

Dielectric Properties of 1,1,1,3,3-Pentafluoropropane (HFC-245fa)[†]

Anely N. Gurova,^{‡,§} Filipe E. de Brito,[‡] Carlos A. Nieto de Castro,^{§,||} and Umesh V. Mardolcar^{*,‡,§}

Instituto Superior Técnico, Departamento de Física e Nucleo de Termofísica, Av. Rovisco Pais, 1049-001 Lisboa, Portugal, Departamento de Química e Bioquímica and Centro de Ciências Moleculares e Materiais, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

The relative permittivity of 1,1,1,3,3-pentafluoropropane (HFC-245fa), a liquid hydrofluorocarbon developed as a blowing agent for plastic foams, is reported. This fluid is being evaluated as a potential replacement for HCFC-141b (1,1-dichloro-1-fluoroethane). The relative permittivity of HFC-245fa in the liquid phase was measured using the direct capacitance method at temperatures from (217 to 303) K and at pressures up to 16 MPa, for a frequency of 10 kHz. The uncertainty of the dielectric constant measurements is estimated to be $\pm 0.88 \times 10^{-2}$. A complete set of values of the relative permittivity as a function of temperature, pressure, and density is presented that covers the needs for most engineering applications. The results were correlated by polynomial equations as a function of density and temperature and also as a function of pressure and temperature. To study the dependence of relative permittivity on density and temperature on a molecular basis, the theory developed by Vedam et al. and adapted by Diguet was applied to analyze the data. The Kirkwood modification of the Onsager equation was used to obtain the value of its dipole moment in the liquid phase. The apparent dipole moment obtained was $\mu^* = 2.688$ D.

Introduction

The current international agreements addressing global environmental issues (the Montreal and Kyoto Protocols) already provide the guidelines needed to ensure that all refrigerant and blowing agent solutions are environmentally safe. The Montreal Protocol has provided a phase-out of all ozone-depleting substances. Some hydrofluorocarbon (HFC) blowing agents such as HFC-245fa (1,1,1,3,3-pentafluoropropane) in addition to their superior insulating capability also contribute to the reduction of the total greenhouse gas emission. The main application of HFC-245fa is as a blowing agent in building insulation. Foam products used for this purpose include the spray polyurethane foam (SPF) roofing, which is used for commercial building roof insulation, and the polyisocyanurate (PIR) board stock, which is widely used for building wall and roof insulation. The Montreal Protocol phase-out of the CFC-11 foam blowing agent was followed by the widespread use of 1-fluoro-1,1-dichloroethane (HCFC-141b) and cyclopentane. HCFC-141b has one of the highest ozone depletion potential (ODP = capacity of destruction of a given number of ozone molecules by chlorine atoms, calculated through a chemical model for stratospheric ozone, assuming the stationary state of emission and destruction, relative to CFC-11 (trichlorofluoromethane)) values among the transitional alternatives and has been put on an earlier phase-out schedule than other transitional alternatives. The changeover from HCFC-141b to a non-ozone-depleting HFC is currently in process, with full-scale production a few

years off. The HFC blowing agents with the best thermal performance (e.g., HFC-245fa, 1,1,1,3,3-pentafluorobutane (HFC-365mfc)) result in foams having thermal conductivities comparable to those of HCFC-141b foams and about 10% lower than that of cyclopentane blown foam.¹

As a continuation of our previous work,^{2–5} we have studied the dependence of the relative permittivity on density, applying the concept of Eulerian deformation, also named Eulerian strain, based on the work of Vedam et al.^{6,7} and Diguet.⁸ In addition, to contribute to a better understanding of the structure of polar liquids, the apparent dipole moment of 1,1,1,3,3-pentafluoropropane in the liquid phase was estimated by applying the theory of molecular polarizability developed by Kirkwood⁹ on the basis of the definition of Onsager's local field.¹⁰

Experimental Section

The measurements were carried out using the direct capacitance method. The description of the cell has been presented before by Mardolcar et al.,¹¹ and the sample handling, vacuum, and pressure system has been presented by Gurova et al.¹² The measuring process makes use of fully automated instrumentation, described elsewhere.³ Vacuum capacitance was measured as a function of temperature before filling the cell with the fluid. An impedance gain-phase analyzer (Schlumberger, model SI 1260) has been used with an uncertainty of 5×10^{-4} pF. This equipment was calibrated by Laboratório de Metrologia Eléctrica da Companhia Portuguesa Radio Marconi, Lisbon, using the standards of capacitance of 1 pF, 10 pF, 100 pF, 1000 pF, 0.01 μ F, 0.1 μ F, and 1 μ F with an uncertainty of 0.01%. The schematic diagram of the apparatus setup for the measurements of the relative permittivity (ϵ) in the liquid phase is presented in Figure 1.

Honeywell Fluorochemical, Italy, provided the sample used with an estimated purity of 99.9% (mass). The main sources of impurity, as stated by the supplier, are isomers

[†] This contribution will be part of a special print edition containing papers presented at the Fourteenth Symposium on Thermophysical Properties, Boulder, CO, June 25–30, 2000.

* To whom correspondence should be addressed.

[‡] Instituto Superior Técnico. Fax: +351 21 8419013. E-mail: pumesh@alfa.ist.utl.pt.

[§] Centro de Ciências Moleculares e Materiais, Faculdade de Ciências da Universidade de Lisboa.

^{||} Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa.

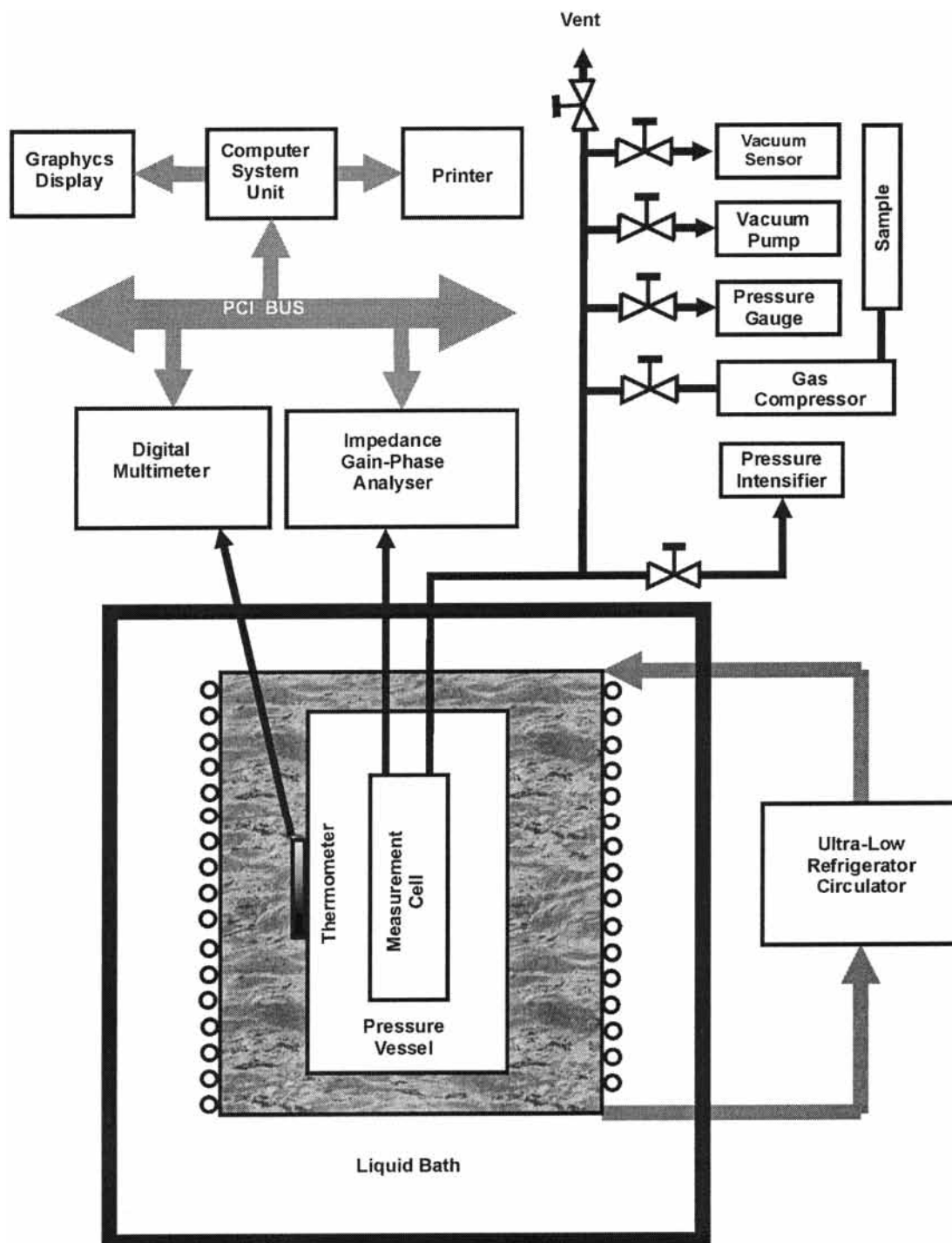


Figure 1. Schematic diagram of the apparatus. The figure is self-contained.

and water (33.5 ppm), although a very small trace of free HCl was found (0.19 ppm). The fluid was measured without further purification, and no further purity checks were performed after handling. The measurements were performed at a frequency of 10 kHz (average of 10 points). A total of 10 isotherms separated by ≈ 10 K, in steps of 1 MPa, from (1 to 16) MPa were obtained. The density values were calculated using the REFPROP database, version 6.01, proposed by McLinden et al.,¹³ which has a range of applicability from (200 to 500) K and pressures to 60 MPa. The temperature was measured with a platinum resistance thermometer calibrated at four temperature points (223, 253, 273, and 303 K) to within 0.01 K, by the Laboratório Central de Metrologia of Instituto Português de Qualidade.

The uncertainties of temperature and pressure are 0.01 K and 10 kPa, respectively. The uncertainty of the experimental measurements of the dielectric constant with the present apparatus was found in previous papers to be better than 0.16%.^{2,13-16} for a confidence interval of 95%. (Here we use the ISO definition of uncertainty, with $k = 2$ (95% confidence). Using the common calculation for accuracy, the values reported must be divided by 2.) This calculation reflects the uncertainty in the temperature, pressure, and capacitance measurements (in the fluid, including the effect of the hydrostatic pressure in the capacitor components, and in a vacuum). The possible uncertainty of the impurities was estimated to be smaller than the repeatability of the measurements (8 parts in 10^4)

and therefore was not included in the uncertainty budget. For the relative permittivity measurements with HFC-245fa the value of the uncertainty is estimated to be $\pm 0.88 \times 10^{-2}$.

Results

The following relation was used to determine the relative permittivity ϵ of the fluid:

$$\epsilon = \frac{C(p, T)}{C_0(T)} \quad (1)$$

where $C(p, T)$ is the geometric capacitance at pressure p and temperature T and $C_0(T)$ is the capacitance under vacuum at the temperature T . Table 1 presents the data obtained as a function of pressure and density for each isotherm, for the fluid studied. T_n is the nominal temperature. All the experimental points measured at a given temperature T , close to T_n , were adjusted to this temperature, by using

$$\epsilon(T_n, p) = \epsilon(T, p) + \left(\frac{\partial \epsilon}{\partial T}\right)_p (T_n - T) \quad (2)$$

In the absence of a full equation of state the density was obtained from the REFPROP database.¹⁷ Figure 2 gives the graphical representation of relative permittivity as a function of density. The experimental data of the relative permittivity were fitted by an iterative χ^2 method (each iteration implemented by a Levenberg–Marquart procedure) to a function of density ρ and temperature, of the following empirical form (this form has proven, as previously stated, to reproduce the experimental data within their uncertainty):

$$\epsilon(\rho, T) = \frac{a_1}{T} + a_2\rho + \frac{a_3\rho}{T} \quad (3)$$

The coefficients (a_1 , a_2 , and a_3) of this fit and their uncertainties are given in Table 2. The standard deviation of the fit is 0.07%. For industrial needs the data were also fitted to a function of pressure and temperature according to the empirical equation (p in MPa and T in K)

$$\epsilon(p, T) = b_0 + \frac{b_1}{T} + b_2p + \frac{b_3p}{T} \quad (4)$$

These coefficients (b_0 , b_1 , b_2 , and b_3) and their uncertainties are given in Table 2. The standard deviation of the fit is 0.25%.

As a continuation of our previous work,^{2–5} we have studied the dependence of the relative permittivity on density, applying the concept of Eulerian deformation, also named Eulerian strain, based on the work of Vedam et al.^{6,7} and Diguët.⁸ The theory shows that the variation of the relative permittivity with pressure is a function of the deformation of the volume, showing a nonlinear behavior in the case of liquids. It is possible to reduce this nonlinearly when the variation of ϵ , Δ , is analyzed as a function of the Eulerian deformation, Σ . We can verify that Σ provides a linear relation for Δ independently of the type of molecules that compose the fluid. We have used the relation between $\epsilon^{1/2}$ and the Eulerian strain, Σ , which is

defined, according to the Vedam relation, as

$$\Delta = \epsilon^{1/2}(\rho) - \epsilon^{1/2}(\rho_0) = A\Sigma + B \quad (5)$$

$$\Sigma = \frac{1}{2} \left[\left(1 - \frac{\rho}{\rho_0} \right)^{2/3} \right] \quad (6)$$

Here ρ_0 is the reference density, taken in this case as the saturation value for each isotherm. The saturation density data of R245fa were calculated using the equation of state provided by Defibaugh and Moldover¹⁸ and implemented in the REFPROP database.¹⁷

The calculations show that the function Δ indeed represents a linear variation with the Eulerian strain, Σ , as can be seen in Figure 3. Table 3 presents the values of the coefficients A and B of the Vedam equation for each isotherm. The y -crossing values are close to zero for all isotherms, $B \cong 0$. The slope of the linear variation of Δ with Σ is negative for all temperatures, decreasing linearly with the increase of temperature, as expected from the theory. Assuming that $B = 0$ (eq 5), it is possible to use the Vedam relation to estimate the relative permittivity values. We have estimated the new value of A' , by fitting the experimental results as a function of Σ and forcing the constant B to be equal to zero. In this case the Vedam equation takes the following form:

$$\Delta = A'\Sigma \quad (7)$$

The new values of the slope A' according to eq 7 are also presented in Table 3. We can estimate the variation of the relative permittivity with density for each isotherm. Figure 4 presents the deviations between the estimated values and the experimental data of relative permittivity calculated according to this model. As can be seen, they are smaller than 0.25%. However a systematic deviation does exist because of the constrained regression. This systematic deviation is never present if we use the full equation (eq 5) for correlating the data. Either equation is very useful for interpolation, and these relations can be improved in the future if a reliable equation of state is available.

In the present work, the apparent dipole moment of HFC-245fa in the liquid phase was estimated by applying the theory of molecular polarizability developed by Kirkwood⁹ on the basis of the definition of Onsager's local field.¹⁰ The relative permittivity of a polar fluid can be related to the apparent dipole moment μ^* through the equation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} \left(\frac{M}{\rho} \right) = \frac{N_0}{3} \left[\alpha + \frac{(\mu^*)^2}{3\epsilon_0 k_B T} \right] \quad (8)$$

Here M is the relative molar mass of the fluid, N_0 is Avogadro's number, α is the molecular polarizability of the molecule, ϵ_0 is the electric permittivity in a vacuum, T is the absolute temperature, and k_B is the Boltzmann constant. The apparent dipole moment is $\mu^* = g^{1/2}\mu$, where μ is the dipole moment in the ideal gas state and g is the Kirkwood correlation parameter that measures the restriction to rotation imposed by a cage of molecules surrounding a given one. By performing a linear regression of the Kirkwood relation as a function of $1/T$, the value of μ^* can be evaluated. Figure 5 shows the plot of the Kirkwood function versus $1/T$ for HFC-245fa. The value of the apparent dipole moment was found to be $\mu^* = 2.688$ D (D). Using the value of the dipole moment ($\mu = 1.549$ D) in the gas phase,¹⁷ the value of the Kirkwood parameter g was found to be equal to 3.01.

Table 1. Experimental Values of the Relative Permittivity, ϵ , along Isotherms from (218 to 302) K and up to 16 MPa, of HFC-245fa

T K	P MPa	ρ kg·m ⁻³	$\epsilon(T,P)$	$\rho(T_n,P)$ kg·m ⁻³	$\epsilon(T_n,P)$	T K	P MPa	ρ kg·m ⁻³	$\epsilon(T,P)$	$\rho(T_n,P)$ kg·m ⁻³	$\epsilon(T_n,P)$
$T_n = 302.84$ K						$T_n = 253.01$ K					
302.83	16.00	1370.84	6.7895	1370.81	6.7893	253.01	16.00	1481.03	8.7395	1481.03	8.7395
302.82	15.00	1368.39	6.7698	1368.34	6.7694	253.01	15.00	1479.43	8.7250	1479.43	8.7250
302.82	14.00	1365.88	6.7500	1365.84	6.7497	253.01	14.00	1477.81	8.7112	1477.81	8.7112
302.82	13.00	1363.33	6.7295	1363.29	6.7292	253.01	13.00	1476.19	8.6948	1476.19	8.6948
302.82	12.00	1360.74	6.7093	1360.69	6.7090	253.01	12.00	1474.54	8.6775	1474.54	8.6775
302.82	11.00	1358.10	6.6886	1358.05	6.6883	253.01	11.00	1472.88	8.6605	1472.88	8.6605
302.82	10.00	1355.41	6.6679	1355.37	6.6676	253.01	10.00	1471.21	8.6436	1471.21	8.6436
302.82	9.00	1352.68	6.6465	1352.63	6.6462	253.00	9.00	1469.54	8.6255	1469.52	8.6253
302.82	8.00	1349.89	6.6244	1349.84	6.6241	253.01	8.00	1467.82	8.6081	1467.82	8.6081
302.82	7.00	1347.05	6.6024	1347.00	6.6020	253.01	7.00	1466.09	8.5911	1466.09	8.5911
302.82	6.00	1344.15	6.5801	1344.10	6.5798	253.00	6.00	1464.38	8.5719	1464.36	8.5717
302.82	5.00	1341.20	6.5576	1341.14	6.5572	253.01	5.00	1462.60	8.5529	1462.60	8.5529
302.82	4.00	1338.18	6.5336	1338.13	6.5333	253.02	4.00	1460.81	8.5354	1460.83	8.5357
302.82	3.00	1335.09	6.5107	1335.04	6.5104	253.01	3.00	1459.04	8.5171	1459.04	8.5171
302.82	2.00	1331.94	6.4860	1331.89	6.4857	253.01	2.00	1457.23	8.4986	1457.23	8.4986
303.13	1.00	1327.86	6.4496	1328.66	6.4544	253.01		1455.41	8.4798	1455.41	8.4798
$T_n = 293.23$ K						$T_n = 243.02$ K					
293.23	16.00	1392.66	7.1302	1392.66	7.1302	243.03	16.00	1502.23	9.2058	1502.25	9.2060
293.22	15.00	1390.41	7.1113	1390.39	7.1112	243.03	15.00	1500.77	9.1895	1500.79	9.1897
293.23	14.00	1388.09	7.0921	1388.09	7.0921	243.02	14.00	1499.32	9.1731	1499.32	9.1731
293.23	13.00	1385.76	7.0734	1385.76	7.0734	243.02	13.00	1497.83	9.1567	1497.83	9.1567
293.22	12.00	1383.41	7.0539	1383.39	7.0537	243.02	12.00	1496.34	9.1399	1496.34	9.1399
293.23	11.00	1380.98	7.0337	1380.98	7.0337	243.02	11.00	1494.83	9.1247	1494.83	9.1247
293.23	10.00	1378.54	7.0135	1378.54	7.0135	243.02	10.00	1493.31	9.1110	1493.31	9.1110
293.23	9.00	1376.05	6.9932	1376.05	6.9932	243.02	9.00	1491.77	9.0949	1491.77	9.0949
293.22	8.00	1373.55	6.9727	1373.53	6.9725	243.02	8.00	1490.23	9.0781	1490.23	9.0781
293.22	7.00	1370.99	6.9518	1370.96	6.9516	243.02	7.00	1488.67	9.0610	1488.67	9.0610
293.22	6.00	1368.37	6.9303	1368.35	6.9302	243.02	6.00	1487.10	9.0438	1487.10	9.0438
293.22	5.00	1365.72	6.9094	1365.69	6.9092	243.02	5.00	1485.51	9.0259	1485.51	9.0259
293.22	4.00	1363.01	6.8873	1362.99	6.8871	243.02	4.00	1483.91	9.0085	1483.91	9.0085
293.22	3.00	1360.26	6.8641	1360.23	6.8639	243.02	3.00	1482.30	8.9907	1482.30	8.9907
293.22	2.00	1357.45	6.8433	1357.42	6.8431	243.02	2.00	1480.68	8.9728	1480.68	8.9728
293.24	1.00	1354.53	6.8154	1354.56	6.8156	243.02	1.00	1479.04	8.9552	1479.04	8.9552
$T_n = 283.19$ K						$T_n = 233.12$ K					
283.20	16.00	1415.14	7.5012	1415.16	7.5014	233.14	16.00	1522.97	9.7015	1523.01	9.7021
283.20	15.00	1413.07	7.4832	1413.09	7.4833	233.14	15.00	1521.64	9.6858	1521.68	9.6864
283.19	14.00	1410.98	7.4648	1410.98	7.4648	233.13	14.00	1520.32	9.6695	1520.34	9.6698
283.19	13.00	1408.85	7.4464	1408.85	7.4464	233.13	13.00	1518.97	9.6543	1518.99	9.6546
283.19	12.00	1406.69	7.4273	1406.69	7.4273	233.13	12.00	1517.61	9.6380	1517.63	9.6383
283.19	11.00	1404.50	7.4086	1404.50	7.4086	233.12	11.00	1516.26	9.6223	1516.26	9.6223
283.19	10.00	1402.28	7.3891	1402.28	7.3891	233.12	10.00	1514.88	9.6055	1514.88	9.6055
283.19	9.00	1400.03	7.3698	1400.03	7.3698	233.12	9.00	1513.49	9.5890	1513.49	9.5890
283.19	8.00	1397.75	7.3498	1397.75	7.3498	233.12	8.00	1512.09	9.5721	1512.09	9.5721
283.18	7.00	1395.45	7.3299	1395.43	7.3297	233.12	7.00	1510.69	9.5564	1510.69	9.5564
283.18	6.00	1393.10	7.3094	1393.08	7.3093	233.11	6.00	1509.29	9.5436	1509.27	9.5433
283.18	5.00	1390.71	7.2891	1390.69	7.2889	233.12	5.00	1507.84	9.5291	1507.84	9.5291
283.18	4.00	1388.29	7.2684	1388.27	7.2682	233.11	4.00	1506.43	9.5117	1506.40	9.5114
283.18	3.00	1385.83	7.2470	1385.80	7.2468	233.11	3.00	1504.98	9.4944	1504.96	9.4941
283.19	2.00	1383.30	7.2258	1383.30	7.2258	233.11	2.00	1503.52	9.4780	1503.50	9.4777
283.19	1.00	1380.76	7.2014	1380.76	7.2014	233.11	1.00	1502.05	9.4607	1502.03	9.4604
$T_n = 273.12$ K						$T_n = 224.16$ K					
273.13	16.00	1437.41	7.8934	1437.43	7.8936	224.15	16.00	1541.58	10.1922	1541.56	10.1919
273.13	15.00	1435.51	7.8747	1435.53	7.8749	224.15	15.00	1540.36	10.1763	1540.34	10.1760
273.13	14.00	1433.58	7.8568	1433.60	7.8570	224.16	14.00	1539.12	10.1602	1539.12	10.1602
273.12	13.00	1431.65	7.8389	1431.65	7.8389	224.16	13.00	1537.89	10.1441	1537.89	10.1441
273.12	12.00	1429.68	7.8207	1429.68	7.8207	224.16	12.00	1536.65	10.1284	1536.65	10.1284
273.12	11.00	1427.69	7.8023	1427.69	7.8023	224.16	11.00	1535.40	10.1123	1535.40	10.1123
273.12	10.00	1425.67	7.7836	1425.67	7.7836	224.16	10.00	1534.15	10.0965	1534.15	10.0965
273.12	9.00	1423.62	7.7649	1423.62	7.7649	224.15	9.00	1532.90	10.0809	1532.88	10.0806
273.12	8.00	1421.55	7.7460	1421.55	7.7460	224.15	8.00	1531.64	10.0643	1531.61	10.0640
273.11	7.00	1419.48	7.7266	1419.46	7.7264	224.15	7.00	1530.36	10.0477	1530.34	10.0474
273.12	6.00	1417.33	7.7073	1417.33	7.7073	224.15	6.00	1529.07	10.0312	1529.05	10.0309
273.12	5.00	1415.18	7.6877	1415.18	7.6877	224.17	5.00	1527.74	10.0137	1527.76	10.0140
273.12	4.00	1413.00	7.6678	1413.00	7.6678	224.17	4.00	1526.44	9.9965	1526.46	9.9968
273.12	3.00	1410.79	7.6478	1410.79	7.6478	224.17	3.00	1525.13	9.9837	1525.15	9.9840
273.12	2.00	1408.55	7.6275	1408.55	7.6275	224.17	2.00	1523.81	9.9673	1523.83	9.9676
273.13	1.00	1406.26	7.6055	1406.28	7.6057	224.17	1.00	1522.49	9.9501	1522.51	9.9504
$T_n = 263.00$ K						$T_n = 218.53$ K					
263.00	16.00	1459.51	8.3091	1459.51	8.3091	218.57	16.00	1553.02	10.5064	1553.10	10.5076
263.00	15.00	1457.77	8.2921	1457.77	8.2921	218.54	15.00	1551.93	10.4929	1551.95	10.4932
263.00	14.00	1456.01	8.2738	1456.01	8.2738	218.54	14.00	1550.78	10.4782	1550.80	10.4785
263.00	13.00	1454.23	8.2566	1454.23	8.2566	218.55	13.00	1549.60	10.4625	1549.64	10.4632
263.00	12.00	1452.43	8.2388	1452.43	8.2388	218.56	12.00	1548.42	10.4461	1548.48	10.4471
263.00	11.00	1450.61	8.2212	1450.61	8.2212	218.59	11.00	1547.18	10.4291	1547.31	10.4310
263.00	10.00	1448.77	8.2030	1448.77	8.2030	218.60	10.00	1545.98	10.4121	1546.13	10.4143
263.00	9.00	1446.91	8.1850	1446.91	8.1850	218.61	9.00	1544.78	10.3955	1544.95	10.3980
263.00	8.00	1445.03	8.1668	1445.03	8.1668	218.61	8.00	1543.58	10.3791	1543.76	10.3816
263.00	7.00	1443.14	8.1481	1443.14	8.1481	218.60	7.00	1542.41	10.3634	1542.56	10.3656
263.00	6.00	1441.22	8.1295	1441.22	8.1295	218.61	6.00	1541.18	10.3474	1541.35	10.3499
263.00	5.00	1439.28	8.1107	1439.28	8.1107	218.54	5.00	1540.12	10.3324	1540.14	10.3327
263.00	4.00	1437.31	8.0917	1437.31	8.0917	218.48	4.00	1539.04	10.3195	1538.93	10.3180
263.00	3.00	1435.33	8.0726	1435.33	8.0726	218.42	3.00	1537.95	10.3072	1537.70	10.3038
263.00	2.00	1433.32	8.0528	1433.32	8.0528	218.34	2.00	1536.90	10.2951	1536.47	10.2891
263.00	1.00	1431.29	8.0335	1431.29	8.0335	218.28	1.00	1535.80	10.2890	1535.24	10.2811

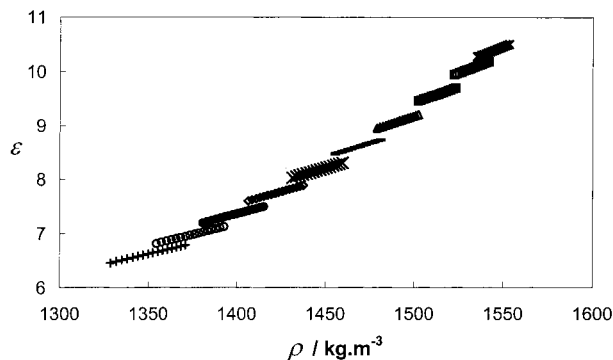


Figure 2. Relative permittivity of 1,1,1,3,3-pentafluoropropane, ϵ , as a function of density, ρ , for the different isotherms: +, 303.84 K; ○, 293.23 K; ●, 283.19 K; ◇, 273.12 K; ×, 263.00 K; −, 253.01 K; △, 243.02 K; ■, 233.12 K; □, 224.16 K; *, 218.53 K.

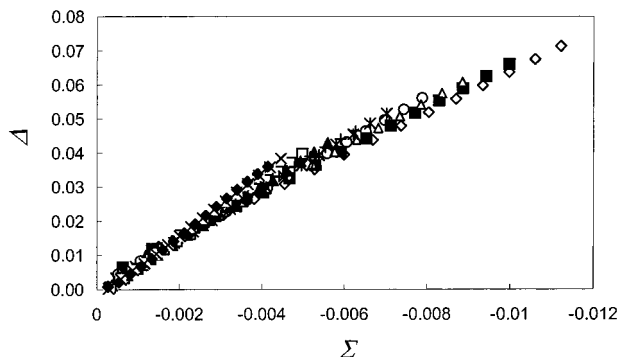


Figure 3. Variation of $\Delta = \epsilon^{1/2}(\rho) - \epsilon^{1/2}(\rho_0)$ with the Eulerian strain, Σ (eq 5), for the various isotherms: ◇, 303.84 K; ■, 293.23 K; △, 283.19 K; ○, 273.12 K; *, 263.00 K; +, 253.01 K; ◆, 243.02 K; □, 233.12 K; ×, 224.16 K; ▲, 218.53 K.

Table 2. Coefficients of the Dielectric Equations of State (Eqs 3 and 4)

	a_1/K	$10^{-3}a_2/\text{kg}^{-1}\cdot\text{m}^3$	$a_3/\text{K}\cdot\text{m}^3\cdot\text{kg}^{-1}$
	-1505.2 ± 23.5	1.8618 ± 0.0256	2.038 ± 0.0097
	b_0	$10^{-2}b_2/\text{MPa}^{-1}$	$b_3/\text{K}\cdot\text{MPa}^{-1}$
	-3.345 ± 0.037	2980.4 ± 9.51	-4.5909 ± 0.984

Table 3. Values of the Constants A and B of the Vedam Equation (Eq 5) and A' in Eq 7

T_n/K	$\rho_{\text{sat}}/\text{kg}\cdot\text{m}^{-3}$	$\epsilon(\rho_{\text{sat}})$	A	B	A'
302.84	1325.95	6.4224	-6.090	0.003 05	-6.4771
293.23	1352.00	6.7815	-6.327	0.002 97	-6.7513
283.19	1378.39	7.1717	-6.647	0.002 01	-6.9714
273.12	1404.11	7.5814	-6.986	0.000 89	-7.1471
263.00	1429.30	8.0146	-7.347	-0.000 15	-7.3166
253.01	1453.60	8.4670	-7.643	-0.000 85	-7.4482
243.02	1477.41	8.9478	-7.918	-0.001 47	-7.5386
233.12	1500.56	9.4565	-8.342	-0.002 12	-7.7256
224.16	1521.18	9.9487	-9.152	-0.002 61	-8.3058
218.53	1534.00	10.2755	-9.405	-0.003 05	-8.3408

When compared with the previous study of HFC-125¹⁶ ($g = 2.52$), it is possible to conclude that for HFC-245fa there is a more restricted rotation of the molecule in the liquid state due to the surrounding molecules,^{2-4,14-16,19} a fact that is quantified by the bigger value of the parameter g . Comparison with previous works by the authors also shows that HFC-245fa has more restricted rotation in the liquid state than 1,1,1-trifluoro-2,2-dichloroethane (HFC-123), 1,1-difluoro-1-chloroethane (HCFC-142b), 1,1-dichloro-1-fluoroethane (HCFC-141b), 1,1,1-trifluoroethane (HFC-143a), and 1,1-difluoroethane (HFC-152a).^{19,20} Investigation of the reasons for this fact is under way, by performing theoretical calculations.²¹ However, the big value of g

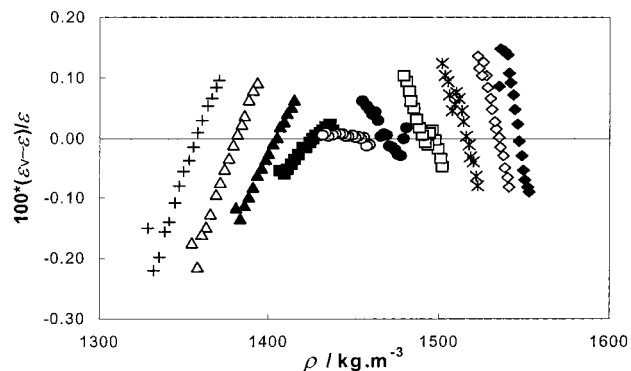


Figure 4. Deviations of the experimental data of the relative permittivity, ϵ , from the values obtained through the modified Vedam relation (eq 7): +, 303.84 K; △, 293.23 K; ▲, 283.19 K; ■, 273.12 K; ○, 263.00 K; ●, 253.01 K; □, 243.02 K; *, 233.12 K; ◇, 224.16 K; ◆, 218.53 K.

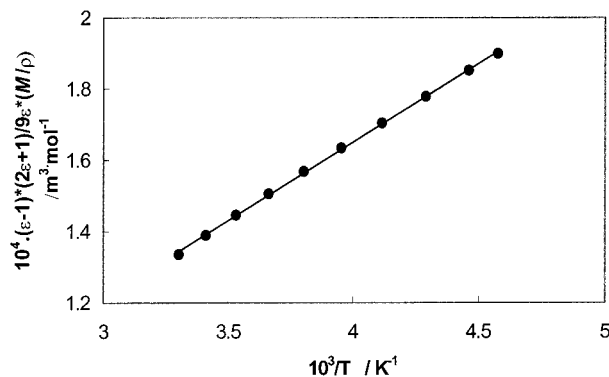


Figure 5. Variation of the Kirkwood function (eq 8) with the reciprocal temperature: ●, experimental values; −, linear fit; $\mu^* = 2.688$ D.

suggests that the C_3 molecule is possibly assuming a trans conformation in the liquid state, caused by the steric hindrance.

Conclusions

The relative permittivity of an environmentally acceptable blowing agent for rigid insulating foams HFC-245fa has been measured in the liquid phase. It is being studied as a potential replacement fluid for HCFC-141, partially due to its environmental properties (zero ozone depletion potential and low global warming potential). Our paper presents accurate relative permittivity measurements in the temperature range (218–303) K and at pressures from (1 to 16) MPa. The uncertainty of the dielectric constant measurements is estimated to be $\pm 0.88 \times 10^{-2}$.

The experimental values were correlated as a function of density and temperature and as a function of pressure and temperature, generating two different dielectric equations of state for this fluid.

The Eulerian formalism has been applied to analyze the data, concluding that it represents a successful estimation method for the dependence of the relative permittivity on density.

The Kirkwood function allows the determination of the value of the apparent dipole moment μ^* , found to be 2.688 D. This theory was also applied to calculate the Kirkwood correlation factor, g , which is equal to 3.01, suggesting that the molecule of HFC-245fa has restricted rotation in the liquid state due to the steric hindrance of the surrounding molecules.

Acknowledgment

The authors would like to thank Dr. Sergio Bobbo from CNR-ITEF, Padova, Italy, for supplying the sample of HFC245fa.

Literature Cited

- (1) Dieckmann, J.; Little, A.; Hillel, M. Global Comparative Analysis of HFC and Alternative Technologies for Refrigeration, Air Conditioning, Foam, Solvent, Aerosol Propellant, and Fire Protection Applications. *Final Report to the Alliance for Responsible Atmospheric Policy*; Arlington, VA, 1999.
- (2) Barão, M. T.; Mardolcar, U. V.; Nieto de Castro, C. A. The Dielectric Constant of Liquid HFC 134a and HCFC 142b. *Int. J. Thermophys.* **1996**, *17*, 573–585.
- (3) de Brito, F. E.; Gurova, A. N.; Mardolcar, U. V.; Nieto de Castro, C. A. Dielectric Constant of Nearly Azeotropic Mixture R-410A. *Int. J. Thermophys.* **2000**, *21*, 415–427.
- (4) de Brito, F. E.; Gurova, A. N.; Mardolcar, U. V.; Nieto de Castro, C. A. Dielectric constant and dipole moment of hydrofluorocarbon refrigerant mixtures R404A, R407C and R507. *High Temp.—High Pressures* **2000**, *32*, 631–651.
- (5) Barão, M. Constante Dielectrica de Refrigerantes Alternativos. Ph.D. Thesis, University of Lisbon, 1996.
- (6) Vedam, K. *CRC Crit. Rev. Solid Mater. Sci.* **1983**, *11*, 1–17.
- (7) Vedam, K.; Chen, C. Importance of using Eulerian representation of strain in high-pressure studies on liquids. *J. Chem. Phys.* **1982**, *77*, 1461–1463.
- (8) Diguët, R. Density Dependence of Refractive Index and Static Dielectric Constant. *Physica* **1986**, *139 & 140B*, 126–130.
- (9) Kirkwood, J. G. The Dielectric Polarization of Polar Liquids. *J. Chem. Phys.* **1939**, *7*, 911–919.
- (10) Onsager, L. Electric moments of molecules in liquids. *J. Am. Chem. Soc.* **1936**, *58*, 1486–1491.
- (11) Mardolcar, U. V.; Nieto de Castro, C. A.; Santos, F. J. Dielectric Constant of Toluene and Benzene. *Fluid Phase Equilib.* **1992**, *79*, 255–264.
- (12) Gurova, A. N.; Barão, M. T.; Mardolcar, U. V.; Nieto de Castro, C. A. The Thermal Conductivity and Dielectric Constant of HCFC 141b, HCFC 123, HCFC 142b and HFC 134a. *High Temp.—High Pressures* **1994**, *26*, 25–34.
- (13) Barão, T.; Nieto de Castro, C. A.; Mardolcar, U. V.; Okambawa, R.; St-Arnaud, J. M. Dielectric Constant, Dielectric Virial Coefficients and Dipole Moments of HFC 134a. *J. Chem. Eng. Data* **1995**, *40*, 1242–1248.
- (14) Barão, M. T.; Nieto de Castro, C. A.; Mardolcar, U. V. Molecular Properties of Alternative Refrigerants Derived from Dielectric Constant Measurements. *Int. J. Thermophys.* **1997**, *18*, 419–438.
- (15) Barão, T.; Mardolcar, U. V.; Nieto de Castro, C. A. Dielectric Constant and Dipole Moments of 1,1,1-Trifluoro-2,2-dichloroethane (HCFC 123) and 1,1-Difluoroethane (HFC 152a) in the Liquid Phase. *Fluid Phase Equilib.* **1998**, *150–151*, 753–762.
- (16) Pereira, L. M.; de Brito, F. E.; Gurova, A. N.; Mardolcar, U. V.; Nieto de Castro, C. A. The dipole moment of pentafluoroethane (HFC 125) in the liquid state. *Int. J. Thermophys.*, submitted.
- (17) McLinden, M. O.; Klein, S. A.; Lemmon, E. W.; Peskin, A. P. REFPROP—Thermodynamic and transport properties of refrigerant and refrigerant mixtures. *NIST, Standard Reference Database 23—version 6.01*; 1998.
- (18) Defibaugh, D.; Moldover, M. Compressed and Saturated Liquid Densities for 18 Halogenated Organic Compounds. *J. Chem. Eng. Data* **1997**, *42*, 160–168.
- (19) Mardolcar, U. V.; Nieto de Castro, C. A. Dielectric Properties of Halogenated Hydrocarbons and Some of Their Mixtures. Paper presented at the 1st Workshop on Thermochemical, Thermodynamic and Transport Properties of Halogenated Hydrocarbons and Mixtures, Pisa, 15–18 December, 1999.
- (20) Costa Cabral, B. J.; Pai-Panandiker, R. S.; Nieto de Castro, C. A. Calculation of the Polarizability and Dipole Moments of Halocarbons in the Liquid State. *Phys. Chem. Chem. Phys.*, submitted.

Received for review August 4, 2000. Accepted February 13, 2001. A.N.G. gratefully acknowledges FCT (PRAXIS XXI), Portugal, for a postdoctoral research grant.

JE000250V