

DIELECTRIC CONSTANT AND DIPOLE MOMENT OF HFC-143a¹

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ABSTRACT¹

From the theoretical point of view, dielectric studies are important to understand molecular interactions in the liquid phase. Dielectric constant measurement complemented with neutron diffraction studies can be used to analyse correlation factors and the formation of dimmers. For industrial purposes, the electrical permittivity of refrigerants is necessary for the project and design of machinery used in the refrigeration industry.

This paper reports the dielectric constant data of R143a (1,1,1-Trifluoroethane), a hydrofluorocarbon (HFC) developed as a refrigerant which has zero ozone depletion potential. The static dielectric constant of HFC-143a in the liquid phase was measured using a direct capacitance method at temperatures from 218 to 294K and under pressures up to 15 MPa. The uncertainty of the measurements is estimated to be within $\pm 0.1\%$ and the repeatability of 0.01% [1]. We provide a complete set of tables of experimental data as a function of temperature, pressure and density, which cover dielectric property needs for most engineering applications. The data obtained was correlated as a function of density and temperature and as a function of pressure and temperature by polynomial equations. In order to study the dependence of dielectric constant on density and temperature on a molecular basis, the theory developed by Vedam et al. [2,3] and adapted by Diguët [4] was applied to analyse the data. The Kirkwood theory based on the Onsager equation [5,6] was used to obtain the value of its apparent dipole moment in the liquid phase, which was found to be equal to 3.29 Debye.

KEY WORDS: HFC-143a, dielectric constant, Kirkwood equation, Vedam equation, dipole moment.

1. INTRODUCTION

Due to the fact that traditional working fluids in heat pumps, refrigeration plants and air conditioning will be forbidden for environmental reasons, there is an urgent need for alternative fluids. Pure HFCs and mixtures of HFCs can be used, but one of the restrictions is to find a compressor oil that is compatible with the working fluid. Many important factors when selecting a successful compressor oil are dependent on the working fluid's solubility in the compressor oil. To minimize costly experimentation, new thermodynamic tools that can predict the behaviour of HFCs and compressor oils will be very useful. The relative permittivity is a property that represents the electric properties of the compressor lubricants where the refrigerants are soluble. The fluid studied in this work is a refrigerant substituting for R-502 as a component in alternative refrigerant blends. R143a mixed with other HFC (R125, for example) can replace R-502 in commercial refrigeration (supermarket freezers and display cases, transport refrigeration, cold stores) and in industrial refrigeration plants. Due to its flammability, HFC143a is not used yet as a pure substance.

In the present study we have measured the dielectric constant of liquid R143a in the thermodynamic range from 218K to 294K along 9 isotherms and pressures from 2 to 15 MPa in steps of 1 MPa, using a direct capacitance method.

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2. EXPERIMENTAL

The experimental setup was described in previous publications [7-9]. In the present work the refrigerant used was supplied by Elf Atochem and has a purity of 99.5 mass % according to the supplier. The fluid was analysed without further purification. Dielectric constant measurements are performed with a direct capacitance method. The schematic diagram of the apparatus setup can be seen in figure 1. The density data was calculated using REFPROP database, version 6.01, proposed by McLinden et al. [10], which has a range of applicability from 162 to 500 K, pressures to 60 MPa and density up to 1331 kgm⁻³.

These density values are based on a 32-term modified Benedict-Webb-Rubin (MBWR) equation of state, presented by Outcalt and McLinden [11] which represents available experimental data from 162 to 346 K and pressures to 35 MPa with a maximum deviation of $\pm 0.3\%$.

3. RESULTS AND DISCUSSION

Dielectric constant values are evaluated from the capacitance ratio of the cell with the fluid and the same one under vacuum:

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

where $C(p,T)$ is the geometric capacitance at pressure p and temperature T and $C_0(T)$ is the capacitance under vacuum at a temperature T . Table 1 presents the data obtained as a function of pressure and density for each isotherm, for the refrigerant studied.

The experimental data of the dielectric constant was fitted by an iterative χ^2 method, each iteration implemented by a Levenberg-Marquardt procedure, to a function in density and temperature, of the following form (T in K and ρ in kg m⁻³):

$$\varepsilon(\rho,T) = a_0 + \frac{a_1}{T} + a_2 \rho + \frac{a_3 \rho}{T} \quad (2)$$

with a standard deviation of 0.19%. For industrial needs the data was also fitted to a function in pressure and temperature according to the polynomial equation (p in MPa and T in K):

$$\varepsilon(p,T) = b_0 + \frac{b_1}{T} + b_2 p + \frac{b_3 p}{T} \quad (3)$$

with a standard deviation of 0.27%. The coefficients of eq.2 and eq.3 with their uncertainties are given in Table 2.

An analysis of the dielectric constant data is presented in this paper as a function of density based on Vedam formalism [3,4]. The variation of dielectric constant with pressure is a function of the deformation of the volume, showing a non-linear behaviour in the case of the liquids. This nonlinearity can be reduced when the variation of ε , Δ , is analysed as a function of the Eulerian deformation, Σ . It is possible to verify that Σ provides a linear relation for Δ independently of the type of molecules that compose the fluid. We have used the relationship between $\varepsilon^{1/2}$ and Σ which is defined, according to the Vedam relation, as:

$$\Delta = \varepsilon^{1/2}(\rho) - \varepsilon^{1/2}(\rho_0) = A\Sigma + B \quad (4)$$

$$\Sigma = \frac{1}{2} \left[\left(1 - \frac{\rho}{\rho_0} \right)^{2/3} \right] \quad (5)$$

Here ρ_0 is the reference density, taken as the saturation value for each isotherm. The saturation density data was calculated using the equation of state provided by Outcalt and McLinden [11]. The calculations show that the function Δ indeed represents a linear variation with Σ , as can be seen in figure 2. Table 3 presents the values of the coefficients A and B of Vedam equation for each isotherm. The y-crossing (vertical axis) values are close to zero for all isotherms, $B \cong 0$. Assuming that $B=0$ (eq.4) it is possible to use Vedam relation to estimate dielectric constant values. We have evaluated the new values of A', by fitting the experimental results as a function of Σ and forcing the constant B to be equal to zero. The new form of Vedam equation is:

$$\Delta = A' \Sigma \quad (6)$$

The new values of the slope A' according to eq.6 are presented also in Table 3. We can estimate the variation of the dielectric constant with density with deviations smaller than 0.5%.

For the calculation of the dipole moment in the liquid phase we have applied the theory of molecular polarizability developed by Kirkwood [6] after the definition of Onsager's local field [5]. In this theory, an apparent dipole moment of the liquid μ^* is calculated from the following relation:

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} \left(\frac{M}{\rho} \right) = \frac{N_0}{3} \left[\alpha + \frac{(\mu^*)^2}{3\varepsilon_0 k_B T} \right] \quad (7)$$

where M is the relative molar mass of the fluid, N_0 is the Avogadro number, α is the molecular polarizability of the molecule, ε_0 the electric permittivity in vacuum, T the absolute temperature, k_B the Boltzmann constant, μ^* the apparent dipole moment ($\mu^* = g^{1/2} \mu$, where μ is the dipole moment in the ideal gas state) and g is the Kirkwood correlation parameter. According to Kirkwood theory g measures the restriction to rotation imposed by a cage of molecules surrounding a given one. The value of μ^* can be calculated by a linear regression of the left-hand side of eq.7 as a function of $1/T$. Figure 3 shows the plot of Kirkwood function vs. $1/T$ and the value of the apparent dipole moment $\mu^* = 3.293$ Debye. Using the value of dipole moment of HFC-143a ($\mu = 2.340$ D) in the gas phase [10], the value of Kirkwood parameter g was found to be equal to 1.98.

4. CONCLUSIONS

This paper contributes to increase our knowledge about the behaviour of polar fluids in the liquid state. We present dielectric constant data of HFC-143a, in the temperature range 218-294 K and pressure from 2 to 15 MPa with an uncertainty of 0.1%. 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. The Eulerian formalism was used to analyse the data and it is possible to conclude that it represents an estimation method for the dependence of the dielectric constant with density. Kirkwood theory, which allows the evaluation of the apparent dipole moment μ^* , was also applied to calculate the Kirkwood correlation factor, g , found to be 1.98. When compared with the previous study of HCFC-123, HFC-152a, HFC-32, HCFC-141b, HCFC-142b and HFC-134a [12] it is possible to conclude that there is some restricted rotation of the molecule in the liquid state.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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Table 1. Experimental data of dielectric constant of HFC-143a¹

| p (MPa) | ρ (kg m ⁻³) | ϵ | p (MPa) | ρ (kg m ⁻³) | ϵ | p (MPa) | ρ (kg m ⁻³) | ϵ |
|--------------------------|------------------------------|------------|--------------------------|------------------------------|------------|--------------------------|------------------------------|------------|
| T _n =294.11 K | | | T _n =263.03 K | | | T _n =233.00 K | | |
| 15.00 | 1031.77 | 10.58454 | 15.00 | 1112.55 | 12.82066 | 15.00 | 1185.67 | 15.69510 |
| 14.00 | 1027.36 | 10.52670 | 14.00 | 1109.48 | 12.77723 | 14.00 | 1183.43 | 15.65750 |
| 13.00 | 1022.79 | 10.46930 | 13.00 | 1106.34 | 12.73270 | 13.00 | 1181.16 | 15.62100 |
| 12.00 | 1018.05 | 10.41000 | 12.00 | 1103.13 | 12.68430 | 12.00 | 1178.85 | 15.58114 |
| 11.00 | 1013.13 | 10.34653 | 11.00 | 1099.84 | 12.63636 | 11.00 | 1176.51 | 15.54380 |
| 10.00 | 1008.00 | 10.28121 | 10.00 | 1096.47 | 12.58563 | 10.00 | 1174.13 | 15.50325 |
| 9.00 | 1002.65 | 10.21324 | 9.00 | 1093.02 | 12.53640 | 9.00 | 1171.70 | 15.46528 |
| 8.00 | 997.04 | 10.14120 | 8.00 | 1089.47 | 12.48505 | 8.00 | 1169.24 | 15.42460 |
| 7.00 | 991.16 | 10.06597 | 7.00 | 1085.83 | 12.43111 | 7.00 | 1166.74 | 15.38730 |
| 6.00 | 984.95 | 9.98643 | 6.00 | 1082.08 | 12.37884 | 6.00 | 1164.20 | 15.34340 |
| 5.00 | 978.39 | 9.90193 | 5.00 | 1078.23 | 12.31920 | 5.00 | 1161.61 | 15.29900 |
| 4.00 | 971.40 | 9.81370 | 4.00 | 1074.25 | 12.26435 | 4.00 | 1158.98 | 15.25430 |
| 3.00 | 963.91 | 9.71832 | 3.00 | 1070.15 | 12.20277 | 3.00 | 1156.29 | 15.20850 |
| 2.00 | 955.83 | 9.61637 | 2.00 | 1065.91 | 12.14430 | 2.00 | 1153.56 | 15.16570 |
| T _n =283.17 K | | | T _n =253.14 K | | | T _n =223.99 K | | |
| 15.00 | 1060.93 | 11.39860 | 15.00 | 1137.07 | 13.66800 | 15.00 | 1206.88 | 16.72900 |
| 14.00 | 1057.07 | 11.34690 | 14.00 | 1134.31 | 13.62784 | 14.00 | 1204.83 | 16.69410 |
| 13.00 | 1053.09 | 11.29440 | 13.00 | 1131.50 | 13.58560 | 13.00 | 1202.75 | 16.65810 |
| 12.00 | 1048.99 | 11.23970 | 12.00 | 1128.63 | 13.54290 | 12.00 | 1200.65 | 16.62130 |
| 11.00 | 1044.75 | 11.18310 | 11.00 | 1125.70 | 13.49958 | 11.00 | 1198.52 | 16.58320 |
| 10.00 | 1040.37 | 11.12540 | 10.00 | 1122.71 | 13.45461 | 10.00 | 1196.35 | 16.54810 |
| 9.00 | 1035.83 | 11.06554 | 9.00 | 1119.65 | 13.40660 | 9.00 | 1194.16 | 16.50640 |
| 8.00 | 1031.12 | 11.00151 | 8.00 | 1116.53 | 13.36170 | 8.00 | 1191.93 | 16.48720 |
| 7.00 | 1026.23 | 10.93589 | 7.00 | 1113.34 | 13.31138 | 7.00 | 1189.68 | 16.43270 |
| 6.00 | 1021.12 | 10.86703 | 6.00 | 1110.06 | 13.26300 | 6.00 | 1187.38 | 16.38990 |
| 5.00 | 1015.78 | 10.79520 | 5.00 | 1106.71 | 13.20942 | 5.00 | 1185.06 | 16.35030 |
| 4.00 | 1010.19 | 10.71980 | 4.00 | 1103.27 | 13.15953 | 4.00 | 1182.70 | 16.30890 |
| 3.00 | 1004.30 | 10.64060 | 3.00 | 1099.74 | 13.10640 | 3.00 | 1180.30 | 16.26740 |
| 2.00 | 998.08 | 10.56710 | 2.00 | 1096.12 | 13.04930 | 2.00 | 1177.86 | 16.22810 |
| T _n =274.43 K | | | T _n =243.16 K | | | T _n =218.25 K | | |
| 15.00 | 1083.63 | 11.89540 | 15.00 | 1161.35 | 14.62830 | 15.00 | 1220.23 | 17.42660 |
| 14.00 | 1080.15 | 11.84680 | 14.00 | 1158.87 | 14.58960 | 14.00 | 1218.29 | 17.38970 |
| 13.00 | 1076.56 | 11.79820 | 13.00 | 1156.34 | 14.55233 | 13.00 | 1216.33 | 17.35620 |
| 12.00 | 1072.89 | 11.74922 | 12.00 | 1153.77 | 14.51023 | 12.00 | 1214.35 | 17.32350 |
| 11.00 | 1069.10 | 11.69630 | 11.00 | 1151.15 | 14.46915 | 11.00 | 1212.34 | 17.29450 |
| 10.00 | 1065.21 | 11.64357 | 10.00 | 1148.49 | 14.42948 | 10.00 | 1210.30 | 17.26020 |
| 9.00 | 1061.20 | 11.58782 | 9.00 | 1145.77 | 14.38570 | 9.00 | 1208.24 | 17.22090 |
| 8.00 | 1057.05 | 11.52870 | 8.00 | 1143.00 | 14.34020 | 8.00 | 1206.15 | 17.18100 |
| 7.00 | 1052.77 | 11.47140 | 7.00 | 1140.18 | 14.29775 | 7.00 | 1204.03 | 17.14190 |
| 6.00 | 1048.34 | 11.41046 | 6.00 | 1137.30 | 14.25398 | 6.00 | 1201.88 | 17.10370 |
| 5.00 | 1043.74 | 11.34639 | 5.00 | 1134.36 | 14.20252 | 5.00 | 1199.70 | 17.06620 |
| 4.00 | 1038.96 | 11.28370 | 4.00 | 1131.36 | 14.15763 | 4.00 | 1197.50 | 17.03210 |
| 3.00 | 1033.98 | 11.21420 | 3.00 | 1128.30 | 14.10805 | 3.00 | 1195.26 | 16.99170 |
| 2.00 | 1028.77 | 11.14020 | 2.00 | 1125.16 | 14.06137 | 2.00 | 1192.98 | 16.95330 |

¹ T_n is a nominal temperature. All experimental points measured at a given temperature T, close to T_n, where adjusted to this temperature, by using $\epsilon(T_n, p) = \epsilon(T, p) + \left(\frac{\partial \epsilon}{\partial T}\right)_p (T_n - T)$.

Figure 1. Schematic diagram of the apparatus.

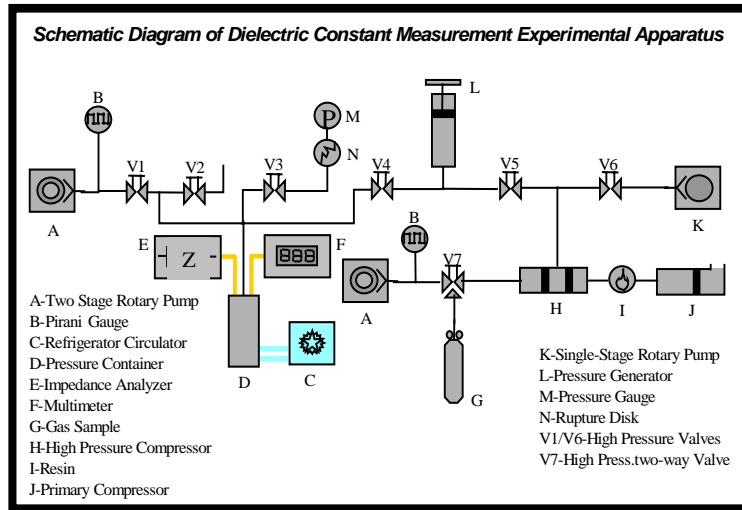


Table 2. Coefficients of the dielectric equations of state (eq.2 and eq.3)

| a_0 | a_1 / K | $10^{-3}a_2/\text{kg}^{-1} \text{ m}^3$ | $a_3/ \text{K m}^3 \text{ kg}^{-1}$ |
|---------------------|------------------|---|-------------------------------------|
| 11.990 ± 0.604 | -4004 ± 189 | -10.3034 ± 0.489 | 6.508 ± 0.148 |
| b_0 | b_1 / K | $10^{-2}b_2/\text{MPa}^{-1}$ | $b_3/ \text{K MPa}^{-1}$ |
| -11.464 ± 0.084 | 6187 ± 20.7 | 16.000 ± 0.893 | -27.468 ± 2.201 |

Table 3. Values of the constants A and B of Vedam equation (eq.4) and values of the constant A' in eq.6

| T (K) | ρ_{sat} (kg m ⁻³) | $\epsilon(\rho_{sat})$ | A | B | A' |
|---------|------------------------------------|------------------------|---------|----------|---------|
| 294.11 | 948.25 | 9.5878 | -5.7983 | -0.01068 | -5.2886 |
| 283.17 | 990.36 | 10.4063 | -6.0515 | 0.00837 | -6.5476 |
| 274.43 | 1021.32 | 11.0960 | -6.2730 | -0.00825 | -5.7003 |
| 263.03 | 1059.01 | 12.0575 | -6.6087 | -0.00208 | -6.4340 |
| 253.14 | 1089.77 | 12.9603 | -6.8151 | -0.00056 | -6.7606 |
| 243.16 | 1119.38 | 13.9483 | -7.0238 | 0.00295 | -7.3596 |
| 233.00 | 1148.34 | 15.0477 | -7.2673 | 0.00426 | -7.8265 |
| 223.99 | 1173.10 | 16.1103 | -7.5519 | 0.00439 | -8.2037 |
| 218.25 | 1188.50 | 16.8362 | -7.5290 | 0.00467 | -8.2771 |

Figure 2. Variation of Δ with Eulerian Strain Σ (eq.4).

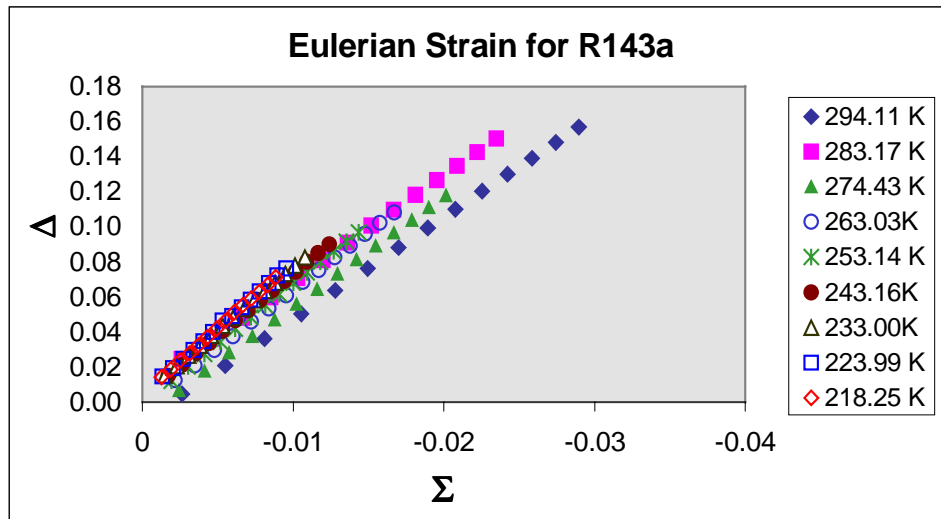


Figure 3. Kirkwood function vs. 1/T for HFC-143a.

