International Journal of Thermophysics, Vol. 20, No. 1, 1999

Relative Permittivity and Resistivity of Liquid HFC Refrigerants Under High Pressure[1]

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The static relative permittivity (dielectric constant) and the resistivity of HFC-236ea (CF_3–CHF–CHF_2) and HFC-245fa (CF_3–CH_2–CHF_2) in the liquid phase were studied at temperatures from 293 to 343 K and pressures from 0.1 to 50 MPa. The relative permittivity was measured by a concentric-cylinder-type capacitance cell with an LCR meter with an uncertainty of less than 0.1%. The resistivity was measured by a high resistance meter using plane-parallel platinum electrodes installed in a borosilicate glass syringe. It was found that the relative permittivities and the resistivities of liquid HFC-236ea and HFC-245fa at 303 K and 0.101325 MPa are about 5.13 and 6.54 and 1.5×10^{10} and $0.2 \times 10^{10}\ \Omega \cdot \mathrm{cm}$, respectively. The relative permittivity and the resistivity increase monotonically with increasing pressure and decreasing temperature.

KEY WORDS: dielectric constant; electrical resistivity; HFC-236ea; HFC-245fa; hydrofluorocarbon; permittivity; high pressure; refrigerants.

1. INTRODUCTION

The relative permittivity and the resistivity of environmentally acceptable refrigerants are necessary to study and interpret the electrical properties of these polar fluids, and to give operational values for some of the design parameters of machinery used in the airconditioning and refrigeration industry. The high electrical resistivity of working fluids is favorable in closed systems. The temperature, pressure, and density dependences of these properties will also permit the application of molecular theories of polar fluids.

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[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.

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In this work the relative permittivity and the resistivity of HFC-236ea (1,1,1,2,3,3-hexafluoropropane) and HFC-245fa (1,1,1,3,3-pentafluoropropane) in the liquid phase have been measured at temperatures from 293 to 343 K and pressures from 0.1 to 50 MPa. HFC-236ea has been proposed as a replacement for CFC-114. HFC-245fa is one of the leading candidates for a new blowing agent for rigid polyurethane foams as a replacement for HCFC-141b.

2. EXPERIMENTAL

The relative permittivity was measured by a three-terminal concentric-cylinder-type capacitance cell. The apparatus and procedure have been described in detail in a previous work [1]. Capacitance measurements were made with a multifrequency LCR meter (HP 4274A) using 100 kHz with an uncertainty of less than 0.1%.

The schematic diagram of the resistivity measuring system [2] is shown in Fig. 1. The conductivity measurements were carried out with plane-parallel platinum electrodes (area = 1 cm^2, electrode separation = 0.3 cm). The electrodes were placed in a borosilicate glass syringe. The sample liquid was filled both inside and outside of the syringe and isolated from the pressure medium (oil) by a bellows-type pressure transmitter in order to avoid contamination. The resistivity was measured by a high-resistance meter (HP 4339A) with a voltage of 10 V and at a frequency of 60 Hz in order to suppress the enhanced conduction due to electroconvection and the electrochemical polarization at the electrodes. The application of a voltage to a liquid layer can produce many phenomena that modify electric charge carrier generation, transport, or elimination. Therefore, the conduction current is time dependent and, to measure the actual conductivity, several conditions on the experimental parameters such as the applied voltage and the electrode gap distance must be satisfied [3–5]. Experiments carried out in an extended range of electrode gap distance from 3 to 8 mm, and of voltage from 500 mV to 300 V, demonstrated that our conductivity cell does measure the ohmic conduction of the sample liquids. A detailed analysis of the influence of electrode gap distance, applied voltage, and frequency of the voltage on the measurements is given by Tobazeon et al. [5]. The conductivity cell was thermostatted in a liquid bath controlled within ± 0.03 K. The temperature was measured using a platinum resistance thermometer calibrated by a standard thermometer with an uncertainty of $\pm$ 0.01 K. The pressure was measured with a Heise Bourdon gauge and a strain-gauge-type pressure transducer with an uncertainty of $\pm 0.1\%$. The cell constant of the conductivity cell was determined using the reference aqueous solution of KCl. As a check on the performance of the conductivity

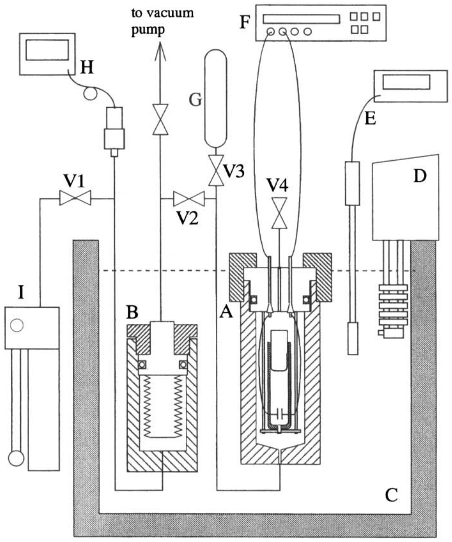

Fig. 1. Schematic diagram of the resistivity measuring system. (A) conductivity cell; (B) bellows pressure transmitter; (C) water bath; (D) temperature controller; (E) quartz thermometer; (F) high-resistance meter; (G) sample cylinder; (H) pressure indicator; (I) oil pump. V1 to V4: valves.

cell, the resistivity of benzene and cyclohexane was measured at temperatures from 298 to 323 K at atmospheric pressure. The experimental results for benzene at 298 K agree with literature values [6–8] within 1%.

The sample fluids of HFC-236ea and HFC-245fa were supplied by Daikin Industries, Ltd., and had a purity of 99.9 mol%. These samples were used without further purification. Benzene and cyclohexane were obtained from commercial sources with a specification of minimum purity of 99.9%. They were used after purification by fractional crystallization.

3. RESULTS AND DISCUSSION

3.1. Static Relative Permittivity

The static relative permittivity of a liquid, ε, is defined by the ratio of the capacitance between two electrodes filled with the liquid C to that in vacuum, C_0,

$$\varepsilon = C/C_0 \tag{1}$$

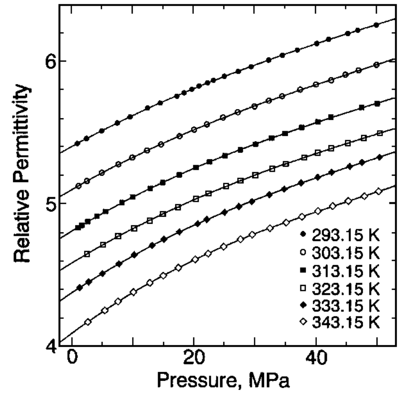

Fig. 2. Static relative permittivity of liquid HFC-236ea as functions of temperature and pressure.

The experimental data for HFC-236ea and HFC-245fa are shown in Figs. 2 and 3, respectively, as functions of temperature and pressure. In both cases, every isotherm increases monotonically with increasing pressure with a slight negative curvature. Under these experimental conditions, the relative permittivity decreases almost linearly with increasing temperature along each isobar. The relative permittivity of HFC-245fa is systematically larger than that of HFC-236ea at the same condition. However, the pressure coefficient of the relative permittivity $(\partial\varepsilon/\partial P)_T$ is quite similar for each.

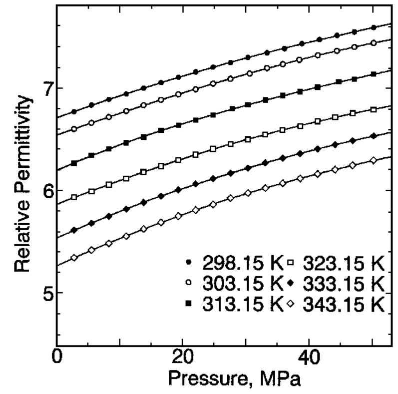

Fig. 3. Static relative permittivity of liquid HFC-245fa as functions of temperature and pressure.

Table I. Empirical Coefficients of Owen–Brinkley Eq. (2) for Liquid HFC-236ea

	Temp. (K)					
	293.15	303.15	313.15	323.15	333.15	343.15
P_0 (MPa)	0.171	0.244	0.338	0.456	0.603	0.783
ε_0	5.4038	5.1043	4.8161	4.5986	4.3946	4.1095
C	0.15627	0.15271	0.14760	0.15571	0.15064	0.13721
B (MPa)	35.41	30.84	25.96	26.20	21.82	15.23
Max. dev. (%)	0.066	0.098	0.085	0.077	0.077	0.089
Mean dev. (%)	0.026	0.026	0.025	0.028	0.025	0.030

The isotherm of ε versus pressure can be represented by several empirical expressions. The Owen–Brinkley equation [9, 10] is a representative one.

$$\frac{\varepsilon-\varepsilon_0}{\varepsilon}=C\ln\left(\frac{B+P}{B+P_0}\right) \tag{2}$$

where ε_0 is the relative permittivity at a reference pressure P_0 (saturated vapor pressure) and P is the pressure in MPa. The coefficients C and B were determined by least-squares fitting. The empirical coefficients are given in Tables I and II together with the mean and the maximum deviations of the experimental data from Eq. (2).

In Fig. 4, the pressure dependences of the relative permittivity at 298.15 K for several fluorocarbon refrigerants in the liquid phase are compared. Judging from the molecular structures of these refrigerants and the electronegativities of F(4.0), Cl(2.5), and H(2.1), it is quite reasonable

Table II. Empirical Coefficients of Owen–Brinkley Eq. (2) for Liquid HFC-245fa

	Temp. (K)					
	298.15	303.15	313.15	323.15	333.15	343.15
P_0 (MPa)	0.152	0.182	0.254	0.347	0.466	0.613
ε_0	6.7110	6.5424	6.2037	5.8722	5.5505	5.2821
C	0.15079	0.16642	0.13911	0.15452	0.15655	0.16429
B (MPa)	42.79	45.77	31.25	34.12	29.84	28.64
Max. dev. (%)	0.093	0.129	0.085	0.171	0.135	0.197
Mean dev. (%)	0.036	0.047	0.042	0.056	0.065	0.082

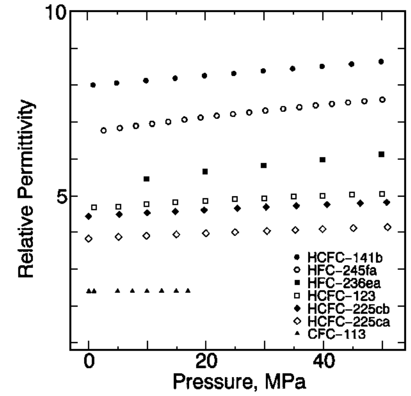

Fig. 4. Static relative permittivity of liquid fluorocarbon refrigerants as a function of pressure at 298.15 K. HCFC-141b [1], HFC-245fa, HFC-236ea [this work], HCFC-123 [1], HCFC-225ca [11], HCFC-225cb [11], and CFC-113 [1].

that the relative permittivity of HCFC-141b (CH_3–CCl_2F) [1], whose molecular structure is quite asymmetric, is significantly larger, and that the relative permittivity of CFC-113 ($CClF_2$–CCl_2F) [1] is clearly smaller, than those of HCFC-123 ($CHCl_2$–CF_3) [1], HFC-236ea (CF_3–CHF–CHF_2), HFC-245fa (CF_3–CH_2–CHF_2), HCFC-225ca ($CHCl_2$–CF_2–CF_3) [11], and HCFC-225cb ($CHClF$–CF_2–$CClF_2$) [11]. Among four halogenated propane derivatives, HFC-236ea and HFC-245fa have larger relative permittivities than HCFC-225ca and HCFC-225cb since the first two HFCs have more hydrogen atoms and the molecular structures are more asymmetric than for the last two HCFCs.

From the theory of molecular polarizability developed by Kirkwood [12] after the definition of Onsager's local field in a liquid assembly of permanent dipoles [13], it is possible to correlate the relative permittivity of the polar liquid with the apparent dipole moment μ^* through the equation [14, 15]

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

where M is the relative molar mass, N_0 is Avogadro's number, α is the molecular polarizability, ε_0 is the relative permittivity of vacuum, and k_B is the Boltzmann constant. The density ρ of HFC-236ea was calculated from the equation of state of Defibaugh et al. [16, 17]. The value of μ^* was calculated for HFC-236ea by a linear regression of the Kirkwood function as a function of $1/T$. It was found that HFC-236ea has an apparent dipole moment $\mu^* = 2.50D$.

3.2. Resistivity

In well-filtered high-insulating liquids, charge carriers are ions or ionic associations of higher order (multipoles), which result from the spontaneous dissociation of tiny amounts of ionizable substances or of the action of natural radiation. Electron or hole conduction will never occur in common situations because the electron life time is lower or much lower than 10^{-4} s, even in ultrapurified liquids [3–5].

The volume conductivity $\sigma = 1/\rho$ of a medium containing i dissociable species generating a volume charge density q_i of free carriers of mobility k_i is

$$\sigma_0 = \sum k_i q_i \tag{4}$$

The resistivity is a characteristic of a dielectric fluid only at the thermodynamic equilibrium of charge carrier dissociation and recombination in the bulk, if the measuring conditions do not modify significantly the density and mobility of free carriers by displacement of the thermodynamic equilibrium, interfacial phenomena at the solid walls, or electroconvection. If the applied voltage is low enough, the electric field E does not significantly disturb the thermodynamic equilibrium and Ohm's law is obeyed

$$j_0 = \sigma_0 E \tag{5}$$

with j_0 being the current density. Therefore, σ_0 can be derived from the measurement of the current I_0 flowing through the cell containing the sample liquid. If the voltage is applied for a long enough time, the initial conduction current I_0 decreases with time and the current reaches the limiting value I_s. The following relation is found between the initial conduction current I_0 and the conduction current I at a time t.

$$I_0 = I(bt + 1) \tag{6}$$

Therefore, the actual value of the conduction current I_0 can be determined by extrapolation of time t to zero. The resistivity ρ is calculated from the resistance $R = 1/I$ by the following equation:

$$R = \rho(d/A) \tag{7}$$

Table III. Resistivity of Liquid Benzene

P (MPa)	$\rho \times 10^{-14}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-14}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-14}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-14}$ ($\Omega \cdot$cm)
298.15 K		303.15 K		313.15 K		323.15 K	
0.10	0.902	0.10	0.846	0.10	0.800	0.10	0.737
10.1	1.06	10.0	0.966	10.0	0.919	10.0	0.890
20.0	1.22	20.1	1.10	20.0	1.03	20.1	0.992
30.1	1.30	30.1	1.16	30.0	1.10	30.0	1.05
40.0	1.43	40.0	1.31	40.0	1.18	40.0	1.13
50.1	1.52	50.0	1.35	50.0	1.22	50.0	1.20

where A is an area of plane-parallel electrodes and d is the electrode gap distance.

The resistivity of benzene and cyclohexane was measured first at temperatures from 298 to 323 K and pressures from 0.1 to 50 MPa. The experimental results are reported in Tables III and IV, respectively. Although experimental data are very scarce in the literature, our results at 298.15 K at atmospheric pressure are found to be consistent within 1% with literature values [6–8]. The progressive improvement in the purification techniques of dielectric liquids renders the measurement of their resistivity more and more difficult with conventional equipment, especially at room temperature or below [3]. In the present work the scatter of data is more remarkable at 298 and 303 K as compared with 313 and 323 K. The shapes of the isotherms at 298 and 303 K are considerably different from those at 313 and 323 K.

The numerical data of the resistivity of HFC-236ea and HFC-245fa are listed in Tables V and VI, respectively. The pressure and temperature

Table IV. Resistivity of Liquid Cyclohexane

P (MPa)	$\rho \times 10^{-17}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-17}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-17}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-17}$ ($\Omega \cdot$cm)
298.15 K		303.15 K		313.15 K		323.15 K	
0.10	1.19	0.10	1.01	0.10	0.936	0.10	0.833
10.0	1.24	10.0	1.06	10.0	0.984	10.0	0.891
20.0	1.28	20.0	1.11	20.0	1.03	20.0	0.941
30.0	1.34	30.0	1.16	30.1	1.05	30.0	0.980
40.0	1.38	40.0	1.21	40.0	1.08	40.0	1.00
50.0	1.41	50.1	1.24	50.1	1.10	50.0	1.03

Table V. Resistivity of Liquid HFC-236ea

P (MPa)	$\rho \times 10^{-10}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-10}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-10}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-10}$ ($\Omega \cdot$cm)
298.15 K		303.15 K		313.15 K		323.15 K	
5.0	1.48	5.0	1.45	5.0	1.37	5.00	1.28
10.1	1.53	10.1	1.47	10.0	1.38	10.0	1.29
20.0	1.56	20.0	1.50	20.1	1.39	20.0	1.31
30.1	1.60	30.1	1.53	30.0	1.42	30.1	1.32
40.1	1.63	40.0	1.55	40.1	1.43	40.0	1.34
50.0	1.66	50.0	1.57	50.0	1.45	50.3	1.35

Table VI. Resistivity of Liquid HFC-245fa

P (MPa)	$\rho \times 10^{-9}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-9}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-9}$ ($\Omega \cdot$cm)	P (MPa)	$\rho \times 10^{-9}$ ($\Omega \cdot$cm)
298.15 K		303.15 K		313.15 K		323.15 K	
0.13	2.00	4.99	1.95	5.05	1.63	5.01	1.44
5.00	2.05	10.0	1.99	10.0	1.67	10.0	1.48
10.1	2.09	20.0	2.09	20.0	1.76	20.0	1.55
20.1	2.19	30.1	2.15	30.0	1.83	30.0	1.61
30.1	2.24	40.0	2.21	40.1	1.89	40.0	1.67
40.0	2.30	50.0	2.27	50.2	1.95	50.0	1.71
50.0	2.36						

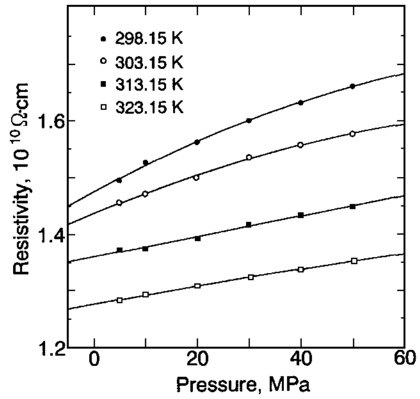

Fig. 5. Resistivity of liquid HFC-236ea as functions of temperature and pressure.

dependences of the resistivity of HFC-236ea are shown in Fig. 5. The behavior of the resistivity of HFC-245fa is similar to Fig. 5.

The resistivity isotherm increases monotonically with increasing pressure, with a small negative curvature. It may be due to the suppression of the charge carrier propagation caused by the decrease of the intermolecular space with increasing pressure. The resistivity decreases with increasing temperature. It may be ascribed to the activation of Brownian movement of free ions between electrodes.

4. CONCLUSIONS

New data for the relative permittivity and the resistivity of liquid HFC-236ea and HFC-245fa have been presented in the temperature range from 293 to 343 K, with pressures up to 50 MPa. Recently the authors have measured the density of liquid HFC-245fa. The details of the experimental results for the density and the data analysis of the relative permittivity of HFC-236ea and HFC-245fa in terms of the density dependence will be published elsewhere.

ACKNOWLEDGMENT

The authors wish to express their sincere appreciation to Daikin Industries, Ltd., for kindly furnishing the refrigerant samples.

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