01	25.05	−1.47	318.15	65.86	65.86	0.00	63.27	2.59
298.09	29.28	29.31	−0.03	30.46	−1.18	323.13	78.91	78.99	−0.08	74.61	4.30
302.98	36.19	36.16	0.03	36.80	−0.61	328.11	94.08	94.09	−0.01	87.47	6.61
307.97	44.38	44.41	−0.03	44.30	0.08	333.10	111.39	111.37	0.02	101.97	9.42
					C_9F_{20} − Perfluoro-*n*-nonane						
288.18	0.68	0.69	−0.01	0.76	−0.08	313.17	3.06	3.02	0.05	3.06	0.00
293.18	0.94	0.95	−0.01	1.02	−0.08	318.22	3.99	3.96	0.03	3.96	0.03
298.11	1.29	1.28	0.01	1.36	−0.07	323.15	5.14	5.14	0.00	5.07	0.07
303.1	1.71	1.71	0.00	1.79	−0.08	328.15	6.59	6.64	−0.04	6.46	0.13
308.19	2.32	2.29	0.03	2.35	−0.04	333.15	8.42	8.52	−0.10	8.19	0.23
					$C_{10}F_{18}$ − Perfluorodecalin						
288.25	0.57	0.52	0.05	0.60	−0.03	313.22	2.05	2.10	−0.05	2.22	−0.16
293.25	0.73	0.71	0.02	0.79	−0.06	318.21	2.66	2.70	−0.04	2.81	−0.15
298.21	0.91	0.94	−0.03	1.04	−0.13	323.18	3.45	3.44	0.01	3.52	−0.08
303.29	1.25	1.25	0.00	1.35	−0.11	328.17	4.41	4.35	0.06	4.40	0.01
308.23	1.59	1.62	−0.04	1.74	−0.15	333.20	5.47	5.47	0.00	5.46	0.01
					$C_8F_{17}Br$ − 1Br-Perfluoro-*n*-octane						
288.22	0.38	0.38	0.00	0.49	−0.11	313.18	1.67	1.72	−0.05	1.97	−0.30
293.20	0.54	0.53	0.01	0.67	−0.13	318.09	2.24	2.24	0.00	2.52	−0.28
298.08	0.69	0.72	−0.03	0.88	−0.19	322.92	2.89	2.88	0.01	3.18	−0.29
303.26	0.98	0.98	0.00	1.17	−0.19	327.88	3.69	3.69	0.00	4.01	−0.32
308.22	1.30	1.31	−0.01	1.53	−0.23	332.78	4.70	4.68	0.02	5.01	−0.31
					$C_8F_{17}H$ − 1H-Perfluoro-*n*-octane						
288.35	1.18	1.18	0.00	1.21	−0.03	313.13	4.87	4.87	0.00	4.76	0.12
293.26	1.60	1.60	0.01	1.62	−0.01	318.06	6.22	6.28	−0.06	6.08	0.14
298.26	2.18	2.15	0.04	2.15	0.03	323.01	8.07	8.03	0.04	7.73	0.34
303.19	2.84	2.84	0.00	2.82	0.02	328.00	10.25	10.25	0.00	9.76	0.49
308.15	3.72	3.74	−0.02	3.68	0.04	332.89	12.83	12.83	0.00	12.18	0.65
					C_7F_8 − Perfluorotoluene						
288.23	2.18	2.22	−0.04	2.38	−0.20	313.15	8.43	8.37	0.06	8.61	−0.18
293.20	2.95	2.95	0.00	3.14	−0.19	318.15	10.69	10.62	0.07	10.84	−0.15
298.28	3.87	3.91	−0.04	4.12	−0.25	323.15	13.38	13.36	0.02	13.54	−0.16
303.18	5.09	5.07	0.02	5.30	−0.21	328.45	16.86	16.89	−0.03	16.99	−0.13
308.15	6.54	6.54	0.00	6.78	−0.24	333.93	21.31	21.33	−0.02	21.31	0.00

[a] $\Delta P = P_{\mathrm{exptl}} - P_{\mathrm{calcd}}$.

Literature data used were calculated with the equations reported by the authors to be the best fit to their experimental data. Absolute deviations between experimental and literature data are shown in Figure 2. Data from Ambrose et al.[11] are not included in the Figure because they coincide with the data from Ambrose.[10] From these results, an accuracy of better than 0.1 kPa can be stated for the measurements performed in this work.

The vapor pressures for the compounds studied are reported in Table 2 along with values calculated with the Antoine equation

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

where P is the vapor pressure, T is the temperature, and A, B, and C are adjustable constants. The Antoine constants adjusted to the experimental data are reported in Table 3.

The soft-SAFT equation of state (EoS)[4,5] was used to correlate the experimental data measured. The soft-SAFT EoS is generally formulated in terms of the residual molar Helmholtz energy, A^{res}, defined as the molar Helmholtz energy of the fluid relative to that of an ideal gas at the same temperature and density. A^{res} is written as the sum of three contributions

$$A^{\mathrm{res}} = A^{\mathrm{total}} - A^{\mathrm{ideal}} = A^{\mathrm{ref}} + A^{\mathrm{chain}} + A^{\mathrm{assoc}} \tag{2}$$

Table 3. Constants for the Antoine Equation

	Antoine constants			
compound	A	B	C	δ^{a}
C_6F_{14}	13.719	2442.990	−61.853	0.033
C_9F_{20}	21.373	7498.037	56.755	0.042
$C_{10}F_{18}$	15.938	4525.811	−15.354	0.037
$C_8F_{17}Br$	15.330	4001.198	−42.571	0.021
$C_8F_{17}H$	16.905	4487.951	−20.213	0.026
C_6F_6	14.271	2885.821	−54.500	0.048
C_7F_8	15.239	3549.981	−42.445	0.035

[a] $\delta = [\sum (p_{\mathrm{exptl}} - p_{\mathrm{calcd}})^2/n]^{0.5}$, where n is the number of experimental points.

A^{ref} accounts for the pairwise intermolecular interactions of the reference system, which in the case of the soft-SAFT EoS is a Lennard-Jones (LJ) monomer fluid accounting both for repulsive and attractive interactions. A^{chain} evaluates the free energy due to the formation of a chain from units of the reference system, and A^{assoc} takes into account the contribution due to site−site association. For molecules that do not associate, as is the case in this work, the association term is null.

The application of the soft-SAFT model to perfluoroalkane systems has already been discussed in previous work.[13] The molecular parameters m, σ, and $\epsilon/\kappa_{\mathrm{B}}$ were adjusted using the experimental vapor pressure and density data measured in this work and are given in Table 4. The vapor-pressure values calculated with the soft-SAFT

Table 4. Molecular Parameters Adjusted for the Studied Compounds

compound	m	σ (Å)	ϵ/κ_B (K)	vapor pressure δ^a	density δ^a ($\times 10^{-3}$)
C_6F_{14}	2.832	4.479	236.6	4.07	1.06
C_9F_{20}	3.901	4.525	246.5	0.10	0.65
$C_{10}F_{18}$	2.696	4.999	310.1	0.10	1.27
$C_8F_{17}Br$	3.522	4.652	268.9	0.24	0.91
$C_8F_{17}H$	3.522	4.492	253.6	0.28	0.96
C_6F_6	3.148	3.647	253.6	0.15	0.71
C_7F_8	3.538	3.764	253.0	0.18	2.15

[a] $\delta = [\sum(\text{exptl} - \text{calcd})^2/n]^{0.5}$, where n is the number of experimental points.

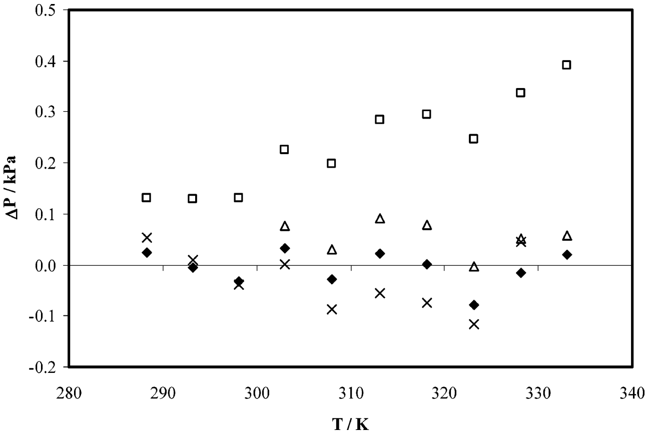

Figure 3. Comparison between correlated experimental and literature vapor pressure data of perfluoro-*n*-hexane: ◆, this work; □, Stiles et al.;[16] △, Dunlap et al.;[14] ×, Crowder et al.[15] $\Delta P = P_{\text{exptl}} - P_{\text{calcd}}$.

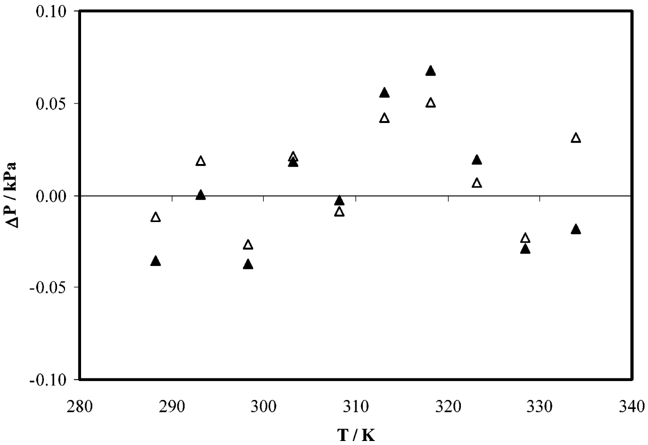

Figure 4. Comparison between correlated experimental and literature vapor pressure data of perfluorotoluene: ▲, this work; △, Ambrose et al.[17] $\Delta P = P_{\text{exptl}} - P_{\text{calcd}}$.

EoS are presented in Table 2. The soft-SAFT EoS correlates experimental vapor-pressure data accurately for all of the compounds studied, although it presents higher deviations for perfluoro-*n*-hexane. When adjusting the molecular parameters, care was taken to obtain the lowest deviations for the density correlation and to obtain a correct sequence for the molecular parameters along the linear perfluoroalkane series from C_1 to C_8. Those restrictions led to a higher deviation in the vapor-pressure data correlation.

Vapor-pressure data were found in the literature for perfluoro-*n*-hexane and perfluorotoluene, and comparisons with the data measured in this work are made in Figures 3 and 4, respectively. No vapor-pressure data for the other compounds studied were found in the literature.

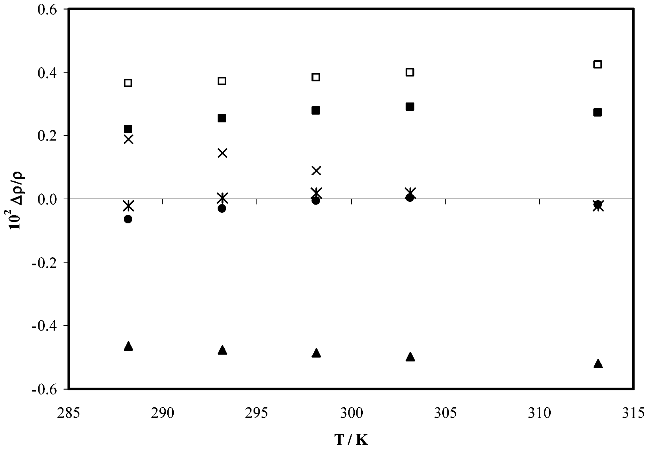

Figure 5. Comparison between experimental and literature density data of perfluoro-*n*-hexane: *, this work; ■, Dunlap et al.,[14] air-saturated sample; □, Dunlap et al.,[14] degassed sample; ▲, Stiles et al.;[16] ●, Piñeiro et al.;[18] ×, Kennan et al.[19]

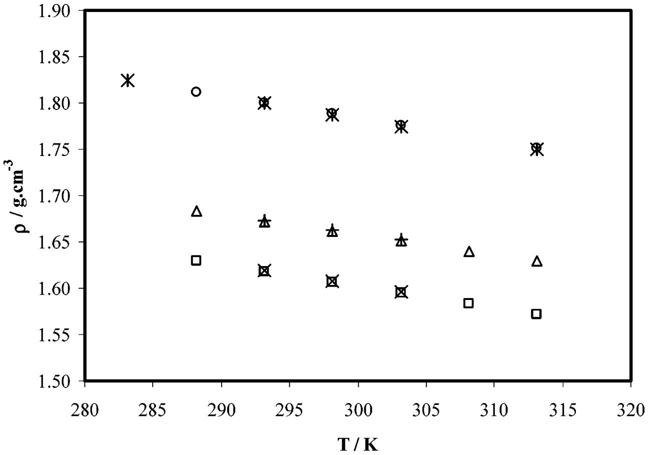

Figure 6. Comparison between experimental density data. This work: ○, perfluoro-*n*-nonane; □, perfluorobenzene; and △, perfluorotoluene. Literature data: *, Piñeiro et al.,[18] perfluoro-*n*-nonane; ×, Hales et al.,[20] perfluorobenzene; +, Hales et al.,[20] perfluorotoluene.

Experimental data obtained for perfluoro-*n*-hexane are in good agreement with data measured both by Dunlap et al.[14] and Crowder et al.[15] The authors used, respectively, the static and ebulliometric methods to perform the measurements, and both of them used mercury manometers to read the pressure. Larger deviations are found when comparisons with the data measured by Stiles et al.[16] using the static method are made.

Vapor-pressure data measured for perfluorotoluene agree, to within the accuracy stated for the method, with data measured by Ambrose et al.,[17] whose measurements were performed using comparative ebulliometry.

Densities. Density data measured in this work is presented in Table 5. For the temperature range studied in this work, experimental data were found to be correctly described by a linear equation of the type

$$\rho_{\text{calcd}} = A - BT \tag{3}$$

where T is the temperature. Coefficients for eq 3 are reported in Table 6.

Table 5 also presents the values calculated with the soft-SAFT EoS using the molecular parameters reported in Table 4.

Table 5. Experimental and Calculated Liquid Densities of the Studied Compounds

T	ρ_{exptl}	ρ_{calcd} (eq 2)	$\Delta\rho^a$	ρ_{calcd} (soft-SAFT)	$\Delta\rho^a$	T	ρ_{exptl}	ρ_{calcd} (eq 2)	$\Delta\rho^a$	ρ_{calcd} (soft-SAFT)	$\Delta\rho^a$
K	g·cm^{-3}	g·cm^{-3}	g·cm^{-3}	g·cm^{-3}	g·cm^{-3}	K	g·cm^{-3}	g·cm^{-3}	g·cm^{-3}	g·cm^{-3}	g·cm^{-3}
C_6F_{14} − Perfluoro-*n*-hexane											
288.15	1.7056	1.7056	0.00072	1.7042	0.00138	303.15	1.6611	1.6611	−0.00074	1.6612	−0.00013
293.15	1.6910	1.6910	0.00043	1.6900	0.00095	313.15	1.6302	1.6302	−0.00285	1.6318	−0.00159
298.15	1.6761	1.6761	−0.00006	1.6757	0.00045						
C_9F_{20} − Perfluoro-*n*-nonane											
288.15	1.8122	1.8122	−0.00016	1.8132	−0.00108	303.15	1.7757	1.7757	0.00012	1.7760	−0.00027
293.15	1.8001	1.8001	0.00001	1.8009	−0.00078	313.15	1.7509	1.7509	−0.00015	1.7508	0.00011
298.15	1.7879	1.7879	0.00011	1.7884	−0.00051						
$C_{10}F_{18}$ − Perfluorodecalin											
288.15	1.9528	1.9529	−0.00008	1.9510	0.00178	303.15	1.9192	1.9191	0.00007	1.9183	0.00091
293.15	1.9417	1.9417	0.00002	1.9401	0.00156	313.15	1.8966	1.8966	−0.00007	1.8965	0.00005
298.15	1.9305	1.9304	0.00007	1.9292	0.00126						
$C_8F_{17}Br$ − 1Br-Perfluoro-*n*-octane											
288.15	1.9386	1.9386	−0.00006	1.9397	−0.00114	303.15	1.9028	1.9027	0.00014	1.9037	−0.00088
293.15	1.9267	1.9266	0.00007	1.9277	−0.00102	308.15	1.8908	1.8907	0.00008	1.8916	−0.00087
298.15	1.9148	1.9147	0.00013	1.9157	−0.00093	313.15	1.8786	1.8787	−0.00007	1.8795	−0.00091
$C_8F_{17}H$ − 1H-Perfluoro-*n*-octane											
288.15	1.7736	1.7738	−0.00016	1.7748	−0.00113	303.15	1.7379	1.7378	0.00008	1.7387	−0.00082
293.15	1.7618	1.7618	−0.00002	1.7628	−0.00101	308.15	1.7258	1.7258	0.00000	1.7266	−0.00077
298.15	1.7499	1.7498	0.00007	1.7508	−0.00090	313.15	1.7136	1.7138	−0.00018	1.7144	−0.00076
C_6F_6 − Perfluorobenzene											
288.15	1.6289	1.6289	−0.00009	1.6299	−0.00105	303.15	1.5948	1.5947	0.00005	1.5953	−0.00058
293.15	1.6175	1.6175	−0.00001	1.6184	−0.00091	308.15	1.5833	1.5833	0.00001	1.5837	−0.00039
298.15	1.6062	1.6061	0.00005	1.6069	−0.00075	313.15	1.5718	1.5719	−0.00010	1.5711	−0.00020
C_7F_8 − Perfluorotoluene											
288.15	1.6828	1.6829	−0.00015	1.6865	−0.00369	303.15	1.6509	1.6509	0.00003	1.6521	−0.00120
293.15	1.6722	1.6723	−0.00004	1.6751	−0.00286	308.15	1.6402	1.6402	−0.00003	1.6406	−0.00038
298.15	1.6616	1.6616	0.00002	1.6636	−0.00202	313.15	1.6294	1.6295	−0.00016	1.6290	0.00042

[a] $\Delta\rho = \rho_{exptl} - \rho_{calcd}$.

Table 6. Constants for the Density Correlation Using Equation 3

compound	A	B ($\times 10^{-3}$)	δ^a ($\times 10^{-3}$)
C_6F_{14}	2.5754	3.0172	0.30
C_9F_{20}	2.5182	2.4497	0.12
$C_{10}F_{18}$	2.6015	2.2509	0.07
$C_8F_{17}Br$	2.6295	2.3976	0.11
$C_8F_{17}H$	2.4654	2.4002	0.10
C_6F_6	2.2867	2.2827	0.06
C_7F_8	2.2984	2.1359	0.09

[a] $\delta = [\Sigma(\rho_{exptl} - \rho_{calcd})^2/n]^{0.5}$, where n is the number of experimental points.

The literature density values for perfluoro-*n*-hexane, perfluoro-*n*-nonane, perfluorobenzene, and perfluorotolueneare are compared in Figures 5 and 6 with the data measured in this work. For simplicity, comparisons for perfluoro-*n*-nonane, perfluorobenzene, and perfluorotoluene are shown in the same Figure once only one set of literature data was found for each compound.

Experimental data obtained for perfluoro-*n*-hexane agree to within 0.7 mg·cm^{-3} with data measured by Piñeiro et al.,[18] whose measurements were performed with the same method used in this work with a degassed sample. Also, the obtained data are systematically higher than the data measured by Kennan et al.[19] and Dunlap et al.[14] for both an air-saturated and a degassed sample and lower than those measured by Stiles et al.[16] The authors used pycnometers to perform their measurements. Kennan et al.[19] and Stiles et al.[16] do not refer the degree of air saturation of their samples.

For perfluoro-*n*-nonane, density data were compared with the only data found in the literature,[18] and the agreement is of the same order of magnitude as in the case of perfluoro-*n*-hexane. The author used the same method and the same perfluoro-*n*-nonane purity as the ones used in this work.

Hales et al.[20] measured the density of degassed samples of perfluorobenzene and perfluorotoluene by weighing with and without the activation of a solenoid, which maintains a magnetically controlled float in the center of the sample according to a procedure described elsewhere.[21] The densities measured for those compounds in the present work are in both cases systematically lower, by 1.2 mg·cm^{-3}, than the ones measured by these authors.

The effect of dissolved air on the density of perfluoro-*n*-hexane and perfluorobenzene was studied by Dunlap et al.[14] and Hales et al.,[20] respectively. In the case of perfluoro-*n*-hexane, densities of the degassed sample were about 2.0 mg·cm^{-3} higher than those of the air-saturated sample. In the case of perfluorobenzene, differences between degassed and air-saturated samples were about 0.75 mg·cm^{-3}. Those differences are related to the solvent's capacity to dissolve components of the air and are higher in the case of perfluoro-*n*-hexane.[2,22] This observation cannot entirely justify the differences between density data measured in this work and literature data. In fact, differences observed for perfluorobenzene and perfluorotoluene, around 1.2 mg·cm^{-3}, are higher than would be expected considering the effect of dissolved air in the sample. For perfluoro-*n*-hexane, data measured by Dunlap et al.[14] for an air saturated sample are lower than the data obtained in this work. Also, comparisons between data measured in this work and by Piñeiro et al.[18] show no differences between degassed and air-saturated samples. It seems that the different methods used to measure the densities are mainly responsible for the differences observed.

The boiling temperature and the enthalpies of vaporization at 298 K calculated from eq 1 are given in Table 7. The enthalpies of vaporization were calculated by means

Table 7. Derived Boiling Temperatures, T_b, Standard Molar Enthalpies of Vaporization at 298.15 K, ΔH^{vap}, and Coefficients of Thermal Expansion at 298.15 K, α, of the Studied Compounds

	T_b(K)		ΔH^{vap}(kJ/mol)		α(K^{-1}), (× 10^{-3})	
	equation 1	SAFT	equation 1	SAFT	equation 3	SAFT
C_6F_{14}	330.29 ± 0.02	332.89	32.47 ± 0.11	29.42	1.87 ± 0.05	1.75
C_9F_{20}	390.76 ± 0.02	394.79	45.27 ± 0.23	41.55	1.38 ± 0.04	1.41
$C_{10}F_{18}$	415.17 ± 0.03	419.99	41.54 ± 0.52	40.35	1.12 ± 0.03	1.14
$C_8F_{17}Br$	416.11 ± 0.02	417.67	45.63 ± 0.36	42.50	1.26 ± 0.03	1.26
$C_8F_{17}H$	385.48 ± 0.02	388.26	43.35 ± 0.19	39.18	1.38 ± 0.03	1.39
C_6F_6	353.47 ± 0.02	353.16	36.08 ± 0.07	35.43	1.43 ± 0.02	1.45
C_7F_8	376.70 ± 0.03	378.22	40.52 ± 0.18	39.37	1.29 ± 0.02	1.39

of the Clapeyron equation, assuming that the vapor behaves as an ideal gas. The coefficients of thermal expansion along the saturation curve at 298.15 K computed from eq 2 are also listed in Table 7. A comparison between these calculated values and the ones estimated by the soft-SAFT EoS are also presented in Table 7. This EoS is able to predict the derived properties with average absolute deviations equal to 0.5% for the boiling temperatures, 5.5% for the enthalpies of vaporization, and 3.0% for the coefficients of thermal expansion.

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