The Dielectric Properties of Compressed Fluoromethane

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The dielectric constant, dielectric loss, and density of compressed fluoromethane have been measured at 50°C and 75°C in the pressure range 20 to 160 atmospheres. The ratio $(\epsilon-1)/d(\epsilon+2)$ shows a large and regular decrease as the density increases. The theories of Debye, Onsager, and Kirkwood have been applied to the results. Evidence of the restriction of molecular rotation at high densities is adduced.

INTRODUCTION

THERE is considerable information[1] on the dielectric properties of polar liquids and of their vapors at atmospheric pressure. Behavior in the range of densities between these two states is of great interest and can be observed by the study of compressed gases. It appears, however, that the only polar gas for which such measurements have been made is ammonia, as reported by Keyes and Oncley.[2]

This paper reports measurements on fluoromethane, which was chosen for its conveniently low critical temperature, 44.55°C,[3] its high dipole moment, 1.81×10^{-18} esu,[4] and its lack of reactivity.

EXPERIMENTAL

CH_3F was prepared by heating an equimolecular mixture of sodium methyl sulfate and sodium fluoride to 250°C.[5,6]

The gases evolved were passed through two wash bottles containing conc. H_2SO_4 and two containing 40 percent NaOH solution to remove the byproducts of the reaction, $(CH_3)_2O$, HF, SO_2, and SiF_4. The CH_3F was dried by magnesium perchlorate, led at atmospheric pressure through a dry ice and alcohol trap, finally condensed on a liquid air trap and permanent gases were pumped off. It was then fractionally distilled and stored in the manner previously described for ethylene.[7]

The vapor pressure of a sample of the fluoromethane at dry ice temperature agreed with that of a sample prepared by the decomposition of tetramethylammonium fluoride.[8]

Capacity and Density Measurements

Simultaneous measurements of pressure (P) and capacity were made in the manner previously reported for ethylene.[7] Since no P-V-T data were available for fluoromethane, measurements of the density (d) were made by the constant volume method. (Holborn[9] and Bartlett[10]). A 2-cc high pressure gas pipette was connected to the gas condenser and pressure balance through a needle valve. When capacity and pressure measurements were completed the valve was closed, this action causing a negligible pressure change in the system. The quantity of gas thus enclosed in the pipette was later determined by expanding it to atmospheric pressure in a 1-liter gas burette. Pressure in the burette was measured by a mercury manometer. The pipette and burette were mounted in the same thermostat as the condenser.

Dielectric Loss Measurement

During the course of the capacity measurements it was found that the minimum anode current in the Henriquez oscillator[11] increased with increasing density. This implied[12] that a power loss was occurring in the gas condenser. To measure the loss the gas condenser was replaced by an equal low loss capacitor and variable series resistor. The resistor was adjusted until the same minimum anode current was obtained. From the values of resistance and capacitance the power factor could be estimated.

At densities greater than the critical, the power loss in the gas condenser was found to cause an error in the capacity as measured, owing to the change in the characteristics of the measuring circuit. A series of measurements of the magnitude of this error at various densities was made at the same time as the power loss measurements. From a smooth curve drawn through these points a correction was applied to the dielectric constant results. The correction amounted to about $1\frac{1}{2}$ percent in the factor $(\epsilon-1)/d(\epsilon+2)$ at the highest densities.

RESULTS

Dielectric Constant and Density

The results are shown in Tables I and II. In the calculation of densities from the gas burette measure-

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TABLE I. Dielectric constant and density of fluoromethane at 50.00°C.

P (Int. ats.)	ϵ	d (moles/liter)	$(\epsilon-1)/d(\epsilon+2)$ (cc/mole)	PV/RT[a]
21.706	1.2176	0.960	70.4	0.853
29.919	1.3330	1.433	69.7	0.787
36.512	1.4477	1.879	69.1	0.733
41.373	1.5512	2.265	68.5	0.689
45.463	1.6572	2.646	67.9	0.648
49.400	1.7834	3.084	67.1	0.604
53.068	1.9313	3.570	66.4	0.561
55.683	2.0669	3.997	65.6	0.525
57.970	2.2206	4.474	64.6	0.4887
60.819	2.4956	5.29	62.9	0.4337
63.530	2.979	6.60	60.2	0.3628
63.630	3.001	6.65	60.1	0.3606
64.799	3.420	7.69	58.1	0.3178
64.721	3.414	7.70	57.9	0.3170
65.468	3.811	(8.67)[b]	(55.8)	(0.2849)
65.541	3.828	8.68	55.9	0.2848
65.826	4.019	9.24	54.3	0.2686
65.962	4.123	9.51	53.6	0.2616
66.190	4.210	9.69	53.4	0.2577
66.636	4.496	10.28	52.4	0.2445
67.287	4.726	10.79	51.4	0.2353
68.670	5.143	11.68	49.67	0.2218
69.052	5.214	11.78	49.57	0.2210
70.948	5.541	12.40	48.55	0.2157
71.724	5.659	12.68	47.99	0.2134
73.480	5.843	12.97	47.62	0.2137
74.993	5.992	13.29	47.00	0.2128
77.205	6.163	13.55	46.67	0.2149
79.830	6.340	13.90	46.08	0.2167
81.402	6.422	14.02	45.91	0.2189
118.25[c]		16.05		0.2779
160.42[c]		17.14		0.3531

[a] Calculated as P/dRT using $R=82.053$ cc atmos/mole as given by J. A. Beattie in *Temperature* (Reinhold Publishing Corporation, New York, 1941), p. 87.
[b] This density was found by interpolation in the d/P data.
[c] The capacities here were beyond the range of the apparatus.

ments the variation of PV with P was allowed for. The values of the second virial coefficient $B(T)$ used in doing this were taken from earlier low pressure measurements made in this laboratory.[8] The figures were

$$B(323.16) = -171 \text{ cc/mole},$$
$$B(348.16) = -141 \text{ cc/mole}.$$

TABLE II. Dielectric constant and density of fluoromethane at 75.00°C.

P (Int. ats.)	ϵ	d (moles/liter)	$(\epsilon-1)/d(\epsilon+2)$ (cc/mole)	PV/RT
28.885	1.2552	1.190	65.9	0.850
39.664	1.3902	1.762	65.3	0.788
54.288	1.6359	2.724	64.2	0.698
63.930	1.8611	3.535	63.1	0.633
71.993	2.1143	4.396	61.6	0.573
77.687	2.3463	5.15	60.1	0.528
78.556	2.3865	5.25	60.2	0.524
81.365	2.5289	5.68	59.4	0.501
85.623	2.7732	6.44	57.7	0.4657
90.681	3.1138	7.41	55.8	0.4286
93.086	3.303	7.88	55.1	0.4136
98.526	3.736	8.98	53.1	0.3840
102.92	4.061	9.79	51.6	0.3680
107.80	4.390	10.60	50.0	0.3560
115.10	4.809	11.58	48.32	0.3480
122.68	5.141	12.37	46.88	0.3471
133.63	5.530	13.22	45.51	0.3539
147.73	5.920	14.00	44.38	0.3695

Included in the tables are the values of PV/RT for the various densities. The variation of this factor with pressure is shown in Fig. (1), which illustrates the relation of the region studied to the critical point. For each temperature the values of PV corresponding to the seven lowest densities were fitted to a curve of the form

$$PV = RT + a(T)d + b(T)d^2 + c(T)d^3$$

by the method of least squares. The second virial coefficient was calculated from the relationship $B(T) = a(T)/RT$. The following values were obtained:

$$B(323.16) = -168 \text{ cc/mole},$$
$$B(348.16) = -140 \text{ cc/mole}.$$

These are in good agreement with the low pressure values quoted above.

The difference between the density of the gas in the high pressure pipette and that in the gas condenser, due
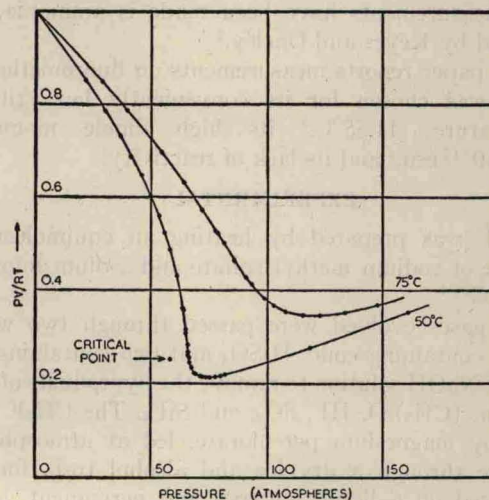

FIG. 1. Isotherms for fluoromethane.

to the head of gas between them, was calculated to be never greater than 0.01 percent and was therefore neglected.

Dielectric Loss

The variation of the tangent of the loss angle δ with density is shown in Table III and in Fig. (2). It must be emphasized that these measurements were made by an extempore method and the results can only be regarded as approximate. They are, however, of considerable interest qualitatively. The power loss is zero until the critical density is approached and then increases rapidly with increasing density, the rate of increase being more pronounced at 50°C than at 75°C ($T_c = 44.55°C$).

APPARENT DIPOLE MOMENT

The most extensively applied theories of polarization in dipolar media are those of Debye and Onsager. Both