

THE TEMPERATURE VARIATION OF THE ELECTRIC  
MOMENT OF ETHYLENE CHLORIDE

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## ABSTRACT

Observations of the molecular polarization of ethylene chloride vapor have been made over a temperature range from 32° to 270°C and over a considerable pressure range at each temperature. These observations show a definite departure from the Debye theory, since the Debye function plotted against temperature gives a definitely curved line. The data might be explained as approximately consistent with an electric moment of value zero and a value of the constant part of the polarization equal to about twice that of the optical refractivity; but for reasons discussed this interpretation is disregarded. It seems necessary to assume that the electric moment varies with temperature, as suggested by Eucken and Meyer. This was to be expected as a result of the hindrance of free rotation due to the interaction of the two atomic groups rotating around the single bond between the two carbon atoms. The possibility of the existence of disturbing effects such as association and adsorption is discussed, but is shown to be improbable, if not untenable. The values of the electric moment are then calculated by the use of a value for the constant part of the polarization, 23.9 cm<sup>3</sup>, determined by C. S. Hitchcock from the solid state. In the observed temperature interval the electric moment increases with the temperature from 1.1 to  $1.5 \times 10^{-18}$  c.g.s.e.s. u.; whereas the value calculated by Meyer for truly free rotation is  $2.4 \times 10^{-18}$ . This suggests that the rotation is considerably hindered; and in fact the results are entirely in accord with the predictions of Eucken and Meyer. The interaction energy may, however, be sufficiently great that it may be necessary, in order to obtain an accurate theory of this effect, to take into consideration the quantum theory rather than the classical theory of Meyer. The interpretation of other observations, of Meyer and of Sängner, is discussed with reference to certain inconsistencies which have been observed.

THE phenomenon of free rotation around single bonds in complex molecules has received considerable attention recently in connection with dipole moments calculated from Debye's equation. The effect of such rotations on observed moments has been discussed by Højendahl, Hückel, Ebert, Williams, Eucken and Meyer, and others.<sup>1</sup> Particularly, Højendahl has pointed out that the two rotating parts of a molecule may interact with one another and therefore cause a partial hindrance of the free rotation. Williams, and Eucken and Meyer have shown that, if the rotation is truly free, the observed moment is to be regarded as the square root of a random average of the square of the moment, over all possible values of the rotational angle.

<sup>1</sup> Højendahl, Studies of Dipole-moment. Copenhagen 1928, and Phys. Zeits. **30**, 391 (1929); W. Hückel, Zeits. f. Phys. Chem. (B) **2**, 451 (1929); L. Ebert, Leipziger Vorträge 1929. Hirzel 1929, page 44; J. W. Williams, Zeits. f. Phys. Chem. **138**, 75 (1928); Eucken and Meyer, Phys. Zeits. **30**, 397 (1929); C. T. Zahn, Phys. Rev. **37**, 1516 (1931). An excellent résumé of this subject has been given by H. Sack, Ergebnisse der Exakten Naturwissenschaften, Band VIII, 337 (1930).

Eucken and Meyer have also pointed out that, if there is sufficient interaction between the two mutually rotating dipoles, one should expect the observed moment to differ from this random root mean square value and possibly to vary with the temperature. For example, this possibility was discussed for the cases of the COOH group and for ethylene chloride.

Several observers have made experiments to determine whether such a temperature variation actually exists in the observable interval. Meyer<sup>2</sup> has determined the molecular polarization of ethylene chloride in benzene and hexane solutions. In benzene the calculated electric moment is practically constant,  $1.83 \times 10^{-18}$ ; whereas in hexane the moment is considerably smaller and varies from  $1.26$  to  $1.42 \times 10^{-18}$  in the temperature interval from  $-75^\circ$  to  $40^\circ\text{C}$ . If the rotation were truly free the value  $2.4 \times 10^{-18}$  should be expected from a calculation after the manner of Eucken and Meyer, based on the addition of vector moments characteristic of the individual chemical bonds and the method of random averaging over the rotational angle. Meyer interpreted these results as indicating an actual temperature variation of electric moment.

Now it is well known that calculations of electric moment from the interpolated values of molecular polarizations of solutions are subject to the following possible errors. (1) Since the concentration of the solute in the liquid state is large compared to that in the gaseous state, there is the possibility of association of the solute molecules both with one another and with the solvent molecules. (2) Since the Debye theory applies rigorously only to the gaseous state, there has always existed the possibility that the strong innermolecular field could be different from the Lorentz value  $4\pi P/3$ . (3) There is also the possibility of the formation of adsorbed layers on the condenser plates, which have been observed even in the gaseous state. Nevertheless, in many cases the experiments on solutions have led to very nearly the same values as those on the gaseous state. The customary test for the validity of the former values has been to determine the moment in several different solvents. If there is agreement between the various values so obtained it seems reasonable to assume that the values are the true non-associated molecular moments. In fact, it is just such cases, where different solvents have led to different values of the electric moment, which have also shown the most marked disagreement with the moments obtained from experiments on the gaseous state. For example, this has been borne out particularly clearly in the case of the fatty acids. Wolf<sup>3</sup> has given the value 1.21 for the moment of formic acid and values around  $0.8 \times 10^{-18}$  for several of the higher members of the series. Also Smyth<sup>4</sup> has made experiments on solutions of acetic acid in benzene and in ether. The observations on the benzene solutions were in general abnormal and led to a value of the electric moment around  $0.7 \times 10^{-18}$ ; whereas those on the ether solutions were normal and indicated a moment of  $1.40 \times 10^{-18}$ . On the other

<sup>2</sup> L. Meyer, *Zeits. f. Phys. Chem. (B)* **8**, 27 (1930).

<sup>3</sup> K. L. Wolf, *Phys. Zeits.* **31**, 227 (1930).

<sup>4</sup> C. P. Smyth and H. E. Rogers, *Jour. Amer. Chem. Soc.* **52**, 1824 (1930).

hand experiments by the author<sup>5</sup> on acetic acid vapor led to an even higher value. These latter experiments indicated also what was *originally* interpreted to be a temperature variation of electric moment from  $1.4$  to  $1.7 \times 10^{-18}$  in the interval from  $300^\circ$  to  $500^\circ\text{K}$ . Later experiments on formic and propionic acid vapors<sup>6</sup> have made it seem highly probable that this temperature variation really does not exist, but that the effect is due to a considerable amount of association. If this interpretation is correct, the moments are approximately  $1.51$  for formic acid,  $1.73$  for acetic acid, and  $1.74 \times 10^{-18}$  for propionic acid. All of these values are considerably higher than those of Wolf, and the value for formic acid relative to that of the other members of the series is even reversed.

Since no association of ethylene chloride in the gaseous state has been reported from vapor density measurements or otherwise, it was thought that it might not exist to an appreciable extent, and that it would be particularly easy to determine whether or not the temperature variation reported by Meyer is a bona fide non-associated molecular effect. For this reason the following measurements on ethylene chloride vapor were undertaken. In the meantime Sanger<sup>7</sup> published the results of similar experiments. The interpretations of these and other experiments have led to inconsistencies.<sup>8</sup> Sanger's experiments indicate normal behavior according to the Debye theory, but lead to a value of the constant part of the polarization almost twice that of the optical refractivity. His calculated value of the electric moment is  $1.1 \times 10^{-18}$ . Since he obtains different values of the polarization for two different densities, he believes his results are somewhat falsified by association, and that the true value should lie between  $1.2$  and  $1.4 \times 10^{-18}$ . On the other hand Meyer's values of molecular polarization from the liquid state are considerably higher than those of Sanger and consequently lead to higher values of the electric moment,  $1.83$  in benzene and  $1.26$  to  $1.42 \times 10^{-18}$  in hexane. He does not believe that Sanger's assumption of association is valid for his own experiments, since he thinks the amount of association necessary to explain the observed difference in polarization is too great. Sanger suggests that part of the discrepancy in the two experiments may be due to adsorption on the condenser plates. This *might* be greater in the liquid state and therefore give higher values for the molecular polarization. But in this latter case the effect of a given percentage adsorption should be less than in the gaseous state, since the amount of solute is actually measured by weighing. Then any effect here must be due entirely to a change in the property of the molecule on adsorption. In the gaseous state the density value is obtained from a measurement of the pressure and temperature of the vapor and does not therefore include the increase in average density due to the adsorption.

<sup>5</sup> C. T. Zahn, Phys. Rev. **35**, 1047 (1930).

<sup>6</sup> C. T. Zahn, Phys. Rev. **37**, 1516 (1931).

<sup>7</sup> R. Sanger, Phys. Zeits. **32**, 21 (1931).

<sup>8</sup> L. Meyer, Phys. Zeits. **32**, 260 (1931); R. Sanger, Phys. Zeits. **32**, 414 (1931).

## EXPERIMENTAL RESULTS AND INTERPRETATIONS

The experiments<sup>9</sup> here described were made over a temperature and pressure range as large as feasible. The pressure curves are of particular interest in connection with the possibility of association or adsorption. They are, however, not conclusive in this connection, since apparently linear pressure curves have previously lead to false interpretations, as in the case of acetic acid vapor.<sup>6</sup> The large observed temperature range from 305° to 543°K enables one to obtain a better test of the Debye equation than was possible in the previous experimental interval 333° to 453°K. The experimental conditions for these experiments were as good as any ever obtained by the author, as regards both steadiness of the electric circuits and reproducibility. A relatively large range of pressure was also studied; for the lower temperatures it was possible to approach saturation in order to search for a curvature effect due to possible association or adsorption. All of the pressure curves of electric

TABLE I. *Ethylene chloride.*

$T^{\circ}\text{K}$	$P$	$PT$	max. $p$ (cm Hg)	$\mu \times 10^{18}$ c.g.s.e.s.u.
304.95	49.47	15086	7	1.12
341.03	51.92	17706	37	1.24
376.25	52.54	19768	74	1.32
419.00	52.74	22098	68	1.40
456.96	52.48	23981	68	1.45
479.82	51.87	24888	49	1.48
484.82	51.74	25085	58	1.48
543.66	50.74	27585	59	1.54

polarization were so perfectly linear that it is to no purpose here to record the data for the individual pressures. The data for the different temperatures are shown in Table I. In order to determine the molecular polarization,  $P$ , the pressures were corrected for departures from the ideal gas values before plotting the pressure curves. For this purpose the van der Waals constants were used as described in a previous article.<sup>9</sup> From the table it is seen that the values of  $P$  vary relatively slightly (about 10%), having a maximum around 150°C. The curves obtained by plotting  $P$  and  $PT$  against  $T$  (shown in Fig. 1) show a definite departure from the Debye theory.

Purified ethylene chloride was obtained by fractional distillation of a specimen from the Eastman Kodak Company, both at room pressure and under its own pressure.

Now even if one supposes that the curvature of  $PT$  is due to experimental error (about 3 percent) and passes a straight line approximately through the observed values, the resulting values of the constant polarization,  $A$ , and the electric moment,  $\mu$ , are unreasonable, as was the case for Sanger's value of  $A$ . Actually this straight line passes almost through the origin (a rough estimate gave even a small negative intercept), and the electric moment has a value

<sup>9</sup> For experimental methods see previous articles: Phys. Rev. **24** 400 (1924); Phys. Rev. **35**, 848 (1930).

zero. On the other hand the value of  $A$  is equal to about  $52 \text{ cm}^3$ , which is more than twice the value of the optical refractivity, with which it should agree to within probably about a 10 percent difference due to infrared terms. The molecular refractivity of ethylene chloride is about  $21 \text{ cm}^3$  and if one were to add 10 percent in order to estimate the value of  $A$ , one would obtain a value of 23. This is in approximate agreement with a recent value of  $A$ , 23.9, obtained by C. S. Hitchcock from measurements of electric polarization in the solid state. Apart from the above mentioned curvature of the Debye line, it does not seem possible that the moment is zero, and that the atomic polarization in the gaseous and liquid states is of the same order as that of the electronic polarization, while that in the solid state is of the ordinary order of magnitude, 10 percent of the refractivity.

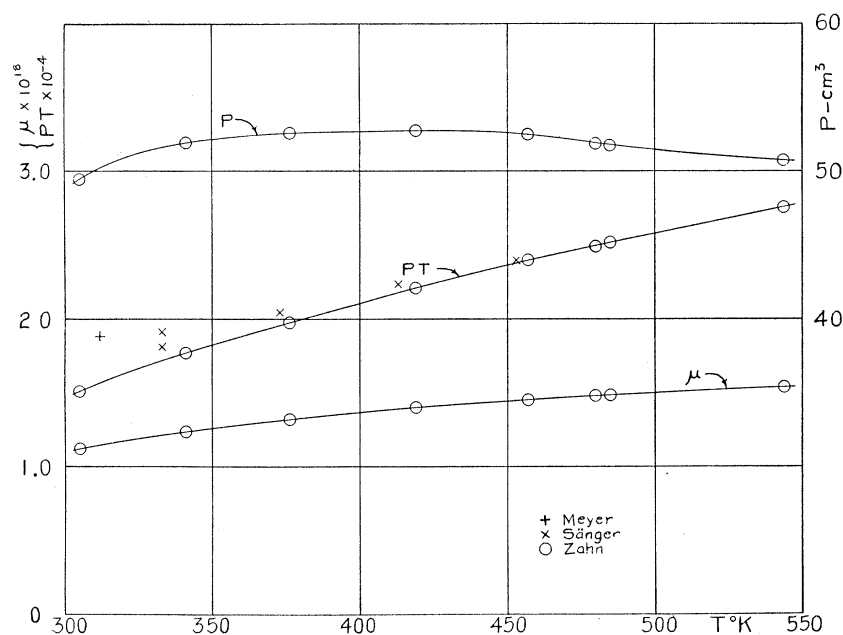


Fig. 1.

Disregarding this possibility, one is left to conclude that the electric moment actually increases with the temperature in accord with Meyer's suggestion, unless one supposes that the experimental data are falsified by either adsorption or association. Considering the value of  $P$  at the high temperatures to be free from error, the possibility that the effect is due chiefly to adsorption is excluded by the fact that such an effect should give abnormally high values at the *low* temperatures, whereas the reverse is true. The question of association is more difficult. First of all one must make a plausible assumption as to the effect of association on  $P$ . As a fair approximation one can assume that  $A$  is doubled on association into double molecules. This gives a value 47.8, which is very little smaller than the value of total  $P$  observed at

the lowest temperature. As regards the change in electric moment on association one could assume either (1) that the moment is reduced to zero, or (2) that the moment of the double molecule has some value different from zero, probably of the order of that of the single molecule. For case (1) it would be necessary to assume a very large and seemingly improbable amount of association in order to explain the observed data. For case (2) the association would lead to abnormally large values of  $P$  at *low* temperatures, which is again in contradiction to the observed facts. In this connection it is hoped that in the near future measurements of the refractivity of ethylene chloride vapor will be made in this laboratory in order to determine in what amount, if any, associated molecules are present.

All of the above assumptions regarding plausible sources of error can therefore be said to lead to contradictions; and it seems necessary to assume a temperature variation of electric moment, which has been expected for some time to exist in certain molecules. There is, in fact, a further argument in favor of this conclusion. All of the experiments of the various observers mentioned above lead to values of electric moment considerably lower than that corresponding to truly free rotation,  $2.4 \times 10^{-18}$ . For example, by assuming Hitchcock's value for  $A$  the present data show a variation of electric moment from 1.1 to  $1.5 \times 10^{-18}$ . The largest value reported is that of Meyer for the benzene solution,  $1.83 \times 10^{-18}$ . These values of moment indicate that the rotation is not truly free. Neither is it completely hindered; for then the moment should be zero. Now since the actual observed data correspond to the intermediate case, it seems very probable that a temperature variation should be observable in such a large range of temperature as  $250^\circ\text{C}$ . One could, of course, raise the objection that these low values may be due to distortions of the two rotating parts; but this would require a strong interaction, which would probably lead back to the necessity of hindered rotation and consequent temperature variation of electric moment.

Finally there seems to be no plausible way to avoid making the assumption that the electric moment of ethylene chloride varies with temperature. In fact, the observations here described present no objections to this conclusion. Still it remains to discuss the observations of other experimenters. If one accepts the proposed interpretation of the data here given, it would seem that the interpretations of both Meyer and Sanger are in part correct. As regards the observations of Meyer, since his values of moment differ widely for the two different solvents, benzene and hexane, there is probably some effect present tending to give abnormally high values of  $P$ , and even in the hexane solution. For example, a similar situation was found for the fatty acids as mentioned above. Still the temperature variation of the moment reported by Meyer exists, but because of the disturbing effect, to a different degree from that given by him. With the uncertainties mentioned his results could hardly be considered as conclusive evidence in favor of such a temperature variation. Whether or not these high values are due to association, adsorption, or to a misapplication of the Debye theory, it is difficult to say. It would seem, as Meyer has pointed out, that too great a degree of associ-

ation is necessary to explain them, and similarly for adsorption. The following suggestion is here offered: that the innermolecular forces in the liquid state may be of such a nature as to shift the potential energy function (as dependent upon rotational angle) and thereby produce a change in the rotational hindrance and a change in the actual observed electric moment.

While Sanger's experiments cover a considerable range of temperature, they are practically all made at the same density. One observation at a different density was made and this was not in agreement with the other at the same temperature. Inasmuch as the author has over a considerable range of temperature and pressure found no such disagreement, it seems that this effect must not be real. Sanger's value of  $P$  at the highest temperature is in almost perfect agreement with that here observed (see Fig. 1). His two values at the lowest temperature differ by about the same amount as one of them differs from the author's. If this disagreement is to be explained by some effect such as mentioned in connection with the observations of Meyer, this effect must be either association or adsorption, since the innermolecular field is almost negligible in the vapor state. Association seems to be excluded by the previous discussion of the author's results. Adsorption may exist in both Sanger's and the present results, but if this is the case, it must exist to a smaller extent in the latter. Furthermore in the present experiments no evidence of adsorption was detected, at least as a departure from the linearity of the pressure curves. However, if Sanger's data were used to calculate the electric moment as in the present case, one would obtain a temperature variation of electric moment, but the values of the moment would be somewhat different.