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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 information¹ 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

CH₃F 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. H₂SO₄ and two containing 40 percent NaOH solution to remove the byproducts of the reaction, (CH₃)₂O, HF, SO₂, and SiF₄. The CH₃F 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. (Holborn⁹ and Bartlett¹⁰). 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 oscillator¹¹ increased with increasing density. This implied¹² 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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⁷ H. G. David, S. D. Hamann and J. F. Pearse, J. Chem. Phys. **19**, 1491 (1951).

⁸ S. D. Hamann and J. F. Pearse, Trans. Faraday Soc. (to be published).

⁹ L. Holborn and H. Schultze, Ann. Physik (4) **47**, 1089 (1915).

¹⁰ E. P. Bartlett, J. Am. Chem. Soc. **49**, 687 (1927).

¹¹ P. Cohen Henriquez, Physica **2**, 429 (1935).

¹² J. Reilly and W. N. Rae, *Physico-Chemical Methods* (D. Van Nostrand Company, Inc., New York, 1939), Vol. II, p. 513.

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°		16.05		0.2779
160.42°		17.14		0.3531

^a Calculated as P/dRT using $R=82.053$ cc atm/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

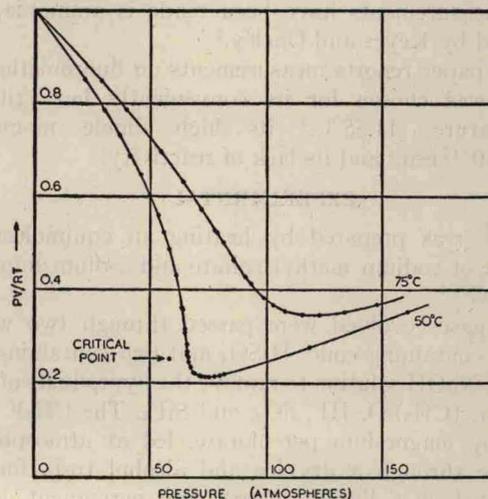


FIG. 1. Isotherms for fluoromethane.

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 ($T_c = 44.55^\circ\text{C}$).

APPARENT DIPOLE MOMENT

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

theories are approximate and a discussion of their relative merits is found in the Faraday Society's "General Discussion on Dielectrics."¹³ If the molecular dipole moment were constant, Debye's theory would require that the Clausius-Mosotti function $(\epsilon-1)/d(\epsilon+2)$ be independent of density at a given temperature. Tables I and II show that there is a large decrease in the C-M ratio for CH_3F with increasing density. It is noteworthy that Keyes and Oncley² report an increase in this ratio for NH_3 . Onsager's theory would require the function $(\epsilon-n^2)(2\epsilon+n^2)/\epsilon d(n^2+2)^2$ to be similarly independent of density (here n is the refractive index). For the present case this function increases by 7 percent. These effects might arise either from the inadequacy of the theories or from changes in the dipole moment of CH_3F with density.

There is no reason to suppose that the dipole moment, μ , of a CH_3F molecule in the compressed gas is the same as that of an isolated molecule since a variation of μ with density might easily occur if the molecules were

TABLE III. Dielectric absorption in fluoromethane at 1 megacycle.^a

50°C		75°C	
Density (moles/l)	tan δ	Density (moles/l)	tan δ
≤6.6	0.00000	≤6.9	0.00000
7.03	0.00022	7.70	0.00009
7.40	0.00046	8.38	0.00030
7.94	0.00128	9.05	0.00072
8.43	0.00176	9.67	0.00164
8.93	0.00227	10.30	0.00312
9.50	0.00330	10.87	0.00504
10.06	0.00444	11.42	0.00787
10.58	0.00518	11.94	0.01022
11.03	0.00669		
11.51	0.00935		

^a Measurements to 5 megacycles showed an increase in the absorption with frequency in this range.

distorted by the intermolecular forces. In this respect the apparent dipole moments calculated from the Debye and Onsager theories and given in Table IV are of interest. The change in the Debye values is larger than would be expected from considerations of the magnitude of the intermolecular forces in the pressure range studied. Onsager's model leads to a smaller apparent change in μ and appears to be the more satisfactory in the present case.

If it were possible to calculate the distribution function for compressed CH_3F , Kirkwood's precise treatment^{13,14} of polar fluids could be applied to the experimental data to find the real change in μ . This calculation is unfortunately exceedingly difficult. In the next section the theory is used in the opposite way, assuming μ to be constant, to find the change in Kirkwood's correlation parameter, g .

¹³ "General Discussion on Dielectrics," Trans. Faraday Soc. 42A (1946).

¹⁴ J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939).

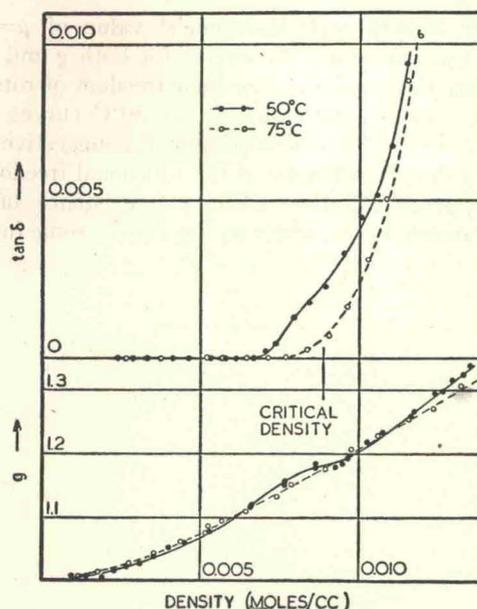


FIG. 2. Dielectric loss and correlation parameter for fluoromethane.

RESTRICTED ROTATION NEAR THE CRITICAL POINT

In an earlier note¹⁵ the sudden development of the dielectric loss near the critical density of CH_3F was taken as evidence of a fairly sharp transition between free and restricted rotation of the dipolar molecules. Some further evidence of this is found in the change of ϵ with density. Kirkwood,^{13,14} allowing for the effects of hindered rotation on the dielectric constant, obtained the expression

$$(2\epsilon+1)(\epsilon-1)/9\epsilon d = {}_D P + 4\pi N_0 g \mu^2 / 9kT,$$

where ${}_D P$ is the molar distortion polarization, N_0 is Avogadro's number, and μ is the dipole moment of an isolated molecule. The correlation parameter g can be related to the forces restricting the rotation of the molecules. Its divergence from unity is a measure of the extent of the restriction.

Figure (2) shows g as a function of density and temperature. It was calculated on the assumption that μ is

TABLE IV. Apparent dipole moment of fluoromethane.

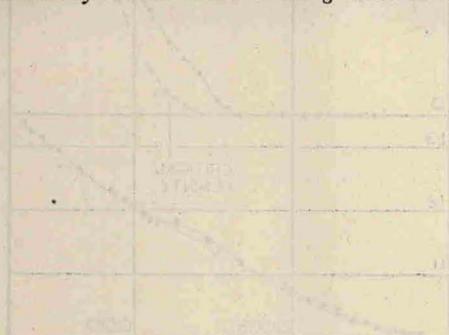
d (moles/l)	50°C		d (moles/l)	75°C	
	μ_{App} (esu $\times 10^{-18}$) ^a Debye	Onsager ^b		μ_{App} (esu $\times 10^{-18}$) ^a Debye	Onsager ^b
0.960	1.806	1.813	1.190	1.804	1.813
3.570	1.745	1.819	3.535	1.759	1.825
7.69	1.615	1.857	6.44	1.670	1.838
10.28	1.517	1.859	9.79	1.562	1.863
12.40	1.449	1.876	11.58	1.500	1.865
14.02	1.400	1.889	14.00	1.423	1.869

^a Smyth and McAlpine's figure (see reference 4) for the distortion polarization ${}_D P = 8.95$ cc/mole was used in calculating μ_{App} .

^b An "effective" refractive index n was calculated from the relationship $(n^2-1)/d(n^2+2) = {}_D P$.

¹⁵ David, Hamann, and Pearse (to be published).

constant. Smyth and McAlpine's⁴ value of $\mu = 1.81 \times 10^{-18}$ esu was used. The curves for both g and $\tan \delta$ show that the molecules lose their freedom of rotation at high densities. In addition, the 50°C curves have shoulders near the critical density, d_c , suggestive of a fairly sudden loss of some of the rotational freedom as d_c is approached. To confirm the existence of the comparatively low shoulder on the g curve some further



RESTRICTED ROTATION NEAR THE CRITICAL POINT

In an earlier note,¹ the sudden disappearance of the dielectric loss near the critical density of CCl₄ was taken as evidence of a fairly sharp transition between free and restricted rotation of the dipolar molecules. Some further evidence of this is found in the change in the dielectric loss near the critical density of a dipolar liquid. The dielectric loss near the critical density of a dipolar liquid is shown in Figure 17. The dielectric loss near the critical density of a dipolar liquid is shown in Figure 17. The dielectric loss near the critical density of a dipolar liquid is shown in Figure 17.

where μ is the dipole moment, V is the volume of an elementary cell, and N is the number of dipolar molecules. The dielectric loss near the critical density of a dipolar liquid is shown in Figure 17. The dielectric loss near the critical density of a dipolar liquid is shown in Figure 17.

Figure 17 shows a shoulder in the dielectric loss near the critical density of a dipolar liquid. It was interpreted as being due to the presence of a small amount of restricted rotation.

Table IV. Dielectric loss near the critical point.

Temperature (°C)	Density (g/cm ³)	Dielectric loss
50	0.85	0.10
50	0.90	0.20
50	0.95	0.30
50	1.00	0.40
50	1.05	0.50
50	1.10	0.60
50	1.15	0.70
50	1.20	0.80
50	1.25	0.90
50	1.30	1.00

The dielectric loss near the critical point of a dipolar liquid is shown in Figure 17. The dielectric loss near the critical point of a dipolar liquid is shown in Figure 17. The dielectric loss near the critical point of a dipolar liquid is shown in Figure 17.

measurements were made several weeks after the original series. These gave results in complete agreement with the earlier ones.

The authors wish to thank Professor R. J. W. Le Fèvre for suggestions leading to this investigation and for some helpful discussions.

The advice and assistance of Dr. J. S. Dryden in the dielectric absorption measurements were of great value.

The dielectric loss near the critical point of a dipolar liquid is shown in Figure 17. The dielectric loss near the critical point of a dipolar liquid is shown in Figure 17. The dielectric loss near the critical point of a dipolar liquid is shown in Figure 17.

Table V. Dielectric loss near the critical point.

Temperature (°C)	Density (g/cm ³)	Dielectric loss
50	0.85	0.10
50	0.90	0.20
50	0.95	0.30
50	1.00	0.40
50	1.05	0.50
50	1.10	0.60
50	1.15	0.70
50	1.20	0.80
50	1.25	0.90
50	1.30	1.00

The dielectric loss near the critical point of a dipolar liquid is shown in Figure 17. The dielectric loss near the critical point of a dipolar liquid is shown in Figure 17. The dielectric loss near the critical point of a dipolar liquid is shown in Figure 17.

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