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PρT Measurements of Nonafluorobutyl Methyl Ether and Nonafluorobutyl Ethyl Ether between 283.15 and 323.15 K at Pressures up to 40 MPa[1]

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In this paper, experimental densities for nonafluorobutyl methyl ether and nonafluorobutyl ethyl ether from 283.15 to 323.15 K at pressures up to 40 MPa are reported. The density measurements were performed by means of a high pressure vibrating tube densimeter. Data reliability was checked by comparing experimental results obtained for tetrachloromethane—whose density is close to those of the fluids studied—with recommended literature data. Furthermore, the isobaric thermal expansion, isothermal compressibility, and internal pressure have been calculated from these density data.

KEY WORDS: density; isobaric thermal expansion; isothermal compressibility; internal pressure; nonafluorobutyl ethyl ether; nonafluorobutyl methyl ether.

1. INTRODUCTION

Recent developments on the search for new environmental friendly fluids have focused increasing attention on hydrofluoroethers (HFEs). These substances present many optimal features that make them suitable for consideration as substitutes of many other commonly used fluids that present more harmful environmental effects. The U.S. Environmental Protection Agency (EPA) included HFEs among those candidates to be

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considered for future replacement in different applications of hydrofluorocarbons (HFCs) and related substances [1]. Over the last two decades, intensive efforts have been devoted to the task of identifying and characterizing new families of potential environmentally friendly substitutes [2]. Although HFCs present zero ozone depletion potential (ODP), which is the main reason that motivated their widespread application, rising concerns about global warming have brought controversy on their use, and will probably result in international restrictions. From this point of view, HFEs, in addition to their good thermophysical characteristics, they have shorter average lifetimes [3] than HFCs and other related substances.

In this work, attention is focused on two segregated HFEs, namely nonafluorobutyl methyl ether and nonafluorobutyl ethyl ether. These two products are currently used as precision electronic components cleaning agents replacing, for example, CFC-113 and HCFC-141b. Both of them have been also proposed for use as low temperature heat exchange fluids in heat transfer devices, in indirect refrigeration or air-conditioning applications using secondary loops. But despite their range of application, almost no thermophysical properties data for these two fluids can be found in the literature, which means that an accurate description of their thermodynamic behavior over broad ranges of temperature and pressure is not currently available. As a result, a first step on thermophysical characterization of these compounds was undertaken through $p\rho T$ measurements. In order to verify the reliability of the experimental procedure, measurements were performed on tetrachloromethane CCl_4, and the results were compared with recommended literature data. Furthermore, isobaric thermal expansion α_p, isothermal compressibility κ_T, and internal pressure π values estimated from the experimental density data are reported.

2. EXPERIMENTAL

2.1. Materials

Tetrachloromethane was obtained from Aldrich, (mole fraction purity > 0.996). Nonafluorobutyl methyl ether and nonafluorobutyl ethyl ether were obtained from TCI. The supplier (TCI) informs that these products are actually mixtures of inseparable structural isomers, with the same physical properties, providing for the first one a purity of 99.8% (39.1% of nonafluorobutyl methyl ether ($CF_3(CF_2)_3OCH_3$, CAS No. 163702-07-6) and 60.7% of nonafluoroisobutyl methyl ether ($(CF_3)_2CFCF_2OCH_3$, CAS No. 163702-08-7), and no purity value is supplied for the second one, composed of nonafluorobutyl ethyl ether ($CF_3(CF_2)_3OCH_2CH_3$, CAS No. 163702-05-4) and nonafluoroisobutyl ethyl ether ($(CF_3)_2CFCF_2OCH_2CH_3$, CAS No. 163702-06-5). All chemicals were degassed in an ultrasonic bath before use.

2.2. Apparatus

The density was measured as a function of pressure and temperature using an Anton Paar DMA 512 P/60 vibrating tube densimeter. The high-pressure densimeter cell DMA512P enables measurements over broad ranges of pressure (0.1 to 70 MPa) and temperature (273.15 to 423.15 K). The well-known measurement principle consists of determining the oscillation period of a U-shaped tube (with an inner volume of 2.5 cm^3, approximately), which contains the sample. The densimeter measuring unit DMA60 provides the period of oscillation of this U-shaped tube to seven significant digits. The temperature regulation is achieved through a jacket filled with water that surrounds the experimental cell, whose temperature is controlled by a Prolabo Thermostat. The temperature is measured by a CKT100 platinum thermometer, placed close to the experimental cell and previously calibrated, with an uncertainty estimated to be less than 0.05 K, whereas the pressure is controlled by a HBM manometer connected close to the experimental cell, which had been calibrated using a double weight gauge (Budenberg, uncertainty of 0.05 MPa). The complete experimental assembly containing the densimeter cell, the pressure pump, and the buffer volume that separates the hydraulic fluid (mercury) from the sample has been previously described in detail [4].

2.3. Experimental Method

Using this experimental technique, the density is linearly related to the square of the measured period of oscillation by the equation,

$$\rho(p,T) = K_1(p,T)\,\Lambda^2(p,T) - K_2(p,T) \tag{1}$$

where $\rho(p,T)$ is the density of the sample, $\Lambda(p,T)$ is the oscillation period of the densimeter cell, and $K_1(p,T)$ and $K_2(p,T)$ are characteristic parameters that are determined typically using two calibrating fluids of well-known densities in the entire ranges of pressure and temperature. Nevertheless, a new calibration method was proposed [5] that showed that the parameter $K_1(T)$ is independent of pressure. With this method, the characteristic parameters can be evaluated from the density of a single reference fluid (water) over the whole range of pressure and temperature with the additional knowledge of the temperature dependence of the experimental oscillation period for another reference fluid. Thus, the oscillation periods were measured for the whole temperature range for vacuum.

So, with Eq. (1) applied, respectively, to water and vacuum, the following equation can be used to calculate the sample density,

$$\rho(p,T)=\rho_{\text{water}}(p,T)+\rho_{\text{water}}(0.1\text{ MPa},T)\cdot\left[\frac{\Lambda^2(p,T)-\Lambda^2_{\text{water}}(p,T)}{\Lambda^2_{\text{water}}(0.1\text{ MPa},T)-\Lambda^2_{\text{vacuum}}(T)}\right]. \tag{2}$$

2.4. Experimental Uncertainty and Choice of Calibration Fluid

Taking into account the uncertainties in temperature (± 0.05 K) and pressure (± 0.05 MPa) and with the excellent reproducibility of the oscillation periods, the main contribution to the experimental uncertainty of the sample density is due to the uncertainty in the density of the calibration fluid. Water was chosen since its density is known with excellent accuracy (uncertainty of $10^{-5}\ \text{g}\cdot\text{cm}^{-3}$) over wide ranges of pressure and temperature [6]. Thus, taking water as the calibrating fluid, a simple error propagation on Eq. (2) shows that the estimated uncertainty in density is about $10^{-4}\ \text{g}\cdot\text{cm}^{-3}$.

In the current study, the densities of the analyzed samples are larger than that of water. Thus, the use of Eq. (2) involves an extrapolation on density as a function of period. Tetrachloromethane (CCl_4) was chosen as a reference fluid to check the validity of this extrapolation, not only because of the accuracy of its density data, compiled by Cibulka et al. [7] but also due to the fact that its density range is similar to that of the studied samples. Comparisons of measured and literature values shown in Table I indicate excellent agreement between the two sets of data (average percent deviation APD $= 0.0145\%$, root mean square deviation RMSD $= 3\times10^{-4}\ \text{g}\cdot\text{cm}^{-3}$), while the authors show RMSD $= 6.41\times10^{-4}\ \text{g}\cdot\text{cm}^{-3}$.

Table I. Experimental Densities ρ ($\text{g}\cdot\text{cm}^{-3}$) for Tetrachloromethane at 293.15 K, Compared with Values from the Correlation in Ref. 7

p (MPa)	Exp. ($\text{g}\cdot\text{cm}^{-3}$)	Ref. 7 ($\text{g}\cdot\text{cm}^{-3}$)	Percent deviation
0.1	1.5935	1.5942	0.04
5	1.6018	1.6021	0.02
10	1.6095	1.6098	0.02
20	1.6242	1.6243	0.009
30	1.6378	1.6378	0.0003
40	1.6505	1.6505	0.002
50	1.6625	1.6623	0.01
60	1.6739	1.6735	0.02

These comparisons demonstrate that this procedure using only water as a calibrating fluid is reliable within the uncertainty estimates. Furthermore, it should be noted that the density values for CCl_4 are not of as high accuracy as those for water—and are not available over the entire (p, T) range needed for a fluid used for calibration.

3. RESULTS AND DISCUSSION

3.1. Densities

Densities were measured for nonafluorobutyl methyl ether and nonafluorobutyl ethyl ether for pressures ranging from 0.1 to 40 MPa, and at temperatures varying from 283.15 to 313.15 K for the former, and from 283.15 to 323.15 K for the latter. All experimental values are listed in Table II, and plotted in Figs. 1 and 2. These measurements were fitted by the widely used modified Tait equation [7],

$$\rho(p, T) = \frac{\rho(p_0, T)}{1 - C \ln\left(\frac{B(T)+p}{B(T)+p_0}\right)}, \tag{3}$$

where C is a constant independent of temperature, and

$$B(T) = \sum_{i=0}^{2} B_i T^i \tag{4}$$

$$\rho(p_0, T) = \sum_{i=0}^{2} \rho_{0i} T^i \tag{5}$$

$\rho(p_0, T)$ stands for the densities considered at the reference pressure $p_0 = 0.1$ MPa over the entire temperature range. The set of coefficients for all compounds, as well as the absolute average deviations (AAD), which remain always below the experimental uncertainty, and the absolute percent deviations (APD (%)) between the experimental and the correlated values are listed in Table III.

3.2. Derived Thermodynamic Properties

Considering their definitions, the internal pressure π, the isobaric thermal expansion α_p, and the isothermal compressibility κ_T can be derived from the data for the volumetric behavior versus pressure and temperature.

Table II. Experimental Densities ($g \cdot cm^{-3}$) for Nonafluorobutyl Methyl Ether and Nonafluorobutyl Ethyl Ether

Nonafluorobutyl methyl ether

	T (K)				
p (MPa)	283.15	288.15	298.15	303.15	313.15
0.1	1.5541	1.5282	1.5153	1.5020	1.4751
1	1.5570	1.5315	1.5188	1.5058	1.4793
2	1.5600	1.5347	1.5220	1.5093	1.4832
3	1.5628	1.5378	1.5254	1.5128	1.4871
4	1.5656	1.5409	1.5287	1.5162	1.4908
5	1.5682	1.5440	1.5318	1.5195	1.4945
7.5	1.5750	1.5512	1.5394	1.5275	1.5033
10	1.5814	1.5582	1.5467	1.5351	1.5116
12.5	1.5876	1.5649	1.5537	1.5424	1.5194
15	1.5934	1.5713	1.5603	1.5493	1.5270
17.5	1.5992	1.5776	1.5667	1.5560	1.5342
20	1.6047	1.5834	1.5730	1.5624	1.5411
22.5	1.6101	1.5891	1.5789	1.5686	1.5477
25	1.6153	1.5946	1.5847	1.5744	1.5540
27.5	1.6203	1.6000	1.5902	1.5801	1.5601
30	1.6252	1.6053	1.5955	1.5855	1.5660
32.5	1.6300	1.6103	1.6007	1.5910	1.5717
35	1.6346	1.6152	1.6057	1.5962	1.5772
37.5	1.6390	1.6200	1.6106	1.6013	1.5826
40	1.6434	1.6245	1.6153	1.6062	1.5877

Nonafluorobutyl ethyl ether

	T (K)					
p (MPa)	283.15	288.15	298.15	303.15	313.15	323.15
0.1	1.4565	1.4340	1.4227	1.4111	1.3877	1.3639
1	1.4593	1.4369	1.4255	1.4143	1.3914	1.3678
2	1.4620	1.4398	1.4287	1.4174	1.3949	1.3717
3	1.4647	1.4426	1.4317	1.4207	1.3984	1.3755
4	1.4672	1.4455	1.4347	1.4237	1.4018	1.3793
5	1.4696	1.4483	1.4376	1.4267	1.4050	1.3830
7.5	1.4760	1.4550	1.4446	1.4341	1.4130	1.3918
10	1.4818	1.4615	1.4513	1.4411	1.4205	1.4000
12.5	1.4876	1.4676	1.4577	1.4477	1.4277	1.4077
15	1.4931	1.4736	1.4639	1.4541	1.4346	1.4150
17.5	1.4984	1.4793	1.4698	1.4602	1.4411	1.4221
20	1.5036	1.4848	1.4755	1.4661	1.4475	1.4287
22.5	1.5085	1.4901	1.4810	1.4718	1.4536	1.4352
25	1.5134	1.4951	1.4863	1.4772	1.4593	1.4414
27.5	1.5180	1.5001	1.4913	1.4824	1.4649	1.4473
30	1.5227	1.5049	1.4963	1.4876	1.4703	1.4531
32.5	1.5271	1.5096	1.5011	1.4926	1.4755	1.4586
35	1.5313	1.5141	1.5058	1.4974	1.4806	1.4639
37.5	1.5354	1.5186	1.5104	1.5020	1.4856	1.4691
40	1.5396	1.5228	1.5147	1.5066	1.4903	1.4741

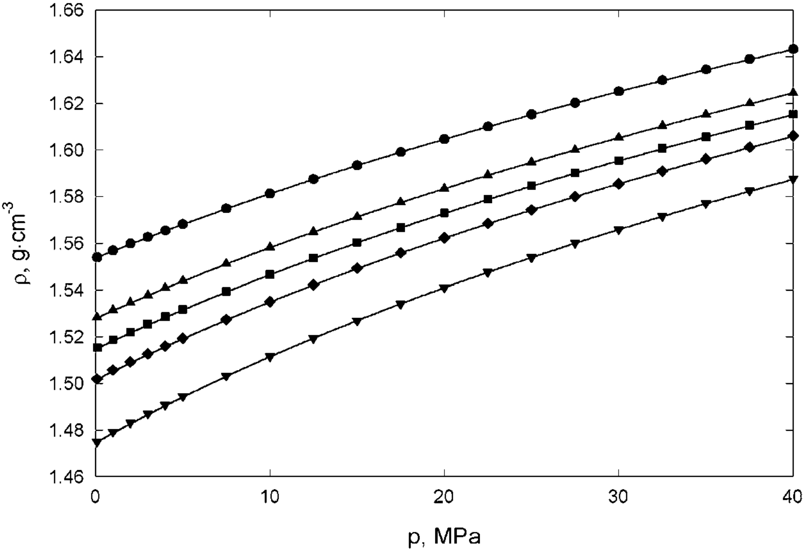

Fig. 1. Experimental density ρ for nonafluorobutyl methyl ether: ●, 283.15 K; ▲, 293.15 K; ■, 298.15 K; ◆, 303.15 K; ▼, 313.15 K; and correlation with Tait equation (solid line).

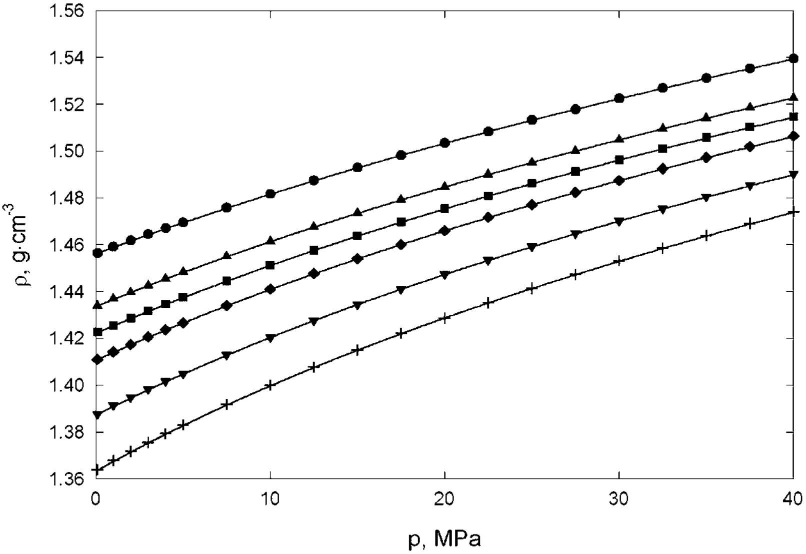

Fig. 2. Experimental density ρ for nonafluorobutyl ethyl ether: ●, 283.15 K; ▲, 293.15 K; ■, 298.15 K; ◆, 303.15 K; ▼, 313.15 K; +, 323.15 K; and correlation with Tait equation (solid line).

Table III. Coefficients for Eq. (3), Absolute Average Deviations (AAD, $g \cdot cm^{-3}$), and Average Percent Deviations (APD, %)

	Nonafluorobutyl Methyl Ether	Nonafluorobutyl Ethyl Ether
C	8.0337×10^{-2}	8.2020×10^{-2}
B_0 (MPa)	326.26	286.53
B_1 ($MPa \cdot K^{-1}$)	−1.5210	−1.2628
B_2 ($MPa \cdot K^{-2}$)	1.8166×10^{-3}	1.4199×10^{-3}
ρ_{00} ($g \cdot cm^{-3}$)	2.0494	1.9022
ρ_{01} ($g \cdot cm^{-3} \cdot K^{-1}$)	-9.4968×10^{-4}	-9.2332×10^{-4}
ρ_{02} ($g \cdot cm^{-3} \cdot K^{-2}$)	-2.8237×10^{-5}	-2.2989×10^{-5}
AAD	1×10^{-4}	8×10^{-5}
APD	7×10^{-3}	5×10^{-3}

Isothermal compressibilities κ_T were determined by analytical differentiation of the Tait equation versus pressure:

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T = \frac{C}{(1 + C \ln[(B(T)+p)/(B(T)+p_0)])(B(T)+p)} \tag{6}$$

This procedure is certainly the most direct way [8] to obtain reliable values of the isothermal compressibility κ_T. Indeed, the Tait equation is an integrated form of an empirical equation representative of the isothermal compressibility behavior versus pressure. Calculated values of κ_T are represented in Fig. 3.

In a similar way, the isobaric themal expansivity α_p can be derived from an analytical derivation of the Tait equation versus temperature. Nevertheless, the function $B(T)$ and the parameter C used in Eq. (3) are interpolated forms with adjusted coefficients without any physical significance. In this context, the isobaric thermal expansion α_p is determined, from its own definition, both by numerical derivation and by analytical differentiation of the Tait equation:

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{7}$$

The values obtained with the two procedures agree to within experimental error, i.e., within $5 \times 10^{-4}\ K^{-1}$. It is worth adding that the relatively narrow temperature range investigated can explain reliable values derived in this case from the analytical form. Therefore, the numerical calculation remains the most coherent procedure, generally advised for thermal expansivity calculations. α_p values for the studied compounds are plotted in Fig. 4.

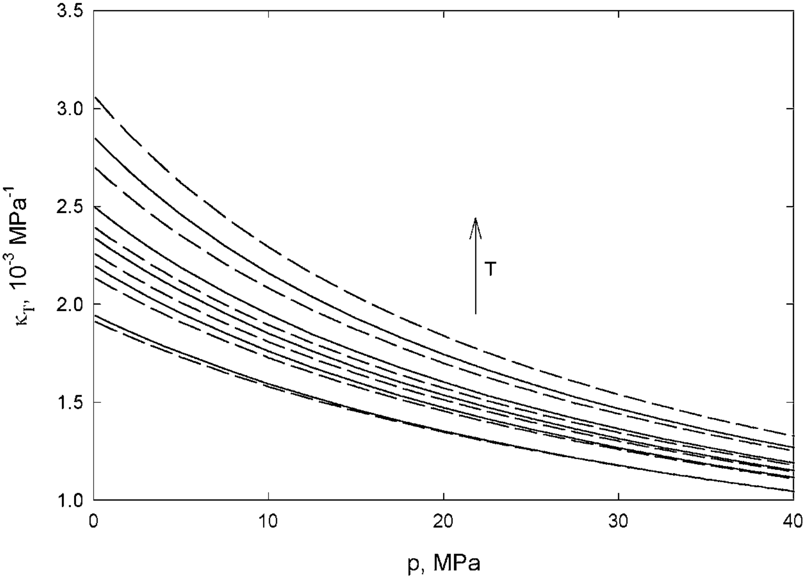

Fig. 3. Isothermal compressibility κ_T, calculated at different temperatures for nonafluorobutyl methyl ether (solid line) and nonafluorobutyl ethyl ether (dashed line).

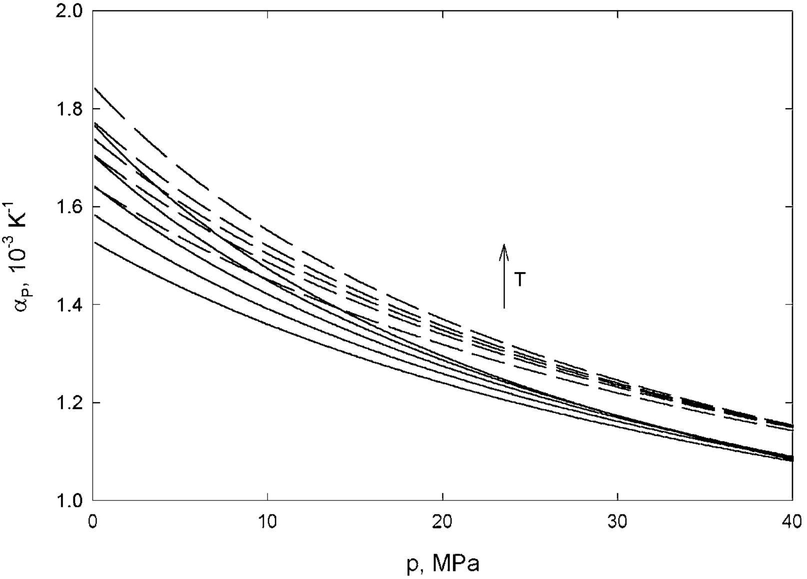

Fig. 4. Isothermal expansion coefficient α_p, calculated at different temperatures for nonafluorobutyl methyl ether (solid line) and nonafluorobutyl ethyl ether (dashed line).

Finally, on the basis of these thermoelastic coefficients, the internal pressure can be determined according to the following expression:

$$\pi = \left(\frac{\partial U}{\partial V_m}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = T\,\frac{\alpha_P}{\kappa_T} - p \tag{8}$$

The values of the internal pressure π were first estimated using the calculated values of isothermal compressibility and thermal expansivity. These results were then confirmed from those obtained from the corresponding Tait equation, taking p as a function of T and ρ and by performing the analytical differentiation of this expression. The error is estimated to be about 1 MPa over the entire pressure and temperature range.

It is particularly useful to plot (Fig. 5) internal pressure $\pi = (\frac{\partial U}{\partial V_m})_T$ against molar volume, taking into consideration both pressure and temperature dependences. The characteristics of these curves provide qualitative information about the microscopic properties of the liquid [9]. The behavior of this property can be explained in terms of competition between two contributions, due to attractive and repulsive internal energy terms. The decrease of the internal pressure with molar volume (Fig. 5) corresponds to a negative $(\frac{\partial^2 U}{\partial V^2})_T < 0$ which indicates that both HFEs behave like

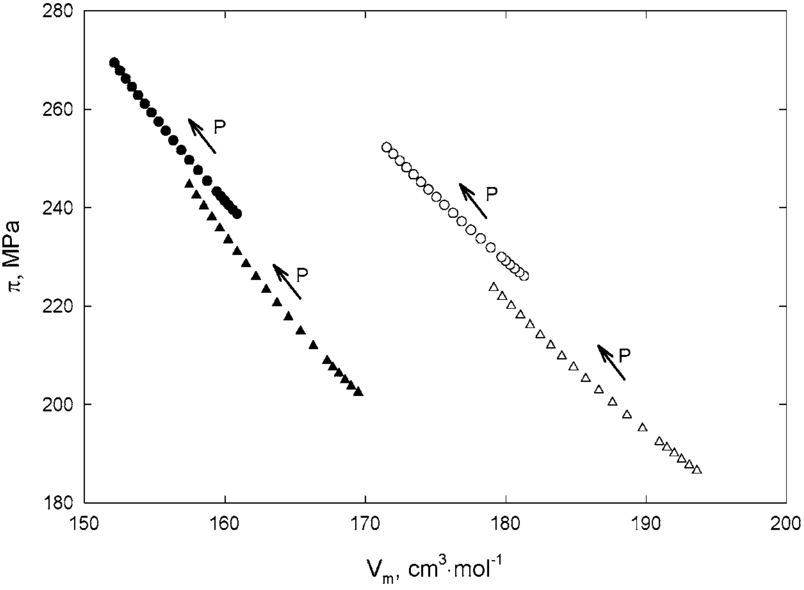

Fig. 5. Internal pressure, π, plotted against molar volume, for nonafluorobutyl methyl ether: ●, 283.15 K; ▲, 313.15 K; and nonafluorobutyl ethyl ether: ○, 283.15 K; △, 323.15 K. The arrows show the direction of increasing pressure for each isotherm.

non-structured or non-associated fluids [9–11]. The linear perfluorinated chain could lead to the assumption of the existence of an orientation order in these molecules. However, it is worth noting that in the temperature range of the current study, close to the boiling temperature of both fluids, the main contribution results from repulsive interactions. At lower temperatures, the combination of both order-orientational forces and an attractive energetic term due to the association energy of the ether group should be predominant. Moreover, a decrease of the internal pressure with temperature is observed, i.e., a diminution of the contribution of cohesive forces with temperature. It is also convenient to emphasize that the impact of the association term must be reduced in the case of the perfluorinated chains when compared to the case of a linear hydrogenated chain, because the size of the contributing groups causes a steric hindrance effect, diminishing the possibility of this potential associative effect.

4. CONCLUSION AND FUTURE WORK

Experimental compressed liquid densities are presented over ranges of pressure and temperature for nonafluorobutyl methyl ether and nonafluorobutyl ethyl ether, useful for their industrial applications. These *pvT* data, as well as the derived thermophysical properties, isobaric thermal expansion coefficient, isothermal compressibility, and internal pressure, provide the first information for these fluids for developing theoretical models. Further measurements will be devoted to the calorimetric properties of these pure compounds, before carrying out experimental studies on the excess properties of mixtures containing HFEs and *n*-alkanes.

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