

Molecular Properties of Alternative Refrigerants Derived from Dielectric-Constant Measurements¹

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A review of the current work in Lisbon on the measurement of the dielectric constant of the liquid phase of some environmentally acceptable refrigerants proposed as alternative replacements of the chlorofluorocarbons (CFCs), responsible for the destruction of the ozone layer, is presented. Measurements on HCFC 141b, HCFC 142b, HCFC 123, HFC 134a, HFC 152a, and HFC 32 samples of stated purities of 99.8 mass% or better were performed as a function of pressure and temperature, in the temperature range from 200 to 300 K and at pressures up to 20 MPa. The ratio of the capacitances of a cell filled with the sample and under vacuum was measured with a direct capacitance method. The dielectric-constant measurements have a repeatability of 0.003% and an accuracy of 0.1%. The theory developed by Vedam et al. based on the Eulerian Strain and the Kirkwood equation for the variation of the modified molar polarization with temperature and density were applied to obtain the dipole moments of the refrigerants in the liquid state, to obtain a physical insight of the molecular behavior, and to understand the equilibrium configuration of these liquids.

KEY WORDS: dielectric constant; dipole moment; HCFC 141b; HCFC 123; HCFC 142b; HFC 134a; HFC 152a; HFC 32.

1. INTRODUCTION

The dielectric constant of environmentally acceptable refrigerants in the liquid state is needed to study and interpret the electrical properties of

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these polar fluids and to give operational values for some of the design parameters of machinery used in air-conditioning and the refrigeration industry. A study of its dependence on temperature, pressure, and density will also permit the application of molecular theories of polar liquids.

These theories are approximate and usually relate the dielectric constant and the molar polarization with the density, temperature, polarizability, and dipole moment. Several attempts have been made in the past to develop correlating equations for these properties, however not always with success. Among the most successful, the equation of Vedam et al. [1, 2], adapted by Diguët [3], and the Kirkwood modification of the Onsager equation [4–6] were chosen, as they have been proven to be the most reliable approaches to the problem in the range of frequency used. To test the application of these theories over wide ranges of temperature and pressure, we decided to measure the dielectric constant of several halocarbons over a wide range of densities. The dipole moments of these compounds are only known in the gas phase [7, 8], and no reference has been found for the liquid phase.

In our current program of research on the thermophysical properties of environmentally acceptable refrigerants, the dielectric constant of liquid samples of HCFC 141b, HCFC 142b, HCFC 123, HFC 134a, HFC 152a, and HFC 32 has been measured in the temperature range from 200 to 300 K and at pressures up to 20 MPa using a direct capacitance method. The data on the saturation line for some of these refrigerants have been presented elsewhere as correlating functions of temperature or density [9].

2. EXPERIMENTAL PROCEDURE

A complete description of the dielectric constant cell has been provided by Mardolcar et al. [10]. Two concentric cylinders made from stainless steel act as electrodes insulated between them and from the pressure vessel body by two Teflon rings reinforced with glass fiber. The gap between the cylinders was 2.50 mm, its capacitance at room temperature being of the order of 6 pF. All the electric wires were soldered with silver. The top flange of the pressure vessel includes two electric feedthroughs, constructed from Cr–Ni wire insulated with magnesia (MgO) powder and surrounded by a 3-mm-OD stainless-steel tube.

The capacitance of the cell was measured with an Impedance Analyser (Schlumberger, Type SI 1260), operating in a four-terminal mode with an uncertainty of 5×10^{-4} pF, to avoid residual electrical capacitances of the wires. The impedance analyzer was calibrated by the Laboratório de Metrologia Eléctrica da Companhia Portuguesa Radio Marconi, Lisbon, Portugal, using the standards of capacitance of 1, 10, 100, and 1000 pF and

Table I. Stated Purity of Refrigerants

| Fluid | Purity (mass %) | Estimated water content (ppm) |
|-----------|--------------------|-------------------------------------|
| HCFC 141b | 99.8 | 20 |
| HCFC 123 | 99.8 | 25 |
| HCFC 142b | 99.9 | 10 |
| HFC 134a | 99.8 | 4 |
| HFC 152a | 99.9 | — |
| HFC 32 | — | — |

— Under current analysis.

0.01, 0.1, and 1 μF , with an uncertainty of 0.01 %. The temperature of the cell 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 the Instituto Português da Qualidade. The measuring system includes a high-pressure line, composed of a HIP liquid pressure generator and a Newport Scientific gas compressor and a pressure transducer from Setra Systems with an accuracy of 10 kPa. Details of the pressure block and cryostat can be found in Ref. 9. The purity of the fluids studied, in mass %, is given in Table I. The analyses were made by chromatography and mass spectrometry, by the manufacturer, Solvay Fluor und Derivative, GmbH, Germany. The fluids were used without further purification, except for the use of special molecular sieves (Dupont, USA) for water extraction. As water has a significant dielectric constant, this procedure was crucial for the accuracy of the determinations.

Measurements were made at an average of 12 isotherms separated by 10 K, in steps of 1 MPa, from slightly above the saturation pressure to 20 MPa, between 200 and 300 K. The temperature for each pressure level did not differ by more than 0.04 K from the value shown on Table II. The dielectric constant ϵ was calculated from the ratio between the measured capacitance with the cell filled with the liquid, C , and under vacuum, C_0 :

$$\epsilon = \frac{C(T, p)}{C(T, 0)} = \frac{C(T, p)}{C_0} \quad (1)$$

The values of $C_0(T)$ were determined at a pressure of 1 Pa, in the temperature range studied. A linear variation with temperature was found, with a root mean-square deviation of 0.0003 pF. Before each isotherm the value of C_0 was confirmed, and no significant deviations were ever found.

Table II. Experimental Data for HCFC 141b

| T (K) | p (MPa) | ρ ($\text{kg} \cdot \text{m}^{-3}$) | z |
|------------|--------------|---|---------|
| 298.25 | 0.20 | 1235.6 | 8.12196 |
| | 0.61 | 1236.5 | 8.12912 |
| | 1.11 | 1237.5 | 8.13745 |
| | 2.15 | 1239.7 | 8.15474 |
| | 3.11 | 1241.7 | 8.17086 |
| | 4.11 | 1243.8 | 8.18652 |
| | 5.28 | 1246.1 | 8.20554 |
| | 6.18 | 1247.9 | 8.21921 |
| | 7.11 | 1249.7 | 8.23487 |
| | 8.11 | 1251.7 | 8.24999 |
| | 9.16 | 1253.7 | 8.26602 |
| | 10.19 | 1255.6 | 8.28169 |
| | 11.20 | 1257.5 | 8.29681 |
| | 12.09 | 1259.1 | 8.30930 |
| | 13.09 | 1260.9 | 8.32361 |
| 283.99 | 14.11 | 1262.8 | 8.33837 |
| | 15.11 | 1264.5 | 8.35240 |
| | 0.10 | 1273.0 | 8.72910 |
| | 0.20 | 1273.2 | 8.72940 |
| | 0.30 | 1273.4 | 8.73050 |
| | 0.50 | 1273.8 | 8.73270 |
| | 0.70 | 1274.1 | 8.73580 |
| | 0.90 | 1274.5 | 8.73880 |
| | 1.10 | 1274.9 | 8.74380 |
| | 1.93 | 1276.5 | 8.75770 |
| | 2.04 | 1276.7 | 8.75930 |
| | 2.13 | 1276.8 | 8.76020 |
| | 2.25 | 1277.1 | 8.76240 |
| | 2.33 | 1277.2 | 8.76310 |
| | 2.40 | 1277.3 | 8.76420 |
| | 2.44 | 1277.4 | 8.76480 |
| | 2.62 | 1277.8 | 8.76790 |
| | 2.65 | 1277.8 | 8.76830 |
| 2.98 | 1278.4 | 8.77280 | |
| 3.86 | 1280.0 | 8.78830 | |
| 4.06 | 1280.4 | 8.79340 | |
| 4.13 | 1280.5 | 8.79140 | |
| 5.06 | 1282.2 | 8.80800 | |
| 5.92 | 1283.7 | 8.81700 | |
| 7.23 | 1286.1 | 8.83490 | |
| 3.29 | 1279.0 | 8.77590 | |
| 8.20 | 1287.7 | 8.84770 | |
| 8.74 | 1288.7 | 8.85530 | |

Table II. (Continued)

| T (K) | p (MPa) | ρ ($\text{kg} \cdot \text{m}^{-3}$) | c |
|------------|--------------|---|----------|
| 273.23 | 10.29 | 1291.3 | 8.87590 |
| | 11.33 | 1293.0 | 8.88970 |
| | 12.40 | 1294.8 | 8.90380 |
| | 13.17 | 1296.1 | 8.91410 |
| | 14.18 | 1297.7 | 8.92710 |
| | 15.10 | 1299.2 | 8.93880 |
| | 0.21 | 1281.6 | 9.24035 |
| | 1.10 | 1283.1 | 9.25430 |
| | 2.16 | 1284.9 | 9.26879 |
| | 3.14 | 1286.6 | 9.28283 |
| | 4.16 | 1288.3 | 9.29687 |
| | 5.16 | 1290.0 | 9.31001 |
| | 6.13 | 1291.6 | 9.32350 |
| | 7.15 | 1293.2 | 9.33782 |
| | 8.14 | 1294.8 | 9.35095 |
| 9.15 | 1296.4 | 9.36436 | |
| 10.14 | 1298.0 | 9.37731 | |
| 11.01 | 1299.3 | 9.38945 | |
| 12.13 | 1301.1 | 9.40276 | |
| 13.10 | 1302.5 | 9.41499 | |
| 14.10 | 1303.1 | 9.42722 | |
| 15.09 | 1305.5 | 9.43954 | |
| 263.24 | 0.20 | 1299.6 | 9.74300 |
| | 1.12 | 1301.1 | 9.75569 |
| | 2.11 | 1302.7 | 9.76964 |
| | 3.11 | 1304.2 | 9.78305 |
| | 4.13 | 1305.8 | 9.79700 |
| | 5.13 | 1307.4 | 9.80995 |
| | 6.12 | 1308.9 | 9.82336 |
| | 7.14 | 1310.5 | 9.83622 |
| | 8.12 | 1311.9 | 9.84836 |
| | 9.15 | 1313.5 | 9.86141 |
| | 10.13 | 1314.9 | 9.87328 |
| | 11.15 | 1316.4 | 9.88614 |
| | 12.11 | 1317.8 | 9.89756 |
| | 13.21 | 1319.2 | 9.91006 |
| | 14.12 | 1320.7 | 9.92238 |
| 15.12 | 1322.1 | 9.93434 | |
| 253.10 | 0.22 | 1317.9 | 10.28607 |
| | 1.09 | 1319.2 | 10.29721 |
| | 2.13 | 1320.7 | 10.31053 |
| | 3.12 | 1322.2 | 10.32312 |
| | 4.15 | 1323.7 | 10.33608 |
| | 5.13 | 1325.1 | 10.34895 |

Table II. (Continued)

| T (K) | p (MPa) | ρ ($\text{kg} \cdot \text{m}^{-3}$) | z |
|------------|--------------|---|----------|
| | 6.13 | 1326.5 | 10.36109 |
| | 7.11 | 1327.9 | 10.37323 |
| | 8.12 | 1329.4 | 10.38556 |
| | 9.14 | 1330.8 | 10.39806 |
| | 10.11 | 1332.1 | 10.40902 |
| | 11.12 | 1333.5 | 10.42153 |
| | 12.13 | 1334.9 | 10.43349 |
| | 13.13 | 1336.2 | 10.44499 |
| | 14.14 | 1337.5 | 10.45659 |
| | 15.14 | 1338.9 | 10.46855 |
| 243.47 | 0.21 | 1335.1 | 10.83103 |
| | 1.10 | 1336.4 | 10.84236 |
| | 2.11 | 1337.8 | 10.85459 |
| | 3.11 | 1339.2 | 10.86719 |
| | 4.12 | 1340.6 | 10.87951 |
| | 5.12 | 1341.9 | 10.89138 |
| | 6.12 | 1343.3 | 10.90380 |
| | 7.12 | 1344.6 | 10.91576 |
| | 8.11 | 1345.9 | 10.92709 |
| | 9.12 | 1347.2 | 10.93887 |
| | 10.13 | 1348.6 | 10.95120 |
| | 11.13 | 1349.8 | 10.96243 |
| | 12.15 | 1351.1 | 10.97276 |
| | 13.11 | 1352.4 | 10.98346 |
| | 14.12 | 1353.6 | 10.99479 |
| | 15.11 | 1354.9 | 11.00611 |
| 232.84 | 0.21 | 1354.3 | 11.49563 |
| | 1.10 | 1355.5 | 11.50641 |
| | 2.14 | 1356.9 | 11.51856 |
| | 3.12 | 1358.1 | 11.53035 |
| | 4.12 | 1359.4 | 11.54203 |
| | 5.10 | 1360.6 | 11.55364 |
| | 6.12 | 1361.9 | 11.56542 |
| | 7.12 | 1363.1 | 11.57666 |
| | 8.12 | 1364.4 | 11.58735 |
| | 9.11 | 1365.6 | 11.59823 |
| | 10.11 | 1366.8 | 11.60928 |
| | 11.09 | 1368.0 | 11.61970 |
| | 12.15 | 1369.2 | 11.63031 |
| | 13.12 | 1370.4 | 11.64136 |
| | 14.11 | 1371.5 | 11.65224 |
| | 15.11 | 1372.7 | 11.66294 |
| 233.66 | 0.21 | 1370.9 | 12.11590 |
| | 1.12 | 1372.0 | 12.12568 |

Table II. (Continued)

| T (K) | p (MPa) | ρ ($\text{kg} \cdot \text{m}^{-3}$) | z |
|------------|--------------|---|----------|
| | 2.13 | 1373.3 | 12.13746 |
| | 3.11 | 1374.5 | 12.14815 |
| | 4.11 | 1375.7 | 12.15974 |
| | 5.11 | 1376.9 | 12.17134 |
| | 6.10 | 1378.1 | 12.18239 |
| | 7.12 | 1379.3 | 12.19344 |
| | 8.14 | 1380.5 | 12.20431 |
| | 9.12 | 1381.6 | 12.21445 |
| | 10.11 | 1382.7 | 12.22614 |
| | 11.12 | 1383.9 | 12.23810 |
| | 12.13 | 1385.0 | 12.24870 |
| | 13.12 | 1386.2 | 12.25911 |
| | 14.13 | 1387.3 | 12.26935 |
| | 15.11 | 1388.4 | 12.27940 |
| 214.30 | 0.20 | 1388.0 | 12.82728 |
| | 1.12 | 1389.1 | 12.83789 |
| | 2.12 | 1390.2 | 12.84841 |
| | 3.12 | 1391.4 | 12.85875 |
| | 4.11 | 1392.5 | 12.87045 |
| | 5.14 | 1393.7 | 12.88251 |
| | 6.12 | 1394.8 | 12.89348 |
| | 7.12 | 1396.0 | 12.90436 |
| | 8.11 | 1397.1 | 12.91451 |
| | 9.10 | 1398.1 | 12.92485 |
| | 10.10 | 1399.2 | 12.93400 |
| | 11.09 | 1400.3 | 12.94588 |
| | 12.13 | 1401.4 | 12.85649 |
| | 13.11 | 1402.5 | 12.96628 |
| | 14.11 | 1403.5 | 12.97607 |
| | 15.13 | 1404.6 | 12.98586 |
| 207.34 | 0.21 | 1400.9 | 13.40243 |
| | 1.12 | 1401.9 | 13.41140 |
| | 2.13 | 1403.0 | 13.42183 |
| | 3.12 | 1404.1 | 13.43180 |
| | 4.13 | 1405.2 | 13.44223 |
| | 5.13 | 1406.3 | 13.45193 |
| | 6.13 | 1407.4 | 13.46154 |
| | 7.15 | 1408.4 | 13.47297 |
| | 9.12 | 1409.5 | 13.48212 |
| | 9.13 | 1410.6 | 13.49110 |
| | 10.10 | 1411.6 | 13.50099 |
| | 11.12 | 1412.6 | 13.51079 |
| | 12.12 | 1413.7 | 13.52002 |
| | 13.12 | 1414.7 | 13.52873 |
| | 14.10 | 1415.7 | 13.53779 |
| | 15.09 | 1416.7 | 13.54677 |

Table II. (Continued)

| T (K) | p (MPa) | ρ ($\text{kg} \cdot \text{m}^{-3}$) | ϵ |
|------------|--------------|---|------------|
| 202.25 | 0.21 | 1410.4 | 13.85150 |
| | 1.10 | 1411.4 | 13.86129 |
| | 2.14 | 1412.5 | 13.87199 |
| | 3.11 | 1413.5 | 13.88097 |
| | 4.11 | 1414.6 | 13.89094 |
| | 5.11 | 1415.6 | 13.90010 |
| | 6.11 | 1416.6 | 13.90861 |
| | 7.12 | 1417.6 | 13.91531 |
| | 8.12 | 1418.6 | 13.92202 |
| | 9.11 | 1419.6 | 13.93173 |
| | 10.10 | 1420.7 | 13.94298 |
| | 11.13 | 1421.7 | 13.95350 |
| | 12.11 | 1422.7 | 13.95965 |
| | 13.11 | 1423.7 | 13.97000 |
| | 14.10 | 1424.7 | 13.98024 |
| 15.10 | 1425.7 | 13.99040 | |

This procedure also guarantees the nonexistence of “floating capacitances” in the overall system during the measurements.

The experimental data were obtained at a frequency of 10 kHz with a repeatability of 0.01 % and an accuracy better than 0.1 %. The density was calculated from the universal correlation scheme for the estimation of the densities of refrigerants developed by Fialho and Nieto de Castro [11],

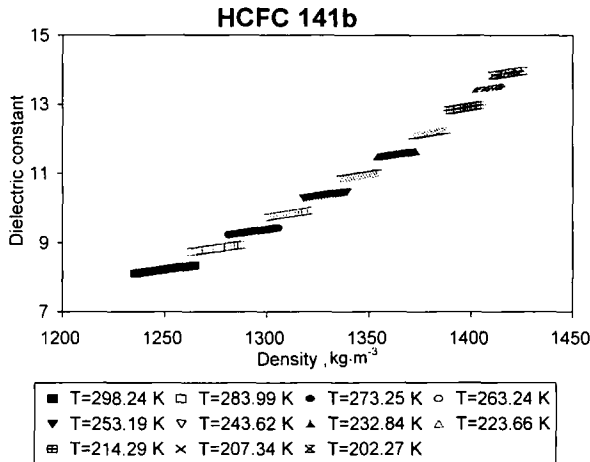


Fig. 1. The dielectric constant of HCFC 141b as a function of density for several temperatures.

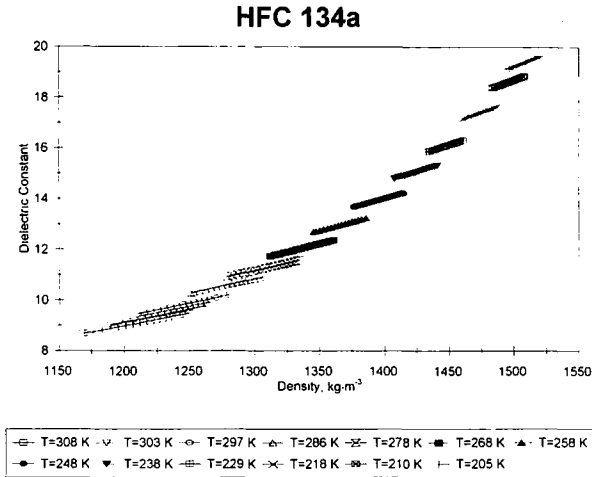


Fig. 2. The dielectric constant of HCFC 134a as a function of density for several temperatures.

except for HFC 134a and HFC 32, where equations developed by Tillner-Roth and Baehr [12] and by Outcalt and McLinden [13] were used. For the case of HFC 134a and 152a, the comparison with equations of state developed by Tillner-Roth and Baehr [12, 14] gave differences in the density that did not deviate by more than 0.2% from the predicted values. The

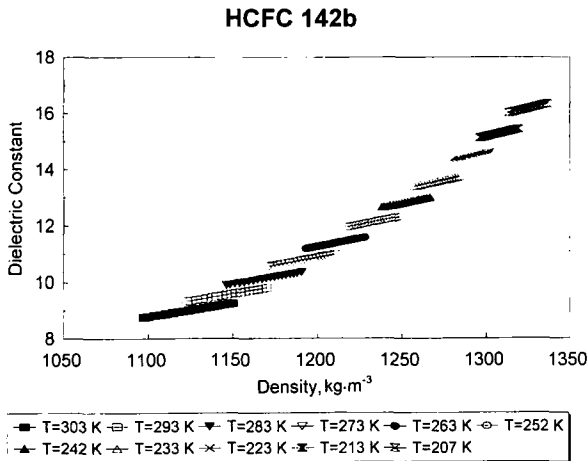


Fig. 3. The dielectric constant of HCFC 142b as a function of density for several temperatures.

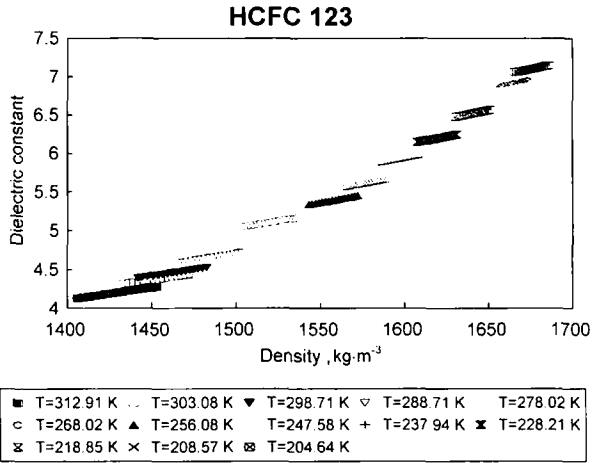


Fig. 4. The dielectric constant of HCFC 123 as a function of density for several temperatures.

accuracy of the prediction scheme for these fluids in the temperature range studied is of the order of 0.8% [15].

The experimental data for HCFC 142b and HFC 134a have been presented earlier [16, 17]. We report here only the experimental data obtained for HCFC 141b. Results for HCFC 123, HFC 152a, and HFC 32 will be presented elsewhere [18, 19].

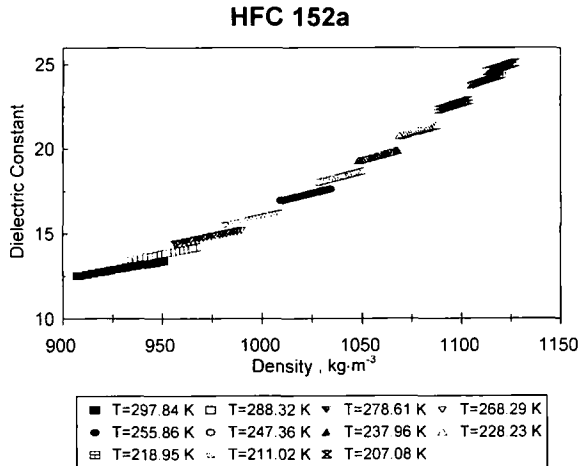


Fig. 5. The dielectric constant of HFC 152a as a function of density for several temperatures.

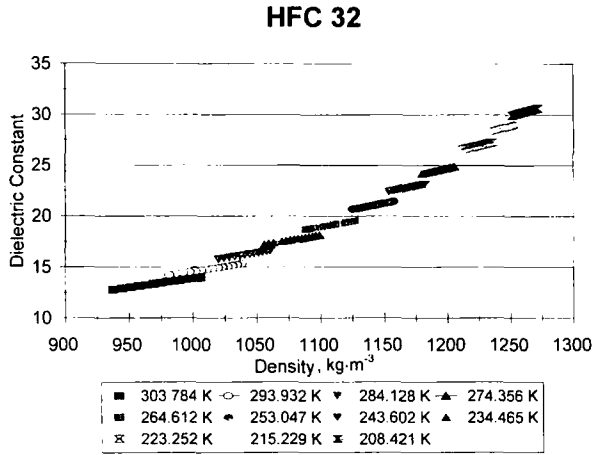


Fig. 6. The dielectric constant of HCFC 32 as a function of density for several temperatures.

Table II presents the data obtained in this work. Figures 1 to 6 show the dependence of the dielectric constant of the refrigerants on density, ρ , for different temperatures, T . Figure 7 shows the variation of the dielectric constant of HFC 32 with pressure, p , also for different temperatures.

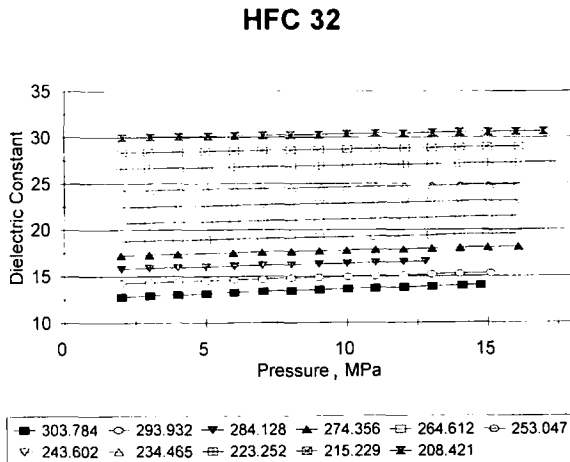


Fig. 7. The dielectric constant of HFC 32 as a function of pressure for several temperatures.

3. DISCUSSION

The pressure dependence of the dielectric properties of liquids has been studied in the past, both for highly associated liquids, like water and the alcohols [1–3, 20–22], and for nonassociated polar and nonpolar liquids [1, 2, 23–25]. For the case of halocarbons, polar nonassociated liquids, the study by Vij [26] on the pressure and temperature dependence of the dielectric-constant and dipole moment of 1,1-dimethoxy-2-propanone is also important. Studies of the liquid phase of halocarbons have been presented by Makita et al. [27] for CFC 12, CFC 13, HCFC 22, and HFC 23. Kashiwagi et al. [28], for HCFC 113, HCFC 114, HCFC 115, HCFC 124, and HFC 116, and by Tanaka et al. [29] for HCFC 123, HCFC 141b, and HFC 134a.

The dependence of the dielectric constant on density has been investigated by the use of the formalism of Vedam et al. and Diguët [1–3]. Vedam and Chen [2] have found that the Eulerian representation of strain in liquids under pressure is very convenient to describe the optical and electrical properties of liquids, because the increase in pressure only rearranges the molecules, decreasing the “free volume” available to them and conditioning their movement. Following these authors, we have used the relation between $\varepsilon^{1,2}$ and the Eulerian strain Σ , defined as

$$\Delta = \varepsilon^{1,2}(\rho) - \varepsilon^{1,2}(\rho_0) = A'\Sigma + B \quad (2)$$

with

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

where ρ_0 is a reference density, chosen in this work to be the saturation density at each isotherm. The value is obtained from the correlation as a function of density. This linear dependence of Δ on Σ was encountered in several organic fluids, but it was not tested for the same fluid over wide ranges of temperature and pressure. From the data obtained it can be concluded that the derivative $(\partial\varepsilon/\partial P)_T$ is always positive, and that $(\partial\varepsilon/\partial T)_P$ is always negative. The derivative $(\partial\varepsilon/\partial\rho)_T$ is also always positive. Figures 8–12 show the variation of the function Δ with the Eulerian strain Σ for all the refrigerants measured, with the exception of HFC 32 where the calculations are presently being made. This variation is linear, with a negative slope ($A' < 0$) and a value of the intercept about the same for all the temperatures, and $B \approx 0$. This fact is consistent with Eq. (2), and minor deviations from the linearity should be attributed to the combined inaccuracies

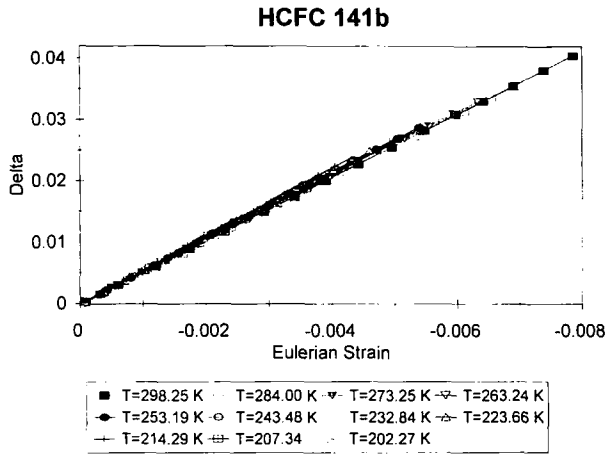


Fig. 8. The function Δ as a function of the Eulerian strain for HCFC 141b.

of the dielectric constant measurements and the equations of state used to calculate the densities.

The parameter A' has a very regular and smooth variation with temperature, and attempts to correlate this value with the molecular properties of each refrigerant showed that with $B=0$ and with a new fit to obtain a value A'_0 , it is possible to calculate the dielectric constant of all refrigerants within the experimental accuracy (0.1%) [30].

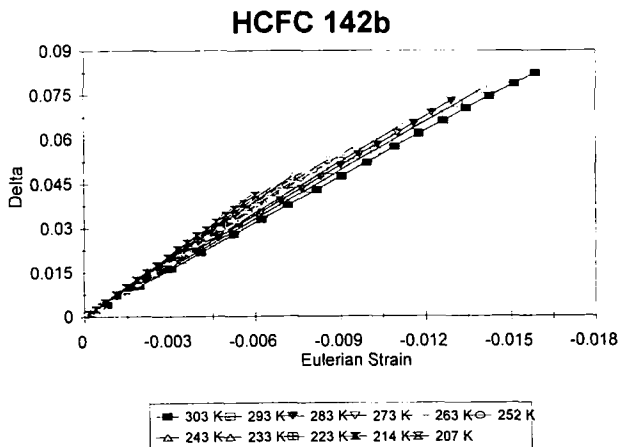


Fig. 9. The function Δ as a function of the Eulerian strain for HCFC 142b.

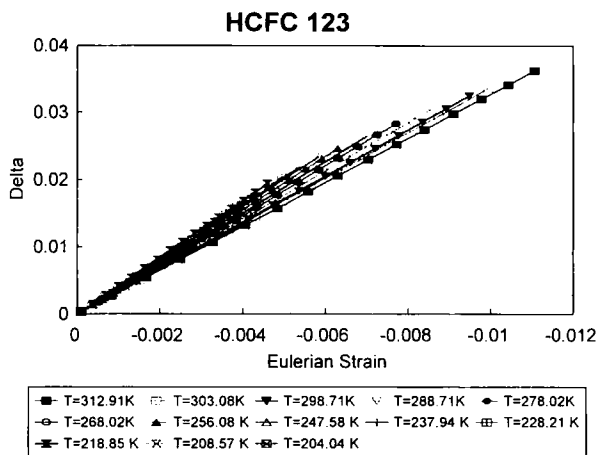


Fig. 10. The function Δ as a function of the Eulerian strain for HCFC 123.

We note here that Δ' varies more with temperature for HCFC 142b, HFC 134a, and HFC 152a, being approximately constant for HCFC 141b. The regularities found for the dependence of Δ on the Eulerian strain are also impressive, a fact already reported from less systematic data by other authors. A molecular interpretation for this fact is under study.

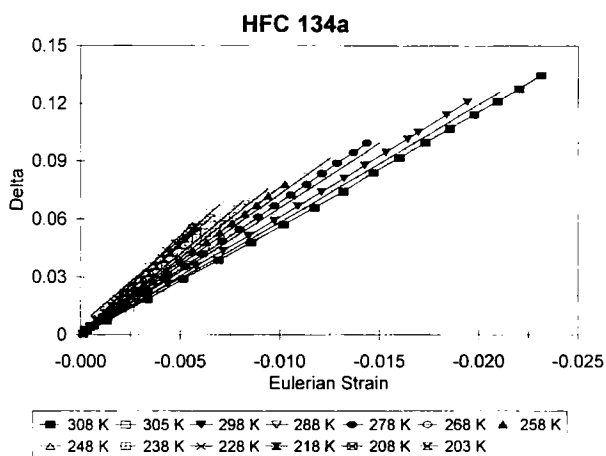


Fig. 11. The function Δ as a function of the Eulerian strain for HFC 134a.

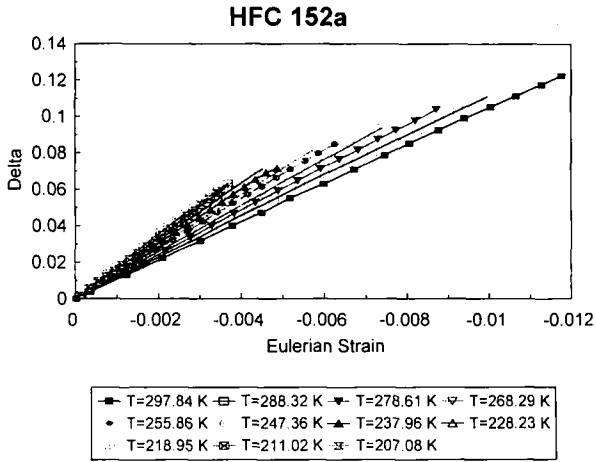


Fig. 12. The function A as a function of the Eulerian strain for HFC 152a.

From the theory of molecular polarizability developed by Kirkwood [5], which uses the definition of the Onsager local field in a liquid assembly of permanent dipoles [4], it is possible to correlate the dielectric constant of the polar liquid with the apparent dipole moment μ^* through the equation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} \left(\frac{M}{\rho} \right) = \frac{N_0}{3} \left(\alpha + \frac{\mu^{*2}}{3\epsilon_0 k_B T} \right) \tag{4}$$

In this equation M is the relative molar mass of the liquid, N_0 the Avogadro number, α the molecular polarizability of the molecule, ϵ_0 the electrical permittivity of vacuum, and k_B the Boltzmann constant. The apparent dipole moment μ^* is defined as $\mu^* = g^{1/2} \mu$, where μ is the dipole moment at the ideal gas state and g is the Kirkwood correlation parameter, which measures the restrictions to rotation imposed by a cage of molecules in a given molecule. Kirkwood, on the basis of a quasicrystalline model, defined this parameter g as

$$g = \frac{\mu^{*2}}{\mu^2} = 1 + \sum_{i=1}^{\infty} z_i \langle \cos \gamma_i \rangle \tag{5}$$

where z_i is the number of neighbours to the central molecule under consideration in the i th coordination shell, and $\langle \cos \gamma_i \rangle$ is the average cosine angle γ formed by the dipole moments of molecules in the i th shell with the

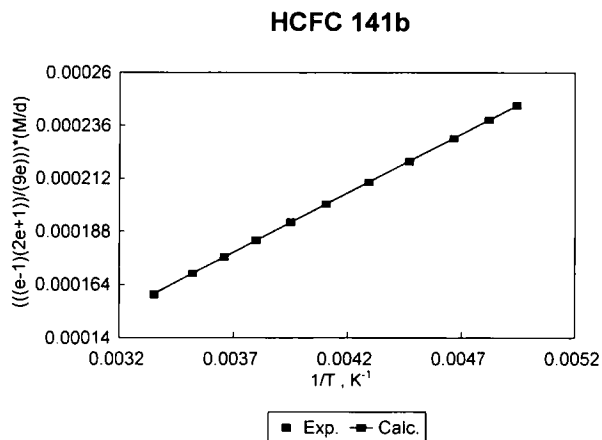


Fig. 13. The Kirkwood function $[(\epsilon - 1)(2\epsilon + 1)/9e](M/\rho)$ for HCFC 141b as a function of $1/T$.

dipole of the central molecule. For liquids with a high dielectric constant $\epsilon \propto g\mu^2$, and g and μ depend on the structure of the liquid. For nonpolar or nonassociated liquids $g \approx 1$, but for polar liquids it may considerably differ from unity. Although possible, g has rarely been calculated rigorously, so we have opted to determine it from the experiment.

The value of μ^* was obtained for all the refrigerants, except for HFC 32, by a linear regression of the Kirkwood function as a function of $1/T$. It is noteworthy that the value of this function was independent of the

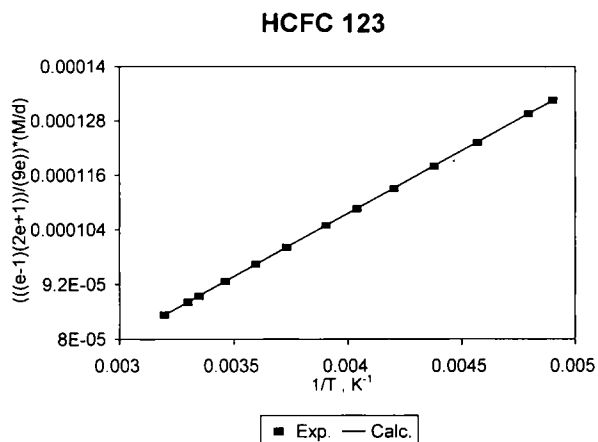


Fig. 14. The Kirkwood function $[(\epsilon - 1)(2\epsilon + 1)/9e](M/\rho)$ for HCFC 123 as a function of $1/T$.

density within the error of the density calculations. Figures 13–17 show the corresponding plots and Table III shows the values obtained for μ^* and g , with the values of μ taken from the work of Meyer and Morrison [7, 8].

The refrigerants studied have dipole moments in the gaseous phase in the following order:

$$123 < 32 < 141b < 134a < 142b < 152a$$

while the values obtained for the liquid phase follow a different order, where the positions of HCFC 142b and HFC 134a are reversed:

$$123 < 141b < 142b < 134a < 152a$$

As a consequence, the values of the Kirkwood correlation parameter, g , have an interesting order:

$$141b < 142b < 123 < 152a < 134a$$

The parameter g measures the restrictions to rotation imposed by a cage of molecules in a given molecule. The results obtained suggest, therefore, that HCFC 141b, 1-fluoro-1,1-dichloroethane, has the greatest mobility in the liquid state, while HFC 134a, 1,1,1,2-tetrafluoroethane, is the most restricted to rotation. This should also be consistent with the fact that a greater apparent dipole moment μ^* introduces bigger electrostatic forces between a given molecule and the cage that surrounds it, but there is HCFC 123, 2,2-dichloro-1,1,1-trifluoroethane, which has the smallest value

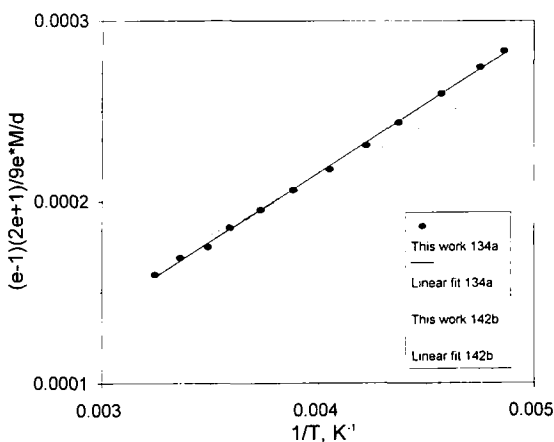


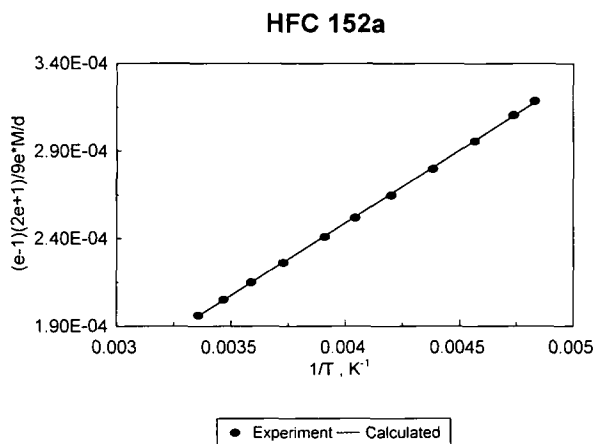
Fig. 15. The Kirkwood function $[(\epsilon - 1)(2\epsilon + 1)/9\epsilon](M/p)$ for HFC 134a and HCFC 142b as a function of $1/T$.

Table III. Dipole Moments and Kirkwood Correlation Factors for HFC 134a and HCFC 142b

| Fluid | μ^* | μ/D [7, 8] | g |
|-----------|---------|----------------|------|
| HCFC 141b | 2.96 | 2.01 | 2.17 |
| HCFC 123 | 2.13 | 1.36 | 2.48 |
| HCFC 142b | 3.17 | 2.14 | 2.20 |
| HFC 134a | 3.54 | 2.06 | 2.96 |
| HFC 152a | 3.69 | 2.26 | 2.67 |
| HFC 32 | — | 1.98 | — |

and HFC 152a, 1,1-difluoroethane, the highest. In addition, HCFC 141b, 1-fluoro-1,1-dichloroethane, and HCFC 142b, 1,1-difluoro-1-chloroethane, differ only by the change of one chlorine atom by a fluorine atom, in the same carbon atom. The values of g are very similar, although both μ and μ^* increase. The replacement of a CH_3 group in HCFC 141b by a CF_3 group in HCFC 123, 2,2-dichloro-1,1,1-trifluoroethane, decreases μ and μ^* but increases g . Pople [31] applied the Kirkwood theory to liquid water, assuming a structure consisting of a water molecule hydrogen bonded to four neighbors and found a value of $g = 2.6$. The values obtained for the refrigerants studied are close to this value.

Returning to the variation of the dielectric constant with density, it can be seen that HCFC 123 has the smallest range of variation of ϵ (4–7), while the HFCs have the largest (134a, 8–20; 152a, 12–25; 32, 12–30). This

**Fig. 16.** The Kirkwood function $[(\epsilon - 1)(2\epsilon + 1)/9\epsilon](M/\rho)$ for HFC 152a as a function of $1/T$.

fact is consistent with the high value of g for these compounds and a weaker dipole moment in gaseous (freely rotating) and liquid (restricted rotation) phases for HCFC 123. The determination of the polarizability α could give some insight into the total explication of the dielectric behavior of the halocarbons, but it is extremely difficult to obtain it with a good accuracy from the liquid-phase dielectric constant measurements, without information regarding refractive index dependence on temperature and pressure.

Finally, Vij [26] considered for 1,1-dimethoxy-2-propanone, a non-associated polar liquid as the halocarbons, $g = 1$. This hypothesis is, in our opinion, incorrect, because it puts all the dependence of the structure on the value of μ^* , a fact that masks the physical meaning of the apparent dipole moment.

4. CONCLUSIONS

New data for the dielectric constant of liquid HCFC 141b, HCFC 123, HCFC 142b, HFC 134a, HFC 152a, and HFC 32 have been presented in the temperature range 200 to 300 K, at pressures up to 20 MPa. The estimated accuracy of the data is 0.1%. Values of the dipole moments in the liquid phase were obtained for all refrigerants except for HFC 32, presently under study.

The molecular interpretation of the dependence of the dielectric constant on density and temperature suggested the following conclusions.

(a) The use of the concept of Eulerian strain seems to be completely successful for interpretation of the dependence of the dielectric constant on density. However, there is some theoretical work yet to be done to obtain accurate information on the molecular properties of the polar liquids studied. The choice of the reference density is very important and the possibility of determining universal behavior is encouraging from the results presented in Figs. 8–12. In addition, it may be possible to use the Vedam relation as a predictive tool for dielectric constants of refrigerants, which will be reported in the near-future.

(b) The use of the Kirkwood theory was much more rewarding, as values of the apparent dipole moments in the liquid phase could be obtained, which seem to be consistent with the present knowledge of the molecular structure of these molecules in the liquid phase.

Further studies are needed to confirm the conclusions found in this work.

REFERENCES

1. K. Vedam, *CRC Crit. Rev. Solid Mater. Sci.* **11**:1 (1983).
2. K. Vedam and C. Chen, *J. Chem. Phys.* **77**:1461 (1982).
3. R. Diguët, *Physica* **139/140B**:126 (1986).
4. L. Onsager, *J. Am. Chem. Soc.* **58**:1486 (1936).
5. J. G. Kirkwood, *J. Chem. Phys.* **7**:911 (1939).
6. B. Hilzler and J. Malecki, *Electrets* (PWN Polish Scientific, Warsaw, 1986).
7. C. W. Meyer and G. Morrison, *J. Phys. Chem.* **95**:3860 (1991).
8. C. W. Meyer and G. Morrison, *J. Chem. Eng. Data* **36**:409 (1991).
9. A. Gurova, T. Barão, U. V. Mardolcar, and C. A. Nieto de Castro, *High Temp.-High Press.* **26**:25 (1994).
10. U. V. Mardolcar, C. A. Nieto de Castro, and F. J. V. Santos, *Fluid Phase Equil.* **79**:255 (1992).
11. P. S. Fialho and C. A. Nieto de Castro, *Fluid Phase Equil.* (1995), in press.
12. R. Tillner-Roth and H. D. Baehr, *J. Phys. Chem. Ref. Data* **20**:1088 (1991).
13. S. Outcalt and M. McLinden, *Int. J. Thermophys.* **16**:79 (1995).
14. R. Tillner-Roth and H. D. Baehr, *Int. J. Thermophys.* **16**:91 (1995).
15. P. S. Fialho and C. A. Nieto de Castro, in *Proc. 19th Congr. IIR IIF, Vol. IVa*, The Hague, Aug. 20-25 (1995), p. 187.
16. M. T. Barão, U. V. Mardolcar, and C. A. Nieto de Castro, *Int. J. Thermophys.* **17**:573 (1996).
17. M. T. Barão, C. A. Nieto de Castro, U. V. Mardolcar, R. Okambawa, and J. M. St-Arnaud, *J. Chem. Eng. Data* **40**:1242 (1995).
18. M. T. Barão, C. A. Nieto de Castro, and U. V. Mardolcar, in preparation (1995).
19. U. V. Mardolcar, F. J. Vieira dos Santos, and C. A. Nieto de Castro, in *Proc. 19th Congr. IIR IIF, Vol. IVa*, The Hague, Aug. 20-25 (1995), p. 436.
20. B. K. P. Scaife, *Proc. Phys. Soc. London Sec. B* **68**:790 (1955).
21. P. Johari and W. Dannhauser, *J. Chem. Phys.* **48**:5114 (1968).
22. K. Vij, W. G. Scaife, and J. H. Calderwood, *J. Phys. D* **11**:545 (1978).
23. F. I. Mopsik, *J. Chem. Phys.* **50**:2558 (1969).
24. J. K. Vij and W. G. Scaife, *J. Chem. Phys.* **64**:2226 (1976).
25. W. G. Scaife and J. K. Vij, *Dielectric Materials, Measurement and Applications* (IEEE Special Publ., 1975), p. 103.
26. J. K. Vij, *J. Chem. Phys.* **79**:6182 (1983).
27. T. Makita, H. Kubota, Y. Tanaka, and H. Kashiwagi, *Refrigeration* **52**:543 (1977).
28. H. Kashiwagi, N. Harada, Y. Tanaka, H. Kubota, and T. Makita, *Trans. JAR* **1**:29 (1984).
29. Y. Tanaka, T. Tsujimoto, S. Matsuo, and T. Makita, *Fluid Phase Equil.* **80**:107 (1992).
30. M. T. Barão, *Propriedades Dielétricas de Refrigerantes Ambientalmente Aceitáveis*, Ph.D. Thesis (University of Lisbon, Lisbon, 1995).
31. A. Pople, *Proc. Roy. Soc.* **A205**:163 (1951).