THE DIELECTRIC CONSTANT AND ELECTRIC MOMENT OF SOME ALCOHOL VAPORS

By John B. Miles, Jr.

Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del.

ABSTRACT

The dielectric constant and electric moment of methyl, ethyl, n-propyl, n-butyl alcohol vapors.—Measurements of the dielectric constant of these alcohol vapors were made at several temperatures. A new method was used for measuring the pressure of the hot vapor. The agreement with Debye's equation for the dielectric constant of gases is good at higher temperatures where there is no association. Association is discussed. The moments are calculated and the following results obtained: methyl alcohol $A = 1.09 \times 10^{-3}$, $\mu = 1.68_0 \times 10^{-18}$; ethyl alcohol, $A = 1.58 \times 10^{-3}$, $\mu = 1.69_6 \times 10^{-18}$; n-propyl alcohol, $A = 2.30 \times 10^{-3}$, $\mu = 1.65_7 \times 10^{-18}$; n-butyl alcohol, $A = 2.91 \times 10^{-3}$, $\mu = 1.65_9 \times 10^{-18}$.

RECENTLY there have been a considerable number of measurements made on the dielectric constant of liquids with the purpose of obtaining the electric moment. The interpretation has been made on the assumption that for dilute solutions of a polar liquid in a non-polar solute the distance between the polar molecules is sufficient to allow the use of Debye's[1] well known equation for the dielectric constant of gases and its temperature variation, i.e.

$$3 \left(\frac{\epsilon - 1}{\epsilon + 2} \right) v = A + \frac{B}{T}$$

where ϵ is the dielectric constant, v is the specific volume measured in terms of an ideal gas at S.P.T. (i.e. $v = V/V_0$ where V is the specific volume and V_0 is the specific volume of an ideal gas, equal to RT/P) and T is the absolute temperature. In this expression A and B are constants for the gas the values of which are given by $A = 4\pi N_0 \lambda$ and $B = 4\pi N_0 \mu^2 / 3K$ where N_0 is the number of molecules per cc of an ideal gas at S.P.T., λ is a constant, K the Boltzmann constant and μ the permanent electric moment of the molecule measured in e.s.u. Theoretically the constant A is equal to $3(n^2 - 1)/(n^2 + 2)$ or, when n^2 is sufficiently near one, to $n^2 - 1$, n being the refractive index extrapolated to infinite wave-length.

Two methods have been used to determine the electric moment of molecules in the liquid state. One is to determine the value of $A + B/T$ at one temperature and to use the value of A as determined by optical data and so obtain B/T and consequently μ. The other is to measure $A + B/T$ at various temperatures and so to obtain $A + B/T$ entirely from measurements of the dielectric constant. The measurements are complicated by the fact

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[1] Marx, Handbuch der Radiologie, **6**, 614 (1925).

that as the concentration of the polar liquid is decreased the value of ϵ per molecule plotted against the concentration does not follow the straight line which might be expected at low concentrations. Consequently the value of ϵ for the polar molecule is obtained by extrapolating the value of ϵ for the mixture to zero concentration of the solute. The principal measurements by the first method are by Williams.[2] In these measurement he uses various solvents as benzene, CCl_4, CS_2 and hexane and obtains fairly consistent results.

Lange,[3] Smyth, Morgan and Boyce,[4] and Stranathan[5] have made observations on the dependence of the dielectric constant on temperature. On account of the small temperature range that can be used the assistance of the refractive index value of A is usually necessary in order to obtain a value of μ at all accurately. Stranathan[5] discusses this subject at some length.

Because Debye's equation is known to hold well for gases, it was thought to be of interest to make measurements on the vapors of some liquids which
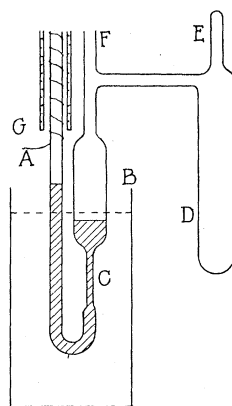

Fig. 1

had been carefully investigated in dilute solutions and so to find how justifiable is the application of the equation to such solutions. The primary alcohols were chosen for this purpose.

EXPERIMENTAL METHOD

The apparatus used was the heterodyne null-beat arrangement described by Zahn in a previous communication[6] and used to measure the dielectric constant of several gases.[7] In order to prevent condensation of the vapors it was of course necessary to keep all parts of the gas system at a temperature

[2] J. W. Williams, Jour. Am. Chem. Soc. **49**, 1676 (1927); Phys. Zeits. **29**, 174 (1928); Phys. Zeits. **29**, 683 (1928).

[3] L. Lange, Zeit. f. Physik **33**, 169 (1925).

[4] Smyth, Morgan and Boyce, Jour. Am. Chem. Soc. **50**, 1550 (1928).

[5] J. D. Stranathan, Phys. Rev. **31**, 653 (1928).

[6] C. T. Zahn, Phys. Rev. **24**, 400 (1924).

[7] C. T. Zahn and J. B. Miles, Jr., Phys. Rev. **32**, 497 (1928).

above that of condensation. This was accomplished by winding the glass tubing with Nichrome wire and covering this with asbestos. The part of the tubing inside the shielding box was kept hot by a gentle stream of hot air.

The method of measuring the pressure of the vapor should be mentioned. Since all parts of the tubing had to be kept hot it was impossible to use a mercury manometer directly. It was also desired to keep away from stopcocks and the resulting grease, since considerable trouble from this source had been experienced in previous measurements, notably in CS_2.[7]

The arrangement used is illustrated in Fig. 1. The liquid whose vapor was to be investigated was introduced at E into the bulb D where it was frozen with liquid air. The opening E was then sealed off and the system evacuated to less than 10^{-4} mm of mercury. The liquid air was then removed and the liquid allowed to come to room temperature while some of the liquid boiled away and the absorbed air was pumped off. This process of freezing and melting was repeated several times in order to get rid of the air. The U tube was then surrounded by ice and sufficient of the liquid distilled over in vacuo to bring the level to the height shown.

As described in the previous communication[6] the readings on the variable condenser were taken for zero beats with high and low pressures of the gas in the condenser. In order to vary the pressure dried air was let in slowly on the side F of the U, forcing the liquid upward toward the part of the tube A which was kept heated to about 150°C, the liquid evaporating and filling the condenser until an equilibrium pressure was established. The pressure of the air was then read on a mercury manometer and was equal to the pressure of the vapor plus the difference in level of the liquid, which was read on a scale directly behind the U. A temperature correction for the density of the liquid was negligible since little of the liquid was at a temperature different from 0°C, the temperature gradient from 150°C to 0°C being established over a distance of about 3 cm. To obtain a low pressure the air was pumped off at F, both levels of the liquid being brought down below that of the ice and a pressure as low as the vapor pressure of the liquid at 0°C was obtainable. In practice a pressure about 1 cm higher was used because of the time necessary, due to the slow condensation, to obtain equilibrium at low pressures. Difficulty was experienced in increasing the pressure because a too rapid boiling at A would drive the liquid around the bottom of the U and allow air to enter the condenser. Several designs of tube were tried and the one used successfully was about 8 in. (20.3 cm) from G to the bottom of the U which was of 3/16 inch (4.5 mm) tubing with a section at C of about 3 in. (7. 5cm) of 1/16 inch (1.5 mm) tubing and one at B of about 3 in. of 3/4 inch (1.9 cm) tubing.

EXPERIMENTAL RESULTS

In the calculation of the results use was made of the complete equation as given by Zahn in his original paper.[6] This was necessary on account of the large value of the dielectric constant for the alcohols. It is

$$\epsilon' - 1 = -\frac{C^2}{C_0} \frac{K}{(K+K'+C)\Delta K + (K+K')^2}$$

where the letters have the same meaning as in that paper; K is the capacity of the variable condenser at the high pressure of the gas, K' the fixed capacity in parallel with it, ΔK the change in the variable condenser with the decrease of the gas pressure and C the capacity of the gas condenser including lead capacity, C_0 being the part of this capacity changed by the gas. C was determined after each run because it had a slight temperature coefficient. Here $\epsilon' - 1$ is of course not that of the gas at the given pressure because the readings are not taken from vacuum but from a pressure of 2 or 3 cm. It is therefore the change due to the change in pressure. The value of $\epsilon - 1$ for the high pressure was obtained by extrapolating, linearly with pressure, to vacuum. The results are given in Table I.

TABLE I

$T°$K	$(\epsilon-1)\times10^{-6}$	p (cm. Hg)	$3\dfrac{\epsilon-1}{\epsilon+2}v\times10^6$	$3\dfrac{(\epsilon-1)vT}{\epsilon+2}$
		Methyl alcohol		
344.7	2740	33	7875	2.715
344.8	2640	32	7880	2.717
399.3	4765	75	6946	2.774
413.2	4493	76.1	6731	2.782
435.2	4015	75.4	6407	2.788
437.1	3966	76.1	6391	2.794
478.9	3418	75.4	6004	2.878
501.9	3112	75.4	5738	2.880
		Ethyl alcohol		
351.0	5985	64.2	9150	3.135
359.2	2779	33	8515	2.974
402.8	5032	74.2	7524	3.031
430.6	4476	75	7096	3.055
462.5	3882	73.8	6723	3.109
499.3	3377	73.7	6332	3.162
		n-Propyl alcohol		
376.0	3261	40.5	8356	3.142
416.9	5168	75.7	7835	3.265
471.7	4160	76.2	7105	3.351
504.9	3669	75.5	6813	3.440
		n-Butyl alcohol		
384.6	2784	33.1	8950	3.442
415.9	5500	75.1	8386	3.488
449.1	4836	75.3	7969	3.579
490.2	4194	75.3	7559	3.705

All the alcohols, except n-butyl, were pure commerical alcohols and were boiled for 24 hours with calcium oxide to get rid of water. They were then distilled off, only the middle fraction being used for the experiments. As a test of the water content the alcohols were left in contact with anhydrous copper sulphate for several days and no green color was observed. The n-butyl alcohol was loaned by Professor C. P. Smyth, and showed no trace of water.

It is important to note that only the approximate values of the pressure are given in the third column. Actually the pressures were read to 0.1 mm of Hg and the value of $3v(\epsilon-1)/(\epsilon+2)$ calculated for each reading and averaged. The deviations from the mean are of such an order as to give a probable error varying from about 0.1 to 0.5 percent in $\epsilon-1$. The values of v were calculated by using the van der Waal equation in the approximate form

$$v = \frac{RT}{p}\left[1 - \frac{(a/vp - b)}{v}\right]$$

and the approximate value of $v = RT/p$ used on the right side. a and b were obtained from Landolt-Börnstein's tables and in the case of n-butyl alcohol extrapolated from the other alcohols. $a = 3600 \times 10^{-5}$ and $b = 5300 \times 10^{-6}$ were the values used. The values obtained by extrapolating from the other normal alcohols and from iso-butyl alcohol on the basis of normal and iso-propyl alcohol both give values approximately the above. The errors introduced from this consideration are certainly less than 0.1 percent.

In Fig. 2 are plotted the values of $3vT(\epsilon-1)/(\epsilon+2)$ against T. The moments are obtained from the values of B. Here

$$\mu = \left(\frac{3KB}{4\pi N_0}\right)^{1/2} = 1.100 \times 10^{-18} B^{1/2}.$$
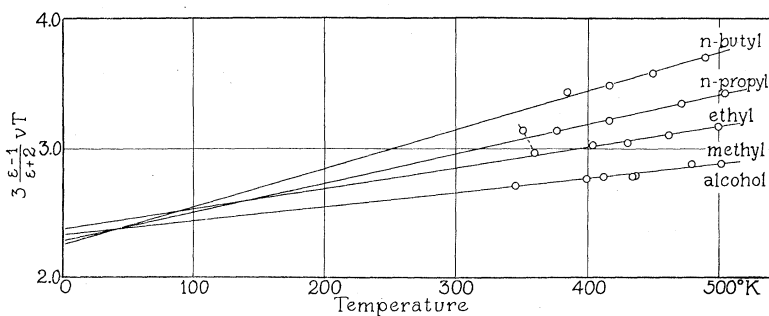
The values of B and A were obtained by the method of least squares, the points being weighted according to their individual probable errors. They are

	B	$A \times 10^3$	$\mu \times 10^{18}$
Methyl alcohol	2.332	1.088	1.680
Ethyl alcohol	2.378	1.578	1.696
n-propyl alcohol	2.269	2.302	1.657
n-butyl alcohol	2.275	2.913	1.659

The probable errors based on the consistency of the readings themselves and the deviations from the straight line are as large as 5 in the last place for μ and 2 in the third place for A only in the case of n-propyl alcohol. In the other determinations they are less. This does not, of course, include the possible errors due to calibration, etc.

In calculating A and B all the points were used in the case of methyl and n-propyl alcohol and the points at the three and four higher temperatures were used in the case of n-butyl and ethyl alcohol respectively. A possible explanation of the deviation of the points at lower temperature from the expected straight line is association.

Association

From the law of mass action if we have association into double molecules, and if p_1 and p_2 are the partial pressures of the single and double molecules respectively

$$Kp_2 = p_1{}^2$$

where K is given by the equation of van't Hoff

$$\frac{d \log K}{dT} = -\frac{Q}{RT^2}$$

Q being the heat absorbed by a gram molecule in the dissociation from double to sincle molecules. On integrating and neglecting the variation of Q with temperature,

$$\log K = Q/RT + \text{const}.$$

In the case of two kinds of molecules Debye's equation takes the form

$$3\frac{\epsilon - 1}{\epsilon + 2}N_0 = N_1 A_1 + N_2 A_2 + \frac{N_1 B_1 + N_2 B_2}{T}$$

where the letters have the same meaning as before, and the subscripts 1 and 2 refer to single and double molecules respectively, N_1 and N_2 are the numbers of each per cc. If P is the total pressure and N the total number of molecules $p_1/P = N_1/N$ and $p_2/P = N_2/N$ and the equation becomes

$$3\frac{N_0(\epsilon - 1)}{N(\epsilon + 2)}P = p_1 A_1 + p_2 A_2 + \frac{p_1 B_1 + p_2 B_2}{T}$$

but $p_1 = P - p_2 = P - p_1{}^2/K$ and, since p_1 is nearly equal to P and K is large,[8] then approximately

$$p_1 = P - P^2/K \; ; \qquad p_2 = P^2/K .$$

The equation becomes

$$3\frac{(\epsilon - 1)N_0}{(\epsilon + 2)N} = A_1 + \frac{P}{K}(A_2 - A_1) + \frac{B_1}{T} + \frac{P}{KT}(B_2 - B_1) .$$

From this equation it will be seen that $v(\epsilon - 1)/(\epsilon + 2)$ is not independent of the pressure at which it is measured, but that a linear term is involved which becomes increasingly important at lower temperatures (the Q involved in K is a negative quantity.) It will be noticed in the case of ethyl alcohol,

[8] For case of water, E. Bose, Zeits. f. Eletrochemie **14**, 269 (1908).

referring to Table I, that the point at lowest temperature which lies considerably above the line is at almost twice the pressure of the point next higher in temperature. This is probably also the reason the lowest point for n-butyl alcohol is above the line determined by the other three points and is the reason why it was not used in calculating A and B.

Before the possibility of association and its effect was realized, many measurements were made in water vapor without its being possible to fit any straight line to the values of $vT(\epsilon-1)(/(\epsilon+2)$ when plotted against T. It is planned, by measuring the dielectric constant at several pressures at each temperature, to obtain all four constants A_1, A_2, B_1 and B_2. Preliminary measurements show that $v(\epsilon-1)/(\epsilon+2)$ at one temperature is linear with pressure. Bose[8] has shown that considerable association is to be expected.

TABLE II. *Comparison with other measurements.*

Observer	Method		A'	$\mu \times 10^{18}$
	Methyl alcohol			
Jona[10]	Vapor			1.61
Debye[1]	Vapor (one temperature)	From refractive index		1.64
Stranthan[5]	Liquid in benzene	8.2 (refractive index)		1.64
"	" " CCl$_4$	" " "		1.67
Miles	Vapor	8.13		1.68$_0$
	Ethyl alcohol			
Debye	Vapor (one temperature)	From refractive index		1.66
Williams[11]	Liquid (one temperature)	" " "		1.63
Stranathan	Liquid in Benzene	12.7 (refractive index)		1.74
Sänger[12]	Vapor	36.4		1.11
Miles	"	11.8		1.69$_6$
	n-Propyl alcohol			
Debye	Vapor (one temperature)	From refractiveindex		1.66
Lange[3]	Liquid in Benzene	Extrapolated temperature coefficient used		1.53
Williams	Liquid (one temperature)	From refractive index		1.66
Stranthan	Liquid in Benzene	17.4 (refractive index)		1.75
Miles	Vapor	17.2		1.65$_7$
	n-Butyl alcohol			
Lange	Liquid in Benzene	Extrapolated temperature coefficient used		1.65
Mahant and Des Gupta[13]	Liquid (method not published)			1.62
Miles	Vapor	21.76		1.65$_2$

Other possible explanations of the anomaly are conductivity introduced by an adsorbed layer on the quartz insulation or an effective change in the plate separation due to the layer. Near saturation, direct-current conductivity was found and all measurements were made at pressures such

[9] J. H. Frazer, Phys. Rev. **33,** 97 (1929).
[10] M. Jona, Phys. Zeits. **20,** 14 (1919).
[11] J. W. Williams, Phys. Zeits. **29,** 204 (1928).
[12] R. Sänger, Phys. Zeits. **28,** 455 (1927).
[13] P. N. Ghosh, Nature **123,** 413 (1929).

that the direct-current resistance of the condenser was greater than about 500 megohms. According to Frazer[9] for water and methyl alcohol at about 50 percent saturation the thickness of an adsorbed layer on glass is of the order of 10A and therefore negligible from this point of view. Of course the adsorbed layer on metal may be quite different from that on glass.

In Table II is given a comparison with other measurements made both upon the liquid and the vapor. Column three gives the value for A' which corresponds to the A used in this article but referred to the dielectric constant per mol, i.e., $A' = 22.4A/3$.

In most cases the agreement is surprisingly good between the measurements in the liquid and in the vapor. In the case of methyl alcohol Stranathan obtains the same value for the moment using CCl_4 as the solvent as this investigation gives but he considers the results with benzene as solvent more nearly correct. Sänger's results with ethyl alcohol are difficult to explain. There seems to be no generalization as to whether the moments obtained from liquids are larger or smaller than those from the vapor. It is interesting to note that in every case the value for A' resulting from these investigations is slightly smaller than that obtained from refractive-index data. The values of $n^2 - 1$ for the vapors extrapolated to infinite wavelength from data given in Landolt-Börnstein are 1.07×10^{-3} and 1.64×10^{-3} for methyl and ethyl alcohol respectively, both being larger than the values given for A in this paper. The reason for this is difficult to explain, since one would expect that the degrees of freedom involved in the vibration levels and not appearing in the visible region where the refractive index is measured would make A slightly larger than $n^2 - 1$ extrapolated.

It is probable that the results given in this paper fall within the experimental error or the error introduced by association in the liquids investigated by the observers mentioned in Table II. In the case of Stranathan[5] when he depends entirely on his own observations this is true. Mahant and Des Gupta[13] do not give their experimental error. From this point of view the results of Länge[3] appear to be in disagreement in some cases.

The fact that the alcohols all have nearly the same moment has been mentioned by previous investigators of the liquids. It has been already mentioned that the moment is ascribed to the OH radical and the addition of the CH_2 groups to the chain does not change this moment appreciably.