The Frequency Variation of the Dielectric Constant of Dilute Non-Aqueous Solutions*

J. L. ONCLEY[1] AND JOHN WARREN WILLIAMS, *Laboratory of Physical Chemistry, University of Wisconsin*

(Received November 26, 1932)

For systems containing polar molecules it has been found that there is a wave-length region in which the dielectric constant decreases with increasing frequency. This wave-length region, dependent upon the size of the orienting molecule and the viscosity of the medium, determines a time of relaxation for the polar molecules which has been evaluated by Debye using the law of Stokes for the rotation of a particle in a viscous medium. The purpose of the present research is to test the dipole theory by making measurements of the frequency variation of the dielectric constant for viscous solutions of various polar substances in nonpolar solvent media. To this end it was necessary to devise an accurate method of measurement for the dielectric constant of a liquid system at frequencies as high as 2×10^7 cycles per second. The apparatus used is briefly described. The dielectric constants of rosin solutions in mineral oils of varying viscosity are tabulated and calculations for the inner-frictional constant for these systems are made. The effect of viscosity upon the behavior of mixtures of "floricin," paraffin oil and vaseline is also investigated. It is found to have little effect, a fact of considerable interest with regard to the inner structure of these solutions. An explanation for the failure to observe an expected dispersion in several experiments is attempted. The comparison of the experimental results with the requirements of the Debye theory leads to several interesting conclusions. There are objections to the use of the ordinary coefficient of viscosity of the medium to measure the frictional resistance to the rotation of a molecule when the discontinuities of the fluid are large compared with the size of the rotating particle and probably in other cases as well. Calculations from the experimental data make possible a differentiation between systems in which the suspended particles are all of one size or monodisperse, and in which they are polydisperse. Finally, there is suggested the type of experiment which must be made if a quantitative verification of the theory is sought.

INTRODUCTION

DRUDE[2] was the first to observe an anomalous dispersion in liquids with short radio waves when he found that many polar substances, such as propyl alcohol, glycerol, etc., showed a decrease in dielectric constant with increasing frequency. Since that time other investigators have made similar observations. However, an explanation of this dispersion was not given until 1913, when Debye[3] attributed it to a transition from the combined effect of deformation and orientation of polar molecules to the effect of the deformation alone. When both deformation and orientation contributions are operative, that is, when the dipoles are swinging with the applied field, the maximum or static dielectric constant is obtained. As the frequency of the applied field is increased the inner-frictional forces between the molecules become effective, and there is produced a phase retardation between the orientation and the applied field. The less complete orientation of the dipoles results in a lower value for the dielectric constant, and an absorption of energy due to this phase difference. When the frequency is increased still further the time between periods becomes so small that no orientation can occur, thus we have only the deformation or distortion effect due to the applied field, resulting in the low, or "optical" dielectric constant. Debye further pointed out that the dispersion caused by this transition will fall in a frequency region determined by the size of the orienting molecule and the frictional constant of the medium. The equation obtained for the dispersion region is

$$0.1<\chi<10, \tag{1}$$

where

$$\chi=[\pi\zeta\nu(\epsilon_0+2)]/[kT(\epsilon_\infty+2)]. \tag{2}$$

In this equation, ϵ_0 is the dielectric constant at

* This article comprises a portion of a thesis presented by J. L. Oncley to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1932.

[1] Charles A. Coffin Fellow in Chemistry, 1931–32.

[2] Drude, Zeits. f. physik. Chemie **23**, 267 (1897) and other references.

[3] Debye, Ber. deut. physik. Ges. **15**, 777 (1913).

zero frequency, ϵ_∞ is the dielectric constant at infinite frequency, k is the Boltzmann constant $=1.37\times10^{-16}$, T is the absolute temperature, ν is the electric frequency in cycles per second, ζ is the "inner-frictional constant," which, when Stokes' law can be applied, is equal to $8\pi\eta r^3$, η is the viscosity of the solution, and r is the particle radius. According to this theory a simple polar molecule, or a monodisperse colloid, should give curves of the forms (a), (b) and (c) of Fig. 1; curve (a) being obtained when we plot the real (observed) dielectric constant (ϵ') against the logarithm of the frequency (log ν), curve (b) when we plot the imaginary dielectric constant (ϵ''), obtained from absorption measurements, against log ν, and curve (c) when we plot the power factor (sin $\tan^{-1}\epsilon''/\epsilon'$) against log ν. If the system is polydisperse, we should find that these curves become flattened out, and that they may be regarded as the result obtained when the simple curves for several particle sizes are added together. Curves of this type are shown by (d), (e) and (f), also of Fig. 1.

The verification of this theory is as yet quite incomplete. Measurements recorded in the literature are sometimes of insufficient accuracy for the purpose because of the unusual experimental difficulties which present themselves, while in other cases the systems studied have hardly conformed to assumptions underlying the theoretical treatment of the problem. Space does not permit review of or even reference to these researches which have been carried out with pure liquids of known chemical composition, articles of commerce such as transformer oils and rubber, and dilute solutions of polar substances in nonpolar solvent media.

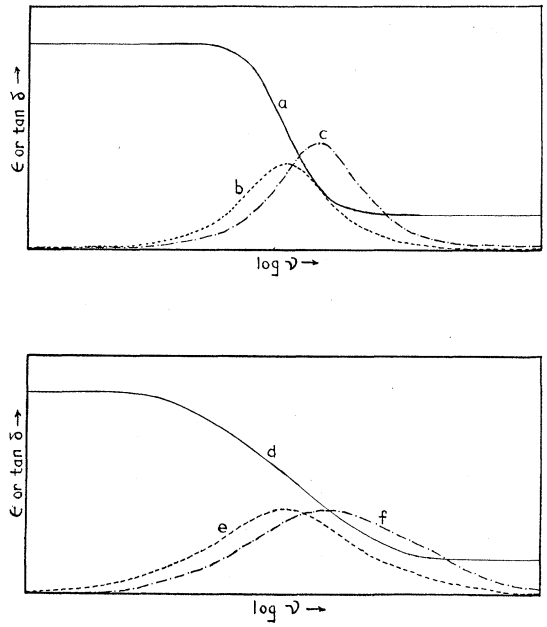

FIG. 1.

The present research was undertaken with the object of finding out what information could be obtained by making accurate measurements of the dielectric constants of viscous solutions of various polar substances in nonpolar solvents. It was decided that the limiting wave-length at which sufficient accuracy could be obtained was about 15 meters. According to the equations of Debye, the frequency ν_c at which the center of the dispersion occurs can be decreased by increasing the inner-frictional constant ζ. If Stokes' law can be applied, this inner-frictional constant is proportional to the viscosity η and to the third power of the radius, r. Accordingly, we should expect a sufficiently high viscosity or a sufficiently large radius to decrease the frequency ν_c until it would fall below 2×10^7 cycles per sec. ($\lambda=15$ meters). When ν_c is found, the value of the inner-frictional constant ζ should be amenable to calculation thus giving a true measure of the friction between solute and solvent molecules or what we may term the "microscopic" viscosity. This microscopic viscosity may then be compared with macroscopic viscosities measured according to well-known procedures.

THEORY

The theory of Debye has been given in detail before,[4] so it will be omitted. Here it is sufficient to say that it leads to the following two equations:

$$\epsilon_{12}' = \epsilon_{12}(\infty) + (\epsilon_{12}(0) - \epsilon_{12}(\infty))/(1+\chi^2), \quad (3)$$

$$\epsilon_{12}'' = \chi[\epsilon_{12}(0)\cdot\epsilon_{12}(\infty)]/(1+\chi^2). \quad (4)$$

In these equations, the subscripts 1 and 2 refer to solvent and solute, respectively, and the subscript

[4] Debye, *Polar Molecules*, Chem. Cat. Co., New York, 1929. It is also reviewed, together with its application to dilute solutions, by Williams and Oncley, Physics 3, 314 (1932).

12 to the binary mixture,

$$\chi = 2\pi\nu\tau_2[\epsilon_{12}(0)+2]/[\epsilon_{12}(\infty)+2],$$

$\tau_2 = (\zeta/2kT)$ is the "time of relaxation" of the polar molecules, which is the time required for $1/e$ of the polar molecules to assume a random distribution after an applied static field has been removed, $\epsilon_{12}(0)$ is the dielectric constant of solution at very low frequencies, $\epsilon_{12}(\infty)$ is the dielectric constant of solution at very high frequencies, $\epsilon_{12}' = \epsilon_{12}'(\nu)$ is the observed ("real") dielectric constant of solution at a frequency ν, $(=[C/C_0] \times[1/(1+4\pi^2\nu^2R^2C^2)])$, $\epsilon_{12}'' = \epsilon_{12}''(\nu)$ is the imaginary dielectric constant of the solution at a frequency ν, $(=[C/C_0][2\pi\nu RC/(1+4\pi^2\nu^2R^2C^2)])$, ζ is the "inner-frictional constant" which, when and if Stokes' law can be applied, is equal to $8\pi\eta r^3$, η is the ordinary macroscopic coefficient of viscosity of the solution, r is the radius of the polar molecules or particles, k is the Boltzmann constant, T is the absolute temperature, ν is the electrical frequency in vibrations per second, C is the pure capacity of cell filled with solution, R is the pure series resistance of cell filled with solution, and C_0 is the capacity of cell in vacuum.

Since each solution has different values of $\epsilon_{12}(0)$ and $\epsilon_{12}(\infty)$, it was found that the calculations could be much simplified by the use of two new functions Δ and Γ, instead of ϵ' and ϵ'', where

$$\Delta = (\epsilon_0 - \epsilon')/(\epsilon_0 - \epsilon_\infty) = \chi^2/(1+\chi^2) \qquad (5)$$

and

$$\Gamma = \epsilon''/(\epsilon_0 - \epsilon_\infty) = \chi/(1+\chi^2). \qquad (6)$$

Further, we have

$$\log\chi = \log\{[\pi(\epsilon_0+2)]/[kT(\epsilon_\infty+2)]\} + \log\zeta + \log\nu. \qquad (7)$$

Now if we plot Δ or Γ against $\log\chi$ we should always arrive at the same form of curve, with changes in ϵ_0, ϵ_∞, and ζ (or τ) causing only a shift of the whole curve along the $\log\chi$ axis. The Δ and Γ curves will have the same general shape as curves *a* and *b* of Fig. 1.

Any monodisperse system (that is, any system with a single value for ζ or for τ) which follows the Mosotti hypothesis should give a curve of this type. Deviations from such a curve can be attributed either to aggregation of the molecules to form polydisperse systems, thus causing several different relaxation times, or to failure for the electrical conditions assumed in the derivation of the Mosotti hypothesis to be satisfied. Thus an extrapolation of deviations from this curve against concentration should give zero as its result. This method has the decided advantage of not employing the molecular weight of either solute or solvent in the calculation—a fact which is of particular use since the molecular weight of the solvent, usually some mineral oil mixture, may be unknown. The calculation of ϵ_2 from ϵ_{12} must involve this molecular weight if it is to be accurate, since the polarization is a partial molar quantity.

It can be seen from Eqs. (3) and (4) that the imaginary dielectric constant will be a maximum, and that the real dielectric constant will take on a mean value at the point where $\chi = 1$. When this is true,

$$[\pi\zeta\nu_c(\epsilon_0+2)]/[kT(\epsilon_\infty+2)] = 1, \qquad (2a)$$

and the critical frequency ν_c is thus given by

$$\nu_c = \frac{\epsilon_\infty+2}{\epsilon_0+2}\frac{kT}{\zeta\pi} = \frac{\epsilon_\infty+2}{\epsilon_0+2}\frac{1}{2\pi\tau}$$

or

$$\nu_c\tau = (\epsilon_\infty+2)/[2\pi(\epsilon_0+2)].$$

After finding this point ν_c where $\chi = 1$, we can calculate ζ from Eq. (2a), since ϵ_0, ϵ_∞, and ν_c are all known. Thus one of the possible applications of these data, which will be discussed further at a later point, is to find this inner-frictional constant, or "microscopic viscosity," ζ.

The Debye theory is not the only theory which accounts for an anomalous dispersion of the dielectric constant and an absorption of energy. However, for the most part, the other theories have been proposed to account for the behavior of complex dielectrics at much lower frequencies. It is well to mention that each of these theories leads to equations of the form

$$\epsilon' = \epsilon_\infty[1+k/(1+4\pi^2\nu^2\tau'^2)] \qquad (8)$$

and

$$\epsilon'' = 2\pi k\nu\tau'\epsilon_\infty/(1+4\pi^2\nu^2\tau'^2), \qquad (9)$$

where ϵ_∞, k, and τ' are given as functions of various measurable quantities, and differ in the

various theories.[5] Gemant[6] has shown that one obtains these equations by simply assuming that the replacement of the equilibrium, when an electrical field is impressed, is an exponential function of the time, thus we have the equation

$$D=\epsilon_\infty(1+k)E-\epsilon_\infty k e^{-(t-t')/\tau'}E, \qquad (10)$$

relating the electric displacement D at the time t to the electric intensity E. Here $\epsilon_\infty(1+k)=\epsilon_0$, τ' is the "time-constant" (or time of relaxation) upon whose value depends the time for equilibrium to be established, and t' is the time at which the field E is applied. This signifies that the displacement at the moment the field is impressed ($t=t'$) is given by $D=\epsilon_\infty E$, and at an infinitely long time ($t=\infty$) by $D=\epsilon_\infty(1+k)E=\epsilon_0 E$.

Thus, any of the important theories of dielectric absorption lead to the same form of frequency dependence of the complex dielectric constant. Accordingly, it can be seen that the only way in which any of these theories can be proved is by the accurate determination of the constants τ', k and ϵ_∞ involved in Eqs. (8) and (9), and subsequent comparison of their values with those calculated by the various theories. Obviously this can only be done for very simple mixtures of pure substances of known composition.

It should be mentioned here that for the most part the Debye theory accounts for losses at very high frequencies (10^8–10^{12} cycles per second), while the others account for losses at much lower frequencies (1–10^6 cycles per second). However, scanty experiments over these ranges indicate that no sharp transition from one region to the other occurs, and that very probably only one absorption region is to be found. Support for the Debye theory may be obtained in that, following arguments based upon the same type of dipole structure, many other effects can be explained. Thus, the data obtained by studies of the Kerr effect, the Stark effect, the infrared rotation bands, and the electric moments of molecules all indirectly support this theory of dielectric absorption of Debye.[7]

Apparatus

The dielectric constants were obtained by determining the capacity of a calibrated cell by means of a modified heterodyne method. The circuit used is given in Fig. 2, and consists of a quartz controlled oscillator and an oscillating detector with one stage of amplification. The quartz crystal vibrated with a fundamental frequency of 1918.9 kilocycles per second ($\lambda=156.2$ meters), and harmonics up to the tenth were present with sufficient intensity to be easily received and used for measurements. The use of the quartz crystal was necessary to insure the stability of frequency in the oscillating circuit. The resonance circuit contained four condensers; an ordinary variable air condenser with which the frequency was adjusted to approximately the proper value, an accurately calibrated standard condenser with a capacity of from 10 to 27 $\mu\mu$f and reading to 0.0066 $\mu\mu$f, a comparison condenser C_4 whose fixed capacity is approximately that of C_x, and a cell C_x into which the solutions were pipetted for the dielectric constant measurements, shown in Fig. 3.

Measurements were made by determining the capacity difference x between C_x and C_4. If the cell is previously calibrated with air and benzene as standards for comparison we can calculate the dielectric constant ϵ of the solution from this difference x in the following manner:

$$\begin{aligned}
&C(\text{air})=C'+C''=C_4+a,\\
&C(\text{benzene})=2.280\times C'+C''=C_4+b,\\
&C'=(b-a)/1.280,\\
&C''=C_4-(b-2.280a)/1.280,\\
&C(\text{unknown})=\epsilon C'+C''=C_4+x,\\
&\epsilon=(C_4-C''+x)/C'=(b-2.280a)/(b-a)\\
&\qquad +1.280x/(b-a)=\alpha+\beta x, \qquad (11)
\end{aligned}$$

where C'' and C' are the fixed and variable portions of cell capacity, respectively, and here equal to approximately 4.9 and 6.1$\mu\mu$f, C(air), C(ben-

[5] Debye's equations (Eqs. (3) and (4)) also reduce to this form, in which case

$$\tau'=\tau(\epsilon_0+2)/(\epsilon_\infty+2) \qquad k=(\epsilon_0-\epsilon_\infty)/\epsilon_\infty \qquad \epsilon_\infty=\epsilon_\infty.$$

[6] Gemant, *Elektrophysik der Isolierstoffe*, J. Springer, Berlin (1930).

[7] For a discussion of such studies, see Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford Press (1932).

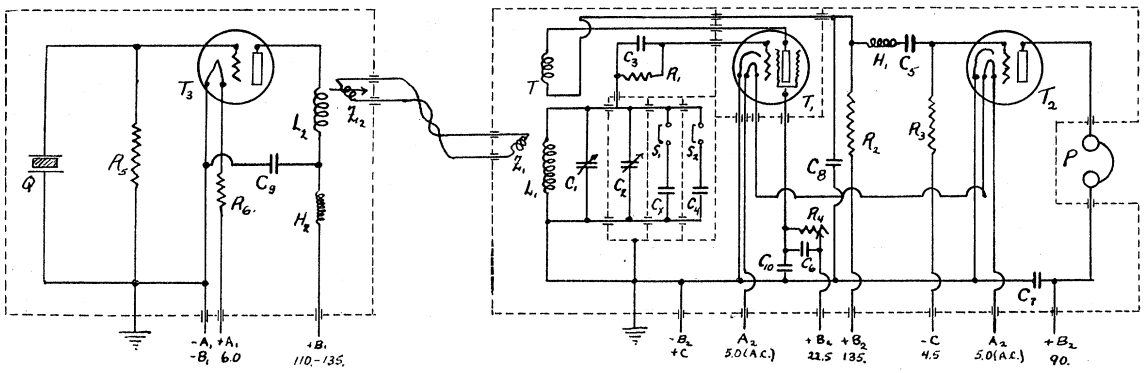

FIG. 2.

C_1 —150$\mu\mu$f variable condenser
C_2 —standard variable condenser
C_3 —250$\mu\mu$f fixed condenser
C_4 —comparison condenser
C_5 —250$\mu\mu$f fixed condenser
C_6 —0.5$\mu\mu$f fixed condenser
C_7 —0.5μf fixed condenser
C_8 —200$\mu\mu$f fixed condenser
C_9 —0.001μf fixed condenser
C_{10}—0.5μf fixed condenser
C_x —cell
H_1 —radiofrequency choke coil
H_2 —radiofrequency choke coil
L_1 —interchangeable inductance coil
L_2 —honey-comb coil tuned to crystal frequency
P —head-phones, 2000 ohms resistance
Q —quartz crystal
R_1 —5×10^6 ohm resistance
R_2 —2.5×10^5 ohm resistance
R_3 —2×10^6 ohm resistance
R_4 —1×10^5 ohm variable resistance
R_5 —2×10^5 ohm resistance
R_6 —5 ohm resistance
S_1 —mercury switch
S_2 —mercury switch
T —tickler coil
T_1 —UV234 vacuum tube
T_2 —UV227 vacuum tube
T_3 —UV171A vacuum tube
Z_1 —pick-up coil
Z_2 —pick-up coil

Batteries as follows:
A_1 —6 volts (storage cells)
A_2 —5 volts a.c. (from transformer)
B_1 —135 volts, or 110 d.c. line
B_2 —135 volts, tapped at 22.5 and 90 volts
C —4.5 volts

zene), and C(unknown) are the capacities of the cell when filled with air ($\epsilon=1$), benzene ($\epsilon=2.280$), and unknown ($\epsilon=\epsilon$). C_4 is the capacity of the comparison condenser, here equal to approximately 17.6$\mu\mu$f, a is the difference in vernier condenser reading (in arbitrary units) when C (air) replaces C_4, b is the difference when C(benzene) replaces C_4, x is the difference when C(unknown) replaces C_4, $\alpha=(b-2.280a)/(b-a)$, and $\beta=1.280/(b-a)$. The accuracy of these measurements, about 1 part in 1000, can be judged from the data of Table I. No corrections for absorption were necessary. Some measurements were also made at two other frequencies, 1000 cycles and 611.1 kilocycles ($\lambda=490.6$ meters), in which cases the customary bridge and resonance methods were used.

The refractive indices were measured with a Pulfrich refractometer in nearly all cases, for the yellow helium line (5876A). In some cases the solutions were not sufficiently clear for this instrument to be used, so that an Abbe refractometer had to be substituted.

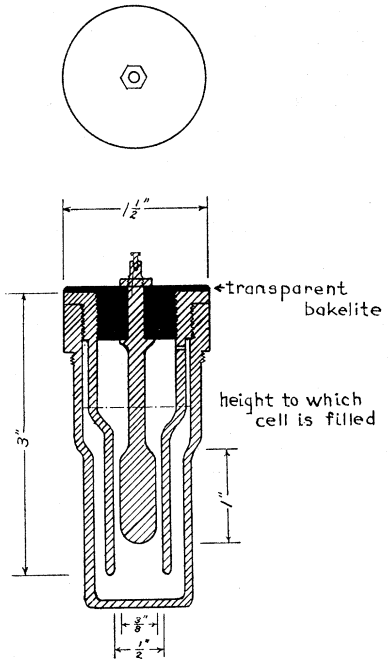

FIG. 3.

The temperature of the cell and of the air used to control the temperature of the crystal oscillator was regulated by means of a thermostat maintained at 25°C. Refractive indices and viscosities were observed at the same temperature. The viscosities were determined by means of a Stormer viscometer, manufactured by the Arthur H. Thomas Company. In this type of instrument the time for 100 revolutions of a cylinder is taken, and from this the viscosity is calculated. The instrument was calibrated by means of sugar solutions of known viscosity.[8] The accuracy of the viscosity determinations was about 5 percent, except in the case of some gels which gave no definite values.

Experimental Data

The experimental results obtained are presented in Tables I–V, inclusive. Table I contains

Table I. *Dielectric constant data for liquids used in this investigation.*

Exp. No.	Substance	ϵ' $\lambda = 156.2$ m	$= 78.12$ m	$= 39.06$ m	$= 26.04$ m	$= 17.36$ m	mean	n^2
1	Paraffin oil	2.196	2.195	2.196	2.194	2.193	2.194	2.194
2	Finoil	2.154	2.151	2.152	2.154	2.154	2.153	2.146
3	Vaseline	2.079	2.079	2.078	2.078	2.078	2.078	2.190
4	Kerosene	2.138	2.134	2.135	2.135	2.134	2.135	2.100
5	Oleic acid	2.507	2.506	2.507	2.505	2.502	2.502	2.122
6	Carbon tetrachloride	2.244	2.243	2.245	2.241	2.246	2.244	2.130
8	Benzene	2.280	2.280	2.280	2.280	2.280	2.280	2.240

dielectric constant data for the solvents used in this investigation, in addition to those for several other substances. These data have the double purpose of testing the purity of the materials[9] used and the accuracy of the apparatus. The results show that the apparatus is capable of an accuracy of approximately 0.1 percent. The values for benzene are assumed. The values for kerosene seem too high when compared to the square of the refractive index n^2. This is probably caused by the presence of traces of polar substances in the commercial oil. Likewise the values for vaseline seem too low, but this is probably due to an error introduced when the cell is filled with a given volume of melted vaseline and then allowed to cool and contract. Otherwise the agreement is very good.

Table II gives results for various solutions of polar molecules dissolved in mineral oils of high viscosity. With the exception of certain cases in which the No. 5182 cable compound[10] was used as a part of the solvent the dielectric constant is constant over the frequency region studied. The significance of these results will be discussed in the next section.

Table III presents data for solutions of rosin in solvents of various viscosities. The purpose of this particular series of measurements was to study the effect of a viscosity change. The work is somewhat incomplete because of a difficulty in the reproduction of results, probably caused by an oxidation or polymerization of the rosin. The rosin used was of a very high grade, and was finely powdered and added to the hot solvent. When it was practically all dissolved the solution was cooled and filtered through ordinary filter paper under suction. The resulting solution was clear and contained no suspended particles visible to the eye. However, upon standing, a heavy layer of light powder was precipitated and showed that some change was taking place. Further discussion of these results is given later.

Table IV indicates the type of the experiments made upon solutions of "floricin" in oils of various viscosity. Floricin is an oil obtained by distilling castor oil (in this case a U.S.P. grade from Schieffelin and Company) at 300°C until it has lost about 10 percent of its weight. It is a

[8] Data of Bingham and Jackson, Int. Crit. Tab. V, McGraw-Hill Book Company, New York (1926).

[9] Wherever possible the chemicals used were subjected to rigorous purification.

[10] Obtained from the Research Laboratory of the General Electric Company, Schenectady, N. Y.

TABLE II. *Dielectric constant data for systems of polar molecules dissolved in mineral oils.*

Exp. No.	Composition	ϵ' $\lambda = 156.2$ m	$= 78.12$ m	$= 39.06$ m	$= 26.04$ m	$= 17.36$ m	mean	n^2
9	2.6% Nitrobenzene 97.4% Paraffin oil ($\eta = 1.0$)	2.542	2.543	2.543	2.547	2.544	2.544	2.198
10	2.5% Nitronaphthalene 97.5% Paraffin oil ($\eta = 1.05$)	2.435	2.437	2.440	2.440	2.438	2.438	2.204
11	7.4% Oleic acid 92.6% Paraffin oil ($\eta = 0.9$)	2.202	2.202	2.202	2.207	2.205	2.203	2.190
12	26.9% Camphor 73.1% Paraffin oil ($\eta = 3.5$)	3.833	3.839	3.840	3.840	3.847	3.840	2.280
14	7.1% Stearic acid 92.9% Paraffin oil ($\eta > 100$)	2.158	2.157	2.160	2.161	2.156	2.158	2.194
15	4.0% Nitrobenzene 20.0% Vaseline 76.0% Paraffin oil ($\eta > 100$) (Temp. = 6°C)	2.933	——	——	——	2.929	2.931	——
16	3.3% Nitronaphthalene 3.4% Vaseline 93.3% Paraffin oil ($\eta = 6.0$) (Temp. = 6°C supersaturated solution)	2.538	——	——	——	2.538	2.538	——
18	2.8% Nitronaphthalene 64.0% Vaseline 33.2% Kerosene ($\eta > 5$)	2.384	2.386	2.387	2.388	2.387	2.386	——
19	6.0% Nitrobenzene 94.0% Vaseline ($\eta > 100$)	2.769	2.770	2.770	2.768	2.770	2.769	2.194
20	2.5% Nitronaphthalene 97.5% Vaseline ($\eta > 100$)	2.326	2.330	2.328	2.328	2.335	2.329	2.195
21	6.5% Nitrobenzene 25.2% No. 5182 Cable compound 68.3% Paraffin oil ($\eta > 20$)	3.037	3.037	3.036	3.033	3.029	——	2.202
22	Same solution after heating	2.921	2.921	2.920	2.921	2.919	——	2.200
23	6.1% Nitrobenzene 33.7% No. 5182 Cable compound 60.2% Paraffin oil ($\eta > 50$)	3.012	3.012	3.013	3.013	3.012	——	——
24	5.8% Nitrobenzene 94.2% No. 5182 Cable compound ($\eta > 100$)	2.923	2.922	2.922	2.923	2.918	——	——
25	5.4% Nitronaphthalene 94.6% No. 5182 Cable compound ($\eta > 100$)	2.628	2.627	2.627	2.628	2.623	——	——

TABLE III. *Dielectric constant data for solutions of rosin in mineral oils.*

Exp. No.	Composition	ϵ' $\lambda=3\times10^5$ m	=490.6 m	=156.2 m	=78.12 m	=39.06 m	=26.04 m	=17.36 m	n^2
26	26.4% Rosin* 73.6% Kerosene	——	——	2.409	2.399	2.393	2.387	2.378	2.173
27	Same one week later	2.427	——	2.422	2.413	2.407	2.402	2.391	2.170
28	20.4% Rosin* 79.6% Finoil	2.309	2.309	2.293	2.288	2.279	2.274	2.271	2.185
29	40.1% Rosin* 59.9% Finoil	——	——	2.403	2.389	2.374	2.364	2.360	2.231
30	26.0% Rosin* 74.0% Paraffin oil	——	——	2.342	2.330	2.323	2.319	2.311	2.233

* Note—The percent rosin refers to the weight of rosin added rather than the weight dissolved.

TABLE IV. *Dielectric constant data for solutions of "floricin" in mineral oils.*

Exp. No.	Composition	ϵ' $\lambda=3\times10^5$ m	=156.2 m	=78.12 m	=39.06 m	=26.04 m	=17.36 m	n^2
31	17.3% Floricin 82.7% Kerosene ($\eta=0.02$)	——	2.375	2.374	2.375	2.375	2.374	2.115
32	16.5% Floricin 82.5% Finoil ($\eta=0.4$)	2.391	2.391	2.390	2.390	2.390	2.381	2.151
33	20.8% Floricin 79.2% Finoil ($\eta=0.5$)	——	2.460	2.458	2.456	2.457	2.450	——
34	15.2% Floricin 84.8% Distilled vaseline ($\eta=0.4$)	——	2.367	2.365	2.364	2.363	2.359	——
35	15.7% Floricin 84.3% Paraffin oil ($\eta=1.3$)	2.427	2.429	2.426	2.421	2.417	2.412	2.190
36	20.8% Floricin 79.2% Paraffin oil ($\eta=1.3$)	——	2.492	2.492	2.491	2.485	2.474	——
37	20.0% Floricin 80.0% Vaseline ($\eta>50$)	——	2.426	2.422	2.419	2.416	2.410	——
38	18.5% Floricin 28.5% Vaseline	——	2.149	2.149	2.152	2.150	2.148	2.148
39	53.0% Kerosene ($\eta>0.4$)	——	2.406	2.406	2.408	2.406	2.406	2.148
40	16.5% Floricin 11.5% Kerosene 72.2% Paraffin oil ($\eta=0.4$)	——	2.417	2.417	2.415	2.412	2.407	——
41	15.1% Floricin 0.8% Vaseline 84.1% Paraffin oil ($\eta>2$)	——	2.468	2.463	2.463	2.457	2.453	——

TABLE IV. (*Continued*).

Exp. No.	Composition	ϵ' $\lambda=3\times10^5$ m	=156.2 m	=78.12 m	=39.06 m	=26.04 m	=17.36 m	n^2
42	18.6% Floricin 1.9% Vaseline 79.4% Paraffin oil ($\eta>5$)	——	2.461	2.459	2.457	2.449	2.445	——
43	8.4% Floricin 2.5% Vaseline 89.1% Paraffin oil ($\eta>10$)	——	2.309	2.308	2.306	2.302	2.297	——
44	11.0% Floricin 3.9% Vaseline 85.1% Paraffin oil ($\eta>10$)	——	2.350	2.347	2.345	2.343	2.339	——
45	10.7% Floricin 6.4% Vaseline 83.0% Paraffin oil ($\eta>10$)	——	2.339	2.336	2.335	2.333	2.330	2.196
46	15.0% Floricin 30.0% Vaseline	——	2.192	2.188	2.188	2.188	2.182	2.192
47	55.0% Paraffin oil ($\eta>50$)	——	2.390	2.387	2.386	2.384	2.383	2.192
48	10.0% Floricin 15.0% No. 5182 Cable compound 75.0% Paraffin oil ($\eta>10$)	——	2.420	2.418	2.418	2.414	2.410	——

TABLE V. *Dielectric constant data for high molecular weight organic substances in low viscosity solvents.*

Exp. No.	Composition	ϵ' $\lambda=3\times10^5$ m	=156.2 m	=78.12 m	=39.06 m	=26.04 m	=17.36 m	n^2
49	Celluloid in dioxane (sat.)	——	2.476	2.477	2.473	2.470	2.465	2.025
50	10% Masticated pale crepe in CCl_4	2.260	2.253	2.252	2.250	2.255	2.255	2.155
51	Hard rubber in CCl_4 (sat.)	——	2.254	2.255	2.255	2.251	2.250	——

yellowish-brown oil, miscible in all proportions with mineral oils or vaseline,[11] has a refractive index of 1.4771, and a dielectric constant of 4.10 at 156 meters. At lower wave-lengths it shows absorption, in fact this absorption was so strong that no measurements could be made with our apparatus. This oil was chosen because it shows absorption in this region, because it gives readily reproducible results showing little or no dielectric constant change over long periods of time, and because it has a viscosity of the same magnitude as that of the solvent.

There are presented in Table V the results of several miscellaneous experiments. The system celluloid in dioxane shows the beginning of an absorption but the work could not be extended to other solvents because of the insolubility of the celluloid. The pale crepe solutions are either non-polar or else possess an inner-frictional constant too high to permit an orientation. The hard rubber is only very slightly soluble and the results can have little significance since the observed value is so near that for pure CCl_4. Traces

[11] Allen, *Commercial Organic Analysis*, 5th Edition, Vol. 2, p. 228, Blakiston, Philadelphia.

of water might cause errors much larger than the differences observed.

With the exception of experiments 15 and 16, which were made at 6°C, our measurements were carried out at 25°. The dielectric cell had to be recalibrated for the measurements at the lower temperature, by using carbon tetrachloride as the standard liquid.

Viscosities could not always be determined because some of the systems were gels and could give no definite results. The measured viscosity of the gels often changed by a factor of 100 or more. In some cases, however, an estimate of a lower limit could be made.

For the most part the data recorded in the tables are averages of from one to ten sets of measurements for the same solution. In two cases (experiments 38 and 46) there are given the results from a single cell filling which differ considerably from the average of about 10 others (experiments 39 and 47). Their significance will be discussed later.

Discussion

Experiments of this type give important information concerning the application of Stokes' law to the rotary motion of polar molecules in such solutions and suspensions. This has been discussed from a theoretical point of view in a previous paper.[12] In that article the conclusion was drawn that any calculations of molecular size from dielectric constant data for systems of small molecules dissolved in solvents whose molecules are of the same or larger size would be of very doubtful significance. Assuming the correctness of Debye's theory (when ζ is used), it can be seen from the data of Table II that either the law of Stokes cannot be applied or the ordinary coefficient of viscosity fails to measure the frictional resistance to the rotation of the polar molecules. Since no dispersion was observed even at 1.727×10^{7} cycles, the value of the inner-frictional constant ζ must be smaller than 10^{-22} since

$$\zeta=[kT\chi(\epsilon_\infty+2)]/[\pi\nu(\epsilon_0+2)]<(1.37\times10^{-16}\times298\times0.1)/(\pi\times1.727\times10^{7})<1\times10^{-22}.$$

Assuming a molecular radius larger than 2×10^{-8} cm, Stokes' law gives

$$\zeta>8\pi\times(2\times10^{-8})^{3}\eta=2\times10^{-22}\eta.$$

Dispersion should therefore be found in the investigated region when η is larger than $\frac{1}{2}$ poise. All the solutions investigated had viscosities higher than this figure, yet with the possible exception of experiments 21–25 inclusive, no dispersion of the dielectric constant is observed. (Systems containing the No. 5182 cable compound (experiments 21–25) are extremely viscous.)

This conclusion is consistent with the results of experiments of Goldammer[13] and of Weigle and Luthi.[14] These investigators have studied similar systems at wave-lengths as low as 50 cm and have found no dispersion. Certain of these results seem to be in partial disagreement with those of Johnstone and Williams,[15] but a possible and even probable explanation of this difference can now be given.

Table VI. *Calculations from data of Johnstone and Williams.*

% $C_6H_5NO_2$	Viscosity (η)	Inner-frictional constant (ζ)$\times10^{22}$	Radii (assuming $\zeta=8\pi\eta a^3$) in A
16.9	7.7	3.9	1.3
8.7	13.0	10.	1.4
3.1	23.0	9.7	1.2

Calculations from the data of Johnstone and Williams show fairly good agreement with the theory of Debye and are shown in Fig. 4.[16] Table VI gives the observed viscosity values of these solutions, the value of ζ calculated from the curves of Fig. 4, and the molecular radii cor-

[12] Williams and Oncley, J. Rheology **3**, 271 (1931).

[13] Goldammer, Phys. Zeits. **33**, 361 (1932).

[14] Weigle and Luthi, Comptes Rendus **49**, 130 (1932).

[15] Johnstone and Williams, Phys. Rev. **34**, 1483 (1929).

[16] Curve I is obtained from Table II of the original article of Johnstone and Williams, curve II from Table IV, and curve III from Table III.

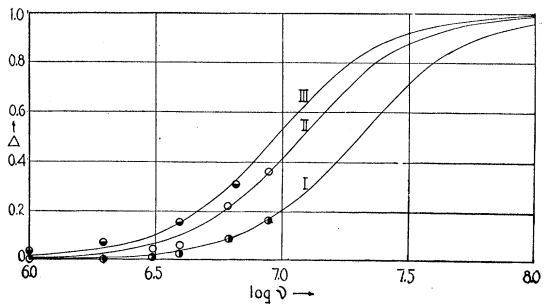

FIG. 4.

responding to these values when Stokes' law in its ordinary form using the macroscopic viscosity of the solution is applied. These radii values are quite small, and should be multiplied by a factor of at least two if agreement with x-ray data is to be obtained. This factor of two then increases ζ by a factor of approximately ten.

Calculations with the data of Mizushima[17] indicate molecular radii of from about 1.7 to 2.5A for the simple alcohols, in good agreement with kinetic theory values. However, at the low temperatures at which the dielectric constant measurements for these substances were made the molecules of these liquids are supposed to be associated. If this is true, one might expect the observed radii to be several times larger than kinetic theory values, which are obtained at much higher temperatures. Accordingly, the application of Stokes' law with the use of the ordinary macroscopic viscosity to measure the frictional rotation of the molecules appears to fail in the determination of ζ by a factor of at least ten. In the case of glycerol this difficulty is much greater, since the calculations give a radius of only 0.35A for this molecule. Another possible explanation of this difficulty in the case of the liquids studied by Mizushima is that it is brought about by the application of the Clausius-Mosotti relationship to polar substances. Experiments of the same type by White and Morgan[18] with certain of the glycols lead to a similar result.

[17] Mizushima, Sci. Papers Inst. Phys. Chem. Research (Tokyo), **5**, 201 (1927); **9**, 209 (1928). Also Debye, *Polar Molecules*, p. 100, Chem. Cat. Co., New York (1929). Recent data of Malsch (Ann. d. Physik [5], **12**, 865 (1932)) are in substantial agreement with these earlier results of Mizushima.

[18] White and Morgan, Physics **2**, 313 (1932). See also the typographical correction in Physics **3**, 53 (1932).

It can be concluded that in the case of all recorded experiments in which the rotation of small molecules has been studied, a failure of Stokes' law by a factor of from ten to several thousand is indicated. This failure may result because such systems do not conform to the law itself or because the use of the macroscopic viscosity in it is not permissible. This discrepancy should be smaller when smaller solvent molecules are used if the application of a law of the form of that of Stokes is justified. Although no definite evidence of this fact is at hand, several of our experiments with floricin and rosin suggest that it is true. We therefore prefer to believe for the present that the discrepancy between theory and experiment has to do with the manner in which in a solution the actual frictional resistance of the solvent molecules to the rotation of the polar solute molecules has been introduced. In other words one might say that the coefficient of viscosity has been introduced into the theory in an inexact way.

The results for the rosin solutions show dispersion, therefore they enable us to see if such systems may be considered theoretically. Since these solutions are probably made up of abiatic acid in various stages of polymerization, we should expect them to behave as polydisperse systems. It can easily be seen that such is the case since the absorption region is spread over a much greater frequency range than for a mono-dispersed system. However, it might be that a single-sized particle would cause absorption in the region investigated. The dielectric constant of any mono-dispersed system can be expressed as a function of the frequency by means of an equation of the form

$$\epsilon(\nu)=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)\left[1+\left(\frac{\epsilon_0+2}{\epsilon_\infty+2}\cdot\frac{\zeta\pi}{kT}\right)^2\nu^2\right]^{-1}. \quad (12)$$

Since we have used harmonics of a fundamental frequency ν_0 in this investigation, we may substitute $\nu_i=n_i\nu_0$, and write (12) in the form

$$\epsilon(n_i\nu_0)=\epsilon_i=c+b/(1+an_i^2),$$

where

$$a=[\zeta\pi\nu_0(\epsilon_0+2)]^2/[kT(\epsilon_\infty+2)]^2, \quad b=\epsilon_0-\epsilon_\infty$$

and $c=\epsilon_\infty$. Since this equation involves the three parameters a, b and c, it will be necessary to solve

three equations simultaneously to find their value. Thus taking

$$\epsilon_i = c + b/(1+an_i^2), \qquad \epsilon_j = c + b/(1+an_j^2), \qquad \text{and} \qquad \epsilon_k = c + b/(1+an_k^2),$$

we obtain the following expression for a:

$$a = \frac{\epsilon_i(n_k^2 - n_j^2) - \epsilon_j(n_k^2 - n_i^2) + \epsilon_k(n_j^2 - n_i^2)}{-\epsilon_i n_i^2(n_k^2 - n_j^2) + \epsilon_j n_j^2(n_k^2 - n_i^2) - \epsilon_k n_k^2(n_j^2 - n_i^2)}.$$

Taking the five values obtained for ϵ_i (at the five harmonics where $n_i = 1$, 2, 4, 6 and 9) in all possible combinations of three at a time, we will obtain $5!/(3!\cdot 2!) = 10$ equations, each giving the proper value for a_{ijk} to exactly represent the three dielectric constants ϵ_i, ϵ_j and ϵ_k. If the solution is monodisperse these values should show a random deviation from a mean value due only to experimental errors. On the other hand if the solution is polydisperse there will be a drift of the values toward smaller values of a at the high frequencies, caused by the fact that smaller particles (and hence a smaller ζ and a) are causing the dispersion at the higher frequencies, while the larger particles (larger a) cause the bulk of the dispersion at lower frequencies. The results of such calculations for experiments 26–30 inclusive are shown in Table VII.

The calculations for the systems represented in experiments 26, 27, and 30 clearly indicate polydisperse systems in which the dispersion of the dielectric constant at one end of the region is caused by one kind of molecule and that at the other end by other kinds. However, the calculations from the data of experiment 28, and perhaps from experiment 29 as well, lead to results characteristic of a monodisperse system, since the quantity a is approximately constant and does not show a gradual decrease at higher frequencies. The data used in experiment 28 are average values obtained from five determinations, while experiment 29 is a result obtained from a single series of measurements. The negative value for a_{345} in experiment 29 is probably due to experimental error since small changes in ϵ_3, ϵ_4 or ϵ_5 would give it a positive value. It leads to an

TABLE VII. *Calculations to show size distribution of particles in rosin suspensions.*

Experiment	26	27	28	29	30
a_{123}	0.607	0.500	0.120	0.223	0.640
a_{124}	.291	.284	.087	.165	.436
a_{125}	.163	.340	.089	.166	.242
a_{134}	.079	.094	.085	.089	.180
a_{135}	.048	.040	.090	.111	.079
a_{145}	.028	.050	.098	.169	.035
a_{234}	.023	.036	.083	.058	.079
a_{235}	.016	.014	.090	.083	.032
a_{245}	.012	.005	.101	.170	.008
a_{345}	.009	.0003	.131	(−.514)	.002
mean a	.13	.12	.097	.137	.17
$\zeta \times 10^{21}$	2.4	2.3	2.1	2.5	2.8

imaginary value for ζ; accordingly it has no significance.

The complete interpretation of these results has not been achieved. The experiments were made with solutions which had stood for varying lengths of time, and since polymerization seemed to take place they might be of quite different nature. The rosin suspensions studied in experiments 26, 28 and 29 were made up from 5 to 24 hours before the dielectric constant measurements were made, but those of experiments 27 and 30 were not made until from 8 to 10 days had passed. There is accordingly no relationship between the data of Table VII and the time the suspensions stood before the experimental observations were made. Another possible explana-

tion, but which seems inconsistent with the chemistry of such systems, would be that the Finoil solvent did not allow certain kinds of molecules which were present to dissolve, while they were soluble in kerosene and paraffin oil.

From the average value of ζ we have calculated ϵ_0 and ϵ_∞, and the values for the dielectric constant ϵ' at the various frequencies. These results are presented in Table VIII. As it to be expected the results for experiments 28 and 29 show very

TABLE VIII. *Observed and calculated dielectric constant values for rosin suspensions.*

Experiment	26		27		28		29		30	
Frequency $(\nu)\times10^{-6}$	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
0	——	2.411	——	2.423	——	2.296	——	2.409	——	2.345
1.919	2.409	2.408	2.422	2.421	2.293	2.293	2.403	2.403	2.342	2.341
3.838	2.399	2.401	2.413	2.415	2.288	2.288	2.389	2.389	2.330	2.332
7.676	2.393	2.391	2.407	2.406	2.279	2.279	2.374	2.374	2.323	2.321
11.51	2.387	2.385	2.402	2.400	2.274	2.274	2.364	2.365	2.319	2.316
17.27	2.378	2.382	2.391	2.396	2.271	2.271	2.360	2.360	2.311	2.313
∞	——	2.378	——	2.392	——	2.268	——	2.356	——	2.311

good agreement, while the others are not as good since ζ is not a constant. Although these deviations between the theoretical and observed values are very small because of the small difference between ϵ_0 and ϵ_∞, they show deviations slightly larger than the errors of observation. The results of the calculation of a are much more significant, and they definitely support our conclusions.

The investigations with floricin solutions show an interesting, but at the same time unexpected, behavior. A change in the viscosity η by a factor of several thousand apparently does not change the inner-frictional constant ζ by any large amount. In order to completely establish this as a conclusion it will be necessary to obtain dielectric constant data over a much wider frequency range than our present experiments. It is a fact, however, that the dispersion appears to be about the same in solutions with a viscosity of only a few poises or with a viscosity of several thousand poises. This clearly indicates that the inner-frictional constant ζ changes but little as the viscosity η of the solution is increased.

It appears that these results may be explained by a consideration of the kinetic theory of liquids. Liquids of high viscosity may contain large molecules but they will also contain some smaller ones. Thus a viscous mineral oil consists of long-chain solid hydrocarbons dissolved in shorter-chain liquid hydrocarbons. In a system consisting of polar molecules dissolved in such a solvent we may expect the arrangement of the polar molecules to be such that the frictional forces would be as small as possible. Thus the molecules will tend to arrange themselves in such a way that the inner-frictional constant ζ will be a minimum. If very large molecules are present they may form pockets in which the smaller molecules would have nearly free rotational movement. Thus a small inner-frictional constant ζ will result from any observation designed to measure it. Very small molecules will also have a small inner-frictional constant. Accordingly an increase in the macroscopic viscosity might either increase or decrease the inner-frictional constant. It may also be expected that a variable time of relaxation τ, or inner-frictional constant ζ might result even though the polar molecules were of only one kind, the difference being due to their movements with respect to solvent molecules of various sizes and shapes.

Two experiments with the floricin systems, 38 and 46, show marked differences from the general behavior. Thus, twice in the course of investigation of some fifty solutions results were obtained which gave a constant dielectric constant, its value being equal to the square of the refractive index. In the attempt to duplicate these experiments different values were obtained. In the first case constant but much higher values resulted, but in the second a normal dispersion from higher values was observed. This behavior might possibly be ascribed to experimental error, since a lower value is found if the cell is filled with an insufficient amount of solution or if the solution does not completely fill the space between the two plates of the condenser. However, both times the usual precautions were taken, and it would

be improbable that both times the value obtained would be constant and within experimental error of the n^2 value. It was also noted that the solutions used in those two experiments seemed to be much less heterogeneous than the other solutions of this type. A possible explanation of this difference in dielectric constant values is that because of some difference in heat treatment or perhaps to traces of impurities, a different sort of gel structure which has a much higher inner-frictional constant is formed. In these cases we were completely beyond the dispersion range, while usually we were near its beginning.

These observations are of interest in connection with the results of experiments 21 to 25 inclusive, and with earlier results of Johnstone and Williams. An attempt was made to repeat the earlier work, but unfortunately a sample of the cable compound used to thicken the solvent, "Insulatum B. B.," could no longer be obtained. A thickening substance of the same type, "Cable Compound No. 5182," was used as a substitute, but with only partial success. Certain experiments with systems in which this substance was used show real evidence of a dispersion (21, 24, 25) while others (22, 23) give a constant dielectric constant. The evidence of a positive dispersion effect in the present experiments depends somewhat upon the fact that in the other experiments whose results are given in Table II the observed dielectric constant is slightly higher at 17.36 and 26.04 meters than it is at 156 meters—in other words the experimental error acts in the direction to make the apparent dispersion effect smaller than the effect which should be observed. A comparison of the results of these experiments with those of Johnstone and Williams indicates that in the present systems the effective inner-frictional constant ζ must have a smaller value, probably because of differences in gel structure. The accuracy of the present experiments is considerably greater than that of the earlier work but both show fairly good agreement with the dispersion theory. In a series of recent experiments made at a temperature of -10°C Weigle and Luthi[14] found dispersion taking place at wave-lengths as high as 300 meters in the case of systems of amyl alcohol suspended in a heavy oil (Shell BL3, viscosity 18 poises at 18°C). The results of experiments in which vaseline-like substances are added to a mineral oil in order to prepare a solvent medium of higher viscosity for the solution of polar molecules must always be of lesser theoretical value because the effective inner-frictional constant will vary in a manner which cannot be controlled. This difficulty results from different heat treatments and different structural formations.

In conclusion, it may be said that these results show that the Debye theory, although theoretically sound, is very difficult to apply quantitatively to the existing dielectric constant data. In fact, there seems to be little chance that any data at frequencies below 3×10^7 cycles per second can be quantitatively treated, unless the viscosity of solutions, always made up by using small solvent molecules, is enormously increased by the use of either very low temperatures or very high pressures. The reason for this statement is that any solutions which will show dispersion at such low frequencies must either contain large polar molecules or be prepared from very viscous solvents. At the present time it does not seem readily possible to obtain monodisperse systems either of large molecules or of particles of colloidal size, in nonpolar solvents. Our ordinary solutions and suspensions will exhibit values of ζ which are not constant since particles of various sizes and shapes will be present. Likewise all very viscous nonpolar solvents known to us are made up of several kinds of molecules so that the inner-frictional constant will be poorly defined. Accordingly, further experiments must be made at still higher frequencies to provide an adequate test of the theory. To accomplish this it will be necessary to develop much more accurate methods of dielectric constant measurement than are now at hand, and this task will be a difficult one. A possibility which has much to recommend it is to prepare colloidal solutions of such substances as NaCl, Na_2SO_4, etc., in benzene, carbon tetrachloride, and other pure, nonpolar solvents. These suspensions can be prepared in monodisperse condition by the use of the centrifuge and proper filters. Such experiments were attempted by us, but apparatus for such a purification was not available.

The work is being continued along the lines suggested in the last paragraph.