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The Dielectric Constant of Ethylene at High Pressures

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The dielectric constant of ethylene has been measured at pressures up to 500 atmospheres and at temperatures of 25°C and 50°C. At both temperatures the Clausius-Mosotti function has been found to pass through a maximum with increasing density. The results have been discussed with reference to Kirkwood's theory of dielectric polarization.

INTRODUCTION

THE study of the dielectric constant of gases over a wide range of densities is of interest in the development of theories of dielectric behavior. A review of work done in this field has been recently given by Miller.¹

The Clausius-Mosotti (C-M) treatment requires that $(\epsilon - 1)/(\epsilon + 2)d$, where ϵ and d are the dielectric constant and density of the gas respectively, should be independent of density. Also for gases with non-polar molecules, the C-M ratio should be independent of temperature. However, variations in the value of the C-M ratio with density have been found for carbon dioxide,^{2,3} ammonia,⁴ and propane.² Several authors have advanced explanations for these variations,⁴⁻⁸ but the agreement between theory and experiment leaves much to be desired.

It was decided in this work to extend the range of experimental data by measuring the dielectric constant of ethylene at various densities and at temperatures of 25°C and 50°C, and to consider the implications of the results.

APPARATUS

The procedure adopted for this study was to confine ethylene at a known temperature and various pressures between the plates of a gas condenser contained in a pressure vessel and to measure the capacity of the condenser and the pressure of the gas. To achieve this, it was necessary to have a supply of pure ethylene, a means of compressing it in the gas condenser, and equipment for accurately measuring temperature, pressure, and capacity.

Gas Condenser

The condenser and containing vessel were similar to those used by Michels.⁹ The former consisted of two

concentric brass cylinders with the outer supported from the inner cylinder by silica disks. The outer cylinder was in electrical contact with the pressure vessel and connection with the inner cylinder was made through a low capacity insulated plug of the type described by Michels.⁹ The design of the condenser was such as to ensure minimum distortion of the cylinders at high gas pressures.

The containing pressure vessel was made of high tensile steel. It was rigidly and independently supported in an oil thermostat. The capacity measuring equipment was mounted on the same support and a rigid coaxial lead connected the gas condenser to this equipment.

The temperature of the oil thermostat was maintained constant to $\pm 0.005^\circ\text{C}$ by an electronic temperature controller (see Wylie).¹⁰ It was measured by a Leeds and Northrup Platinum Resistance Thermometer and G-2 Mueller Bridge. The thermometer and bridge were calibrated by the U. S. National Bureau of Standards and the Ice Point resistance of the thermometer was determined in this laboratory.

Pressure Balance

The pressures were measured by a modified Budenberg-type Pressure Balance which has been described by one of the authors.¹¹ The balance was used in conjunction with a *U*-tube containing mercury and an oil injector as described by Keyes.¹² The pressures were measured over the whole range (20-530 atmospheres) with a piston-cylinder unit of nominal piston area of 0.02 sq. in. It was calibrated against the vapor pressure of carbon dioxide at 0°C (see Bridgman).¹³ In this calibration it was found that a change in the weight on the piston of one part in 95,000 was sufficient to make or break contacts in the *U*-tube and readings were reproducible to one part in 25,000. The calibrated value of the gauge constant was assumed to be correct up to 530 atmospheres. Keyes¹² has shown this assumption to be justifiable.

¹⁰ R. G. Wylie, Natl. Standards Lab. C.S.I.R.O. Report No. PA-2 (1948).

¹¹ J. F. Pearse, submitted for publication in *J. Sci. Instr.*

¹² F. G. Keyes, *Proc. Am. Acad. Arts Sci.* **68**, 505 (1933).

¹³ O. C. Bridgman, *J. Am. Chem. Soc.* **49**, 1174 (1927).

¹ J. G. Miller, *Trans. Am. Soc. Mech. Engrs.* **70**, 621 (1948).
² F. G. Keyes and J. L. Oncley, *Chem. Revs.* **19**, 195 (1936).
³ A. Michels and L. Kleerekoper, *Physica* **6**, 586 (1939).
⁴ F. G. Keyes and J. G. Kirkwood, *Phys. Rev.* **36**, 1570 (1930); **37**, 202 (1931); J. G. Kirkwood, *J. Chem. Phys.* **4**, 592 (1936).
⁵ J. H. Van Vleck, *J. Chem. Phys.* **5**, 556, 991 (1937).
⁶ Michels, de Boer, and Bijl, *Physica* **4**, 981 (1937).
⁷ C. J. F. Böttcher, *Physica* **9**, 937, 945 (1942).
⁸ W. F. Brown, *J. Chem. Phys.* **18**, 1193, 1200 (1950).
⁹ A. Michels and Mrs. C. Michels, *Trans. Roy. Soc. (London)* (A) **231**, 409 (1933).

Mercury Gas-Compressor

This unit was based on a design developed by Michels and described by Tongue.¹⁴ It was used in conjunction with a "Cook" 3000 atmospheres two-stage pump.¹⁵

Ethylene Storage Cylinder and Transfer Vessel

The gas was stored in a high tensile steel pressure vessel of one liter capacity. The transfer vessel, the use of which will be described later, was made of stainless steel and had a capacity of 150 ml.

Electrical Equipment

The method used for capacity measurements was that described by P. Cohen Henriquez.¹⁶ The circuit consisted of a pentode valve, type 6F6G, with a 1000 Kc quartz crystal controlling the grid circuit. The anode circuit was tuned by means of an inductance in parallel with the gas condenser and a standard variable condenser. The anode voltage was supplied by a stabilized power pack and the heater current was taken from a 6-volt battery. Such a circuit exhibits the usual minimum of anode current at the capacity corresponding to the natural frequency of the crystal with the important feature that the slope of the curve on the high capacitance side is very steep. A suitable operating point is chosen on the steepest portion of the curve and capacitance adjusted until the anode current is at the chosen value. To obviate errors in the capacity measurements caused by drifts in the oscillator circuit, a reference condenser was included, as suggested by P. Cohen Henriquez.¹⁶

The standard condenser was constructed from a transmitting condenser. The spindle, supported in a lapped conical bearing, was rotated by a worm and wheel drive fitted with an anti-backlash device. The worm spindle carried a graduated drum on which one division was equivalent to 1/100 $\mu\mu\text{F}$. The instrument was calibrated by the Division of Electrotechnology of the C.S.I.R.O. and found to be consistent to $\pm 0.02 \mu\mu\text{F}$ over a long period. The whole of the capacity measuring equipment was screened.

EXPERIMENTAL PROCEDURE

Preparation of Ethylene

The gas was prepared by the dehydration of ethyl alcohol by Pyro-phosphoric acid at 220–240°C. An apparatus was set up in which to carry out this preparation in a continuous manner. The alcohol was led into a flask containing 100 cc of Pyro-phosphoric acid (prepared *in situ* by dehydration of ortho-phosphoric acid) at the required temperature. The ethylene was passed successively at atmospheric pressure through a dry ice

and alcohol trap, a wash bottle containing concentrated sulfuric acid, another containing 50 percent caustic soda, a further dry ice and alcohol trap, and a liquid air trap in which it was finally condensed.

When sufficient gas had been collected in the last trap, production was ceased and the permanent gases were pumped off. The ethylene was then fractionally distilled in batches in a low temperature fractionating column similar to that described by Lu, Newitt, and Ruhemann.¹⁷ The middle fractions of ethylene were condensed in the gas transfer vessel immersed in liquid air. The vessel was then warmed and the ethylene passed into the mercury gas-compressor and pumped into the gas storage cylinder. One hundred liters of ethylene were prepared. Before preparation and storage of the gas, the glass apparatus was pumped out at a pressure of less than 1/10th micron and flamed and the gas compressor and vessels were pumped out for several days. A sample of the ethylene was analyzed and 99.7 percent by volume was adsorbed by bromine water. The residual gas was shown to be non-condensable at liquid air temperature.

Calibration of Gas Condenser

The vacuum capacity of the gas condenser was determined in the usual way by calibration with benzene.¹⁸ Carefully fractionated benzene, dried for several weeks over sodium, was refluxed and stored over sodium in a glass vessel. It was degassed and distilled in vacuum into the previously evacuated gas condenser. Mercury U-tube valves were used in the system to prevent contamination of the benzene by tap-grease.

The vacuum capacity at 25°C was found to be $148.96 \pm 0.05 \mu\mu\text{f}$ (taking $\epsilon_{25} = 2.2725$ for benzene),¹⁹ compared with the value 149.4 $\mu\mu\text{f}$ calculated from the condenser dimensions. The change in capacity of the evacuated condenser between 25°C and 50°C was found to be +0.04 $\mu\mu\text{f}$ (calculated value, +0.07 $\mu\mu\text{f}$). Since this variation is smaller than the probable error in the calibration, the same value of the vacuum capacity was used at both temperatures.

Capacity Measurements

The condenser was filled from the storage vessel (via the gas compressor) with ethylene at the desired pressure and temperature (25°C or 50°C). Readings of the standard condenser and pressure balance were taken when the values appeared constant. These were checked after an interval of five minutes to confirm that the system was in equilibrium. Measurements were made over a range of pressures, the points being chosen so that the capacity of the gas condenser changed in approximately equal steps ($\approx 5 \mu\mu\text{f}$). Before and after a

¹⁴ H. Tongue, *The Design and Construction of High Pressure Plant* (Chapman and Hall, Ltd., London, 1934).

¹⁵ D. M. Newitt, *High Pressure Plant and Fluids at High Pressures* (Oxford University, New York, 1940).

¹⁶ P. Cohen Henriquez, *Physica* **2**, 429 (1935).

¹⁷ Lu, Newitt, and Ruhemann, *Proc. Roy. Soc. (London)* **A178**, 506 (1941).

¹⁸ R. J. W. Le Fèvre, *Dipole Moments* (Methuen and Company, Ltd., London, 1938).

¹⁹ L. Hartshorn and D. A. Oliver, *Proc. Roy. Soc. (London)* **A123**, 664 (1929).

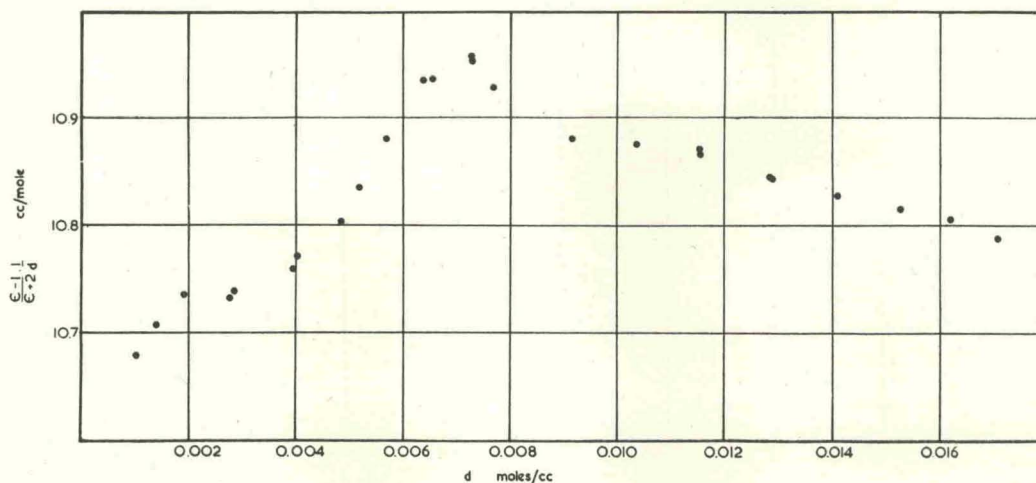


FIG. 1. Clausius-Mosotti function for ethylene at 25°C.

series of observations the gas condenser was evacuated and its capacity in this state checked. Throughout the measurements this value did not vary by more than $\pm 0.03 \mu\text{mf}$.

The change in the condenser dimensions with pressure was shown by calculation to cause negligible error in the capacity measurements even at the highest pressures.

RESULTS

In order to determine densities from measured pressures the P - V - T data of Michels and Geldermans²⁰ for ethylene were used. To convert the values of Amagat density so obtained to densities in moles/liter the normal volume is required. This was calculated from the relationship,

$$V_n = 22.414/(1+\lambda) \text{ liters}, \quad (1)$$

using the value of λ found by Cawood and Patterson.²¹ The figure obtained was 22.251 liters.

The values of the Clausius-Mosotti function are shown in Tables I and II and in Figs. 1 and 2 for the temperatures 25°C and 50°C. For convenience in extrapolation an attempt was made to fit the low density values by a least squares analysis to an expression of the form,

$$(\epsilon-1)/(\epsilon+2)d = A + Bd + Cd^2, \quad (2)$$

d being the density and A , B , and C constants for a given temperature. A reasonable fit was impossible for the 25°C values but was achieved at 50°C with the constants:

$$A = 10.69 \pm 0.01 \text{ cm}^3 \text{ mole}^{-1}$$

$$B = 25 \pm 7 \text{ cm}^6 \text{ mole}^{-2}$$

$$C = 540 \pm 820 \text{ cm}^9 \text{ mole}^{-3}.$$

The curve corresponding to these values is shown in Fig. 2.

It will be noticed that the experimental points do not strictly lie on a smooth curve, but rather on a periodic curve superimposed on a smooth curve. For example, in our results there is a positive "peak" at density 0.002 mole/cc and a negative "peak" at density 0.004 moles/cc on each curve. This phenomenon is noticeable in the results of other workers, e.g., Michels and Kleerekoper³ for CO_2 and Keyes *et al*² for CH_4 , N_2 , CO_2 , and NH_3 .

The evident agreement between the zero-density values of the Clausius-Mosotti function at the two temperatures (see Figs. 1 and 2) is in accord with the known absence of dipole moment in ethylene. The value (10.69) deduced from these measurements agrees well

TABLE I. Clausius-Mosotti function for ethylene at 25.00°C.

Pressure (int. atmos)	Density (moles/liter)	Dielectric constant	Clausius-Mosotti function (cc/mole)
21.696	1.0262	1.0332	10.680
28.221	1.4121	1.0461	10.708
35.593	1.9187	1.0631	10.737
45.530	2.7894	1.0926	10.733
46.209	2.8621	1.0951	10.740
54.615	3.9657	1.1337	10.760
55.083	4.0438	1.1366	10.772
59.263	4.8685	1.1666	10.804
60.606	5.1959	1.1790	10.836
62.426	5.7033	1.1985	10.881
64.491	6.3823	1.2251	10.937
64.924	6.5386	1.2311	10.938
66.888	7.2822	1.2602	10.960
66.908	7.2899	1.2603	10.954
67.930	7.6769	1.2748	10.930
72.839	9.146	1.3316	10.881
80.368	10.359	1.3809	10.876
94.287	11.524	1.4297	10.872
94.564	11.541	1.4303	10.868
125.62	12.851	1.4859	10.846
125.89	12.860	1.4862	10.845
181.59	14.092	1.5402	10.829
272.12	15.247	1.5925	10.816
385.54	16.193	1.6364	10.807
534.27	17.082	1.6778	10.789

²⁰ A. Michels and M. Geldermans, *Physica* **9**, 967 (1942).

²¹ W. Cawood and H. S. Patterson, *J. Chem. Soc.* 619 (1933).

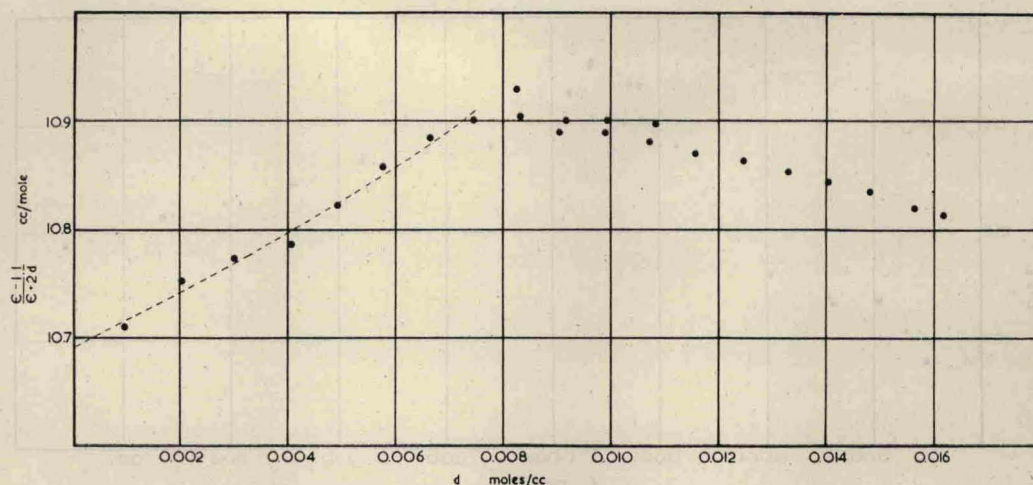


FIG. 2. Clausius-Mosotti function for ethylene at 50°C.

with the existing data²² for 25°C, *viz.*:

Boltzmann	(1874)	9.74 cc/mole
Klemencic	(1885)	10.81 cc/mole
Smyth and Zahn	(1925)	10.72 cc/mole
Watson, Rao, and Ramaswamy	(1934)	10.74 cc/mole

DISCUSSION

The C-M relationship may be written in the form,

$$(\epsilon - 1)/(\epsilon + 2)d = 4\pi\alpha N/3, \quad (3)$$

where ϵ is the dielectric constant of a substance, d is its density in molar units, α is its molecular polarizability and N is Avogadro's number. If α is assumed to be constant the C-M function, $(\epsilon - 1)/(\epsilon + 2)d$, should also

TABLE II. Clausius-Mosotti function for ethylene at 50.00°C.

Pressure (int. atmos)	Density (moles/liter)	Dielectric constant	Clausius-Mosotti function (cc/mole)
23.527	0.9980	1.0324	10.711
42.234	2.0181	1.0665	10.753
56.186	3.0007	1.1002	10.774
67.851	4.0529	1.1372	10.787
75.783	4.9229	1.1688	10.823
82.733	5.7899	1.2013	10.859
89.241	6.6510	1.2342	10.886
95.683	7.4839	1.2665	10.902
102.42	8.2699	1.2981	10.931
102.87	8.3177	1.2993	10.906
110.32	9.045	1.3278	10.891
112.05	9.194	1.3342	10.902
121.50	9.900	1.3626	10.891
121.97	9.931	1.3643	10.902
135.96	10.721	1.3962	10.882
138.62	10.846	1.4021	10.899
157.39	11.593	1.4327	10.872
188.48	12.480	1.4706	10.865
229.19	13.304	1.5064	10.855
277.71	14.029	1.5384	10.846
347.23	14.808	1.5735	10.837
448.26	15.653	1.6118	10.821
529.43	16.186	1.6366	10.815

²² Summarized by Watson, Rao, and Ramaswamy, Proc. Roy. Soc. (London) A143, 558 (1934).

be constant. It has been found experimentally, however, that the function is to some extent dependent on density. Explanations of this effect have been based upon two considerations: (a) that α may vary with density,⁶ (b) that the Lorentz molecular model is not applicable at high densities and the equality (3) does not necessarily hold.^{4, 5, 7, 8} No quantitative information has yet been provided by the first approach and we shall consider our results in the light of the theory which Kirkwood developed to replace the Lorentz derivation of Eq. 3.

Kirkwood⁴ determined statistically the effect of translational fluctuations on the average local electric field in a molecule and obtained an expression of the form:

$$(\epsilon - 1)/(\epsilon + 2)d = P_0(1 + \gamma P_0 d + \delta P_0^2 d^2 + \dots) \quad (4)$$

where d is the density of the gas and P_0 is its molar polarization at zero density. He showed that the coefficient γ is given by

$$\gamma = (P_0/b)[1 + (A/3bRT)] \quad (5)$$

in the special case of a gas consisting of hard spherical molecules with mutual attractive potentials, $V(r)$, which vary inversely as the sixth power of the intermolecular distance, r . A and b are the constants of the van der Waals equation of state.

There is some uncertainty as to the values that should be used for A and b in Eq. (4) and the adequacy of the van der Waals type of intermolecular field is, in any case, rather doubtful.² For these reasons we have calculated γ from equations based upon the more accurate representation of intermolecular forces which is given by the Lennard-Jones²³ expression:

$$V(\rho) = 4E^*(\rho^{-12} - \rho^{-6}) \quad (6)$$

$$\rho = r/r_0.$$

²³ J. E. Lennard-Jones, Proc. Roy. Soc. (London) A106, 463 (1924).

In Eq. (6) $-E^*$ is the minimum potential energy between two molecules and r_0 is their separation when $V(\rho)=0$. Putting (6) into the limiting expression for low densities:

$$\gamma = \frac{3P_0}{b_0} \int_0^\infty \rho^{-4} e^{-\beta V(\rho)} d\rho \quad (7)$$

(where $\beta=1/kT$, $b_0=2\pi N r_0^3/3$) and using the parameters $b_0=115.5$ cc/mole, $E^*/k=199.2^\circ\text{K}$ calculated by Bird, Spatz, and Hirschfelder²⁴ from the second virial coefficient data for C_2H_4 , we find: $\gamma=+0.143$ at 50°C . This figure is somewhat lower than the value $\gamma=+0.22 \pm 0.06$ given by the least squares quadratic fit of our low density experimental data. In this respect our results are qualitatively similar to those of Keyes and Oncley² for CO_2 and C_3H_8 . For these gases γ_{obs} is about twice γ_{calc} .

It is hardly profitable to speculate on these differences since the C-M/ d curves are apparently of quite complex form even at the lowest densities,* and the extrapolated values of γ may be subject to very large errors. There is

²⁴ Bird, Spatz, and Hirschfelder, J. Chem. Phys. 18, 1395 (1950).

* The steps in these curves which are found in nearly all the recorded data suggest that there may be relatively sharp changes in the molecular distribution functions with density.

TABLE III.

Temp.	CO_2		C_2H_4	
	50°C	100°C	25°C	50°C
d (for max. C-M)	0.0123 ^a	0.0135 ^a	0.0070	0.0083 mole/cc
d (critical)		0.0104 ^b	0.0079 ^b	mole/cc

^a The data for CO_2 are taken from A. Michels and L. Kleerekoper, Physica 6, 586 (1939).

^b Values from International Critical Tables 3, 248 (1928).

an obvious need for more accurate C-M measurements in the density range 0–0.002 moles/cc. These were not possible with our apparatus.

A point of interest is that the densities at which the slopes of the C-M/ d plots abruptly change sign correspond quite closely with the critical densities of the gases. This is shown in Table III.

It may also be significant that above this density the C-M function decreases with increasing density, an effect which is generally found in liquid systems.

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