DIELECTRIC CONSTANTS OF DILUTE SOLUTIONS OF POLAR LIQUIDS IN NONPOLAR SOLVENTS

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Abstract

Dielectric constants of solutions of methyl, ethyl, propyl and amyl alcohols in benzene and carbon tetrachloride.—Failure of the Debye theory to represent the behavior of such polar liquids as the alcohols is usually attributed to association. With hope of eliminating the effects of association, the dielectric behavior of dilute solutions of several alcohols in benzene have been studied. Dielectric constants were determined by a heterodyne beat method. Both dielectric and density data were obtained at each 10° temperature interval from freezing to boiling. The molecular polarization found for the dissolved alcohol was plotted against concentration; one such curve was plotted at each 10° interval. With hope of obtaining the polarization of the alcohol in the unassociated state, these curves were extended to cut the zero concentration axis. The resulting intercepts for the various temperatures were checked against theory.

Electric moments of methyl, ethyl, propyl and amyl alcohol molecules.—By taking the contribution due to electron displacement from optical data, it was found that the zero concentration intercepts for methyl, ethyl, propyl, and amyl alcohol (using benzene as solvent) lead to values of the electric moment of the molecule which are essentially independent of temperature. This is in agreement with the Debye theory; it is in contrast to the behavior of the pure liquid alcohols. The moments found are 1.64, 1.74, 1.75, and 1.62×10^{-18} for methyl, ethyl, propyl, and amyl alcohol, respectively. If use of the molecular refraction is avoided by plotting values of P_0T against T, where P_0 is the zero concentration intercept, it is apparent that the data can in no way lead to imaginary electric moments, as do data on the pure liquids. If straight lines with the extreme slopes justified by the data are drawn through the group of points for any alcohol, the zero temperature intercepts so found limit the electric moment to a range whose extremes differ by not more than 20 percent. In every case the moment obtained through use of the molecular refraction falls within this range.

Introduction

THE Debye theory[1] of dielectrics leads to the expression

$$\frac{K-1}{K+2}\,\frac{M}{d}=A+\frac{B}{T}$$

where K is the dielectric constant, M the molecular weight, d the density, and where A and B are constants for a given dielectric. Theoretically, the constant A is equal to the molecular refraction $(M/d)(n^2-1)/(n^2+2)$ extrapolated to infinite wave-length; it includes only the effect of electron displacement, and not that of doublet orientation. The constant B measures the contribution due to the permanent electric moment of the molecule. The moment u is given by

$$u=(9kdB/4\pi NM)^{1/2}=1.27\times10^{-20}B^{1/2}$$

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[1] See, for example, Marx, Handbuch der Radiologie, **6**, 614–619 (1925).

where k is the Boltzmann gas constant per molecule and N the number of molecules per cubic centimeter. The quantity $(M/d)(K-1)/(K+2)$ is known as the molecular polarization P; hence, the first equation may be written

$$PT=AT+B$$

The theory can be tested for agreement with experimental data by plotting values of PT against T; theory demands a straight line with slope A and intercept B. Numerous data on gases by Zahn,[2] Smyth and Zahn,[3] and others, have shown that in general the theoretical expression represents well the experimental findings. The electric moment of the molecule is calculated from the experimental intercept B. In most cases the experimental slope A agrees moderately well with the molecular refraction calculated from optical data.

In general the data on liquids do not agree well with the Debye expression. As an example of a typical failure of the expression, attention is called to the data on liquid ethyl alcohol as quoted by Debye.[4] In this case the data do conform to the linear relationship between PT and T required by theory, but the intercept B is clearly negative. Since the electric moment of the molecule is proportional to the square root of the intercept B, the theory here leads to an imaginary moment. Or, if the value of A be taken over from optical data and B calculated at various temperatures, the resulting electric moment is found to increase with rising temperature. Thus the simple theory is quite inadequate. Similar statements can be made regarding data on liquid methyl alcohol.

The failure of the simple theory in the case of polar liquids is usually attributed to association and changes of the degree and manner of association with temperature. Such changes would clearly result in an electric moment which varies with temperature; the moment measured would be an effective value, averaged over the various types of associated groups present.

Dielectric data on solutions of polar liquids in a nonpolar solvent furnish illuminating data as to the effects of association. The dielectric constant of a solution of known concentration, say alcohol in benzene, may be measured, and thence the molecular polarization P of the mixture calculated; for this calculation the weighted molecular weight $(M_1c_1+M_2c_2)$ is used,[5] where M_1 and M_2 are the molecular weights, and c_1 and c_2 the mole fraction concentrations of the solvent (benzene) and the solute (alcohol), respectively. On the basis of the additive law the polarization P of the mixture is made up of two parts, one due to the solvent, the other due to the solute; that is,

$$P=P_1c_1+P_2c_2$$

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[2] C. T. Zahn, Phys. Rev. **24**, 400 (1924); **27**, 455 (1926).

[3] C. P. Smyth and C. T. Zahn, Jour. Am. Chem. Soc. **47**, 2501 (1925).

[4] Marx, Handbuch der Radiologie, **6**, 625 (1925).

[5] See Marx, Handbuch der Radiologie, **6**, 628 (1925).

where P_1 and P_2 are the molecular polarizations of the solvent and the solute, respectively. P_1c_1 can be calculated from dielectric data on the pure solvent; hence, P_2, the polarization of the alcohol at concentration c_2, can be obtained. Debye[6] and his students have shown that the molecular polarization P_2 depends markedly on concentration; at some concentrations it increases, at others it decreases, as c_2 decreases. This is presumably due to association changes.

Debye has suggested that if the experimental curve of P_2 versus c_2 (for small concentrations) be extrapolated to zero concentration, the molecular polarization of the solute in the unassociated state would be obtained. This is based upon the assumption that association disappears as the concentration approaches zero, an assumption which is in agreement with data[7] on the lowering of the freezing point of benzene due to the addition of alcohol. It would be interesting to know whether these extrapolated values obey the Debye theory. While there is considerable data in the literature on solutions, practically all of it is for much too large concentrations to be useful here. The author is aware of only two works dealing with the subject. Debye[8] has used data of J. C. Philip on several alcohols in benzene and toluene at mole fraction concentrations ranging from somewhat under 0.01 to 0.11. He extrapolates to zero concentration and calculates the electric moment u, taking the constant A as equal to the molecular refraction obtained from optical data. Unfortunately, the data are all at one temperature, and therefore furnish no test of the Debye theory. The second work is that of L. Lange.[9] She has studied solutions of several alcohols in nonpolar solvents, but a great majority of her data pertain to relatively high concentrations. She has never more than three points under a mass concentration 0.10, and never any under 0.031. Data were taken at most at three temperatures, and usually for only one or two. Judging from the data, it would seem quite unreliable to extrapolate using so few points at low concentrations, and to test the Debye theory with data at so few temperatures.

In the present work the author has therefore made an effort to secure accurate data for somewhat more dilute solutions, and at numerous temperatures, for the purpose of checking the zero concentration intercepts against the Debye theory.

Experimental Procedure

Capacity measurements. Because of the fact that a relatively small error in the initial measurements of either the dielectric constant or the density, becomes greatly magnified during the process of calculation, and all the more so as the concentration is lowered, it is essential that the original errors of measurement be small. In view of this, the method used for the measurement of dielectric constant was a heterodyne beat arrangement commonly used for

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[6] Marx, Handbuch der Radiologie, **6**, 627–633 (1925). L. Lange, Zeits. f. Physik **33**, 169–182 (1925).

[7] Cited by Debye, Marx, Handbuch der Radiologie, **6**, 640 (1925).

[8] Marx, Handbuch der Radiologie, **6**, 630 (1925).

[9] L. Lange, Zeits. f. Physik **33**, 169–182 (1925).

measurements on gases.[10] It is true that the sensitivity of this method is far greater than is here necessary, but this is no disadvantage.

The apparatus consisted of two high frequency oscillators, as shown in Fig. 1. The frequency of one oscillator was maintained constant at 476 kilocycles by a quartz crystal, while that of the second could be adjusted at will by variable condensers. The amplified beat note between the two oscillators could be heard from the telephone *T*. The frequency of the second oscillator could be made accurately 1000 cycles less than that of the crystal controlled oscillator, through use of the electrically driven tuning fork *F* coupled electrically to the grid circuit of the last stage amplifier; the note due to this tuning fork also issued from the telephone *T*. The secondary beat-note formed between the tuning fork note and the beat-tone between the two high frequency oscillators, was adjusted to zero by varying the capacity of the second oscillatory circuit. In this way the frequency of the second oscillator could always be brought to a fixed value. The oscillators were shielded, and run from independent batteries to avoid synchronizing effects.

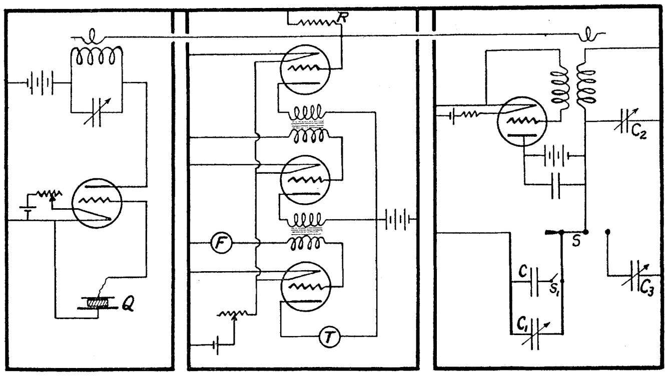

Fig. 1. Diagram of apparatus.

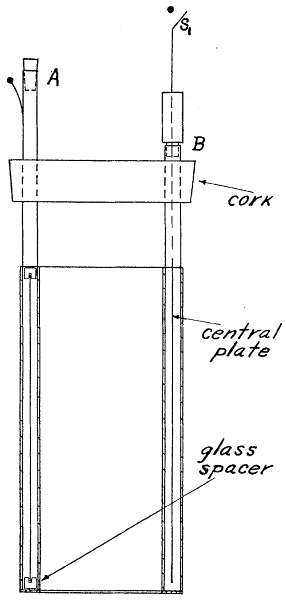

Fig. 2. Test condenser.

The liquid whose dielectric constant was desired was placed in a three plate, cylindrical, brass condenser *C* whose construction is made clear by Fig. 2. The central plate was held in place by three small Pyrex glass spacers at both top and bottom. This condenser was of such dimensions as to fit into a wide mouth quart thermos bottle containing a water (or alcohol) bath. The temperature, which was read from a mercury thermometer projecting through the cork of the thermos bottle, could be

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[10] See, for example, C. T. Zahn, Phys. Rev. **24**, 400 (1924).

adjusted at will by means of an electric heater placed in the bath. Uniformity of temperature was insured by a stirrer projecting through the cork.

The capacity of the test condenser C under any particular conditions was determined by observing the change in capacity of C_1 necessary to compensate for placing the test condenser in parallel with it; the General Radio precision condenser C_1 was readable consistently to 0.1 micro-microfarad. The function of condensers C_3 and C_2 of Fig. 1 was to eliminate any effect of drift in frequency. The circuit including C_3 served as a standard circuit by means of which it could be ascertained whether the tube had drifted in frequency during the process of measurement; C_2, a very small capacity which was always in the oscillatory circuit regardless of the position of switch S, served to compensate for any drift observed.

The capacity of C thus determined must be corrected for both lead capacity and capacity occasioned by the solid dielectric spacers; the glass projecting into the condenser tube at B, Fig. 2, also necessitates a correction. The lead capacity, including that due to the glass at B was determined by direct measurements on a set of dummy leads placed just as were the actual leads during the measurements proper. Several independent sets of measurements gave very consistent results. In order to obtain the capacity correction due to the solid dielectric spacers, use was made of a second cylindrical condenser exactly similar to the one used except that it contained twice as many spacers. The spacers were identical in the two condensers, and they were placed in exactly similar positions. It was therefore assumed that the capacity due to solid dielectric in the second condenser was just twice that in the first. Hence, by expressing the dielectric constant of the same liquid at the same temperature, measured first with one condenser and then the other, in terms of the unknown solid dielectric capacity, and equating the two values of dielectric constant, it is possible to solve algebraically for the solid dielectric capacity. Several measurements gave consistent results. The total correction necessitated by the leads and the spacers was 5.1 micro-microfarads.

The capacity of the empty test condenser, approximately 300 micro-microfarads, was determined for various temperatures ranging from $-30°$ to 80°C. The capacity, corrected for solid dielectric and lead capacity, and also for the air present in the condenser during measurement, was found to be a linear function of the temperature. The temperature coefficient of capacity was 0.0000144 per °C. This is of the same order as the temperature coefficient of linear expansion of brass, as should be expected. An indication of the consistency with which measurements could be duplicated is given by the fact that not one of the 19 experimental points deviates from the straight line by more than one part in 6000.

Mixing of solutions. Solutions of known concentrations were mixed by weighing the components. Great care was exercised in making up the solutions to avoid evaporation of components during the process of weighing and mixing. The best chemically pure materials that could be purchased were used. No further effort was made to remove traces of water except in the case of propyl alcohol, since its presence should cause but insignificant errors.

Density measurements. The densities of solutions were measured by the loss of weight method, using a Pyrex sinker and an analytical balance for weighing. The calibration was obtained by measurements on distilled water at temperatures ranging from 0° to 80°C, the densities of water being taken from tables. The material being tested was maintained at any temperature desired by immersion in a bath contained in a thermos bottle. The temperature could be changed at will by an electric heater immersed in the bath. By comparison with numerous tabular values wherever possible, it appears that the densities thus determined are quite reliable. For example, the present density determinations on benzene as read from a smooth curve at each 10° temperature interval from freezing to boiling, show an average deviation from Young's values[11] of only 3 parts in 10,000. Also, the author's densities of carbon tetrachloride show about the same percent deviation from Young's values.[12]

DATA AND RESULTS

Methyl alcohol in benzene. Nine solutions of methyl alcohol in benzene were mixed, the mole fraction concentration of alcohol ranging from 0.00890 to 0.07135. The dielectric constants of each of these solutions, and of the pure solvent benzene, were determined at temperatures ranging from freezing to boiling. The test condenser was filled, immersed in a bath at about 6°C, and the dielectric constant of the solution measured. The temperature was

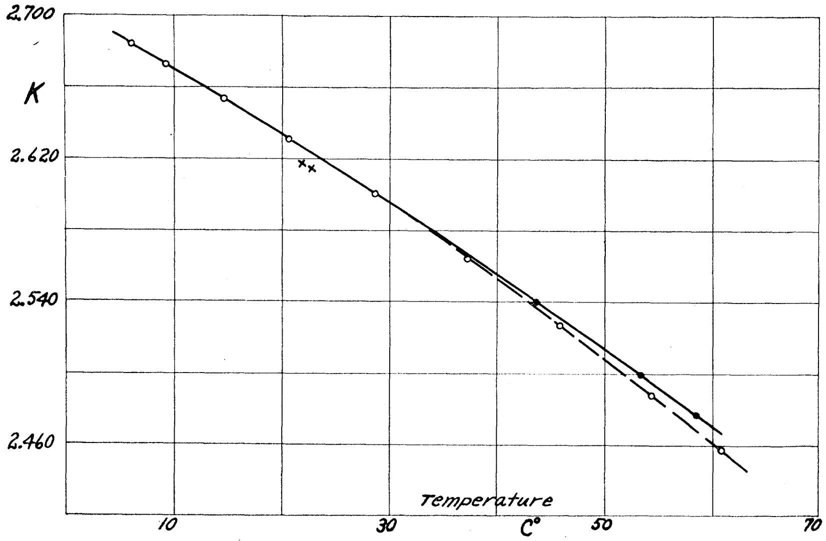

Fig. 3. Correction for evaporation.

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[11] Quoted in Landolt and Börnstein, p. 152, 1912.

[12] Quoted in Landolt and Börnstein, p. 160, 1912.

increased, time allowed for temperature equilibrium, and the measurements repeated. As long as the temperature was never allowed to fall, and as long as no vapor bubbles formed in the liquid, the expansion of the liquid with rising temperature served to keep the test condenser full. Excess liquid forced itself out around the capillary fitting at *B* of Fig. 2. When necessary, additional liquid was put into the condenser through the grounded lead *A*.

Considerable difficulty was experienced, especially with methyl alcohol, due to evaporation of alcohol during the run and the consequent changing of concentration. This was the case in spite of the fact that the lead from the inner plate of the condenser was surrounded by a tight fitting capillary ground to fit tightly into the brass tube of the condenser at *B*, Fig. 2, and the fact that a cork was kept in the tube *A* at all times except when replenishing the solution. The effect of evaporation is shown by Fig. 3, on which points represented by circles are those obtained during a run. The solution was then cooled to room temperature, and the dielectric constant measured; the fact that the two resulting points represented by crosses fall below the original curve indicates that the concentration has decreased. An approximate correction for evaporation would be to raise the curve at the highest temperature point by the same amount that the points represented by crosses deviate from the original curve. As a second, and somewhat better method of correction, the following procedure was adopted. After the first run, the test condenser was refilled with a fresh sample of the solution under test. A point was taken at room temperature (not shown on the curve) to insure that later measurements could be relied upon. The temperature was increased rapidly and a point taken at a temperature somewhat above that at which evaporation began to introduce errors in the original curve. A subsequent measurement at room temperature showed that evaporation had been inappreciable; the time for which the solution had remained at a high temperature was much shorter than for the original measurements. The condenser was again refilled with a fresh sample and the procedure repeated. Points obtained in this way are represented on the curve by black dots. The final curve representing dielectric constant as a function of temperature was drawn through these points rather than the original ones at high temperatures. Dielectric constants were read from this curve at each 10° temperature interval, and tabulated. The procedure was repeated for each of the nine different solutions. The resulting dielectric constants for various concentrations and temperatures are collected in Table 1.

The density of each solution was measured at temperatures ranging from freezing to boiling. The experimental densities for each solution were plotted against temperature, and the density read from the curve at each 10° interval. The densities for the various solutions at any one temperature were then plotted against concentration of alcohol in the solution, and a smooth curve drawn through the points. The density corresponding to any particular concentration and to any particular temperature was then read from these curves. The resulting densities are shown in Table I.

TABLE I

Methyl alcohol in benzene

Summary of dielectric constant and density values. The upper figure in each group of two is the dielectric constant; the lower figure is the density. The same is true for all subsequent tables of this nature.

T	$c_2=0$	.00890	.01507	.01929	.02248	.02929	.03904	.05278	.06266	.07135
10°	2.300 .8897	2.335 .8895	2.362 .8893	2.381 .8892	2.394 .8891	2.426 .8889	2.475 .8887	2.550 .8884	2.610 .8881	2.669 .8879
20°	2.279 .8794	2.313 .8792	2.338 .8790	2.355 .8789	2.369 .8788	2.398 .8786	2.445 .8784	2.517 .8781	2.575 .8778	2.633 .8776
30°	2.258 .8687	2.290 .8685	2.313 .8683	2.329 .8682	2.434 .8681	2.371 .8679	2.415 .8677	2.483 .8674	2.539 .8671	2.595 .8669
40°	2.236 .8579	2.266 .8577	2.288 .8575	2.303 .8574	2.316 .8573	2.342 .8571	2.383 .8569	2.448 .8566	2.501 .8563	2.554 .8561
50°	2.214 .8470	2.243 .8468	2.262 .8466	2.277 .8465	2.289 .8464	2.313 .8462	2.352 .8460	2.414 .8457	2.463 .8454	2.512 8452
60°	2.192 .8361	2.218 .8359	2.237 .8357	2.251 .8356	2.262 .8355	2.284 .8353	2.321 .8351	2.380 .8348	2.425 .8345	2.470 .8343

The procedure followed in calculating the contribution of the dissolved alcohol to the polarization of the mixture, is made clear by Table II. The second and third columns represent experimental data. The fourth is calculated from the second and third. The fifth contains values of molecular

TABLE II

Sample calculations.

Methyl alcohol in benzene $c_2=0.07135$

T	K	d	$\frac{K-1}{K+2}\frac{1}{d}$	P	P_1c_1	P_2c_2	P_2
10°C	2.669	0.8879	0.4026	30.11	24.64	5.47	76.7
20	2.633	.8776	.4016	30.04	24.65	5.39	75.5
30	2.595	.8669	.4004	29.95	24.66	5.29	74.1
40	2.554	.8561	.3986	29.82	24.67	5.15	72.2
50	2.512	.8452	.3965	29.66	24.67	4.99	69.9
60	2.470	.8343	.3942	29.49	24.67	4.82	67.6

$M_1c_1+M_2c_2=78.08\times0.92865+32.04\times0.07135=72.51+2.29=74.80$

polarization of the mixture; these values are obtained by multiplying those of the fourth column by the weighted molecular weight of the solution; the method of weighting is indicated below the table. These values of P include two contributions, one P_1c_1 due to the solvent, the second P_2c_2 due to the dissolved alcohol. Polarizations of the pure solvent at various temperatures are shown in Table III. Values of P_1c_1 are calculated and tabulated in the sixth column of Table II; these are subtracted from the P values to give the contribution P_2c_2. This contribution divided by the concentration of alcohol gives the molecular polarization P_2 of the solute. It will be noticed that the

P_2 values decrease with rising temperature, as should be expected from theory.

Before proceeding further, a word should be said regarding data on the pure solvent, benzene. Theoretically, the molecular polarization of benzene should be independent of temperature. Experimentally, however, it has been shown by Graffunder,[13] Grützmacher,[14] and others, that for carefully dried benzene the molecular polarization increases very slightly with rising temperature. This fact has been verified by the author, who finds a steady increase slightly less than that observed by Graffunder. For benzene not entirely dry the deviation from constancy is less, and seems to reverse sign at high temperatures. (See Table III; the initial increase in P_1 and the subsequent decrease are even more apparent for the benzene used as solvent for ethyl alcohol.) In order to avoid quite appreciable errors which would be introduced if the polarization of the solvent were assumed independent of temperature, the author has determined this polarization at various temperatures, always for the particular sample of benzene used in mixing the solutions. The particular value found for any temperature was then used in calculations at that temperature. This procedure avoids also any effect of slight impurities in the solvent, except the minor effect of these upon the manner of association of the solute.

TABLE III

Polarizations of the benzene used as solvent for methyl alcohol.

T	$\frac{K-1}{K+2}\frac{M}{d}=P_1$
10°C	26.53
20	26.54
30	26.55
40	26.56
50	26.56
60	26.56
70	26.55

The procedure of calculation outlined above was carried out for each of the nine solutions. This all done, there is available a value of P_2 at each 10° interval and for each concentration used. These final values for the polarization of the alcohol for a particular temperature are plotted against concentration in Fig. 4. Smooth curves are drawn through points of equal temperature. The dependence of the polarization of the alcohol on concentration is supposedly due to association. If it be assumed that the effects of association vanish as the concentration approaches zero, the polarization of the alcohol molecules in the unassociated state is represented by the intercepts of these curves on the zero concentration axis. The curves are produced to obtain these intercepts.

Before proceeding further, a word should be said concerning the extrapolation. It is inherent in the method of calculating P_2 that any small error in the original values of K or d for the mixture becomes greatly magnified in the final values of P_2. This magnification of error enters in obtaining the small quantity P_2c_2 by subtracting two large quantities, P and P_1c_1, from one another. The magnification of error becomes greater as the concentration

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[13] W. Graffunder, Ann. d. Physik, **70,** 232 (1923).

[14] M. Grützmacher, Zeits. f. Physik **28,** 349 (1924).

of the alcohol becomes smaller. For this reason the accuracy of points for concentrations under 0.02 is not very good. For the lowest concentration used, 0.00890, the final values of polarization of the alcohol can be expressed to only two significant figures even though the original measurements were to four; and the second place in this final value is none too good. Hence, in extending the curves to the zero concentration axis, much less weight is given the points at low concentrations. In fact, the lower concentration points should be considered more as showing that the data are not inconsistent with the curves drawn that as showing where to draw these curves. Everything considered, the intercepts are rather well defined.

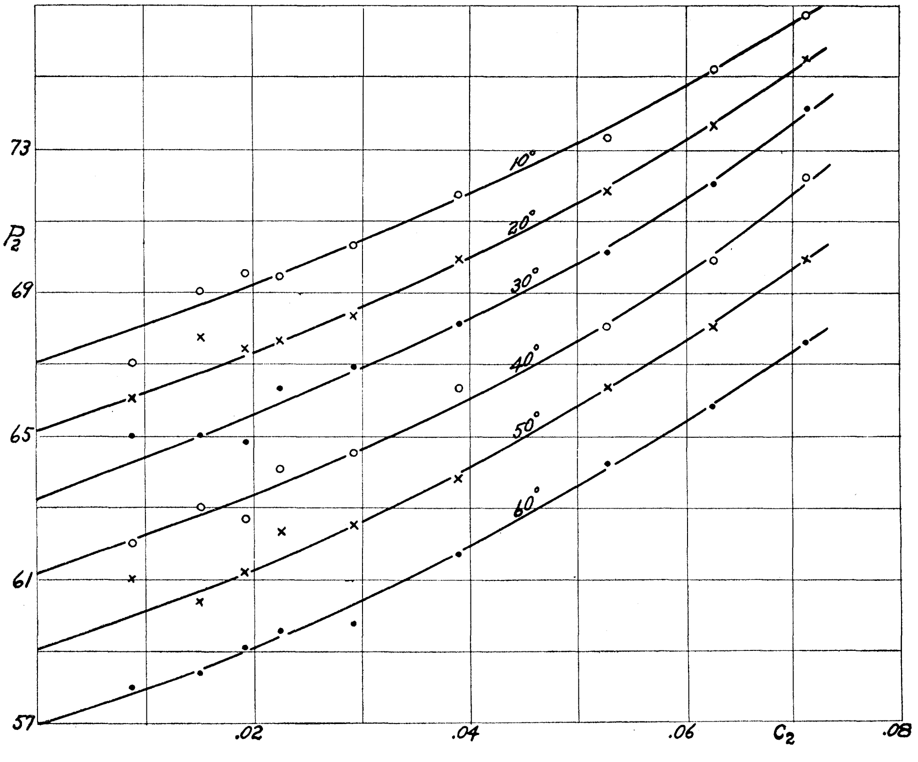

Fig. 4. Polarization curves for methyl alcohol.

The intercepts on the zero concentration axis are read from the curves and tabulated under the heading P_0 in Table IV. In order to check these values against the simple Debye theory, one might proceed in either of two ways. On theory the products P_0T when plotted against T should lead to a straight line whose slope is the molecular refraction extrapolated to long wave-lengths, and whose intercept furnishes a value from which the electric moment u can be calculated. Unfortunately, the data extend over a small temperature range, and the nature of the work is such that precise values of P_0 can not be obtained; such a test is therefore not applicable with any degree of precision. It is true that L. Lange[15] has used the equivalent of this method to calculate the electric moment of the molecule. Critical inspection of her data will show, however, that the intercepts are so poorly defined, due both to extreme scarcity of points under a concentration 0.10 and to inconsistencies in density and dielectric data, that the calculated moments mean little. Even with the present data, which certainly define the zero concentration intercepts better than any data in print, this procedure of calculation leads to values of the electric moment u whose extreme limits may differ by as much as 20 percent in some cases.

Table IV

Methyl alcohol. Calculation of the electric moment u. (Benzene used as solvent).

T	P_0	$(P_0-A)T=B$	u
10°C	67.1	16670	1.64×10^{-18}
20	65.2	16700	1.64
30	63.3	16700	1.64
40	61.2	16590	1.64
50	59.2	16470	1.63
60	57.0	16250	1.62
		Mean value of $u=1.64\times10^{-18}$	

The second method of checking the experimental values of P_0 against theory makes use of the molecular refraction taken from optical data. This procedure is open to the objection that this value may be in error due to infrared absorption; on the other hand, the electric moment u is not seriously affected by small errors in this constant. Following this procedure, the molecular refraction for methyl alcohol, 8.2, is subtracted from the P_0 values. These differences multiplied by the absolute temperature should give a constant B, column three of Table IV. The electric moment is calculated at each temperature, and the results shown in the last column of the table. The constancy is apparent. The slight falling off at the two higher temperatures may possibly be due to inadequate correction for the effects of evaporation.

The present constancy of electric moment is in contrast with the variable value obtained by similar calculations from data for the pure liquid methyl alcohol. As far as the author knows, data on the pure liquid are not available for the temperature range here used. Data cited by Smyth,[16] however, extend from $-100°$ to 20°C. The author has calculated the electric moment at various temperatures from these data, again taking the constant A as 8.2. The results are shown in Table V. These values

Table V

Electric moments of methyl alcohol calculated from data on the pure liquid.

T	u
-100°C	$.839\times10^{-18}$
-70	.926
-40	1.007
-10	1.086
0	1.113
20	1.162

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[15] L. Lange, Zeits. f. Physik **33**, 169–182 (1925).

[16] C. P. Smyth, Phil. Mag. **45**, 860 (1923).

are much lower than those found by the author; furthermore, the moment increases steadily with rising temperature. The average increase for a 10° temperature interval is approximately 0.03×10^{-18}. The last column of Table IV shows that no variation comparable with this exists in the present data. The present average value of 1.64×10^{-18} agrees exactly with the value found by Debye,[17] using the same procedure as here followed, at a single temperature 16°C. It also agrees rather closely with the value 1.61×10^{-18} found by Jona[18] from data on vapor alcohol. The data on vapor are not subject to the effects of association; hence, the agreement may be taken as an indication that these effects have been pretty well eliminated by the low concentration work.

TABLE VI

Methyl alcohol in carbon tetrachloride. Summary of dielectric constant and density values.

T	$c_2=0$	.02219	.02566	.02819	.03867	.04358	.05390	.06162	.07089
−18°	2.297 1.6643	2.351 1.6564	2.358 1.6551	2.365 1.6542	2.396 1.6505	2.409 1.6487	2.447 1.6450	2.476 1.6421	2.514 1.6385
−10°	2.281 1.6505	2.338 1.6428	2.345 1.6416	2.353 1.6407	2.383 1.6371	2.397 1.6354	2.434 1.6317	2.463 1.6289	2.499 1.6254
0°	2.262 1.6322	2.322 1.6248	2.329 1.6236	2.336 1.6228	2.367 1.6193	2.380 1.6176	2.417 1.6141	2.446 1.6114	2.480 1.6081
10°	2.242 1.6130	2.304 1.6060	2.312 1.6048	2.318 1.6041	2.350 1.6006	2.362 1.5991	2.399 1.5957	2.428 1.5930	2.461 1.5898
20°	2.221 1.5938	2.286 1.5871	2.294 1.5860	2.300 1.5852	2.332 1.5820	2.344 1.5804	2.381 1.5772	2.409 1.5747	2.441 1.5716
30°	2.200 1.5746	2.266 1.5681	2.275 1.5671	2.282 1.5663	2.313 1.5632	2.326 1.5618	2.363 1.5587	2.389 1.5563	2.421 1.5533
40°	2.180 1.5554	2.245 1.5492	2.255 1.5482	2.262 1.5475	2.293 1.5446	2.307 1.5432	2.343 1.5402	2.368 1.5379	2.400 1.5351
50°	2.159 1.5360	2.222 1.5301	2.234 1.5292	2.242 1.5285	2.272 1.5257	2.287 1.5243	2.321 1.5216	2.346 1.5194	2.378 1.5165
60°	2.138 1.5166	2.199 1.5111	2.211 1.5102	2.221 1.5095	2.252 1.5068	2.265 1.5055	2.299 1.5029	2.323 1.5008	2.354 1.4981

The author has also tested the present data by plotting P_0T against T. This procedure avoids taking the constant A from refractive data. As has already been mentioned, the intercepts are not sufficiently precise and do not extend over a sufficiently large temperature range to test the linearity of the resulting curve. However, if a straight line be drawn through any pair of points, or an average straight line through the whole group, it is apparent that the data can in no way lead to an imaginary electric moment, as do data on pure liquid methyl alcohol. The extreme values of electric

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[17] Marx, Handbuch der Radiologie, **6**, 627 (1925).

[18] M. Jona, Phys. Zeits. **20**, 19 (1919).

moment which can be obtained by drawing any just straight line through the group of points are 1.60×10^{-18} and 1.75×10^{-18}. The value found above falls within this range.

Methyl alcohol in carbon tetrachloride. A similar procedure was followed, again using methyl alcohol, this time in carbon tetrachloride as solvent. Dielectric constant and density data are summarized in Table VI. The molecular polarization of the particular sample of carbon tetrachloride used here as solvent showed no consistent variation with temperature; the average value 27.91 was therefore used in the calculations. The molecular polarizations calculated for the dissolved alcohol for various concentrations and temperatures are plotted in Fig. 5. The curves are produced to the zero concentration axis as before, though the intercepts are by no means as well defined.

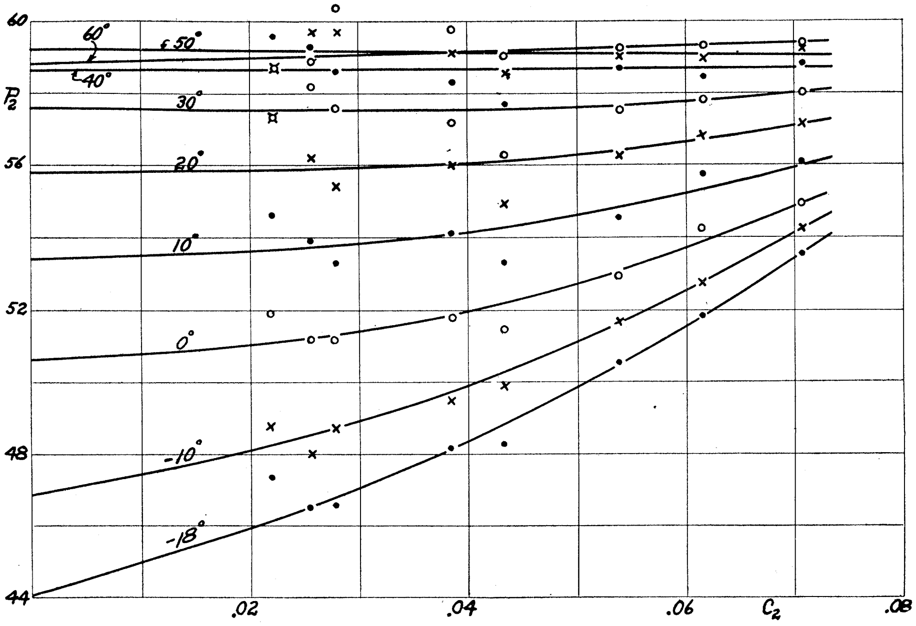

Fig. 5. Polarization curves for methyl alcohol. (Carbon tetrachloride used as solvent).

It is apparent that these data are not even qualitatively in agreement with the simple Debye theory; on theory the molecular polarization should decrease with rising temperature, while actually it increases. The author does not believe this can be construed as evidence against the Debye theory; rather, there are probably large association effects existing at the lowest concentrations used, and the intercepts obtained by extrapolating therefore do not give the polarization in the unassociated state. There are two features of the curves which are noticeable. First and most important, the curves become closer together at high temperatures and even tend to reverse their upward shift with rising temperature, as they would have to do to be qualitatively in accord with theory. Secondly, the curves at the higher temperatures are more nearly horizontal. Each of these facts may be taken as an indication that the effects of association decrease with rising temperature. If the quite reasonable assumption that the effects of association approach zero at sufficiently high temperatures be made, the values of $(P_0-A)T$ plotted against T would be expected to approach a constant value at high temperatures. The experimental values of $(P_0-A)T$ are plotted against T in Fig. 6. The tendency of the curve to become horizontal at high temperatures is quite noticeable. If it be assumed that the value 17,400 approached asymptotically represents the value of $(P_0-A)T$ when the alcohol is unassociated, the electric moment can be calculated. This leads to a value 1.67×10^{-18} which agrees rather well with the value 1.64×10^{-18} found for methyl alcohol when used in benzene.

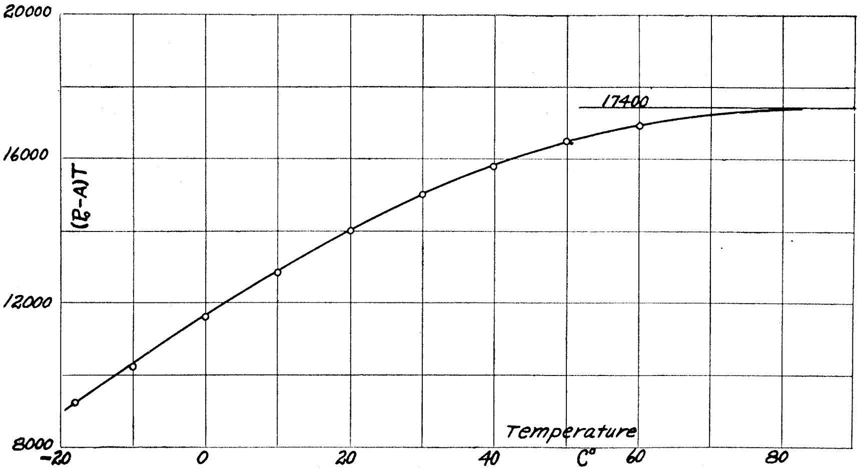

Fig. 6. For methyl alcohol. (Carbon tetrachloride used as solvent).

TABLE VII

Ethyl alcohol in benzene. Summary of dielectric constant and density values.

T	$c_2=0$	.00551	.01000	.01682	.02157	.02709	.03333	.04144	.05133	.05919	.07080
10°	2.300 .8897	2.324 .8895	2.345 .8893	2.375 .8890	2.396 .8888	2.422 .8886	2.451 .8884	2.489 .8881	2.540 .8877	2.581 .8874	2.643 .8870
20°	2.280 .8794	2.302 .8792	2.322 .8790	2.351 .8787	2.371 .8785	2.397 .8783	2.425 .8781	2.462 .8778	2.511 .8774	2.551 .8771	2.611 .8767
30°	2.259 .8687	2.280 .8685	2.299 .8683	2.327 .8680	2.347 .8678	2.371 .8676	2.399 .8674	2.434 .8671	2.481 .8667	2.519 .8664	2.577 .8660
40°	2.238 .8579	2.258 .8577	2.276 .8575	2.303 .8572	2.321 .8570	2.344 .8568	2.370 .8566	2.404 .8563	2.449 .8559	2.485 .8556	2.540 .8552
50°	2.217 .8470	2.236 .8468	2.253 .8466	2.278 .8463	2.295 .8461	2.317 .8459	2.342 .8457	2.374 .8454	2.416 .8450	2.450 .8447	2.503 .8443
60°	2.195 .8361	2.213 .8359	2.229 .8357	2.253 .8354	2.269 .8352	2.289 .8350	2.311 .8348	2.342 .8345	2.381 .8341	2.416 .8338	2.464 .8334
70°	2.172 .8251	2.189 .8249	2.203 .8247	2.226 .8244	2.241 .8242	2.259 .8240	2.281 .8238	2.309 .8235	2.346 .8231	2.377 .8228	2.424 .8224

Ethyl alcohol in benzene. Solutions of ten different concentrations were studied. Dielectric constant and density data for various concentrations and temperatures are collected in Table VII. The molecular polarizations calculated for the dissolved alcohol are plotted in Fig. 7. The curves are again extended to the zero concentration axis to obtain the values P_0, small weight being given to the points at concentrations under 0.02 for the reason already mentioned. The value of A is taken equal to 12.7 from refractive data, and the electric moment calculated for various temperatures. The resulting values are shown in the third column of Table X near the end of the paper. The value is essentially independent of temperature, as it should be on the Debye theory.

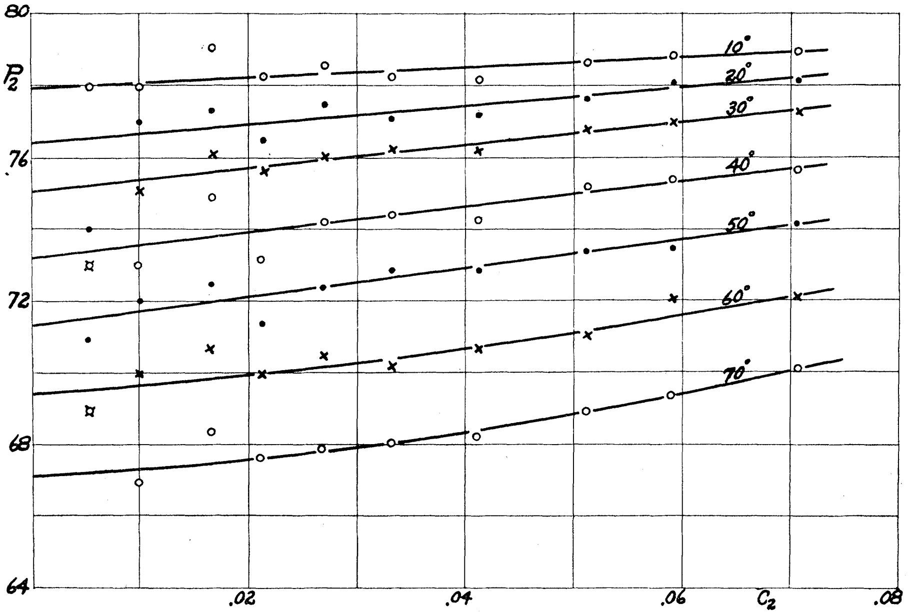

Fig. 7. Polarization curves for ethyl alcohol.

The constancy of the moment found from the present data is in contrast with the variable, and lower value found from data on pure liquid ethyl alcohol. The values[19] for the pure liquid are shown in the fourth column of Table X. The average moment found by the author, 1.74×10^{-18}, agrees fairly well with the value 1.79×10^{-18} as calculated from data by Bädeker[20] on the vapor, using A equal to 12.7. It is somewhat larger than the value 1.66×10^{-18} found by Debye,[21] following the same procedure as here followed, at a single temperature. These values are all markedly higher than the value 1.11×10^{-18} recently reported by Sänger[22] from data on vapor at sufficiently high temperatures.

[19] Calculated from data cited in Marx, Handbuch der Radiologie, **6**, 625 (1925).

[20] K. Bädeker, Zeits. f. Phys. Chem. **36**, 315 (1901).

[21] Marx, Handbuch der Radiologie **6**, 632 (1925).

[22] R. Sänger, Phys. Zeits. **28**, 455 (1927).

As in the case of methyl alcohol, in order to avoid taking the constant A from refractive data, values of P_0T were plotted against T. A straight line drawn through any pair of points, or an average straight line drawn through the group, can in no way lead to an imaginary moment, as do the data on pure liquid ethyl alcohol. The extreme values of electric moment that can be obtained by drawing any just straight line through the group of points are 1.50×10^{-18} and 1.78×10^{-18}. The value found above falls within these limits.

TABLE VIII

Propyl alcohol in benzene. Summary of dielectric constant and density values.

T	$c_2=0$	.01002	.01667	.02205	.02714	.03360	.04402	.05501
10°	2.300 .8897	2.343 .8889	2.374 .8884	2.397 .8880	2.422 .8876	2.449 .8871	2.501 .8864	2.556 .8856
20°	2.280 .8794	2.321 .8786	2.351 .8781	2.373 .8777	2.397 .8773	2.424 .8768	2.475 .8761	2.529 .8753
30°	2.259 .8687	2.298 .8679	2.327 .8674	2.349 .8670	2.372 .8666	2.397 .8661	2.448 .8654	2.501 .8646
40°	2.238 .8579	2.275 .8571	2.303 .8566	2.324 .8562	2.345 .8558	2.370 .8553	2.419 .8546	2.470 .8537
50°	2.217 .8470	2.251 .8462	2.277 .8457	2.297 .8453	2.317 .8449	2.342 .8445	2.388 .8438	2.437 .8429
60°	2.194 .8361	2.227 .8353	2.251 .8348	2.269 .8344	2.289 .8341	2.312 .8336	2.357 .8328	2.404 .8319
70°	2.172 .8251	2.202 .8243	2.225 .8238	2.243 .8235	2.261 .8231	2.281 .8226	2.325 .8218	2.370 .8209

Propyl alcohol in benzene. Solutions of seven different concentrations of iso-propyl alcohol in benzene were studied. Dielectric and density data are collected in Table VIII. The molecular polarizations of the alcohol at various concentrations and temperatures are plotted in Fig. 8.

It should be mentioned here that the author does not consider the dielectric data on propyl alcohol solutions as reliable as that on the other alcohols. Even though an effort was made to remove traces of water from the propyl alcohol, sufficient water remained to cause temporary clouding of the solutions for the higher concentrations. No such clouding occurred in solutions of other alcohols.

Taking A equal to 17.4 from refractive data, values of electric moment u were calculated from the P_0 intercepts at various temperatures; they are shown in column five of Table X. The constancy of u is in agreement with theory. The average moment 1.75×10^{-18} is somewhat higher than the value 1.66×10^{-18} found by Debye,[23] following a similar procedure at a single temperature.

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[23] Marx, Handbuch der Radiologie, **6**, 627 (1925).

In order to avoid taking the constant A from refractive data, values of P_0T were again plotted against T. Straight lines drawn justly through the group of points limit the electric moment to some value between 1.60×10^{-18} and 1.85×10^{-18}. The value found above falls within these limits.

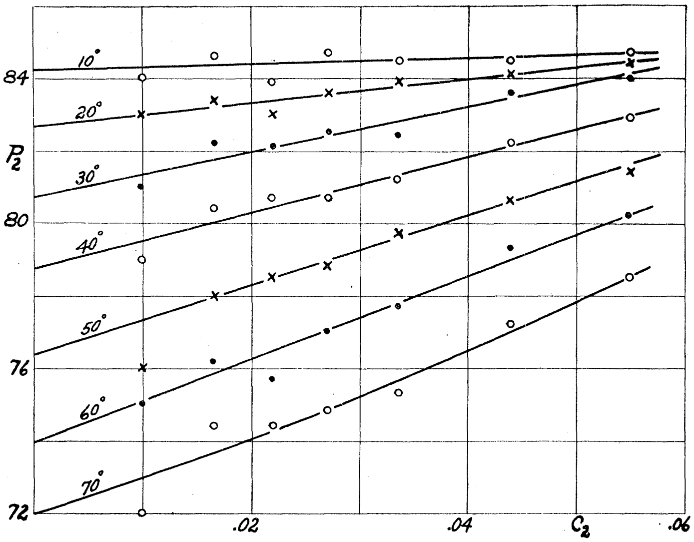

Fig. 8. Polarization curves for propyl alcohol.

Amyl alcohol in benzene. Solutions of eleven different concentrations of iso-amyl alcohol in benzene were studied. Dielectric and density data are summarized in Table IX. The molecular polarizations of the alcohol are plotted in Fig. 9.

Table IX

Amyl alcohol in benzene. Summary of dielectric constant and density values.

T	$c_2=0$	.01028	.01578	.01677	.02261	.02661	.03190	.03662	.04102	.05001	.05906	.06900
10°	2.300 .8897	2.337 .8885	2.357 .8879	2.361 .8877	2.383 .8871	2.398 .8867	2.420 .8861	2.439 .8857	2.457 .8853	2.494 .8846	2.531 .8840	2.573 .8833
20°	2.279 .8794	2.315 .8782	2.334 .8776	2.338 .8774	2.359 .8768	2.374 .8764	2.396 .8758	2.414 .8754	2.432 .8750	2.470 .8743	2.508 .8737	2.550 .8730
30°	2.258 .8687	2.291 .8675	2.310 .8669	2.313 .8667	2.334 .8661	2.349 .8657	2.370 .8651	2.388 .8647	2.406 .8643	2.444 .8636	2.482 .8631	2.525 .8624
40°	2.236 .8579	2.268 .8567	2.286 .8561	2.289 .8559	2.309 .8554	2.323 .8550	2.344 .8544	2.361 .8540	2.379 .8536	2.415 .8529	2.453 .8523	2.497 .8516
50°	2.214 .8470	2.244 .8458	2.262 .8453	2.265 .8451	2.284 .8445	2.298 .8441	2.317 .8435	2.334 .8431	2.351 .8427	2.386 .8420	2.424 .8414	2.466 .8407
60°	2.192 .8361	2.221 .8349	2.237 .8344	2.240 .8342	2.259 .8336	2.272 .8332	2.290 .8326	2.307 .8322	2.323 .8318	2.356 .8311	2.392 .8306	2.433 .8299
70°	2.170 .8251	2.197 .8239	2.213 .8234	2.216 .8232	2.233 .8226	2.246 .8222	2.263 .8217	2.279 .8213	2.294 .8209	2.325 .8202	2.358 .8196	2.396 .8189

Taking A equal to 26.6 from refractive data, values of electric moment were calculated from the P_0 intercepts at various temperatures; they are shown in the last column of Table X. The constancy of the value is in agreement with the demands of the Debye theory. The average moment found is 1.62×10^{-18}.

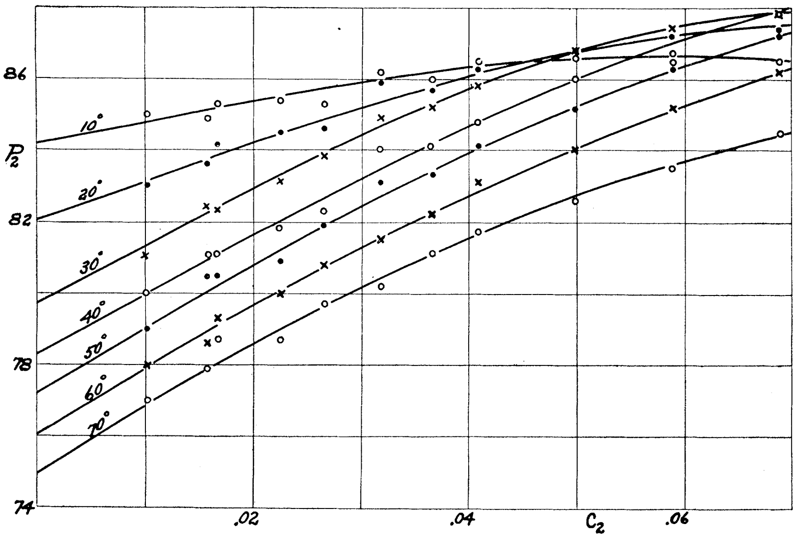

Fig. 9. Polarization curves for amyl alcohol.

In order to avoid taking A from refractive data, values of P_0T were again plotted against T. Straight lines drawn justly through the group of points furnish extreme limits for the moment equal to 1.41×10^{-18} and 1.67×10^{-18}. The value found above falls within these limits.

SUMMARY AND DISCUSSION OF RESULTS

The electric moments of methyl, ethyl, propyl, and amyl alcohol have been determined through a study of dilute solutions of these in benzene, at various temperatures. The moments in each case come out essentially independent of temperature, as is apparent from Table X summarizing results. The

TABLE X

Summary of moments found. The figures given are electric moments times 10^{18}.

T	Methyl alcohol	Ethyl alcohol		Propyl alcohol	Amyl alcohol
10°C	1.64	1.73	1.34*	1.75	1.62
20	1.64	1.73	1.37	1.76	1.62
30	1.64	1.74	1.40	1.76	1.61
40	1.64	1.75	1.42	1.76	1.62
50	1.63	1.75	1.45	1.75	1.62
60	1.62	1.74	1.47	1.74	1.63
70		1.73	1.50	1.74	1.64
Mean	1.64	1.74		1.75	1.62

* Calculated from data on the pure liquid, taking A from refractive data.

independence of moment upon temperature is in agreement with the Debye theory; it is in marked contrast with the variable moments found from data on the pure liquid alcohols; the data therefore lend weight to the supposition that the failure of the simple theory for pure polar liquids is due to association phenomena.

If use of the molecular refraction for the constant A is avoided by plotting P_0T against T, it is apparent that no straight line drawn through any pair of points can lead to an imaginary moment for any of the alcohols studied; data on the pure liquids are known to lead to imaginary moments. If straight lines with the extreme slopes justified by the data be drawn through the group of points for any alcohol, the moment so found is limited to a range whose extremes differ by not more than 20 percent. In every case the moments found through use of the molecular refraction fall within these ranges.

It would be highly desirable to have still more accurate dielectric data over a greater temperature range; this available, the linearity of the P_0T versus T curve could be tested, and the moment could be determined more accurately without making use of the molecular refraction. The greater temperature range might be procured by using a solvent other than benzene. Judging from data here presented, carbon tetrachloride would not be suitable; carbon disulphide or toluene might serve. To define the intercept at any particular temperature more accurately, it is necessary to have dielectric data to more than four significant figures. Two difficulties seem to prohibit this; the first is evaporation of the solute; the second is the formation of vapor bubbles within the liquid in the test condenser at the higher temperatures. Errors due to the first of these could probably be eliminated by suitable precautions. The author found the second difficulty very troublesome. Fortunately, the experimental method was such as to allow rapid adjustment following disappearance of a vapor bubble; the reading corresponding to maximum capacity of the test condenser was taken as that free from the presence of bubbles. Boiling the components of the solution before using eliminated part of the difficulty, possibly by driving off absorbed gases. At best the uncertainty was sufficient to preclude the possibility of obtaining reliable data to more than four significant figures.

Ryerson Physical Laboratory,
University of Chicago,
January 1, 1928.