

ANOMALOUS DISPERSION, ABSORPTION AND KERR EFFECT IN VISCOUS DIELECTRICS

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ABSTRACT

The *temperature variation of the dielectric constant and power factor* of castor oil and rosin, measured at different frequencies from 10^7 to 60 cycles, shows that, in accordance with Debye's theory of polar molecules, the region of anomalous dispersion of these very viscous liquids shifts with decreasing temperatures into the long-wave radio region and even down to audio frequencies. The measurements qualitatively verify the theory. The *influence of viscosity* in solutions of rosin in different oils which have no polar molecules is found in agreement with the theory. The existence of anomalous dispersion in the audio and radio frequency region explains the complicated dielectric behavior of many insulation materials and makes it possible to observe an anomalous behavior of the Kerr effect, or electric double refraction. According to Debye, this effect is due to the orientation of the molecules and should disappear at temperatures and frequencies where the orientation of the dipoles is impossible. We find, as is to be expected, that the regions of anomalous Kerr effect and of anomalous dispersion coincide.

MEASUREMENTS of the dielectric constant δ and of the power factor f of rosin and castor oil, carried out for engineering purposes, led to curious results which, we believe, represent an interesting contribution to Debye's theory of polar molecules.

EXPERIMENTAL METHOD

The experimental arrangement is represented in Fig. 1. A resonant circuit is coupled to a calibrated oscillator, using a 201A tube. The test conden-

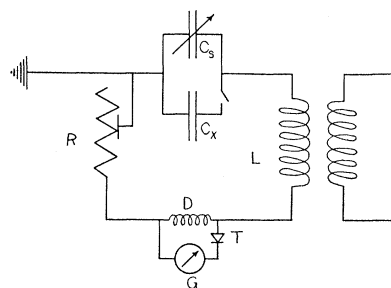


Fig. 1. Experimental arrangement. C_s is the variable standard condenser; C_x , the test condenser; R , the variable resistance; L , inductance; D , drop coil; G , micro-ammeter; T , the crystal rectifier.

ser consisted of two coaxial cylinders. Experiments showed that its vacuum capacity C_v did not vary with temperature.

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Each run was made at constant frequency and varying temperature. The method consisted of tuning the circuit to resonance with C_x connected and $R=0$, and noting the galvanometer deflection. Then, with C_x disconnected, the circuit was again brought to resonance and R varied to bring the galvanometer to the same deflection.

Let ν be the applied frequency; $C_x = C_2 - C_1$ the difference between the two readings of C_s ; R the added resistance; C_v the vacuum capacity of test condenser. Then $R_x = R (C_2/C_x)^2$ is the equivalent series resistance of C_x ; $f = 2\pi\nu C_x R_x$ the power factor; and $\delta = C_x/C_v$ the dielectric constant.

DISCUSSION OF RESULTS

Figs. 2 and 3 show the results obtained on castor oil and Hercules wood rosin "F." Because of the change of density, the normal behavior of the dielectric constant of a liquid is to decrease with increasing temperature. These curves, however, show a temperature region in which the dielectric constant increases. In the same region the power factor has a sharp maximum. The position of this region shifts with higher frequencies to higher temperatures.

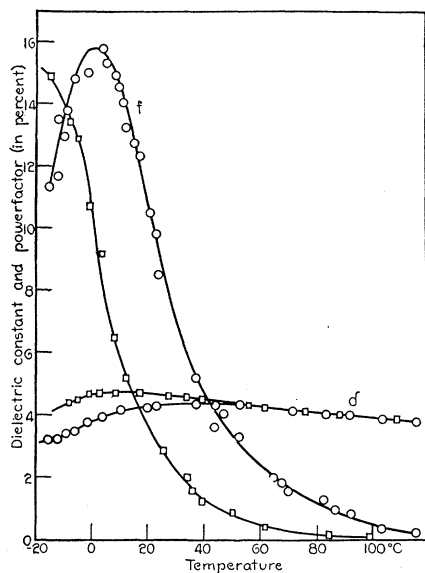


Fig. 2. Dielectric constant and power factor of castor oil as a function of temperature, at (□) 0.4×10^6 cycles, and (○) 10.9×10^6 cycles.

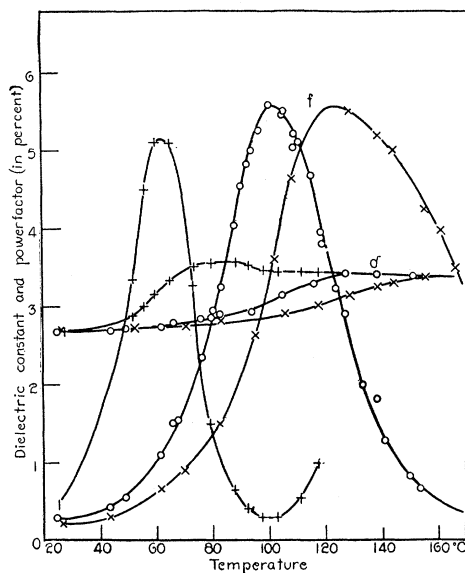


Fig. 3. Dielectric constant and power factor of wood rosin "F" as a function of temperature at (+) 60 cycles, (○) 10^6 cycles, (×) 10^7 cycles.

It is our opinion that this observed behavior cannot be explained on the basis of a heterogeneous dielectric as described, for example, in Maxwell's theory or its modification by K. W. Wagner,¹ Schweidler,² Pellat,³ etc.

¹ K. W. Wagner, *Ann. d. Physik* **40**, 817, 833 (1913).

² Schweidler, *Ann. d. Physik* **24**, 742 (1907).

³ Pellat, *Ann. de chimie et phys.* **18**, 150 (1899).

An explanation of these results, however, can be given on the basis of Debye's⁴ theory of polar molecules, by assuming that the molecules of the main constituents of these liquids are electric dipoles. According to Debye's theory, one part of the dielectric polarization is due to the orientation of the polar molecules. This orientation has a relaxation time τ , which depends on the viscosity of the liquid. Considering the molecules as spheres of radius r turning in a viscous medium, Debye calculates the frequency $\nu_0 = 1/\tau$ corresponding to this relaxation time as

$$\nu_0 = kT/8\pi^2\eta r^3 \quad (1)$$

where $k = 1.37 \times 10^{-16}$ erg is Boltzmann's constant; T , the absolute temperature; η , the viscosity of the liquid; and r , the radius of the molecules.

The polar molecules cannot follow the changes in field for frequencies very much higher than ν_0 . The polarization is then only due to the displacement of the electrons and the dielectric constant has therefore its optical value $\delta_\infty = n^2$. For frequencies very much smaller than ν_0 , the relaxation can be neglected and the dielectric constant becomes independent of the frequency at its larger static value δ_0 . In the neighborhood of ν_0 , the dielectric constant decreases with increasing frequency, producing the so-called anomalous dispersion. In this region the relaxation produces a phase difference between the electric displacement (D) and the field strength (E). Therefore, the absorption coefficient α passes through a maximum in the region of anomalous dispersion.

Since the viscosity η usually decreases very much faster than $1/T$ with increasing temperature, the characteristic frequency ν_0 varies greatly with temperature. Representing, as we do, the dielectric constant at constant frequency as a function of the temperature, we must therefore find a temperature where the applied frequency coincides with ν_0 . In the neighborhood of this temperature the dielectric constant increases, since the dipoles, which are fixed at low temperature, become liberated and, for the same reason as above, the coefficient of absorption or the power factor passes through a maximum. For a higher frequency the corresponding temperature must be higher, and hence the phenomenon shifts to higher temperatures with increasing frequencies.

So we see that Debye's theory explains, at least qualitatively, the observed behavior of the dielectric constant and power factor of rosin and castor oil. To prove rigorously that we are really dealing with the effect of anomalous dispersion, we should be able to check Debye's equation quantitatively.

We cannot, of course, expect to find Debye's equation accurately verified, but must be satisfied with results of the correct order of magnitude, for the following reasons: (1) Debye's equations hold exactly only for a gas in which all the molecules are dipoles. Rosin and castor oil, however, are viscous liquids and are furthermore not chemically uniform. (2) The coefficient of viscosity entering into Debye's formula is not necessarily identical with the

⁴ P. Debye, Theorie der elektrischen und magnetischen Molekulareigenschaften, Marx's Handbuch der Radiologie 6, 597-790. Leipzig, 1925.

macroscopically measured viscosity, and the quantity r is not the actual radius of the molecules but is only a length of the order of magnitude of molecular dimensions. (3) The formulas are applicable to experiments at constant temperature with variable frequency and, therefore, do not directly apply to our measurements. We shall nevertheless use these formulas. By doing so, we neglect the change of density of the liquid—i.e., we consider δ_0 and δ_∞ as independent of the temperature. Since their variations are small in the temperature region under consideration compared to the anomalous increase of δ , this cannot involve an appreciable error.

The position of the anomalous change of the dielectric constant at constant frequency is best characterized by the temperature for which the corresponding power factor is a maximum. This is not the temperature, however, at which the applied frequency coincides with ν_0 but the maximum occurs where

$$\nu = \nu_0 \frac{\delta_\infty + 2}{\delta_0 + 2} \left(\frac{\delta_0}{\delta_\infty} \right)^{1/2} \quad (2)$$

For rosin we have, approximately, $\delta_0 = 3.4$, $\delta_\infty = 2.7$, therefore, $\nu = 0.98 \nu_0$. Since the measurements are subject to a possible error of 3 percent, we can neglect this difference for rosin. For castor oil, however, we have approximately $\delta_0 = 4.5$, $\delta_\infty = 2.5$, therefore, $\nu = 0.93 \nu_0$, and the difference has to be taken into account.

If, in our experiments, we really are dealing with anomalous dispersion, we must show that equation (1) is satisfied, that is, that this equation leads

to a reasonable value for r . Practically all the liquids which have hitherto been investigated show anomalous dispersion in the region of the spectrum between wave-lengths of 10 m and 0.1 cm.⁵ Debye predicted, however, that liquids with large molecules and high viscosity should show the effect at lower frequencies. Castor-oil and rosin evidently satisfy both conditions. Fig. 4 represents our measurements of the viscosity curves of both liquids. These curves differ only slightly from the data given in Landolt-Börnstein. The departure is due to the difference in degree of refinement of the liquids.

The maximum of the power factor of rosin for the frequency $\nu = 10^7$ appears

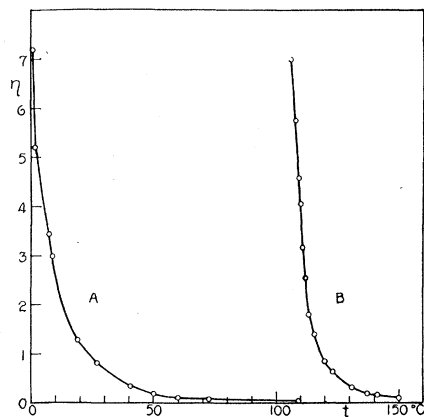


Fig. 4. Viscosity measurements for (A) castor oil and (B) rosin.

⁵ P. Drude, *Zeits. f. Physik. Chemie* **23**, 267 (1897). J. D. Tear, *Phys. Rev.* **21**, 611 (1923). Nichols and Tear, *Phys. Rev.* **21**, 587 (1923). S. Mizushima, *Scientific Papers Inst. of Phys. Chem. Research* **5**, No. 79. Tokyo 1927.

at the temperature $t = 123^\circ\text{C}$ ($T = 396$). At this temperature, the viscosity is 0.63. Introducing these values in equation (1), we find a radius

$$r = (kT/8\pi^2\eta\nu)^{1/3} = 4.8\text{\AA}$$

A molecular radius of rosin of this order of magnitude is certainly reasonable.

For castor oil, the maximum of the power factor for the frequency 10.9×10^6 is at $t = 1^\circ\text{C}$ ($T = 274$), and the viscosity is about 7. By taking into account that $\nu = 0.93 \nu_0$, equation (1) leads to a radius $r = 1.8\text{\AA}$.

The change of the characteristic temperature with frequency is also in good agreement with the theory. From (1) it follows that the temperatures T_1 and T_2 , where the power factor for the frequencies ν_1 and ν_2 are maxima should satisfy the relation.

$$T_1 \cdot \eta(T_2) / T_2 \cdot \eta(T_1) = \nu_1 / \nu_2 \quad (3)$$

For example in the case of rosin we have $T_1 = 396$, $\eta(T_1) = 0.63$, $\nu_1 = 10^7$, $T_2 = 374$, $\nu_2 = 10^6$. The above relation is satisfied if we put $\eta(T_2) = 6.7$. The extrapolation of the viscosity curve, on the other hand, gives a viscosity $\eta(374)$ of about 7.5. Since the temperatures are not very accurately determined, and since the viscosity changes so rapidly with temperature that a small variation of temperature produces a large change of the value of η the agreement must be considered satisfactory.

The shape of the curves dielectric constant and the power factor versus temperature is in accordance with the theory. We notice particularly that at lower temperatures the region of anomalous behavior is smaller. This can be explained by the rate of increase of viscosity with falling temperature. If the viscosity increased exponentially the regions would be of equal width. The viscosity curves however increase in slope more rapidly.

Debye's theory further predicts the magnitude of the maximum in the absorption coefficient.

$$\alpha(\text{max}) = \frac{(\delta_0)^{1/2} - (\delta_\infty)^{1/2}}{(\delta_0)^{1/2} + (\delta_\infty)^{1/2}} \quad (4)$$

Power factor and absorption coefficient are related to each other according to the equation

$$f = 2\alpha / (1 - \alpha^2) \quad (5)$$

Hence the power factor maximum should have the value

$$f(\text{max}) = (\delta_0 - \delta_\infty) / 2(\delta_0\delta_\infty)^{1/2} \quad (6)$$

Since δ_0 and δ_∞ do not vary much in the temperature region investigated, the maximum power factor should be independent of the frequency, as our results show.

$\delta_0 - \delta_\infty$ is the part of the dielectric constant which is due to the orientation of the polar molecules. The larger this part is—i.e., the greater the number of polar molecules per unit volume or the larger the dipole moment of the single

molecules, the larger is the maximum power factor. A comparison of our results on rosin and castor oil verifies this conclusion. For rosin, $\delta_0 - \delta_\infty$ is about 0.7 and for castor oil about 2, while $(\delta_0\delta_\infty)^{1/2}$ has almost the same value. Accordingly, the maximum power factor of rosin is about one-third as great as that for castor oil. The polar molecules in castor oil evidently have a larger dipole moment than those in rosin.

The absolute value of the power factor is of the same order of magnitude as that calculated from equation (6). The observed value for rosin is about one-half the calculated one, namely 5.6 percent instead of 11.2 percent. Such deviations have to be expected in a substance containing different constituents.

A second series of experiments was carried out with solutions of rosin in different oils whose molecules were not polar. These solutions gave similar results—coincidence of maximum power loss and anomalous change of the dielectric constant both effects increasing in a parallel way with increasing concentration of the rosin. By changing the concentration of the solution or by changing the solvent the viscosity curve can be shifted and this offers a very convenient way to prove the importance of the viscosity for the position of anomalous dispersion.

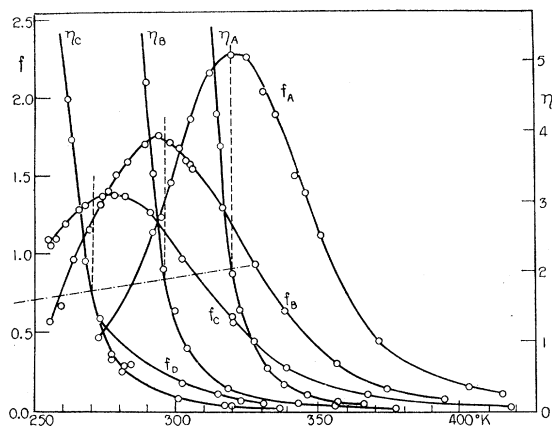


Fig. 5. Viscosity and power factor curves for mixture of rosin oil with transil oil at 10^6 cycles. (A) 100%, (B) 80%, (C) 50%, (D) 20% rosin oil.

Fig. 5 shows the viscosity curves and the power factor curves for one million cycles for three different mixtures of synthetic rosin oil with transil oil, and the power factor curve only for an additional mixture. Since v is constant, the maximum power loss should according to equation (1) occur at those temperatures where the ratio η/T assumes the same value. This fact is illustrated in the diagram. The "dot-dash" line coming from the absolute zero point, intersects the viscosity curves in points where the ratio η/T is the same. In

agreement with the theory, the power factor maxima occur very close to the corresponding temperatures. These curves show very clearly the parallelism between viscosity and position of anomalous dispersion as demanded by Debye's theory.

In Fig. 3 we have also presented the curves power factor and dielectric constant of rosin versus temperature for a frequency of 60 cycles.⁶ These

⁶ For these curves, which were measured in the laboratories of the General Electric Co., we are indebted to the Hercules Powder Co.

curves are extremely interesting, because they show exactly the same features as the curves measured at radio frequencies. We believe therefore that this is a case where anomalous dispersion appears at 60 cycles.

At 60°C where the maximum power loss appears rosin is semi-solid. It assumes the properties of an ordinary liquid only when heated above 100°, but there is no sudden change between these states. All its physical properties vary continuously in the whole temperature region as can be seen in our measurements of the dielectric constant. This indicates that rosin is still a liquid at room temperature but has a tremendous viscosity.

If we assume that Debye's equation (1) is still valid even for this highly viscous liquid, we have to ascribe to rosin at 60°C a viscosity of the order of magnitude of 10^5 . R. Reiger⁷ has calculated from observations of the elastic hysteresis of rosin that its viscosity should be of the order of magnitude of 10^{11} . Since Reiger may have used another kind of rosin and since the viscosity in this temperature region can easily be changed a few thousand times by small temperature variations or small additions of turpentine (which is a constituent of rosin) our value is compatible with Reiger's result. It is, of course, very doubtful that Debye's equation still holds for such very viscous substances, but any any rate it seems very probable that this is a true case of anomalous dispersion at 60 cycles.

In a third set of measurements we have been able to verify this result by means of optical investigations. Rosin and castor oil were two of the first materials in which Kerr⁸ was able to observe electric double refraction. Kerr found that in these two liquids the effect had a different character from that in all other substances. The problem has, however, never been investigated, since the experiments of Quincke made it doubtful, at that time, if in rosin the effect was not due merely to electrostriction and heating⁹. Debye's theory and our recent experiments explain the difficulties involved in these earlier experiments.

According to Langevin, Cotton-Mouton, and P. Debye¹⁰ the Kerr effect is due to the orientation of the asymmetric molecules in the electric field. The effect can also exist in nonpolar substances but is especially strong in liquids with polar molecules. In these substances the effect is mainly due to the orientation of the dipoles. Therefore, the Kerr effect has a relaxation time which is identical with the relaxation time of the electric polarization. This fact has been shown by the experiments of Blondlot¹¹ H. Abraham and Lemoine¹² J. James,¹³ C. Gutton¹⁴, etc. All these investigators measured the relaxation time after a sudden discharge of the Kerr cell and found values of

⁷ R. Reiger, *Phys. Zeits.* **2**, 213 (1900).

⁸ Kerr, *Phil. Mag.* **50**, 337, 446 (1875).

⁹ W. Voigt in Graetz, *Handbuch der Elektrizität und Magnetismus I.*

¹⁰ P. Debye, *loc. cit.* (4).

¹¹ R. Blondlot, *Journal de phys.* **7**, 91 (1888).

¹² H. Abraham and J. Lemoine, *Journal de phys.* **9**, 262 (1900).

¹³ J. James, *Ann. de Physique* **15**, 954 (1904).

¹⁴ C. Gutton, *Journal de phys.* **2**, 51 (1912); **3**, 266, 445 (1913).

τ of the order of 2×10^{-9} sec., corresponding to anomalous dispersion for waves of 60 cm wave-length or $\nu = 5 \times 10^3$ as observed for ordinary liquids.

By producing the Kerr effect with an electric potential of this frequency, one should be able to observe an anomalous Kerr effect, namely a decrease of the Kerr constant with increasing frequency. Since the observation of the Kerr effect requires potentials of at least a few thousand volts, such an investigation is impossible with ordinary liquids. The effect has only been discovered quite recently by C. V. Raman and S. C. Sirkar.¹⁵

The existence of anomalous dispersion in rosin for radio and audio frequencies makes it very easy to demonstrate this "anomalous Kerr effect," and the success of these experiments proves the existence of polar molecules in rosin.

A Kerr cell was filled with commercial white rosin, which is transparent in layers up to 10 cm thickness. The cell was 8 cm long, and the distance between the electrodes was 3 mm. The existence of the Kerr effect was observed in the usual way with help of two crossed nicols. Since rosin is optically active, it was necessary to use monochromatic light. This was obtained from a carbon arc with different light filters. By very slow cooling of the liquid rosin we were able to prevent internal stresses at lower temperatures. The voltage was measured with a spark gap parallel to the cell.

A d.c. voltage of 10 kv., furnished by electrostatic machine, produced at all temperatures an intense Kerr effect. Sixty cycle voltage, however, did not produce the slightest effect at room temperatures though the potential was increased to more than 75 kv. This certainly shows that the double refraction in this case cannot be due to electrostriction.

The effect of relaxation can easily be observed. If the Kerr effect is produced with d.c. and the voltage suddenly removed by closing the spark gap, the Kerr effect disappears gradually. At room temperature (20°C) the effect could still be clearly observed 30 seconds after the closing of the spark gap.

Using 60 cycle a.c. and raising the temperature of the rosin very slowly, the Kerr effect appears at 35°C first very faintly and increases gradually until it has the same intensity at 70°C as for the corresponding d.c. voltage. The temperature at which the effect appears was fixed by leaving the rosin for 24 hours at constant temperature, once at 30° without obtaining any effect, and once at 35° with the first observable result.

These observations are in agreement with our measurements of the anomalous dispersion at 60 cycles. The curves in Fig. 3 show that the orientation of the polar molecules begins at about 35°C and reaches its full value at about 70°C.

We encountered many more difficulties in producing this anomalous Kerr effect with radio waves. For this purpose we built an oscillator, using a UX-852, 75 watt tube. The oscillator was coupled to a Tesla coil whose ends were connected to the electrodes of the Kerr cell. The frequency of the oscillator was adjusted to resonance with the circuit containing the Kerr con-

¹⁵ C. V. Raman and S. C. Sirkar, *Nature* **121**, 794 (May 1928).

denser. The frequency was 1.5×10^6 . According to our results in Fig. 3 the Kerr effect for this frequency should appear at about 100°C . At this temperature the rosin is liquid; since the anomalous dispersion is always connected with a maximum of absorption the high voltage used heats the substance. This heating effect produces a convection of the liquid which makes it almost impossible¹⁶ to observe the Kerr effect. Since the disturbance due to convection requires about one second to appear, the effect can be seen for an instant after the field is applied.

After numerous trials we succeeded in this way in observing the Kerr effect for rosin at radio frequencies. The lowest temperature for which it was clearly seen was 115° . The effect may have existed at somewhat lower temperatures, but the difficulties of observation precluded any definite results.

CONCLUSIONS

The measurement of the dielectric constant and power factor and the observation of the Kerr effect show that castor oil and rosin are liquids with polar molecules. Because of the extremely high viscosity of these substances, the effect of anomalous dispersion and the anomalous change of the Kerr effect can be observed with radio frequencies and on rosin even at 60 cycles. These facts are important in three respects.

1. The existence of anomalous dispersion in the radio and audio region of the spectrum makes it possible to carry out accurate measurements of this effect and to test Debye's theory. Such an investigation is very desirable. We hope to be able to publish in the near future accurate data on chemically uniform materials. Our present measurements agree qualitatively with Debye's theory. The results of this investigation seem to point to the possibility of investigating the anomalous dispersion of practically any substance which may be dissolved in non-polar oils of proper viscosity.

2. The anomalous change of the Kerr effect with temperature and frequency represents a new effect to prove the theory of the orientation of the polar molecules.

3. The existence of anomalous dispersion in rosin at 60 cycles shows the importance of this effect in understanding the dielectric behavior of technical insulation materials. We believe that the curious behavior of many dielectrics as found by electrical engineers can be explained by the fact that polar molecules are present.

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¹⁶ R. Leiser, *Abhandlg. d. Bunsenges.* No. 4, Halle 1910.