

THE VARIATION OF DIELECTRIC
CONSTANT WITH FREQUENCYBy J. H. L. JOHNSTONE AND JOHN WARREN WILLIAMS
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ABSTRACT

Measurements of dielectric constants were made of solutions of nitrobenzene and para-dichlorobenzene in mineral oil of high viscosity at three concentrations. A decrease in dielectric constant of nitrobenzene with increasing frequency is found. Para-dichlorobenzene shows no dispersion effect. An approximate value of the relaxation time for nitrobenzene is calculated from the Debye formula after corrections are made for molecular associations. The diameter of the nitrobenzene molecule calculated from it is of the right order of magnitude.

I. THE SYSTEM NITROBENZENE—MINERAL OIL

A DECREASE in the dielectric constant of certain liquids with increase in frequency of the applied field was first observed by Drude¹ and afterward by others.² An explanation of the effect was proposed by Debye³ which can be briefly summarized as follows: A substance containing dipoles will become polarized in an electric field because the dipole molecule is an electric doublet. There will be polarization due to orientation and deformation respectively.

The polarization due to orientation will decrease as the frequency of the field is increased, and will vanish when the frequency becomes sufficiently high. Under the latter condition the dielectric constant of the medium will become equal to N^2 , where N is its refractive index. The transition from orientation to pure distortion should occur in the frequency region V_c defined by the equation $V_c\tau$ where τ is defined by Debye as the time of relaxation of the liquid, i.e., the time required for the molecules to assume random distribution after the field is cut off.

In his theoretical treatment⁴ Debye assumes the molecule to be a sphere, the dilution to be infinite, the inner friction to be the same as the measured viscosity and the Stokes' formula for inner friction to hold true. By the aid of the Einstein theory of the Brownian movement he derives a partial differential equation defining the distribution function of the dipole moments when affected by a field of variable frequency and shows that

¹ Drude, *Zeits. f. Phys. Chem.* **23**, 267 (1897).

² O. v. Baeyer, *Ann. d. Physik* **17**, 30 (1905); F. Eckert, *Verh. deut. physik. Ges.* **15**, 307 (1913); H. Rubens, *ibid.* **17**, 335 (1915); E. F. Nichols and J. D. Tear, *Phys. Rev.* **21**, 587 (1923); J. D. Tear, *Phys. Rev.* **21**, 600 (1923); R. Bock, *Zeits. f. Physik* **31**, 534 (1925).

³ Debye, *Ber.* **15**, 777 (1913).

⁴ Debye, "Polar Molecules," Chemical Catalog Co. N. Y., 1929, chapter V.

$$\tau = \frac{4\pi\zeta a^3}{kT} \quad (1)$$

where τ is the relaxation time, ζ the inner friction coefficient, a the radius of the molecule, k the Boltzmann constant and T the absolute temperature.

If the period of the external field is greater than τ , the dielectric constant of a dipole liquid should have a high and constant value, but as the period of the field approaches τ , there will be a rapid decrease in dielectric constant and for very high frequencies it will become equal to the square of the refractive index of the substance. The effect is then analogous to anomalous dispersion in optics.

The results of several investigations² have indicated a dispersion effect in polar liquids. The most recent work in this field is by Mizushima⁵ and by Kitchin and Müller.⁶ The former measured the dielectric constant of certain alcohols at different temperatures for wave-lengths of 57.8 cm and 3.08, 9.5 and 50 meters respectively and found a dispersion effect with temperature as would be expected from formula (1). Kitchin and Müller measured the dielectric constant and power factor of rosin oils at different temperatures for frequencies of 60, 10⁶, and 10⁷ cycles.

To make a proper test of the dipole theory of Debye it is necessary to study very dilute solutions of a polar substance in a non-polar solvent. This method of procedure is analogous to that which makes possible the determination of the electric moment of a molecule in dilute solution in a non-polar solvent.^{4,7} It is, of course, impossible to determine the electric moment of a molecule from its dielectric constant and density data as a pure liquid or solid. However, if determinations of the dielectric constant are made at different frequencies for different concentrations it is possible to find by extrapolation the critical frequency for infinite dilution. It was therefore decided to arrange experimental conditions to conform as nearly as possible to these requirements. A mineral oil solvent of high viscosity was selected so that dispersion would begin to show at ordinary room temperature for wave-lengths as long as 34 meters. The dielectric constants were measured at one temperature for three different concentrations of nitrobenzene. In this manner it is possible to find the approximate value of the critical frequency at infinite dilution for nitrobenzene.

2. EXPERIMENTAL METHOD

A simple resonance circuit was used to measure the dielectric constant of solutions of nitrobenzene and of a solution of para-dichlorobenzene in mineral oil. Two variable standard air condensers and a variable experimental condenser or dielectric cell were connected in parallel. The high frequency current in each case was supplied by a quartz crystal oscillator. The wiring diagram is shown in Figure 1. Three different crystals were used in the oscillat-

⁵ Mizushima, Sc. papers Inst. of Phys. & Chem. Res. Japan, **5**, 79, 201, and **9**, 166, 209.

⁶ Kitchin and Müller, Trans. A.I.E.E. **48**, 2, 495. Phys. Rev. **32**, 979 (1928).

⁷ Williams, Phys. Zeits. **29**, 174, 204, 683, (1929).

ing circuit, so that by the use of the fundamentals and second harmonics six wave-lengths were made available for measuring dielectric constants, viz. 154, 98, 77, 68, 49, and 34 meters. Wave-lengths were measured by standard wave meters. Detection of resonance was made by a vacuum tube voltmeter which was found to have advantages as compared with a vacuum thermocouple. All the apparatus was inclosed by an earthed screen. Values of the dielectric constants were also determined by means of a heterodyne heat method previously described by one of us⁸ at 300 and 150 meters respectively. A capacity bridge built by the General Radio Company, Cambridge, Mass. was used for measurements at 1000 cycles.

The following procedure was followed in the determination of a dielectric constant: The dielectric cell was calibrated by measuring its capacity when its plates were covered with carefully purified benzene. The benzene was assumed to have a dielectric constant of 2.280 at 25°C.

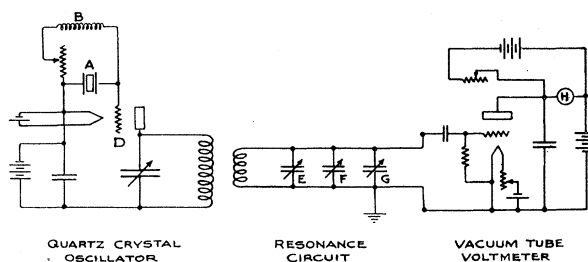


Fig. 1. Wiring diagram. A, quartz crystal; B, 60 M.H. choke; D, PT-210 piotron; E-G, standard condenser; F, test condenser.

The test condenser was filled with benzene and the scale set at zero. The circuit was then brought to resonance by adjusting one of the standard condensers and the reading on the latter noted. The test condenser was then set at 20.0 on the scale and resonance obtained as before. The difference in readings of the standard condenser is the capacity change of the test cell between 0 and 20 on its scale. The test cell is then filled with the liquid of unknown dielectric constant and the same procedure is followed. This method of measurement, already described in the literature,⁹ possesses the great advantage, that it is not necessary to make any correction for the capacity of the lead wires. The error involved in capacity measurement is 1 percent, so that the error in each dielectric constant is of the order of magnitude of 2 percent.

The dielectric constants for each of the solutions studied were measured at 154, 98, 77, 68, 49 and 34 meters respectively and at 25°C. Dielectric constants of benzene and of the mineral oil base were also measured at the different wave-lengths and the values obtained were found independent of wave-length, which is to be expected as they are non-polar liquids. Viscosity

⁸ Williams, Jr. Amer. Chem. Soc. **49**, 1676 (1927), **50**, 2332 (1928).

⁹ Williams and Krchma, Jr. Amer. Chem. Soc. **48**, 1888 (1926).

measurements were made with a Stormer viscosimeter. The refractive indices of the different solutions were measured by an Abbé refractometer.

It would be desirable to have measurements of the dielectric constants of the solutions at shorter wave-lengths than was possible using the quartz crystal controlled oscillators, in order to determine completely the dispersion curve. In the time at our disposal it was not possible to make measurements at shorter wave-lengths. However, in the curves to be presented the approximate courses of the lines from the 34 meter point to the value of the dielectric constant as calculated from the refractive index are shown drawn in dotted line.

As has already been indicated the advantage of working with dilute solutions of a polar liquid in a non-polar solvent is that any effect of molecular associations can be eliminated by an extrapolation to infinite dilution. Another advantage of the method used is that by working at a single temper-

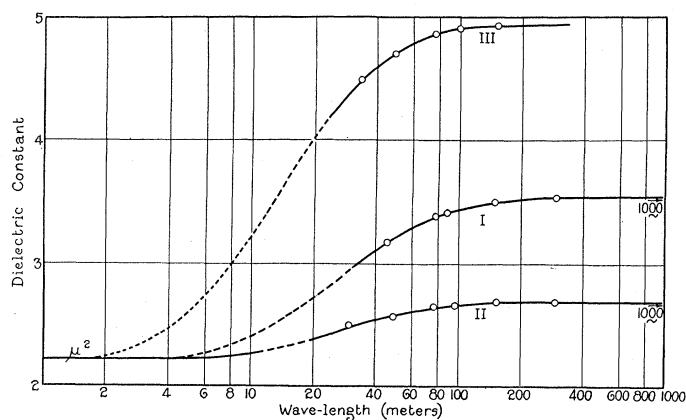


Fig. 2. Variation of dielectric constant with frequency.

ature no corrections will have to be applied because of change of dielectric constant due to density variation with temperature. Correction for the latter effect does not seem to have been made in the work of Mizushima and of Kitchin and Müller, and these investigators, as well as their predecessors, did not work with dilute solutions.

Ordinarily the dielectric constant of a liquid or of a solution decreases with increasing temperature. In the region of anomalous dispersion, however, for a given frequency the dielectric constant will increase as the temperature increases. Therefore, the curve obtained in this region will be the resultant of the two effects, and the dielectric constant curve over a considerable range of temperature for a constant frequency will pass first through a minimum and then through a maximum. Such curves were actually obtained by us, but the correction for the change due to the simple density effect could only make the results more uncertain. It must be pointed out that the formulae of Debye are applicable to experiments at constant temperature with vari-

able frequency, and cannot apply directly to experiments made at constant frequency with variable temperature.

3. RESULTS

The results of the experimental work are given in Figure 2, where curves I, II, and III have been constructed from the data of Tables II, III, and IV. Table I gives the results of measurements made upon the mineral oil base. Table V gives the results of a similar set of measurements upon a solution of para-dichlorobenzene, a non-polar substance, dissolved in the mineral oil base.

TABLE I. *Mineral oil base. 25.5°C. Viscosity 28.7 poises.*

Wave-lengths (meters)	Dielectric Constant
3×10^7	2.13
93	2.16
32	2.15

TABLE II. *20.4 gr. nitrobenzene per 100 gr. of oil. Temp. 25.5°C: $n=1.488$ (Refractive Index). Viscosity 7.7 poises.*

Wave-lengths (meters)	Dielectric Constant
154	4.94
98	4.91
77	4.87
49	4.70
34	4.50
n^2	2.22

TABLE III. *3.2 gr. Nitrobenzene per 100 gr. of oil. Temp. = 23.5°C. Viscosity 23.0 poises.*

Wave-lengths (meters)	Dielectric Constant
3×10^7	2.65
300	2.68
154	2.69
98	2.66
77	2.65
49	2.57
34	2.50

TABLE IV. *9.5 gr. Nitrobenzene per 100 gr. mineral oil. Temp. 25°C. $n=1.485$. Viscosity 13.0 poises.*

Wave-lengths (meters)	Dielectric Constant
3×10^7	3.60
300	3.55
154	3.50
77	3.38
46	3.17
n^2	2.20

TABLE V. *10 gr. para-dichlorobenzene in 100 gr. of oil.*

Wave-lengths (meters)	Dielectric Constant
154	2.29
77	2.33
34	2.32

From curves I, II, and III approximate values for the wave-lengths at which maximum absorption takes place in the different solutions were then found by noting the points of inflection of the different curves. The values so found were then corrected for the viscosity of the particular solution as

compared with that of the mineral oil base since, the nitrobenzene when dissolved in it materially lowers the viscosity of the medium. Since an extrapolation to infinite dilution is to be made, the critical wave-lengths should be adjusted to the viscosity of the medium. The corrected wave-lengths were then plotted against the concentrations of nitrobenzene in the mineral oil base, and by extrapolation of this curve to zero concentration there was obtained the wave-length (or frequency) at which maximum absorption for infinite dilution takes place. This extrapolation is shown in Fig 3, Curve IV.

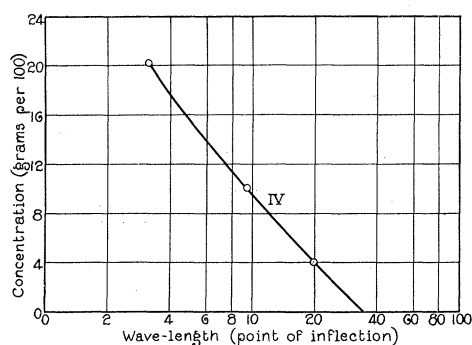


Fig. 3.

It is important to note, Table V, that the dielectric constant of a solution of a non-polar solute, para-dichlorobenzene, in the mineral oil base was constant, within the limits of the experimental error. Since para-dichlorobenzene is a molecule of the same size as nitrobenzene and the solution studied had a viscosity comparable to that of the nitrobenzene solutions, it indicates that the dispersion of the dielectric constant which is the subject of this article is actually caused by the orientation of polar molecules in the field.

4. DISCUSSION OF RESULTS

If the extrapolated value of the wave-length for infinite dilution be changed to its proper frequency and the result substituted in formula (1) the value for the diameter of the nitrobenzene molecule is found to equal 4.8×10^{-8} cm. X-ray studies of carbon compounds indicate the diameter of the nitrobenzene molecule to be between 6×10^{-8} and 8×10^{-8} cm. It is evident then, that the Debye formula when applied to these experiments gives values of the right order of magnitude. However, the evidence from the present experiments is not sufficient to draw definite conclusions as to whether or not the Debye formula in its present form is correct.

The values of molecular radii calculated by Mizushima from his dispersion experiments agree well with those determined by other methods except in the case of glycerine. The calculated radius of the latter molecule, viz. 2.8×10^{-9} cm is obviously much too small. Bock¹⁰ also finds that the Debye

¹⁰ Bock: Zeits. f. Physik 31, 534 (1925).

formula apparently does not hold in the case of glycerine. The suggestion is made that as the viscosity of glycerine is abnormally great, it is very doubtful if ζ in the Eq. (1) is the true inner friction coefficient. Even if corrections could be made for viscosity effects, differences between the actual and experimentally determined molecular radii would probably exist because the above mentioned experiments have not been designed to eliminate the effects due to associations and segregations of molecules. In addition to this, the Debye formula is derived on the basis of the following assumptions which may or may not effect the case under discussion.

I. The molecules are spheres (glycerine molecules must be very irregular in shape).

II. The Stokes' expression is correct for a molecule rotating in a viscous medium consisting of molecules of other odd shapes.

Kitchen and Müller calculate the relaxation time from power factor measurements on wood rosin, mineral oil, and castor oil, instead of using dielectric constant measurements. It appears that their molecular diameters should be larger than they have reported. The formula used by Kitchin and Müller (See also Kitchin *Trans. A. I. E. E.* **48**, 495, (1929)) differs by a factor 2π from formula (1). Using formula (1) the value of the radius of rosin becomes 8×10^{-8} cm instead of 4.8×10^{-8} cm as reported. The value for the radius of castor oil given is 2×10^{-8} cm, and it should be increased by a corresponding amount. Even making these corrections the present authors can not agree with the statement, "The fact that these results are comparable with molecular sizes obtained by entirely different method (x-rays, spreading of oil films, etc.) gives a striking proof of the fundamental correctness of the orientation theory." These substances, rosin and castor oil, in addition to not being pure chemical compounds, consist of molecules containing between eighteen and twenty carbon atoms. One would expect, therefore that their radii would be of the order of magnitude 20×10^{-8} cm to 30×10^{-8} cm.

Mizushima's calculated values of molecular radii for molecules in liquids of low viscosity agree well with the values obtained by other methods. However, if corrections are made for association the calculated radii would be larger. The same considerations apply to the results of Kitchin and Müller.

The Debye theory of dipoles is also of interest from the standpoint of dielectric losses in insulating materials. The problem of the heating of dielectrics in rapidly alternating fields has long engaged the attention of many investigators. It has been assumed by some that power losses are due to so-called dielectric hysteresis and that Joule's law does not apply. Joffé¹¹ and his co-workers have shown that if Joule's law be properly applied it satisfactorily explains the dielectric losses in the substances they have examined. One of us (J. H. L. J.) when working with conducting liquids in high frequency fields, found that the major part of the heat developed in the liquids could be explained on the basis of an RI^2 loss. However, it is probable that a part of the losses are due to dissipation of energy during dipole orientations

¹¹ Joffé, "Physics of Crystals," McGraw-Hill Book Co., 1928, pg. 144.

and a careful investigation should be made of this point. A rough calculation of the heat losses due to dipole orientation can be made. The orientation energy of nitrobenzene molecules for a frequency 10^7 cycles per second would be 5×10^8 clas. per sec. per cubic centimeter, provided all the molecules were oriented. This orientation energy is given by the quantity μF where μ = electric moment of the molecule, and F = field strength of 300 volts per cm. However, only the fraction

$$e^{-\mu F / KT} = 2.5 \times 10^{-6}$$

are oriented, so that the energy dissipation per sec. per cubic centimeter would be approximately 1×10^{-2} cal.

When dielectrics such as water containing ions are placed in a high frequency field it is found that the resulting power losses are very much greater than the value calculated assuming that dipole orientation is the cause of the heating effect. It would appear, therefore, that the contribution of dipole orientation to the dielectric loss in such cases is negligible.

The work is being extended and continued.