

## Dielectric properties of 1,1,1-trifluoroethane (HFC-143a) in the liquid phase

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### ABSTRACT

The relative permittivity ( $\epsilon_r$ ) data of 1,1,1-trifluoroethane (HFC-143a), (CAS N# 420-46-2), a hydrofluoro-carbon (HFC) developed as a refrigerant that has zero ozone depletion potential, is reported. The relative permittivity of HFC-143a in the liquid phase was measured using a direct capacitance method at temperatures from  $T = 218$  to  $294$  K and at pressures up to  $P = 15$  MPa, for a frequency of  $10$  kHz. The uncertainty of the  $\epsilon_r$  measurements is estimated to be better than  $\pm 1.2 \times 10^{-2}$ . A complete set of tables of experimental data as a function of temperature, pressure and density, is presented that covers the dielectric property needs for most engineering applications. To study the dependence of  $\epsilon_r$  on density and temperature on a molecular basis, the theory developed by Vedam et al. and adapted by Diguët was applied to analyse the data. The Kirkwood modification of the Onsager equation was used to obtain the value of its dipole moment in the liquid phase ( $\mu^*$ ). The apparent dipole moment obtained was  $\mu^* = 3.293$  D. The effective dipole in the liquid state predicted by the Kirkwood–Frölich theory is  $2.530$  D. The measured values are compared with density functional and density functional self-consistent calculations (SCIPCM) of the electronic distribution and of the dipole moment of HFC-143a. Finally, the values of the isobaric thermal expansion and isothermal compressibility were estimated from the reported measurements.

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### 1. Introduction

The prohibition to use working fluids in heat pumps, refrigeration plants and air conditioning for environmental reasons, and the selection of alternative replacement fluids justifies the need for their properties, namely those necessary for an optimum technological design. Pure HFC's and mixtures of HFC's can be used, but there are some restrictions related with finding compressor oil that is compatible with the working fluid. Many important factors when selecting successful compressor oil are dependent on the working fluid's solubility in the compressor oil and its dielectric properties. To minimize costly experimentation, new thermodynamic tools that can predict the behavior of HFCs and compressor oils will be very useful.

Relative permittivity ( $\epsilon_r$ ) provides information about the behavior of molecules under an electrical field and it is dependent on chemical structure and molecular interactions [1]. It also represents the electric properties of the compressor lubricants where the refrigerants are soluble. HFC-143a mixed with HFC-125 can replace

R502<sup>1</sup> in commercial refrigeration (supermarket freezers and display cases, transport refrigeration, cold stores) and in industrial refrigeration plants [1]. Due to its flammability, HFC-143a is not used yet as a pure substance.

It is the purpose of this paper to report measurements on the electrical permittivity of 1,1,1-trifluoroethane, HFC-143a in the liquid state, as a function of temperature and pressure, and to contribute to the understanding of the molecular interactions in the liquid state, by calculating the dipole moments using available statistical mechanics theories of Kirkwood and Kirkwood–Frölich [2–4], as well as the Vedam formalism, applying the concept of Eulerian deformation, also named Eulerian strain, developed by Vedam et al. [5,6] and adapted by Diguët [7]. Recent studies of the measurement of the  $\epsilon_r$  in the liquid state and the interpretation of neutron scattering spectral data in conjunction with molecular dynamics simulations have been attempted to elucidate the liquid state structure of these systems. The present calculations of the electronic distribution and of the dipole moment in the liquid state for several alternative refrigerants were reported recently [8,9], and will be integrated in the present discussion. Finally, a recent attempt

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<sup>1</sup> R502 is the azeotropic mixture of HCFC-22 (chlorodifluoromethane) and CFC-115 (chloropentafluoroethane) (48.8% HCFC-22).

**Table 1**  
Physical properties and purity 1,1,1-trifluoroethane (HFC-143a).

Chemical name	1,1,1-Trifluoroethane
ASHRAE nomenclature	R-143a
Molecular formula	CF <sub>3</sub> CH <sub>3</sub>
Relative molar mass (g mol <sup>-1</sup> )	84.041
ODP (CFC-11 = 1)	0
GWP <sup>a</sup> (CO <sub>2</sub> = 1)	3800
Boiling point @ 1 atm (°C)	-47.75
Estimated water content (ppm)	<30 ppm
Purity	99.5%
Sample provider	Elf Atochem

<sup>a</sup> Integrated time horizon = 100 years.

to derive thermodynamic properties from electrical permittivity data [10] was applied to HFC-143a.

## 2. Materials and methods

Measurements of the electrical permittivity ( $\epsilon_r$ ) of liquid of 1,1,1-trifluoroethane (HFC-143a) in the thermodynamic range from  $T=218$  to 294 K along nine isotherms and pressures from 2 to 15 MPa, in steps of 1 MPa, using a direct capacitance method have been performed. The application of this method to refrigerants was recently reviewed by the authors [1], and the experimental method was described in previous publications [9,10] including a schematic diagram of the apparatus setup, described in detail in references [11,12]. Therefore we do not present here the instrument. The most important physical properties, purity and supplier (Elf Atochem, France) are presented in Table 1. The fluid was studied without further purification. The density data were calculated using NIST REFPROP<sup>®</sup> database 23, [13] with a maximum deviation of  $\pm 0.3\%$ .

To apply the Kirkwood–Frölich theory, described below, to obtain the effective dipole in the liquid phase  $\mu_{KF}^*$ , the refractive index ( $n$ ) has been taken from Ref. [14].

## 3. Results and discussion

Relative permittivity values are evaluated from the ratio of the capacitance  $C(P,T)$  of the cell filled with the liquid, at pressure  $P$  and temperature  $T$  and the capacitance,  $C_0(T)$ , under vacuum. All the experimental points measured at a given temperature  $T$ , close to a prescribed nominal temperature  $T_n$ , were adjusted to this temperature using the following relation:

$$\epsilon_r(T_n, P) = \epsilon_r(T, P) + \left( \frac{\partial \epsilon_r}{\partial T} \right)_P (T_n - T) \quad (1)$$

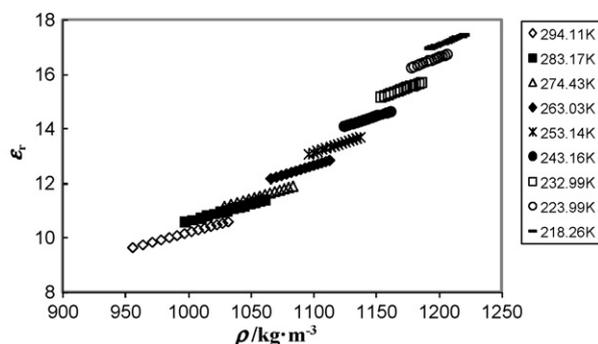
Table 2 presents the data obtained as a function of  $P$  and  $\rho$  for each isotherm, for the refrigerant studied. Fig. 1 shows the experimental data as function of  $\rho$ . The experimental data of the relative permittivity was fitted by an iterative  $\chi^2$  method for a multiparameter and multivariable function in density and temperature (iterations implemented by a Levenberg–Marquardt procedure), of the following form ( $T$  in K and  $\rho$  in kg m<sup>-3</sup>):

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

with a standard deviation of 0.30%. For industrial needs the data were also fitted to a function in pressure and temperature according to the polynomial equation ( $P$  in MPa and  $T$  in K):

$$\epsilon_r(P, T) = b_0 + \frac{b_1}{T} + b_2P + \frac{b_3P}{T} \quad (3)$$

with a standard deviation of 0.38%. The coefficients of Eqs. (2) and (3) are given in Table 3, with their uncertainties.



**Fig. 1.** The relative permittivity of 1,1,1-Trifluoroethane (HFC-143a),  $\epsilon_r$ , as a function of density,  $\rho$ , for the different isotherms. ( $\diamond$ ) 294.11 K; ( $\blacksquare$ ) 283.17 K; ( $\triangle$ ) 274.43 K; ( $\blacklozenge$ ) 263.03 K; ( $\times$ ) 253.14 K; ( $\bullet$ ) 243.16 K; ( $\square$ ) 232.99 K; ( $\circ$ ) 223.99 K; ( $-$ ) 218.26 K.

The uncertainty in the electrical permittivity measurements can be obtained from a careful study of all the contributions to it. The principal variables are  $T$ ,  $P$ ,  $C$  and  $C_0$ . The corresponding uncertainties are, respectively, 0.1 °C, 0.01 MPa, 0.0019 pF and 0.0023 pF [9,15]. The total uncertainty can be calculated following the usual way<sup>2</sup>. The global uncertainty of the measurement can be calculated by using the coverage factor  $k=2$ , for a confidence interval of 95%. The value obtained was  $U = 1.1 \times 10^{-2}$ , a value commensurate with that obtained for other three refrigerants [9].

The presence of water in the samples (<30 ppm) is an additional source of uncertainty. If we assume an ideal model mixture with HFC-143a with water, with a weight fraction of water  $\omega_{H_2O} = 0.00003$ , with a dielectric constant of 78.4 at room temperature and ambient pressure [16] and a value of  $\epsilon_{\text{mix}} \sim 9.600$  (see Table 2), a value of  $\epsilon_{\text{HFC-143a}} \sim 9.598$  is obtained, which suggests an additional contribution to uncertainty of  $2.3 \times 10^{-3}$ . If we assume this further source of uncertainty, the global uncertainty of the measurement is  $U = 1.2 \times 10^{-2}$ .

An analysis of the relative permittivity data as a function of density based on Vedam formalism [5,6] is presented in this paper. The variation of relative permittivity with pressure is a function of the deformation of the volume, showing a nonlinear behavior in the case of the liquids. This nonlinearity can be reduced when the variation of  $\epsilon_r^{1/2}$ ,  $\Delta$ , is analysed as a function of the Eulerian deformation,  $\Sigma$ . In the original model, and has demonstrated previously for many fluids [1],  $\Sigma$  provides a linear relation for  $\Delta$  independently of the type of molecules that compose the fluid. We have used the relationship between  $\epsilon_r^{1/2}$  and  $\Sigma$  which is defined, according to the Vedam relation [5,6], as:

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

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

Here  $\rho_0$  is a reference density, taken usually as the saturation value for each isotherm,  $\rho_0 = \rho^{\text{sat}}(T)$ . The saturation density data was calculated using NIST REFPROP<sup>®</sup> database 23, [13]. The value of  $\epsilon_r(\rho_0)$  was calculated from Eq. (2). Calculations show that the function  $\Delta$  indeed represents a linear variation with  $\Sigma$ , as can be seen in Fig. 2. However, and differently from other alternative refrigerants [1,9–12], the isotherms do not all cross the origin, a fact probably related with the accuracy of density data for this fluid, namely near

<sup>2</sup>  $u_\epsilon^2 = \sum_i \left( \frac{\partial \epsilon_r}{\partial x_i} \right)^2 u_{x_i}^2$ , where  $i$  stands for  $T$ ,  $P$ ,  $C$  and  $C_0$ . The values of the sensitivity coefficients were estimated from the experimental data.  $U = ku_\epsilon$ .

**Table 2**  
Relative permittivity,  $\epsilon_r$ , of HFC-143a, from  $T = 218.26$  to  $294.11$  K and up to  $P = 15$  MPa.

$T$ (K)	$P$ (MPa)	$\rho$ ( $\text{kg m}^{-3}$ )	$\epsilon_r(T,P)$	$\rho(T_n,P)$ ( $\text{kg m}^{-3}$ )	$\epsilon_r(T_n,P)$	$T$ (K)	$P$ (MPa)	$\rho$ ( $\text{kg m}^{-3}$ )	$\epsilon_r(T,P)$	$\rho(T_n,P)$ ( $\text{kg m}^{-3}$ )	$\epsilon_r(T_n,P)$
$T_n = 294.11$ K						$T_n = 283.17$ K					
294.11	15.0	1032	10.585	1032	10.585	283.20	15.0	1060	11.397	1061	11.399
294.12	14.0	1027	10.526	1027	10.527	283.19	14.0	1057	11.346	1057	11.347
294.12	13.0	1023	10.469	1023	10.469	283.19	13.0	1053	11.293	1053	11.295
294.12	12.0	1018	10.409	1018	10.410	283.18	12.0	1049	11.239	1049	11.240
294.11	11.0	1013	10.347	1013	10.347	283.18	11.0	1044	11.183	1044	11.183
294.11	10.0	1008	10.281	1008	10.281	283.18	10.0	1040	11.125	1040	11.126
294.11	9.0	1002	10.213	1002	10.213	283.17	9.0	1035	11.066	1035	11.066
294.12	8.0	997	10.141	997	10.141	283.17	8.0	1031	11.002	1031	11.002
294.11	7.0	991	10.066	991	10.066	283.17	7.0	1026	10.936	1026	10.936
294.11	6.0	985	9.9864	985	9.9864	283.17	6.0	1021	10.867	1021	10.867
294.11	5.0	978	9.9019	978	9.9019	283.16	5.0	1015	10.796	1015	10.795
294.11	4.0	971	9.8137	971	9.8137	283.16	4.0	1009	10.720	1009	10.720
294.10	3.0	963	9.7189	963	9.7182	283.16	3.0	1003	10.641	1003	10.640
294.10	2.0	955	9.6170	955	9.6162	283.16	2.0	997	10.568	997	10.567
$T_n = 274.43$ K						$T_n = 263.03$ K					
274.44	15.0	1083	11.895	1083	11.896	263.03	15.0	1112	12.821	1112	12.821
274.44	14.0	1080	11.846	1080	11.847	263.03	14.0	1109	12.777	1109	12.777
274.44	13.0	1076	11.798	1076	11.799	263.02	13.0	1106	12.733	1106	12.732
274.43	12.0	1072	11.749	1072	11.749	263.02	12.0	1103	12.685	1103	12.684
274.44	11.0	1069	11.696	1069	11.697	263.03	11.0	1099	12.636	1099	12.636
274.43	10.0	1065	11.644	1065	11.644	263.03	10.0	1096	12.586	1096	12.586
274.43	9.0	1061	11.588	1061	11.588	263.04	9.0	1092	12.536	1092	12.537
274.44	8.0	1057	11.528	1057	11.529	263.03	8.0	1089	12.485	1089	12.485
274.43	7.0	1052	11.471	1052	11.471	263.03	7.0	1085	12.431	1085	12.431
274.43	6.0	1048	11.411	1048	11.411	263.03	6.0	1081	12.379	1081	12.379
274.43	5.0	1043	11.346	1043	11.346	263.04	5.0	1077	12.319	1077	12.320
274.42	4.0	1038	11.284	1038	11.283	263.03	4.0	1073	12.264	1073	12.264
274.42	3.0	1033	11.215	1033	11.214	263.03	3.0	1069	12.203	1069	12.203
274.42	2.0	1028	11.141	1028	11.140	263.02	2.0	1065	12.145	1065	12.144
$T_n = 253.14$ K						$T_n = 243.16$ K					
253.13	15.0	1136	13.669	1136	13.668	243.15	15.0	1161	14.629	1161	14.628
253.14	14.0	1134	13.628	1134	13.628	243.15	14.0	1158	14.590	1158	14.589
253.15	13.0	1131	13.585	1131	13.586	243.16	13.0	1156	14.552	1156	14.552
253.14	12.0	1128	13.543	1128	13.543	243.16	12.0	1153	14.510	1153	14.510
253.14	11.0	1125	13.500	1125	13.500	243.16	11.0	1150	14.469	1150	14.469
253.14	10.0	1122	13.455	1122	13.455	243.16	10.0	1148	14.430	1148	14.430
253.13	9.0	1119	13.407	1119	13.406	243.16	9.0	1145	14.386	1145	14.386
253.13	8.0	1116	13.362	1116	13.361	243.17	8.0	1142	14.340	1142	14.341
253.14	7.0	1113	13.311	1113	13.311	243.16	7.0	1139	14.298	1139	14.298
253.13	6.0	1109	13.264	1109	13.263	243.16	6.0	1136	14.254	1136	14.254
253.14	5.0	1106	13.209	1106	13.209	243.16	5.0	1133	14.203	1133	14.203
253.14	4.0	1102	13.160	1102	13.160	243.16	4.0	1130	14.158	1130	14.158
253.14	3.0	1099	13.106	1099	13.106	243.16	3.0	1127	14.108	1127	14.108
253.13	2.0	1095	13.050	1095	13.049	243.16	2.0	1124	14.061	1124	14.061
$T_n = 232.99$ K						$T_n = 223.99$ K					
232.97	15.0	1185	15.697	1185	15.694	223.96	15.0	1206	16.732	1206	16.728
232.97	14.0	1183	15.659	1183	15.657	223.97	14.0	1204	16.696	1204	16.694
232.98	13.0	1180	15.622	1180	15.621	223.97	13.0	1202	16.660	1202	16.658
232.99	12.0	1178	15.581	1178	15.581	223.98	12.0	1200	16.622	1200	16.621
233.00	11.0	1176	15.543	1176	15.544	224.00	11.0	1198	16.582	1198	16.583
232.99	10.0	1173	15.503	1173	15.503	224.00	10.0	1195	16.547	1195	16.548
232.99	9.0	1171	15.465	1171	15.465	224.00	9.0	1193	16.506	1193	16.507
233.00	8.0	1168	15.424	1168	15.425	224.00	8.0	1191	16.486	1191	16.488
233.00	7.0	1166	15.387	1166	15.388	224.00	7.0	1189	16.432	1189	16.433
233.00	6.0	1163	15.343	1163	15.344	224.00	6.0	1186	16.389	1186	16.390
233.01	5.0	1161	15.298	1161	15.300	224.00	5.0	1184	16.349	1184	16.351
233.01	4.0	1158	15.253	1158	15.255	224.00	4.0	1182	16.308	1182	16.309
233.01	3.0	1155	15.207	1155	15.209	224.00	3.0	1179	16.267	1179	16.268
233.01	2.0	1152	15.164	1152	15.167	224.00	2.0	1177	16.227	1177	16.228
$T_n = 218.26$ K											
218.48	15.0	1219	17.403	1220	17.430						
218.45	14.0	1217	17.370	1218	17.393						
218.43	13.0	1215	17.338	1216	17.359						
218.24	12.0	1214	17.326	1214	17.323						
218.18	11.0	1212	17.303	1212	17.293						
218.22	10.0	1210	17.264	1210	17.260						
218.23	9.0	1207	17.224	1207	17.220						
218.23	8.0	1205	17.184	1205	17.181						
218.21	7.0	1203	17.147	1203	17.141						

Table 2 (Continued)

T (K)	P (MPa)	$\rho$ (kg m <sup>-3</sup> )	$\varepsilon_r(T,P)$	$\rho(T_n,P)$ (kg m <sup>-3</sup> )	$\varepsilon_r(T_n,P)$	T (K)	P (MPa)	$\rho$ (kg m <sup>-3</sup> )	$\varepsilon_r(T,P)$	$\rho(T_n,P)$ (kg m <sup>-3</sup> )	$\varepsilon_r(T_n,P)$
218.19	6.0	1201	17.111	1201	17.102						
218.17	5.0	1199	17.076	1199	17.064						
218.16	4.0	1197	17.043	1196	17.030						
218.13	3.0	1194	17.006	1194	16.989						
218.12	2.0	1192	16.968	1192	16.950						

Table 3

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

$a_0$	$a_1$ (K)	$a_2$ (kg <sup>-1</sup> m <sup>3</sup> )	$a_3$ (K m <sup>3</sup> kg <sup>-1</sup> )
11.811 ± 0.674	-3928 ± 210	-0.0102 ± 0.1654	6.4656 ± 0.0006
$b_0$	$b_1$ (K)	$10^{-2}b_2$ (MPa <sup>-1</sup> )	$b_3$ (KMPa <sup>-1</sup> )
-11.468 ± 0.095	6188 ± 23.7	16.450 ± 1.010	-28.678 ± 2.527

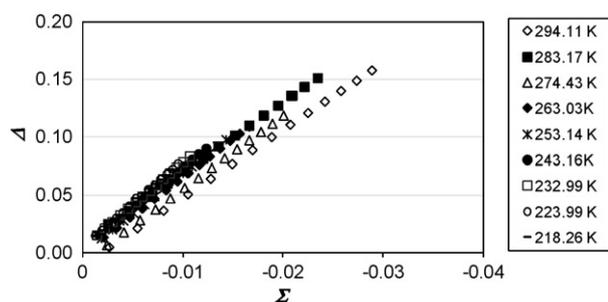


Fig. 2. Variation of  $\Delta = \varepsilon_r^{1/2}(\rho) - \varepsilon_r^{1/2}(\rho_0)$  with the Eulerian Strain,  $\Sigma$  (Eq. (5)) for the various isotherms; ( $\diamond$ ) 294.11 K; ( $\blacksquare$ ) 283.17 K; ( $\triangle$ ) 274.43 K; ( $\blacklozenge$ ) 263.03 K; ( $*$ ) 253.14 K; ( $\bullet$ ) 243.16 K; ( $\square$ ) 232.99 K; ( $\circ$ ) 223.99 K; ( $-$ ) 218.25 K.

saturation. In addition, the function  $\Delta$  seems to be less sensitive to temperature (lines almost parallel). Table 3 presents the values of the coefficients  $A$  and  $B$  of Vedam equation for each isotherm. The intercepts  $B$  are very small for all isotherms,  $B \approx 0$  and the slope of the linear variation of  $\Delta$  with  $\Sigma$  is negative for all temperatures, decreasing linearly with the increase with temperature, as expected from the theory. Assuming that  $B=0$  in Eq. (4), it is possible to use the Vedam relation to estimate the relative permittivity values. As reported before, the values for  $A'$  were estimated by fitting the experimental data as a function of  $\Sigma$  and forcing the constant  $B$  to be equal to zero. Being the case the Vedam equation is of the form:

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

The new values of the slope  $A'$  according to Eq. (6) are also presented also in Table 4. This equation allows the estimation the relative permittivity at any density, for the temperatures measured, to better than 0.5% as shown in Fig. 3.

For the calculation of the dipole moment in the liquid phase we have applied first the theory of molecular polarizability developed

Table 4

Values of the constants  $A$  and  $B$  of Vedam equation (Eq. (4)) and values of the constant  $A'$  (Eq. (6)).

T (K)	$\rho_{\text{sat}}$ (kg m <sup>-3</sup> )	$\varepsilon_r(\rho_{\text{sat}})$	$A$	$B$	$A'$
294.11	946.93	9.5811	-5.7344	-0.01043	-5.2451
283.17	988.99	10.3993	-5.9874	0.00857	-6.4858
274.43	1019.92	11.0888	-6.2051	-0.00804	-5.6573
263.03	1057.58	12.0502	-6.5287	-0.00176	-6.3834
253.14	1088.32	12.9530	-6.7325	-0.00021	-6.7125
243.16	1117.90	13.9408	-6.9235	0.00345	-7.3074
232.99	1146.84	15.0401	-7.1310	0.00494	-7.7648
223.99	1171.62	16.1031	-7.3956	0.00498	-8.1159
218.26	1187.05	16.8297	-7.4609	0.00456	-8.1727

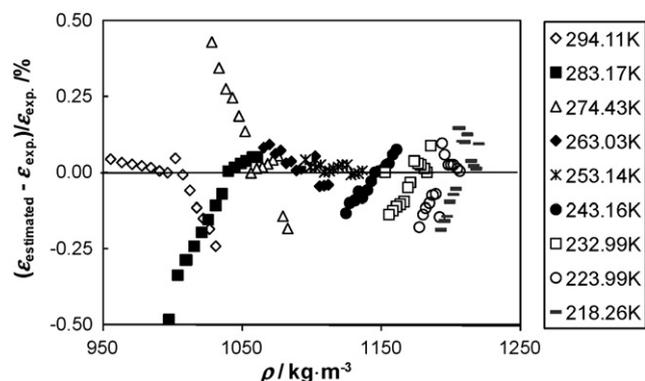


Fig. 3. Deviations of the experimental data of the relative permittivity,  $\varepsilon_r$ , from the values obtained through the modified Vedam relation (Eq. (6)); ( $\diamond$ ) 294.11 K; ( $\blacksquare$ ) 283.17 K; ( $\triangle$ ) 274.43 K; ( $\blacklozenge$ ) 263.03 K; ( $*$ ) 253.14 K; ( $\bullet$ ) 243.16 K; ( $\square$ ) 232.99 K; ( $\circ$ ) 223.99 K; ( $-$ ) 218.25 K.

by Kirkwood [3] after the definition of Onsager's local field [2], as it only needs molecular properties, relative permittivity and density. In this theory, an apparent dipole moment of the liquid  $\mu^*$  is calculated from the following relation:

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

where  $M$  is the relative molar mass of the fluid,  $N_0$  is the Avogadro number,  $\alpha$  is the molecular polarizability of the molecule,  $\varepsilon_0$  the electric permittivity in vacuum,  $T$  the absolute temperature,  $k_B$  the Boltzmann constant,  $\mu_K^*$  the apparent dipole moment ( $\mu_K^* = g_K^{1/2} \mu$ , where  $\mu$  is the dipole moment in the ideal gas state) and  $g_K$  is the Kirkwood correlation parameter. According to Kirkwood theory  $g_K$  measures the restriction to rotation imposed by a cage of molecules surrounding a given molecule. A complete discussion about the importance and the information that  $g$  gives about the hindered rotation in the liquid state can be found in parent publications [1,9]. The value of  $\mu_K^*$  can be calculated by a linear regression of the left-hand side of Eq. (7) as a function of  $T^{-1}$ . In the present paper we use the unit Debye<sup>3</sup>. Fig. 4 shows the plot of Kirkwood function vs.  $T^{-1}$ ,  $\mu_K^* = 3.293$  D. Using the value of dipole moment of HFC-143a ( $\mu = 2.340$  D) in the gas phase [13], the value of Kirkwood parameter  $g_K$  was found to be equal to 1.981. These values differ by about 1.5% from those presented before for HFC-143a [1,17], because the data was reanalysed, and some differences on the density calculations were encountered. Nevertheless, both results, together with the discussion about rotational hindrance in the liquid state for the fluorine derivatives of methane, ethane, propane and butane showed that 1,1,1-trifluoroethane (HFC-134a) is one of the most mobile molecules in the liquid state [1,9], although possessing partially hindered rotation. As stated before [1,10], it seems that the more fluorine atoms, or the bigger the ratio between fluorine and hydrogen atoms in the molecule, the more restricted the rotation in the liquid phase [1]. Molecules like 1,1,1,2-tetrafluoroethane, HFC-

<sup>3</sup> 1D = 3.335640 × 10<sup>-30</sup> C m.

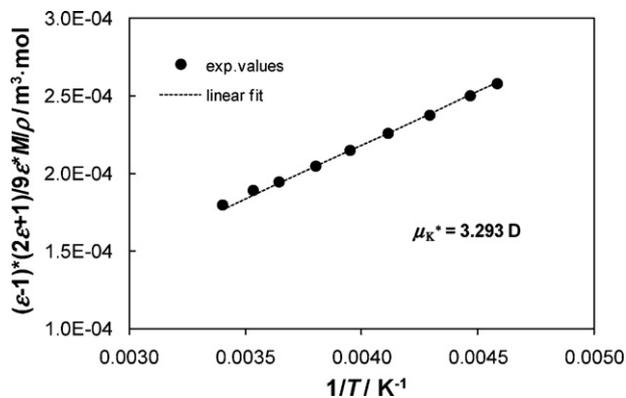


Fig. 4. The variation of the Kirkwood function (Eq. (7)) with the reciprocal temperature; (●) experimental values; linear fit;  $\mu_K^* = 3.293 D$ .

134a, and 1,1-difluoroethane, HFC-152a, have restricted rotation in the liquid state, caused by hydrogen bonding. This was already proved for HFC-134a and HFC-143a [8]. For instance, in HFC-143a, the distances between the active fluorine and hydrogen atoms in the different dimers vary between 0.253 nm and 0.295 nm, values well known in hydrogen bonds in other compounds.

From the theoretical calculations performed before with the Kirkwood theory [1,8] it was concluded that this theory was just a first approximation, and that more reliable values for the dipole moments in the liquid phase should be obtained from the application of Frölich theory [4]. In fact, in the liquid phase the molecules are close to each other, so the orientation polarization of a molecule is influenced by the surrounding dielectric. Onsager has given a more careful treatment of the continuum approach. In his model, a point dipole is placed in the centre of a cavity of relative permittivity  $\varepsilon_{r,\infty}$ , and the effect of the surrounding dielectric is measured by the dielectric response of the polarization charges induced on the wall of the cavity, resulting:

$$\frac{(\varepsilon_r - \varepsilon_{r,\infty})(2\varepsilon_r + \varepsilon_{r,\infty})}{\varepsilon_r(\varepsilon_{r,\infty} + 2)^2} \left(\frac{M}{\rho}\right) = \frac{N_0 g_{KF} \mu^2}{9\varepsilon_0 k_B T} \quad (8)$$

$$KFF = \frac{(\varepsilon_r - n^2)(2\varepsilon_r + n^2)}{\varepsilon_r(n^2 + 2)^2} \left(\frac{M}{\rho}\right) = \frac{N_0 g_{KF} \mu^2}{9\varepsilon_0 k_B T} \quad (9)$$

The high-frequency relative permittivity  $\varepsilon_{r,\infty}$  is commonly calculated from the Maxwell relation  $\varepsilon_{r,\infty} = n^2$ , where  $n$  is the refractive index of the liquid at temperature  $T$ . Eq. (8) is then transformed in the Kirkwood–Frölich equation (9), where KFF is the Kirkwood–Frölich Function. This equation was used to predict the apparent dipole in the liquid state of HFC-143a ( $\mu_{KF}^* = 2.530 D$ ). Fig. 5 shows the experimental measurements and its variation with  $1/T$  for HFC-143a. The Kirkwood–Frölich parameter  $g_{KF}$  obtained is 1.169. The SCIPCM model, developed by Costa Cabral et al., [8] generated a value for the dipole moment in the liquid phase of 2.75 D, smaller than the Kirkwood value, but slightly greater than the Kirkwood–Frölich value (5%), and in excellent agreement with the Kirkwood–Frölich theory. This shows that the Kirkwood theory has several limitations, namely because there is the possibility of formation of dimers or  $n$ -molecule clusters in the liquid state, not accounted for this theory. We therefore recommend the use of the Kirkwood–Frölich theory, whenever the refraction index in the liquid state is known. Application of this theory to most refrigerants measured by this group in the past, shows exactly the same trend and this will be reported soon [18].

As reported before [10], the electrical permittivity data can be used to estimate values for thermodynamic coefficients like the isobaric coefficient of thermal expansion  $\alpha_p$  and of the isothermal

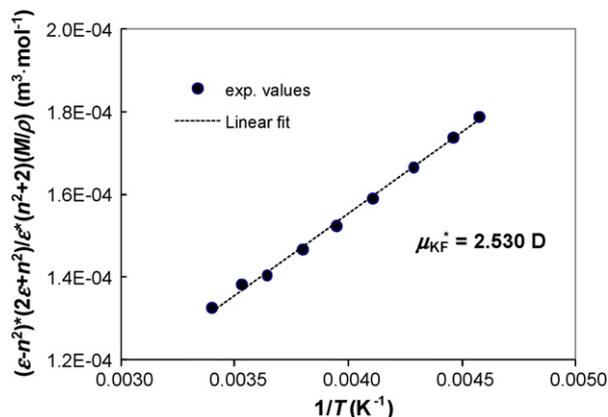


Fig. 5. The variation of the Kirkwood–Frölich function (Eq. (9)) with the reciprocal temperature; (●) experimental values; linear fit;  $\mu_{KF}^* = 2.530 D$ .

compressibility  $\kappa_T$ . This is possible because the accuracy of the  $\varepsilon_r$  data and the quality of density data necessary for the calculations is very high, and, not replacing direct experimental data and/or a very accurate equation of state, can be extremely useful for estimating data for fluids or mixtures, where experimental information is not available. The general approach was described in a recent publication by the authors, and applied to three refrigerant mixtures, of fixed composition [10]. Details of the procedure can be seen in this reference, and will not be repeated here. The main equations used in the calculation, derived from the thermodynamic definitions of the coefficients and from the temperature, pressure and density derivatives of electrical permittivity, calculated from the experimental data and Eqs. (2) and (3) are:

$$\alpha_p = -\frac{(\partial\varepsilon_r/\partial T)_p}{\rho(\partial\varepsilon_r/\partial\rho)_p} \quad (10)$$

and

$$\kappa_T = \frac{(\partial\varepsilon_r/\partial P)_T}{\rho(\partial\varepsilon_r/\partial\rho)_T} \quad (11)$$

Table 5 shows the values obtained for the isobaric expansion coefficient,  $\alpha_p$ , for HFC-143a, as a function of pressure, for different temperatures, calculated with the present scheme, and the values obtained from REFPROP<sup>®</sup> [13]. Fig. 6 shows the deviations between our calculated values and the proposed by NIST, as a function of density, for all the isotherms studied. The deviations amount to  $\pm 3\%$ , with an average deviation of 1.8%. Table 6 shows the calculations performed for the isothermal compressibility,  $\kappa_T$ , and Fig. 7 shows the deviations from REFPROP<sup>®</sup> [13]. Here the deviations are much bigger, within  $\pm 20\%$ , with an average deviation of 10%, showing

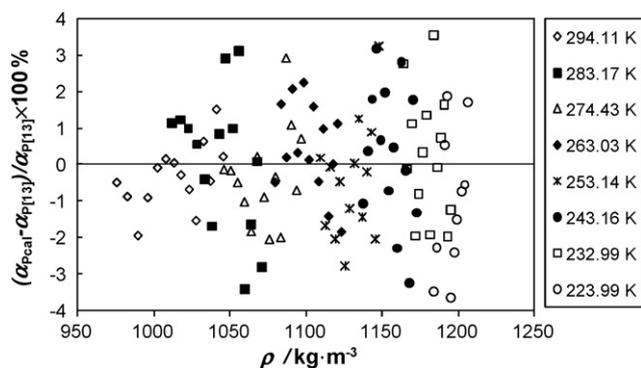


Fig. 6. Deviations between the determined coefficients of thermal expansion and REFPROP7<sup>®</sup> [13], as a function of density, for HFC-143a.

**Table 5**Coefficients of isobaric thermal expansion ( $\alpha_p$ ) calculated from Eq. (10) for HFC-143a, from  $T = 218.26$  to  $294.11$  K and  $P = 2$ – $15$  MPa.

$\alpha_p$ (K <sup>-1</sup> )	$\alpha_p$ (K <sup>-1</sup> ) [13]	$\alpha_p$ (K <sup>-1</sup> )	$\alpha_p$ (K <sup>-1</sup> ) [13]	$\alpha_p$ (K <sup>-1</sup> )	$\alpha_p$ (K <sup>-1</sup> ) [13]	$\alpha_p$ (K <sup>-1</sup> )	$\alpha_p$ (K <sup>-1</sup> ) [13]
$T_n = 294.11$ K		$T_n = 283.17$ K		$T_n = 274.43$ K		$T_n = 263.03$ K	
0.002540	0.002534	0.002343	0.002411	0.002316	0.002300	0.002157	0.002197
0.002634	0.002595	0.002460	0.002458	0.002322	0.002339	0.002254	0.002229
0.002644	0.002656	0.002469	0.002511	0.002408	0.002382	0.002265	0.002264
0.002742	0.002724	0.002479	0.002567	0.002498	0.002428	0.002268	0.002301
0.002758	0.002800	0.002707	0.002626	0.002426	0.002475	0.002364	0.002341
0.002859	0.002879	0.002715	0.002688	0.002517	0.002526	0.002371	0.002382
0.002962	0.002970	0.002839	0.002758	0.002528	0.002581	0.002465	0.002426
0.003062	0.003061	0.002853	0.002829	0.002614	0.002638	0.002474	0.002471
0.003172	0.003167	0.002863	0.002913	0.002709	0.002704	0.002576	0.002520
0.003281	0.003283	0.002986	0.002999	0.002719	0.002770	0.002583	0.002575
0.003391	0.003422	0.003117	0.003100	0.002816	0.002846	0.002684	0.002630
0.003505	0.003575	0.003242	0.003210	0.002911	0.002926	0.002696	0.002691
0.003720	0.003752	0.003372	0.003331	0.003007	0.003013	0.002798	0.002753
0.003934	0.003953	0.003503	0.003464	0.003101	0.003106	0.002809	0.002822
$T_n = 253.14$ K		$T_n = 243.16$ K		$T_n = 232.99$ K		$T_n = 223.99$ K	
0.002181	0.002113	0.002010	0.002037	0.001950	0.001974	0.002106	0.00193
0.002096	0.002141	0.002098	0.002061	0.001955	0.001995	0.002094	0.001948
0.002188	0.002169	0.002018	0.002087	0.002050	0.002017	0.00209	0.001968
0.002196	0.002201	0.002109	0.002113	0.002054	0.002039	0.002021	0.001987
0.002202	0.002235	0.002200	0.002140	0.002059	0.002061	0.001996	0.002007
0.002295	0.002267	0.002118	0.002168	0.002160	0.002086	0.002013	0.002028
0.002304	0.002303	0.002208	0.002197	0.002070	0.002111	0.002022	0.002053
0.002312	0.002341	0.002213	0.002230	0.002167	0.002138	0.002025	0.002075
0.002314	0.002380	0.002306	0.002261	0.002170	0.002163	0.002022	0.002098
0.002413	0.002424	0.002312	0.002297	0.002176	0.002194	0.002163	0.002124
0.002417	0.002467	0.002405	0.002331	0.002177	0.002221	0.002159	0.002148
0.002514	0.002516	0.002411	0.002369	0.002277	0.002252	0.002016	0.002176
0.002521	0.002564	0.002418	0.002409	0.002283	0.002286	0.002154	0.002204
0.002622	0.002617	0.002424	0.002451	0.002383	0.002319	0.002154	0.002231

**Table 6**Coefficients of isothermal compressibility ( $\kappa_T$ ) calculated from Eq. (11) for HFC-143a from  $T = 218.26$  to  $294.11$  K and  $P = 2$ – $15$  MPa.

$\kappa_T$ (MPa <sup>-1</sup> )	$\kappa_T$ (MPa <sup>-1</sup> ) [13]	$\kappa_T$ (MPa <sup>-1</sup> )	$\kappa_T$ (MPa <sup>-1</sup> ) [13]	$\kappa_T$ (MPa <sup>-1</sup> )	$\kappa_T$ (MPa <sup>-1</sup> ) [13]	$\kappa_T$ (MPa <sup>-1</sup> )	$\kappa_T$ (MPa <sup>-1</sup> ) [13]	$\kappa_T$ (MPa <sup>-1</sup> )	$\kappa_T$ (MPa <sup>-1</sup> ) [13]
$T_n = 294.11$ K		$T_n = 283.17$ K		$T_n = 274.43$ K		$T_n = 263.03$ K		$T_n = 253.14$ K	
0.004857	0.004270	0.003777	0.003623	0.002774	0.003209	0.002701	0.002750	0.001762	0.002422
0.003902	0.004446	0.003791	0.003754	0.003711	0.003309	0.002709	0.002822	0.002649	0.002474
0.004900	0.004632	0.003806	0.003891	0.003724	0.003429	0.002716	0.002897	0.002656	0.002538
0.004924	0.004852	0.004778	0.004054	0.002802	0.003538	0.003633	0.002987	0.002663	0.002604
0.004948	0.005085	0.003839	0.004226	0.003749	0.003652	0.002733	0.003081	0.00267	0.002673
0.005970	0.005358	0.004819	0.004407	0.003763	0.003789	0.003656	0.003179	0.002677	0.002744
0.005003	0.005651	0.003872	0.004599	0.003777	0.003932	0.002751	0.003281	0.002685	0.002818
0.006036	0.005965	0.004861	0.004802	0.004742	0.004101	0.003680	0.003389	0.002692	0.002895
0.006073	0.006337	0.004885	0.005042	0.003810	0.004282	0.003693	0.003517	0.0036	0.002988
0.007132	0.006774	0.005894	0.005326	0.004782	0.004473	0.003707	0.003651	0.002709	0.003085
0.007183	0.007292	0.005929	0.005661	0.004805	0.004699	0.003721	0.003793	0.003623	0.003186
0.008273	0.007910	0.005964	0.006025	0.004829	0.004942	0.003735	0.003943	0.002726	0.003292
0.008342	0.008653	0.006000	0.006422	0.004852	0.005202	0.003749	0.004101	0.003646	0.003404
$T_n = 243.16$ K		$T_n = 232.99$ K		$T_n = 218.26$ K		$T_n = 218.26$ K		$T_n = 218.26$ K	
0.002587	0.002137	0.001689	0.001892	0.001660	0.001710	0.001641	0.001594		
0.001729	0.002182	0.002539	0.001931	0.001663	0.001738	0.001643	0.001619		
0.002599	0.002228	0.001696	0.001971	0.001665	0.001766	0.001646	0.001645		
0.002605	0.002285	0.001699	0.002003	0.001668	0.001794	0.001649	0.001674		
0.001741	0.002334	0.002554	0.002045	0.001671	0.001824	0.001652	0.001702		
0.002617	0.002385	0.001706	0.002089	0.002512	0.001861	0.002482	0.001736		
0.002624	0.002448	0.002565	0.002133	0.001678	0.001900	0.001658	0.001772		
0.002630	0.002512	0.001714	0.002179	0.001681	0.001932	0.001661	0.001801		
0.002637	0.002580	0.002576	0.002226	0.002526	0.001973	0.001664	0.001831		
0.002644	0.002650	0.001721	0.002275	0.001688	0.002015	0.001667	0.001862		
0.002651	0.002722	0.002587	0.002325	0.001691	0.002049	0.002505	0.001902		
0.002658	0.002798	0.002594	0.002387	0.002541	0.002094	0.001674	0.001943		
0.002665	0.002876	0.002601	0.002452	0.001698	0.002139	0.001676	0.001976		

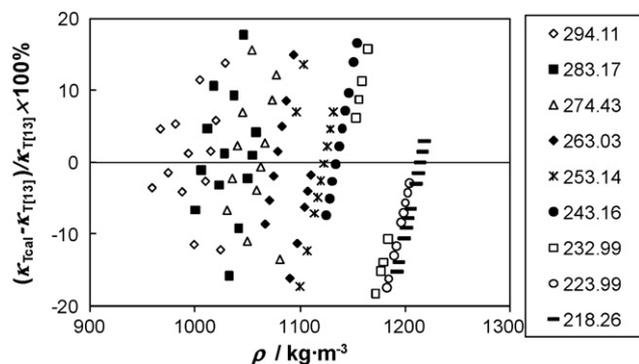


Fig. 7. Deviations between the determined coefficients of compressibility and REFPROP7<sup>®</sup> [13], as a function of density, for HFC-143a.

systematic deviations, for the lower temperature isotherms. These results are about 10 times bigger than those obtained for R408A<sup>4</sup> and R409A<sup>5</sup> [10], a result somewhat surprising, as in principle the EOS of HFC-143a should be more accurate than the prediction of a corresponding states model used for mixtures. However, this might be explained by less accurate values in the densities for these temperatures. Results obtained for other refrigerants show deviations in these thermodynamic coefficients of the order of those reported in reference [10], and will be presented soon [19].

#### 4. Conclusions

This paper contributes to increase our knowledge about the behavior of polar fluids in the liquid state. We present relative permittivity data of HFC-143a, in the temperature range 218–294 K and pressure from 2 to 15 MPa with an uncertainty better than  $\pm 1.2 \times 10^{-2}$ . 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.

The Eulerian formalism was used to analyze the data and it is possible to conclude that it represents an estimation method for the dependence of the relative permittivity with density. The application of Kirkwood and Kirkwood–Frölich theories, and the evaluation of the dipole moments in the liquid state, together with the corresponding correlation factors ( $\mu_K^* = 3.293$  D,  $\mu_{KF}^* = 2.530$  D,  $g_K = 1.981$  and  $g_{KF} = 1.169$ ) permits the discussion about the structure of the molecules in the liquid state.

There has been many changes in the field of dielectric properties of polar liquids since we published in this journal a decade ago the results on the dielectric constant (relative permittivity) and dipole moments of 1,1,1-trifluoro-2,2-dichloroethane (HCFC-123) and 1,1-difluoroethane (HFC-152a) [20]. At that time there were several limitations, namely in density (many times predicted and not experimental) and refractive indices values (almost non-existent), and the first conclusions about hindered or free rotation in the liquid state where still a possible interpretation. Since all the evolution, both on experimental measurements on other refrigerants, on the SCIPCM model and other theoretical calculations, and

the availability of refractive indices for all these fluids, occurred since then, it is now possible to understand clearly the molecular interactions of these molecules in the liquid state, the formation of dimers and  $n$ -sized clusters, the “cage effect”, the hydrogen bonding, and their consequences in the rotation of molecules, free or hindered. For the case here presented, HFC-143a, although the existence of hydrogen bonds was predicted, the rotational mobility of this molecule in the liquid state seems to be quite high. In addition, the predicted values of the dipole moments in the liquid state can be used to derive effective and pair-additive intermolecular potential models, which, can be used to discuss the liquid state properties by means of computer simulations based on Monte Carlo or molecular dynamics techniques. This is a research line that we look forward pursuing in the near future.

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<sup>4</sup> R408A is a zeotropic mixture or blend, with a composition of 7% HFC-125 (pentafluoroethane)+46% HFC-143a (1,1,1-trifluoroethane)+47% HCFC-22 (chlorodifluoromethane).

<sup>5</sup> R409A is a zeotropic mixture or blend, with a composition of 60% HCFC-22 (chlorodifluoromethane)+25% HCFC-124 (chlorotetrafluoroethane)+15% HCFC-142b (1-chloro-1,1-difluoroethane).