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Dielectric Constant, Dielectric Virial Coefficients, and Dipole Moments of 1,1,1,2-Tetrafluoroethane

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In this paper we report measurements of the dielectric constant of 1,1,1,2-tetrafluoroethane, HFC-134a, an environmentally acceptable refrigerant, under consideration as an alternative replacement of the chlorofluorocarbons, CFCs. The dipole moment in the gaseous phase was found to be (1.91 ± 0.19) D, and in the liquid phase (3.54 ± 0.01) D. We present values of the first three dielectric virial coefficients in the gaseous phase.

Introduction

In this paper precise measurements of the dielectric constant in the gaseous phase of HFC-134a are used to obtain accurate values of the density and the isolated molecule dipole moment, while those in the liquid phase can be used to obtain the dipole moment in the condensed phase.

The relation between the density ϱ and the dielectric constant ϵ is given by the Clausius–Mossotti relation

$$P_t = \frac{\epsilon - 1}{\epsilon + 2}\left(\frac{M}{\varrho}\right) = (\mathrm{CM})\left(\frac{M}{\varrho}\right) = A_\epsilon + B_\epsilon\left(\frac{\varrho}{M}\right) + C_\epsilon\left(\frac{\varrho}{M}\right)^2 + ... \quad (1)$$

where P_t is the total molar polarization, M is the relative molecular mass, and A_ϵ, B_ϵ, and C_ϵ are, respectively, the first, second, and third dielectric virial coefficients, expressed in molar units. CM is the Clausius–Mossoti function. The dielectric virial coefficients are independent of pressure and density but are functions of temperature. The first dielectric virial coefficient, A_ϵ, describes the isolated molecule contribution to P_t. The second dielectric virial coefficient, B_ϵ, describes the excess contribution to P_t due to the interaction of molecular pairs. The third dielectric virial coefficient, C_ϵ, describes the interaction of the molecular triplets.

Buckingham and Pople (1955) have derived the first and second dielectric virial coefficients from statistical mechanics. For a homogeneous, isotropic dielectric medium, they obtained

$$A_\epsilon = \frac{4}{3}\pi N_o\left(\alpha + \frac{\mu^2}{3k_B T}\right) \quad (2)$$

where N_o is the Avogadro number, α is the polarizability, μ is the permanent dipole moment, and k_B is the Boltzman constant. The second dielectric virial coefficient, B_ϵ, is given by

$$B_\epsilon = \frac{4\pi N_o^{\,2}}{3\Omega}\left\{\left[\frac{1}{2}\frac{\partial(\bar{\mu}_1 + \bar{\mu}_2)}{\partial \bar{E}_o}\bar{e} - \alpha_o\right] + \frac{1}{3kT}\left[\frac{1}{2}(\bar{\mu}_1 + \bar{\mu}_2)^2 - \mu_o^{\,2}\right]\right\} \exp\left\{-\frac{U_{12}}{k_B T}\right\} \mathrm{d}\tau_2 \quad (3)$$

where $\bar{E}_o$ is the external field, $\bar{\mu}$, and $\bar{\mu}_2$ are, respectively, the mean values of the induced dipole on molecules 1 and 2, $\bar{e}$ is a unit vector in the direction of $\bar{E}_o$, τ is related to the coordinates, and U_{12} is the potential energy due to intermolecular interaction between molecules 1 and 2.

The successive approximations for the density obtained from eq 1 are given by

$$\varrho_1 = (\mathrm{CM})M/A_\epsilon \quad (4)$$

$$\varrho_2 = \varrho_1 - (B_\epsilon/A_\epsilon)\varrho_1^2 \quad (5)$$

$$\varrho_3 = \varrho_2 + [(2B_\epsilon^{\,2} - A_\epsilon C_\epsilon)/A_3^{\,2}]\varrho_1^{\,3} \quad (6)$$

where ϱ_1, ϱ_2, and ϱ_3 are, respectively, the first, second, and third approximations of the density. The value of the total molar polarization can be expressed in terms of the polarizability of the molecule, α, and its dipole moment in the gaseous phase, μ, through the Debye equation

$$P_t = \frac{\epsilon - 1}{\epsilon + 2}\left(\frac{M}{\varrho}\right) = \frac{4\pi N_o}{3}\left(\alpha + \frac{\mu^2}{3k_B T}\right) = A_\epsilon \quad (7)$$

which is the first approximation of eq 1. For the liquid phase, the problem of the interaction of dipoles at a close distance has to be resolved differently. We assume that the theory of molecular polarizability developed by Kirkwood (1939), after the definition of Onsager's local field in a liquid assembly of permanent dipoles (Onsager, 1936), is the most appropriate. In this theory it is possible to correlate the dielectric constant of the polar liquid with the apparent dipole moment μ^* through the equation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon}\left(\frac{M}{\varrho}\right) = \frac{N_o}{3}\left(\alpha + \frac{(\mu^*)^2}{3\epsilon_o k_B T}\right) \quad (8)$$

The apparent dipole moment is $\mu^* = g^{1/2}\mu$, where μ is the dipole moment in the ideal gas state. g is the Kirkwood correlation parameter, and it measures the restrictions to

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Table 1. Measured Values of the Dielectric Constant (ϵ), the First (ϱ_1), the Second (ϱ_2), and the Third (ϱ_3) Approximations of the Density, the Calculated Values (ϱ_{TR}) According to the EOS by Tillner-Roth and Baehr (1991), and Deviations $\Delta\varrho_n = (\varrho_n - \varrho_{TR})/\varrho_{TR}$ of HFC-134a in the Gaseous Phase as a Function of Pressure (P) at 298.15 K

P/MPa ± 0.01%	$\epsilon - 1 \pm 1 \times 10^{-6}$	ϱ_1/(kg m^{-3}) ± 0.05	ϱ_2/(kg m^{-3}) ± 0.05	ϱ_3/(kg m^{-3}) ± 0.05	ϱ_{TR}/(kg m^{-3})	$100\Delta\varrho_1$	$100\Delta\varrho_2$	$100\Delta\varrho_3$
0.6089	0.088 440	29.09	29.44	28.24	29.08	0.0250	1.2350	−2.9937
0.5755	0.082 595	27.27	27.53	26.54	27.21	0.0341	1.1733	−2.4538
0.5503	0.078 284	25.83	26.11	25.26	25.82	0.0357	1.1080	−2.1623
0.5251	0.074 043	24.26	24.71	23.99	24.46	0.0134	1.0312	−1.9073
0.5000	0.069 914	23.13	23.35	22.74	23.13	0.0108	0.9639	−1.6689
0.4751	0.065 862	21.82	22.02	21.51	21.82	−0.0202	0.8804	−1.4605
0.4502	0.061 903	20.53	20.71	20.28	20.54	−0.0480	0.8121	−1.2732
0.4250	0.057 965	19.25	19.40	19.05	19.26	−0.0675	0.7306	−1.1014
0.4000	0.054 131	18.00	18.13	17.85	18.01	−0.0744	0.6741	−0.9300
0.3750	0.050 354	16.77	16.88	16.65	16.78	−0.0836	0.6049	−0.7841
0.3499	0.046 622	15.543	15.64	15.46	15.56	−0.1047	0.5464	−0.6515
0.3254	0.043 040	14.37	14.45	14.30	14.38	−0.1225	0.4811	−0.5492
0.2776	0.036 214	12.12	12.18	12.09	12.13	−0.1281	0.3721	−0.3500
0.2750	0.035 840	11.99	12.05	11.97	12.01	−0.1565	0.3432	−0.3676
0.2500	0.032 358	10.84	10.89	10.82	10.85	−0.1383	0.3055	−0.2748
0.2250	0.0298 924	9.70	9.73	9.69	9.74	−0.1807	0.2180	−0.2434
0.2003	0.025 570	8.58	8.62	8.58	8.60	−0.1699	0.1848	−0.1803
0.1744	0.022 114	7.43	7.45	7.43	7.44	−0.1970	0.1035	−0.1660
0.1398	0.017 565	5.91	5.93	5.92	5.92	−0.1483	0.0986	−0.0764
0.1200	0.015 016	5.06	5.07	5.06	5.06	−0.0987	− 0.1166	−0.0168

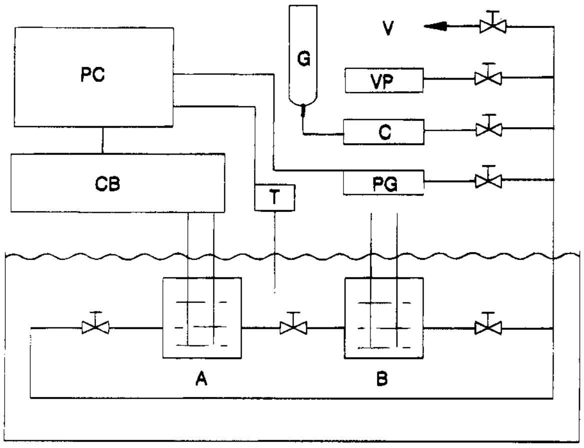

Figure 1. Schematic diagram of the apparatus for the dielectric measurements in the gaseous phase. (A and B) measurement cells; (C) gas compressor; (CB) capacitance bridge; (CTB) controlled temperature bath; (G) gas cylinder; (PC) personal computer; (PG) pressure gauge; (V) vent; (VP) vacuum pump.

rotation imposed by a cage of molecules in a given molecule. The value of μ^* can be calculated for HFC-134a by a linear regression of the left-hand side of eq 8 as a function of $1/T$.

Experimental Procedure

The gas used for these gaseous phase measurements has been obtained from ICI Polymers, Runcorn, U.K., and was prepared in the same way as the one utilized for the round-robin measurements on this refrigerant (Assael et al., 1994). The purity was estimated, by ICI, to be on the order of 99.99%. The gas was used without further purification. For the liquid phase measurements, we obtained a sample from Solvay Fluor und Derivative, Gmbh, Hannover, Germany, with an estimated purity of 99.8%.

The schematic diagram of the apparatus setup for the measurements of the dielectric constant in the gaseous phase is presented in Figure 1. In the gaseous phase, the dielectric measurements were carried out at 1 kHz with a capacitance bridge (Andeen Hagerling, model 2500A). The uncertainty of the capacitance measurement is estimated to be 5 × 10^{-6} pF. The two cells used were of the three-terminal type. Each cell has a set of two parallel plates, 3.18 cm in diameter. The separation between the plates was adjusted to have, under vacuum, a geometrical capacitance of about 10 pF. The plates are made of copper for better thermal conductivity and are gold plated in order to reduce adsorption. Details of the construction may be obtained from Huot and Bose (1991). This system has been used previously for numerous works in the gas phase measurements (St-Arnaud et al., 1992, 1993a,b, 1995). The measurement system (cells, tubes, and valves) was in a controlled temperature bath. Temperature was controlled by a circulating bath to within ±0.01 K and was measured using a thermistor calibrated against a platinum resistance thermometer. The uncertainty in temperature measurements is estimated to be 0.01 K.

The pressure was measured with a quartz pressure transducer (Paroscientific, model 740). The transducer was calibrated against a pressure standard manufactured by Desgranges and Huot (model 5213) with an uncertainty on the order of ±0.005%. For the purpose of calibration, the pressure was represented by a polynomial in terms of the readings on the transducer. Considering the fitting and small errors due to the temperature, the final uncertainty is estimated to be on the order of ±0.01% for pressure above 1.5 MPa. For lower pressures, the uncertainty increases to ±0.05% down to ±0.5 MPa. Below this pressure the calibration is very difficult, and the uncertainty in pressure is on the order of 0.1%.

The experimental apparatus used for the liquid phase measurements, the sample handling, and the apparatus' performance have been described in detail by Gurova et al. (1994), while a description of the cell has been given by Mardolcar et al. (1992). The principal addition to the measuring system was the high-pressure line, composed of a HIP liquid pressure generator, a Newport Scientific gas compressor, and a pressure transducer, from Setra Systems, calibrated at the the LME-ICAT with an accuracy of ±0.01 MPa (traceable to NIST). 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.

Dielectric constants were obtained at a frequency of 10 kHz, with an estimated precision of ±0.01% and an accuracy better than ±0.1%. The density at the various conditions was obtained from the equation of state (EOS) developed by Tillner-Roth and Baehr (1991).

The dielectric constant of the gas is given by the relation

$$\epsilon = C(P,T)/C_0(T) \qquad (9)$$

where $C(P,T)$ is the geometric capacitance at pressure P and temperature T and $C_0(T)$ is the capacitance under vacuum. For all the results reported here, we included a

Table 2. Measured Values of the Dielectric Constant (ϵ), the First (ϱ_1), the Second (ϱ_2), and the Third (ϱ_3) Approximations of the Density, the Calculated Values (ϱ_{TR}) According to the EOS by Tillner-Roth and Baehr (1991), and Deviations $\Delta\varrho_n = (\varrho_n - \varrho_{TR})/\varrho_{TR}$ of HFC-134a in the Gaseous Phase as a Function of Pressure (P) at 308.20 K

P/MPa ± 0.01%	$\epsilon - 1 \pm 1 \times 10^{-6}$	ϱ_1/(kg m^{-3}) ± 0.05	ϱ_2/(kg m^{-3}) ± 0.05	ϱ_3/(kg m^{-3}) ± 0.05	ϱ_{TR}/(kg m^{-3})	$100\Delta\varrho_1$	$100\Delta\varrho_2$	$100\Delta\varrho_3$
0.8112	0.116 621	39.07	39.16	38.33	38.76	0.7985	1.0307	−1.1156
0.7012	0.097 042	32.72	32.78	32.29	32.47	0.7552	0.95363	−0.5617
0.6481	0.088 161	29.81	29.86	29.49	29.59	0.7334	0.9082	−0.3488
0.5470	0.071 858	24.43	24.46	24.26	24.36	0.2959	0.4423	−0.3967
0.4971	0.064 370	21.93	21.96	21.81	21.87	0.2713	0.4048	−0.2702
0.4505	0.057 571	19.66	19.68	19.58	19.61	0.2472	0.3683	−0.1765
0.4247	0.053 894	18.43	18.45	18.36	18.38	0.2441	0.3534	−0.1260
0.4007	0.050 518	17.29	17.31	17.24	17.25	0.2243	0.3222	−0.1005
0.3747	0.046 903	16.07	16.09	16.03	16.04	0.1924	0.2896	−0.0768
0.3497	0.043 495	14.92	14.93	14.89	14.89	0.1868	0.2728	−0.0382
0.3251	0.040 160	13.80	13.81	13.77	13.77	0.1488	0.2343	−0.0323
0.3006	0.036 905	12.69	12.70	12.67	12.67	0.1383	0.2126	−0.0207
0.2750	0.033 528	11.54	11.55	11.53	11.53	0.1009	0.1643	−0.0256
0.2499	0.030 275	10.43	10.44	10.43	10.43	0.0658	0.1288	−0.0181
0.2249	0.027 084	9.34	9.35	9.34	9.34	0.0606	0.1128	−0.0020
0.1999	0.023 921	8.26	8.26	8.26	8.26	0.0082	0.0497	−0.0437
0.1746	0.020 768	7.18	7.18	7.18	7.18	0.0103	0.0620	−0.0206
0.1498	0.017 708	6.13	6.13	6.13	6.13	−0.0193	0.0218	−0.0398
0.1248	0.014 670	5.08	5.08	5.08	5.08	−0.0543	−0.0237	−0.0645

Table 3. Measured Values of the Dielectric Constant (ϵ), the First (ϱ_1), the Second (ϱ_2), and the Third (ϱ_3) Approximation of the Density, the Calculated Values (ϱ_{TR}) According to the EOS by Tillner-Roth and Baehr (1991), and Deviations $\Delta\varrho_n = (\varrho_n - \varrho_{TR})/\varrho_{TR}$ of HFC-134a in the Gaseous Phase as a Function of Pressure (P) at 323.15 K

P/MPa ± 0.01%	$\epsilon - 1 \pm 1 \times 10^{-6}$	ϱ_1/(kgm^{-3}) ± 0.05	ϱ_2/(kgm^{-3}) ± 0.05	ϱ_3/(kgm^{-3}) ± 0.05	ϱ_{TR}/(kgm^{-3})	$100\Delta\varrho_1$	$100\Delta\varrho_2$	$100\Delta\varrho_3$
1.2486	0.181 169	62.18	60.94	61.07	61.39	1.2771	−0.7403	−0.5230
1.1454	0.160 048	55.30	54.32	54.41	54.62	1.2406	−0.5546	−0.3805
1.0400	0.103 33	48.79	48.02	48.09	48.20	1.2169	−0.3707	−0.2373
0.9406	0.123 079	43.02	42.43	42.47	42.53	1.1621	−0.2438	−0.1370
0.8339	0.105 758	37.18	36.73	36.76	36.79	1.0564	−0.1510	−0.0699
0.7239	0.089 142	31.50	31.18	31.20	31.19	1.0010	−0.0186	0.0381
0.6101	0.072 756	25.85	25.63	25.64	25.69	0.6216	−0.2244	−0.1802
0.5476	0.064 315	22.91	22.74	22.75	22.78	0.5802	−0.1679	−0.1351
0.4496	0.051 633	18.47	18.36	18.36	18.37	0.5398	−0.0548	−0.0441
0.4246	0.048 498	17.37	17.27	17.27	17.27	0.5551	−0.0157	0.0057
0.3998	0.045 411	16.28	16.19	16.19	16.19	−0.0076	0.0030	0.3750
0.3750	0.042 346	15.20	15.12	15.12	15.12	0.4923	0.0014	0.0120
0.3219	0.035 913	12.92	12.86	12.86	12.86	0.4152	−0.0074	0.0031
0.3000	0.033 310	11.99	11.94	11.94	11.94	0.3836	−0.0058	0.0047
0.2677	0.029 521	10.64	10.60	10.60	10.60	0.3405	−0.0048	−0.0048
0.2499	0.027 47	9.90	9.87	9.87	9.87	0.3281	0.0046	0.0150
0.2248	0.0245 66	8.87	8.84	8.84	8.84	0.3118	0.0208	0.0208
0.1972	0.021 411	7.74	7.72	7.72	7.72	0.2248	−0.0335	−0.0232
0.1747	0.018 874	6.83	6.81	6.81	6.81	0.1670	−0.0489	−0.0489
0.1457	0.015 649	5.67	5.66	5.66	5.66	0.1499	−0.0373	−0.0343
0.1245	0.013 314	4.82	4.81	4.81	4.82	−0.0596	−0.0596	−0.0596

Table 4. Experimental Values of the First (A_ϵ), Second (B_ϵ), and Third (C_ϵ) Dielectric Virial Coefficients and the Literature Values of the Second (B) and Third (C) Density Virial Coefficients for HFC-134a at Various Temperatures

T/K	A_ϵ/(cm^3 mol^{-1})	B_ϵ/(cm^3 mol^{-1})^2	$C_\epsilon \times 10^6$/(cm^3 mol^{-1})^3	B^a/(cm^3 mol^{-1})	$C^b \times 10^6$/(cm^3 mol^{-1})^2
298.15	100.15 ± 0.13	−4223 ± 200	52.1 ± 10.0	−493.07	14 979
308.20	97.71 ± 0.10	−595 ± 30	14.4 ± 2.9	−448.89	21 456
323.15	93.46 ± 0.06	3112 ± 156	0.46 ± 0.09	−396.60	26 467

[a] Mean value of the measurements by Weber (1989), Goodwin and Moldover (1990), and Tillner-Roth and Baehr (1992). [b] Extrapolated value from the measured values by Goodwin and Moldover (1990).

correction for the effect of the pressure on the plates of the geometric capacitance $C(P,T)$ of the cells. The relation between $C(P,T)$ and $C_0(T)$ is $C(P,T) = C_0(T)\,(1 - \gamma P)$, where γ is the compressibility of copper ($\gamma = 2.4 \times 10^{-6}$ MPa^{-1}). In the gaseous phase this correction did not amount to more than 0.001%, which is commensurate with the error of the capacitance measurement. However, for the sake of consistency, it was applied to all measurements.

The first dielectric virial coefficient, A_ϵ, is obtained from the measurement of the dielectric constant ϵ as a function of pressure. The equation of state

$$P/\varrho RT = 1 + B\varrho + C\varrho^2 + \ldots \qquad (10)$$

where B and C are, respectively, the second and third density virial coefficients and ϱ is the molar density, is combined with the Clausius–Mossotti equation (eq 1) to give

$$CM\left(\frac{RT}{P}\right) = A_\epsilon + \left(\frac{B_\epsilon}{A_\epsilon} - B\right) CM + \left\{\frac{C_\epsilon}{A_\epsilon^2} - \frac{B_\epsilon^2}{A_\epsilon^3} + (B^2 - C)\right\} (CM)^2 + \ldots \qquad (11)$$

In order to determine precisely the second (B_ϵ) and the third (C_ϵ) dielectric virial coefficients, we normally use (St-Arnaud et al., 1994) the expansion technique developed by Buckingham et al. (1970). Unfortunately, the low pressure in the gaseous phase does not allow the use of this technique because the uncertainty is too large. In order to solve this problem, the values of B_ϵ and C_ϵ are obtained

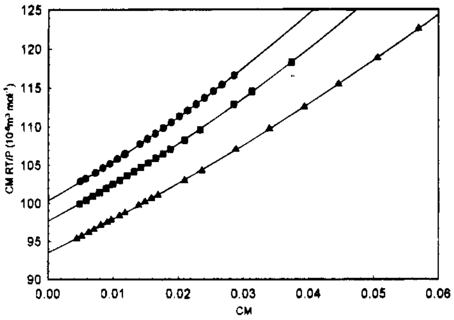

Figure 2. Curves of (CM)RT/P as a function of CM = $(\epsilon - 1)/(\epsilon + 2)$ for gaseous HFC-134a at (●) 298.15 K, (■) 303.15 K, and (▲) 323.15 K.

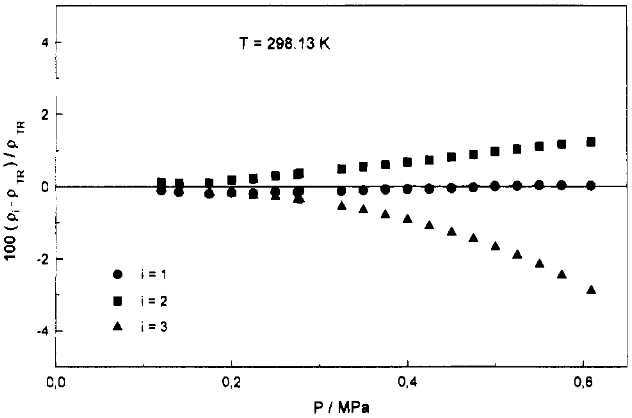

Figure 3. Pressure dependence of the deviations $(\Delta\varrho_n)$ between the three (n = 1−3) approximations of the measured density (ϱ_n) and those calculated (ϱ_{TR}) according to the EOS by Tillner-Roth and Baehr (1991) for gaseous HFC-134a at 298.15 K. Note: $\Delta\varrho_n = (\varrho_n - \varrho_{TR})/\varrho_{TR}$.

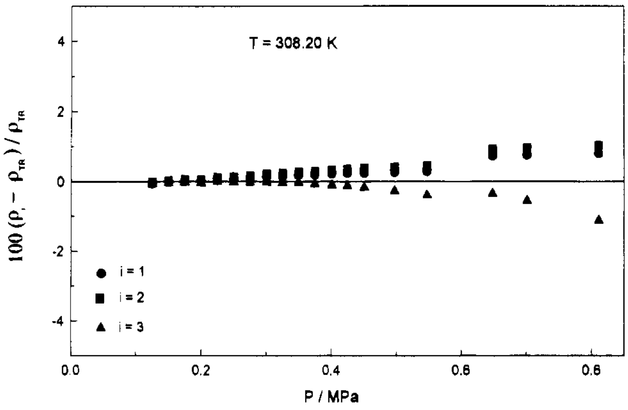

Figure 4. Pressure dependence of the deviations $(\Delta\varrho_n)$ between the three (n = 1−3) approximations of the measured density (ϱ_n) and those calculated (ϱ_{TR}) according to the EOS by Tillner-Roth and Baehr (1991) for gaseous HFC-134a at 303.20 K. Note: $\Delta\varrho_n = (\varrho_n - \varrho_{TR})/\varrho_{TR}$.

by a free fit of the Clausius−Mossotti equation, keeping our measured value of A_ϵ fixed. The B values are the mean values of the measurements by Weber (1989), Goodwin and Moldover (1990), and Tilnner-Roth and Baehr (1992). The C values are those obtained by Goodwin and Moldover (1990) (see Table 4). In eq 11, the dielectric constant values are our measured values while the density values are those calculated from the EOS by Tilnner-Roth and Baehr (1991).

Results and Discussion

In the gaseous phase, the experimental values of $\epsilon - 1$ as a function of P at 298.15, 308.20, and 323.15 K are presented, respectively, in Tables 1−3.

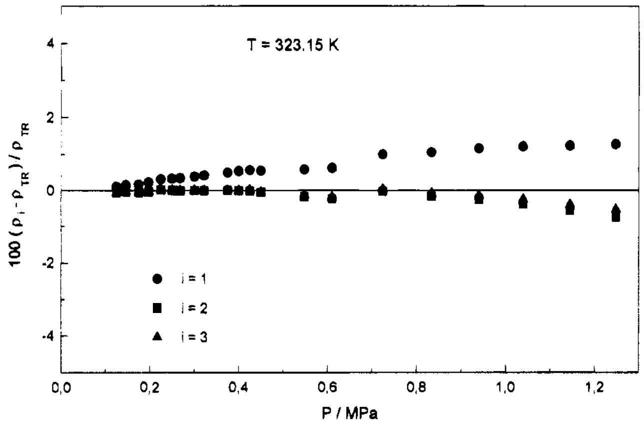

Figure 5. Pressure dependence of the deviations $(\Delta\varrho_n)$ between the three (n = 1−3) approximations of the measured density (ϱ_n) and those calculated (ϱ_{TR}) according to the EOS by Tillner-Roth and Baehr (1991) for gaseous HFC-134a at 323.15 K. Note: $\Delta\varrho_n = (\varrho_n - \varrho_{TR})/\varrho_{TR}$.

Table 5. Dielectric Constant Values for HFC-134a (Liquid) near T = 205 K

T/K	P/MPa	ϱ/(kg m^{-3})	ϵ
205.59	16.09	1520.36	19.645
205.64	15.03	1518.69	19.605
205.63	14.07	1517.31	19.578
205.59	13.07	1515.93	19.556
205.65	12.08	1514.30	19.519
205.66	11.18	1512.91	19.490
205.68	10.11	1511.23	19.453
205.69	9.090	1509.63	19.422
205.70	8.120	1508.10	19.391
205.69	7.090	1506.50	19.359
205.69	6.090	1504.92	19.329
205.70	5.100	1503.40	19.298
205.60	4.100	1501.97	19.269
205.60	3.100	1500.33	19.236
205.60	2.100	1498.66	19.202
205.60	1.090	1496.97	19.168
205.6 0	0.660	1496.24	19.154

Table 6. Dielectric Constant Values for HFC-134a (Liquid) near T = 210 K

T/K	P/MPa	ϱ/(kg m^{-3})	ϵ
210.28	15.53	1507.76	18.871
210.36	15.16	1506.99	18.854
210.37	14.12	1505.38	18.820
210.39	13.15	1503.83	18.789
210.41	12.14	1502.20	18.756
210.41	11.17	1500.67	18.727
210.41	10.13	1499.01	18.695
210.40	9.120	1497.41	18.666
210.39	8.120	1495.81	18.635
210.39	7.110	1494.15	18.606
210.39	6.140	1492.54	18.577
210.38	5.080	1490.79	18.544
210.37	4.110	1489.17	18.513
210.36	3.120	1487.50	18.484
210.35	2.090	1485.73	18.452
210.34	1.120	1484.06	18.423
210.34	0.650	1483.23	18.408

The first dielectric virial coefficient (A_ϵ) is obtained from the intercept by plotting *CM RT/P* as a function of CM, eq 11. Figure 2 shows the curves for the determination of A_ϵ at three temperatures in the gaseous phase, and the values of A_ϵ are presented in Table 4. Values of B_ϵ and C_ϵ obtained from a curve fit of eq 11 using known values of B and C (see Table 4) are also presented in the same table as a function of T.

The calculated values of the first (ϱ_1), the second (ϱ_2), and the third (ϱ_3) approximations of the density calculated from eqs 4−6 are presented in Tables 1−3, respectively,

Table 7. Dielectric Constant Values for HFC-134a (Liquid) near T = 218 K

T/K	P/MPa	ϱ/(kg m^{-3})	ϵ
218.67	16.12	1487.54	17.662
218.67	15.10	1485.87	17.632
218.67	14.11	1484.24	17.603
218.67	13.11	1482.57	17.574
218.67	12.12	1480.90	17.545
218.67	11.10	1479.17	17.514
218.67	10.10	1477.44	17.483
218.67	9.110	1475.72	17.453
218.67	8.100	1473.94	17.420
218.67	7.100	1472.16	17.388
218.68	6.120	1470.37	17.357
218.67	5.120	1468.57	17.325
218.67	4.110	1466.70	17.292
218.67	3.140	1464.89	17.261
218.67	2.090	1462.90	17.225
218.67	1.110	1461.02	17.193
218.67	0.630	1460.09	17.178

Table 8. Dielectric Constant Values for HFC-134a (Liquid) near T = 228 K

T/K	P/MPa	ϱ/(kg m^{-3})	ϵ
228.73	15.22	1460.44	16.324
228.74	14.10	1458.39	16.289
228.74	13.12	1456.59	16.259
228.74	12.12	1454.74	16.228
228.75	11.11	1452.85	16.196
228.75	10.11	1450.93	16.163
228.75	9.100	1448.98	16.131
228.75	8.095	1447.03	16.099
228.75	7.090	1445.05	16.066
228.75	6.090	1443.05	16.033
228.75	5.090	1441.02	16.001
228.75	4.100	1438.99	15.966
228.75	3.080	1436.86	15.931
228.75	2.060	1434.71	15.897
228.75	1.085	1432.62	15.864

Table 9. Dielectric Constant Values for HFC-134a (Liquid) near T = 237 K

T/K	P/MPa	ϱ/(kg m^{-3})	ϵ
237.20	16.24	1440.63	15.330
237.20	15.11	1438.45	15.296
237.20	14.11	1436.49	15.264
237.20	13.13	1434.55	15.233
237.20	12.09	1432.46	15.200
237.21	11.15	1430.52	15.170
237.22	10.14	1428.41	15.136
237.22	9.160	1426.37	15.104
237.22	8.090	1424.10	15.069
237.23	7.180	1422.11	15.037
237.22	6.090	1419.76	15.000
237.22	5.100	1417.56	14.968
237.22	4.100	1415.34	14.935
237.22	3.120	1413.07	14.899
237.22	2.110	1410.72	14.863
237.21	1.110	1408.39	14.828
237.21	0.660	1407.17	14.810

Table 10. Dielectric Constant Values for HFC-134a (Liquid) near T = 248 K

T/K	P/MPa	ϱ/(kg m^{-3})	ϵ
247.62	16.49	1414.28	14.235
247.61	15.12	1411.40	14.194
247.61	14.13	1409.26	14.163
247.60	13.12	1407.07	14.131
247.60	12.12	1404.85	14.099
247.60	11.14	1402.64	14.065
247.61	10.10	1400.23	14.029
247.61	9.080	1397.85	13.995
247.61	8.110	1395.56	13.961
247.61	7.110	1393.15	13.926
247.61	6.120	1390.73	13.891
247.61	5.120	1388.24	13.855
247.61	4.110	1385.68	13.818
247.61	3.100	1383.08	13.783
247.61	2.090	1380.42	13.744
247.61	1.100	1377.77	13.706
247.61	0.600	1376.41	13.688

Table 11. Dielectric Constant Values for HFC-134a (Liquid) near T = 258 K

T/K	P/MPa	ϱ/(kg m^{-3})	ϵ
257.82	15.51	1385.41	13.254
257.81	14.10	1382.08	13.209
257.80	13.10	1379.68	13.175
257.80	12.10	1377.21	13.142
257.80	11.09	1374.68	13.108
257.80	10.11	1372.17	13.072
257.80	9.090	1369.52	13.037
257.80	8.090	1366.88	13.000
257.80	7.120	1364.26	12.965
257.79	6.110	1361.52	12.928
257.79	5.100	1358.68	12.889
257.80	4.110	1355.82	12.850
257.80	3.100	1352.87	12.810
257.79	2.080	1349.85	12.769
257.79	1.100	1346.86	12.728
257.79	0.540	1345.12	12.710

Table 12. Dielectric Constant Values for HFC-134a (Liquid) near T = 268 K

T/K	P/MPa	ϱ/(kg m^{-3})	ϵ
268.37	16.64	1360.16	12.372
268.37	15.55	1357.35	12.336
268.37	14.58	1354.79	12.302
268.37	13.66	1352.33	12.270
268.36	12.61	1349.49	12.234
268.36	11.62	1346.74	12.197
268.36	10.50	1343.55	12.160
268.37	9.640	1341.03	12.124
268.37	8.620	1338.02	12.085
268.37	7.620	1335.00	12.046
268.37	6.620	1331.91	12.007
268.37	5.620	1328.76	11.966
268.37	4.600	1325.46	11.924
268.37	3.600	1322.15	11.882
268.37	2.610	1318.78	11.839
268.37	1.600	1315.26	11.795
268.37	0.640	1311.82	11.752

at 298.15, 303.20, and 323.40 K. We also show the deviations $\Delta\varrho_n = 100[(\varrho_n - \varrho_{TR})/\varrho_{TR}]$ between our values (ϱ_n) of the three approximations (n = 1−3) and those calculated (ϱ_{TR}) using the Tillner-Roth and Baehr (1991) EOS. The deviations in density ($\Delta\varrho_n$) are presented in Figures 3−5, respectively, at 298.15, 308.20, and 323.40 K.

At 298.15 K, we observe that the first approximation (ϱ_1) in density leads to values which are closer ($\Delta\varrho_1$ on the order of 0.05%) to the calculated values (ϱ_{TR}) according to the Tillner-Roth and Baehr (1991) EOS for pressures less than 0.6 MPa. At 308.20 K, the third approximation (ϱ_3) in density leads to the smallest deviations (on the order of 0.5% up to 0.7 MPa and 1.0% at 0.8 MPa). At 323.15 K, it is still the third approximation that gives the smallest deviations up to 1.2 MPa, the maximum pressure that one can reach in the gaseous phase at this temperature.

Figure 6 shows the dielectric constant of HFC-134a as a function of density, for all the isotherms in the liquid state. No values of the dielectric constant in the gaseous phase in the same temperature range were found to test the validity of the excess function formulation. Table 5−17 show the values measured at temperatures near 205, 210, 218, 229, 238, 248, 258, 268, 278, 286, 297, 303, and 308 K.

The dipole moment in the gaseous phase was obtained from eq 7. The value obtained was μ = (1.91 ± 0.19) D and can be compared with the value obtained by Meyer

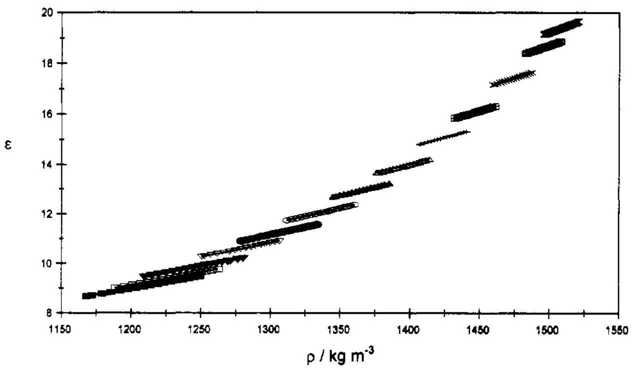

Figure 6. Dielectric constant of HFC-134a in the liquid phase as a function of density for the different temperatures studied. Symbols from bottom to top: T = 268 K, T = 308 K, T = 238 K, T = 303 K, T = 248 K, T = 297 K, T = 258 K, T = 286 K, T = 205 K, T = 229 K, T = 218 K, T = 210 K, T = 278 K.

Table 13. Dielectric Constant Values for HFC-134a (Liquid) near T = 278 K

T/K	P/MPa	ρ/(kg m^{-3})	ϵ
278.21	16.51	1333.38	11.580
278.21	15.58	1330.72	11.547
278.21	14.50	1327.56	11.509
278.21	13.50	1324.58	11.472
278.21	12.50	1321.53	11.435
278.20	11.51	1318.48	11.398
278.21	10.54	1315.37	11.360
278.21	9.560	1312.18	11.321
278.21	8.480	1308.59	11.277
278.21	7.510	1305.27	11.236
278.21	6.460	1301.59	11.193
278.21	5.470	1298.02	11.150
278.21	4.460	1294.29	11.106
278.21	3.550	1290.82	11.065
278.21	2.500	1286.71	11.016
278.21	1.510	1282.66	10.969
278.21	0.650	1279.12	10.929

Table 14. Dielectric Constant Values for HFC-134a (Liquid) near T = 286 K

T/K	P/MPa	ρ/(kg m^{-3})	ϵ
286.36	15.07	1306.58	10.919
286.35	14.07	1303.39	10.881
286.35	13.03	1299.93	10.841
286.35	12.00	1296.48	10.801
286.35	11.04	1293.16	10.762
236.35	10.10	1289.83	10.724
286.35	9.110	1286.24	10.683
286.34	8.100	1282.54	10.640
286.34	7.110	1278.70	10.596
286.34	6.100	1274.71	10.551
286.34	5.100	1270.63	10.504
286.34	4.100	1266.42	10.456
286.34	3.080	1261.92	10.407
286.34	2.060	1257.37	10.355
286.34	1.110	1252.92	10.306
286.34	0.660	1250.76	10.281

Table 15. Dielectric Constant Values for HFC-134a (Liquid) near T = 297 K

T/K	P/MPa	ρ/(kg m^{-3})	ϵ
297.46	16.62	1280.53	10.214
297.45	15.50	1276.62	10.170
297.45	14.05	1271.35	10.113
297.45	13.53	1269.41	10.090
297.45	12.47	1265.38	10.046
297.44	11.47	1261.50	10.004
297.45	10.51	1257.60	9.9605
297.45	9.500	1253.41	9.9160
297.45	8.500	1249.13	9.8702
297.45	7.510	1244.75	9.8240
297.45	6.490	1240.08	9.7739
297.44	5.490	1235.36	9.7266
297.44	4.500	1230.48	9.6766
297.44	3.500	1225.34	9.6190
297.45	2.440	1219.61	9.5594
297.44	1.600	1214.93	9.5120
297.44	0.700	1209.66	9.4583

Table 16. Dielectric Constant Values for HFC-134a (Liquid) near T = 303 K

T/K	P/MPa	ρ/(kg m^{-3})	ϵ
303.33	16.28	1262.60	9.7835
303.33	15.10	1258.13	9.7364
303.33	14.07	1254.10	9.6942
303.33	13.10	1250.20	9.6520
303.34	12.09	1245.99	9.6077
303.34	11.09	1241.73	9.5632
303.34	10.08	1237.27	9.5168
303.34	9.070	1232.67	9.4700
303.35	8.040	1227.77	9.4168
303.34	7.010	1222.74	9.3660
303.34	6.020	1217.69	9.3158
303.34	5.120	1212.90	9.2670
303.34	4.090	1207.19	9.2108
303.33	3.030	1201.06	9.1557
303.34	2.120	1195.45	9.0929
303.34	1.100	1188.88	9.0299

Table 17. Dielectric Constant Values for HFC-134a (Liquid) near T = 308 K

T/K	P/MPa	ρ/(kg m^{-3})	ϵ
308.15	16.48	1249.46	9.4895
308.16	15.49	1245.49	9.4448
308.16	14.54	1241.61	9.4057
308.15	13.52	1237.34	9.3623
308.15	12.53	1233.05	9.3187
308.15	11.54	1228.61	9.2743
308.16	10.54	1223.95	9.2258
308.16	9.580	1219.34	9.1800
308.17	8.510	1213.97	9.1202
308.16	7.510	1208.82	9.0699
308.16	6.500	1203.35	9.0174
308.16	5.480	1197.58	8.9623
308.16	4.500	1191.76	8.9068
308.16	3.510	1185.59	8.8496
308.15	2.550	1179.32	8.7867
308.16	1.520	1172.09	8.7199
308.16	0.950	1167.91	8.6813

and Morrison (1991), μ = (2.06 ± 0.01) D, and Ogata and Miki (1986), μ = (1.80 ± 0.22) D.

As already said the value of the dipole moment for the liquid phase, μ^*, can be calculated for HFC-134a by a linear regression of the left-hand side of eq 8 as a function of $1/T$. It is noteworthy that the value of the Kirkwood function is independent of the density within the error of the density calculations. Figure 7 shows the corresponding plot. The value obtained for μ^* and g using the values of μ obtained in this work were, respectively, (3.54 ± 0.01) D and 3.44. The value of g obtained for HFC-134a is greater than the one obtained for HCFC-142b (Barão et al., 1994). HFC-134a, 1,1,1,2-tetrafluoroethane, is a quasi-symmetrical molecule, while HCFC-142b, 1,1-difluoro-1-chloroethane, is highly asymmetric. This will make the rotation in the liquid phase easier for the latter molecule, which is confirmed by the determination of a smaller correlation coefficient g. The result is coincident if we interpret it on the basis of the apparent dipole moment, much greater for HFC-134a.

To the best of our knowledge, this paper presents the first report of the first three dielectric virial coefficients for HFC-134a and of the dipole moment in the liquid phase.

Conclusion

The small deviations in density between our measured values and those calculated from the Tilnner-Roth and

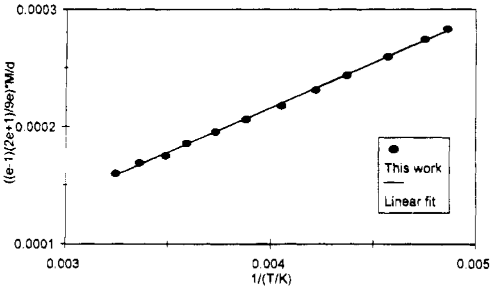

Figure 7. Kirkwood representation (eq 8) for the determination of the dipole moment in the liquid phase.

Baehr EOS show that the accurate dielectric constant measurements are a powerful method for obtaining accurate PVT measurements.

Small deviations between our value of the dipole moment in the gaseous phase and those in the literature prove also that dielectric constant measurements in the gaseous and liquid phases lead to an accurate value of the dipole moment.

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