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# The Variation of the Complex Dielectric Constant with Frequency

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The locus of the complex dielectric constant for the dispersion region of a polar dielectric is found in the "complex dielectric constant plane" following the equation of Onsager (1936), and is compared with the approximate solution of Cole (1938). The curve is plotted for the polar liquids, water, ethyl alcohol, and tertiary butyl alcohol, and compared with the curve deduced from Debye's equation. Calculations are made of the values of the relaxation times. The values of the molecular volume deduced from the Debye expression for the relaxation time are compared with those deduced from the van der Waals  $b$  coefficient.

## INTRODUCTION

THE equation of Debye<sup>1</sup> for the dielectric constant  $\epsilon$  of a polar substance at any frequency  $\omega/2\pi$  is

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} N \left[ \alpha + \frac{\mu_0^2}{3kT} \frac{1}{1 + i\omega\tau} \right]. \quad (1)$$

$N$  is the number of dipoles per cc,  $\alpha$  the molecular polarizability,  $\mu_0$  the dipole moment in the absence of interaction effects,  $k$  Boltzmann's constant,  $T$  the absolute temperature, and  $\tau$  the "relaxation time" of the dipole. Equation (1) reduces to  $\epsilon - \epsilon_0 = (\epsilon_1 - \epsilon_0)/(1 + ix)$ , where  $\epsilon_1$  is the static dielectric constant, measured at frequencies low enough so that  $\omega\tau \ll 1$ ,  $\epsilon_0$  is the optical dielectric constant, given by the square of the refractive index measured for the  $D$  line, and  $x$  is a parameter given by

$$x = \frac{\epsilon_1 + 2}{\epsilon_0 + 2} \omega\tau. \quad (2)$$

It is customary to write  $\epsilon = \epsilon' - i\epsilon''$ , and K. S. Cole and R. H. Cole<sup>2</sup> showed that the locus of  $(\epsilon', \epsilon'')$  considered as a point in the complex dielectric constant plane is a circle with center on the real axis  $[(\epsilon_1 + \epsilon_0)/(2), 0]$  and radius  $(\epsilon_1 - \epsilon_0)/2$ . It was also pointed out by Cole and Cole that the experimental locus of  $(\epsilon', \epsilon'')$  lay below the Debye curve in many cases and could then be fitted by a circular arc with a center below the real axis.

<sup>1</sup> P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929).

<sup>2</sup> K. S. Cole and R. H. Cole, *J. Chem. Phys.* 9, 341 (1941).

## THE USE OF ONSAGER'S EQUATION

The equation of Onsager<sup>3</sup> for  $\epsilon_1$  was suggested as an alternative expression for polar substances: the equation is

$$\frac{(\epsilon_1 - \epsilon_0)(2\epsilon_1 + \epsilon_0)}{\epsilon_1(\epsilon_0 + 2)^2} = \frac{4\pi}{9} N \frac{\mu_0^2}{kT},$$

and can be written as

$$\frac{(\epsilon_1 - \epsilon_0)(2\epsilon_1 + \epsilon_0)}{\epsilon_1(\epsilon_0 + 2)^2} = \beta, \quad (3)$$

where  $\beta$  is a constant. It is assumed that the term  $1/(1 + i\omega\tau)$ , representing the relaxation of the dipoles, enters in the same way as in the Debye equation, and, thus, the Onsager equation for  $\epsilon$  at any frequency  $\omega/2\pi$  can be written

$$\frac{(\epsilon - \epsilon_0)(2\epsilon + \epsilon_0)}{\epsilon(\epsilon_0 + 2)^2} = \frac{\beta}{1 + i\omega\tau}. \quad (4)$$

The problem is to obtain the locus of the point  $(\epsilon', \epsilon'')$  from Eqs. (3) and (4). A solution was given by R. H. Cole<sup>4</sup> by using the approximation

$$3\epsilon/(2\epsilon + \epsilon_0) \approx 3/2, \quad (5)$$

and it was found to be a circle with the same center and radius as the Debye circle, but the parameter describing any point on it was simply  $\omega\tau$  instead of Eq. (2). Cole also introduced a further factor  $q$ , following Van Vleck,<sup>5</sup> to describe the fact that the environment has a discrete structure and is not merely a continuum, but this is omitted in the following argument and the simple Onsager equation is considered.

<sup>3</sup> L. Onsager, *J. Am. Chem. Soc.* 58, 1486 (1936).

<sup>4</sup> R. H. Cole, *J. Chem. Phys.* 6, 385 (1938).

<sup>5</sup> J. H. Van Vleck, *J. Chem. Phys.* 5, 556 (1937).

Reference is made later to the modifications that Kirkwood<sup>6</sup> has suggested to describe this discrete nature of the dielectric. As will be expected from Eq. (5), the solution of Cole<sup>4</sup> and that given below agree for large values of  $\epsilon/\epsilon_0$ .

Combining Eqs. (3) and (4),

$$\frac{\gamma\epsilon}{(\epsilon - \epsilon_0)(2\epsilon + \epsilon_0)} = 1 + i\omega\tau, \quad (6)$$

and

$$R = \frac{\gamma[(2\epsilon' - \epsilon_0)(\epsilon'^2 + \epsilon''^2) - \epsilon'\epsilon_0^2]}{(2\epsilon'^2 - 2\epsilon''^2 - \epsilon'\epsilon_0 - \epsilon_0^2)^2 + (4\epsilon'\epsilon'' - \epsilon''^2\epsilon_0)^2} = 1, \quad (7)$$

$$X = \frac{\gamma[2\epsilon''(\epsilon'^2 + \epsilon''^2) + \epsilon''^2\epsilon_0^2]}{(2\epsilon'^2 - 2\epsilon''^2 - \epsilon'\epsilon_0 - \epsilon_0^2)^2 + (4\epsilon'\epsilon'' - \epsilon''^2\epsilon_0)^2} = \omega\tau. \quad (8)$$

Equation (7) is the locus of the point  $(\epsilon', \epsilon'')$ . The most convenient way of representing any point of the circle (corresponding to the parameter  $x$  of Debye) is through the value of  $\omega\tau$ . This is most directly given by

$$\omega\tau = \frac{X}{R} = \frac{2\epsilon''(\epsilon'^2 + \epsilon''^2) + \epsilon''^2\epsilon_0^2}{(2\epsilon' - \epsilon_0)(\epsilon'^2 + \epsilon''^2) - \epsilon'\epsilon_0^2}. \quad (9)$$

It will be seen that Eq. (7) contains two terms,  $\epsilon_0$  and  $\gamma$ , referring to the particular dielectric, but it can be generalized slightly by the substitutions

$$u = \epsilon'/\epsilon_0, \quad v = \epsilon''/\epsilon_0, \\ \delta = \gamma/\epsilon_0 = [(\epsilon_1/\epsilon_0) - 1][2(\epsilon_1/\epsilon_0) + 1]/(\epsilon_1/\epsilon_0).$$

Equation (7) now becomes

$$\delta[(2u - 1)(u^2 + v^2) - u] \\ = [2u^2 - 2v^2 - u - 1]^2 + (4uv - v)^2, \quad (10)$$

in which only the one term  $\delta$  represents the dielectric. In a similar manner Eq. (9) becomes

$$\omega\tau = \frac{2v(u^2 + v^2) + v}{(2u - 1)(u^2 + v^2) - u}. \quad (11)$$

A solution of (10) is required giving real values of  $v$  for  $1 < u < \epsilon_1/\epsilon_0$ , and it is obtained numerically.

For the purposes of calculation it is convenient to use the fact that Eq. (10) is a quadratic in  $v^2$  and it can be written, after rearrange-

where  $\gamma$  is a constant depending on the dielectric considered.

$$\gamma = [(\epsilon_1 - \epsilon_0)(2\epsilon_1 + \epsilon_0)]/\epsilon_1.$$

On substituting  $\epsilon = \epsilon' - i\epsilon''$ , rationalizing the denominator of the left-hand side, Eq. (6) becomes

$$R + iX = 1 + i\omega\tau,$$

where

ment, as

$$av^4 + bv^2 + c = 0, \quad (12)$$

where

$$\begin{cases} a = 4, \\ b = 8u^2 - u(4 + 2\delta) + (5 + \delta), \\ c = 4u^4 - u^3(4 + 2\delta) + u^2(\delta - 3) + u(\delta + 2) + 1. \end{cases}$$

The solution is given by

$$v^2 = [-b \pm (b^2 - 4ac)^{1/2}]/2a. \quad (13)$$

It is found that

$$b^2 - 4ac = Fu^2 - Gu + H,$$

where

$$\begin{cases} F = 4(\delta^2 + 4\delta + 36), \\ G = 4(\delta^2 + 11\delta + 18), \\ H = (\delta^2 + 10\delta + 9). \end{cases}$$

At this stage a check can be applied to insure that the equation for the locus has been derived correctly. The curve of  $(u, v)$  must go through the points  $(\epsilon_1/\epsilon_0, 0)$  and  $(1, 0)$ . Substituting

$$u = \epsilon_1/\epsilon_0 = p \text{ (say)}$$

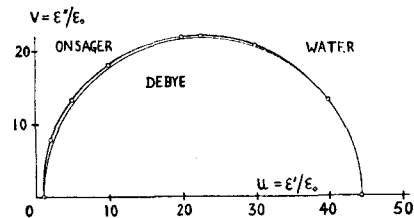


FIG. 1. The theoretical variation of the complex dielectric constant of water.

<sup>6</sup> J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939).

in Eq. (13) it is found that  $v^2=0$  (as required) and  $\frac{1}{4}[(1/p)-6-4p^2]$ . The second branch of the curve is here imaginary. Also, substituting  $u=1$  in Eq. (13) it is found that  $v^2=0$  (as required) and  $\frac{1}{4}(\delta-9)$ . The other branch of the curve can be real at this point, but in computation it is easy to see which branch is the physically possible one. A further check is given by considering what happens to the curve when  $\delta=0$ . First, the equation for  $v^2$  becomes

$$v^2+(u-1)^2=0,$$

which is satisfied by the point (1,0). This is to be expected as the dielectric so considered is non-polar and loss-free. The other solution for  $v^2$  is

$$v^2+(u+\frac{1}{2})^2=0,$$

satisfied by the point  $(-\frac{1}{2},0)$  which is physically meaningless. In the following calculations only the physically significant solution is given, any imaginary branches of the curves being neglected.

#### COMPUTATION OF CURVE

Equation (13) has been used to plot the curve for water, ethyl alcohol, and tertiary butyl alcohol. These three dielectrics were chosen to see how the curve behaved for polar substances of large, medium, and small dielectric constant, and the data about them are reliable. In every case it was found that the positive sign in Eq. (13) gave the physical solution.

For water, the value of  $\epsilon_1$  was taken to be 78.5 at 25°C (Lattey, Gatty, and Davies<sup>7</sup>).  $n_D=1.33$ ,  $\epsilon_0=1.77$ . Various values of  $u$  were taken between 1 and  $\epsilon_1/\epsilon_0=44.3$  and the corresponding values of  $v$  were found. The points  $(u,v)$  are plotted in Fig. 1 and are seen to lie close to the Debye circle whose center is

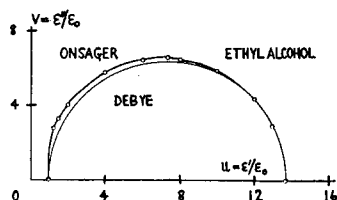


FIG. 2. The theoretical variation of the complex dielectric constant of ethyl alcohol.

<sup>7</sup> R. T. Lattey, O. Gatty, and W. G. Davies, *Phil. Mag.* **12**, 1019 (1931).

( $u=22.65$ ,  $v=0$ ) radius 21.65 and which is also drawn. As a whole the Onsager curve lies above the Debye circle but is closest to it for large  $u$ . This is to be expected as Cole<sup>4</sup> showed that the Onsager curve reduced to the circle if, essentially,  $\epsilon_0$  could be neglected in comparison with  $\epsilon$  and this is true for the right-hand side of the curve for water.

For ethyl alcohol, the value of  $\epsilon_1$  was taken to be 25.3 at 18°C (Akerlof<sup>8</sup>).  $n_D=1.36$ ,  $\epsilon_0=1.85$ . Results are shown in Fig. 2.

Again for large  $u$ , the Onsager curve lies closely beside the Debye circle though the departure from it is more marked than for water. A similar comment applies to tertiary butyl alcohol for which  $\epsilon_1$  is 9.37 at 30°C.<sup>8</sup>  $n_D=1.39$ ,  $\epsilon_0=1.93$ . The results are plotted in Fig. 3. In all three cases the Onsager curve lies above the Debye circle while Cole and Cole<sup>2</sup> showed that the experimental points lie below if not on it for the substances they considered. Considering only the curves as a whole, the Debye theory seems to be the more correct, especially for substances with small dielectric constants.

#### NUMERICAL COMPARISON WITH DEBYE'S EQUATION

A stricter comparison of the two theories is given if the parameters are considered for any point in the dispersion region. The point chosen is that midway between  $\epsilon_0$  and  $\epsilon_1$ , namely, that for which  $u=(1+\epsilon_1/\epsilon_0)/2$  and the value of  $\omega\tau$  is calculated according to both theories. According to Debye, the midpoint of the semicircular arc is given when

$$x=1.$$

Hence from Eq. (2)

$$\omega\tau=(\epsilon_0+2)/(\epsilon_1+2).$$

To find the value of  $\omega\tau$  according to Onsager's

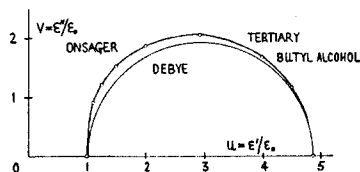


FIG. 3. The theoretical variation of the complex dielectric constant of tertiary butyl alcohol.

<sup>8</sup> G. Akerlof, *J. Am. Chem. Soc.* **54**, 4125 (1932).

TABLE I.

	$\omega\tau$ from	
	Onsager	Debye
Water	0.99	0.047
Ethyl alcohol	0.97	0.14
Tertiary butyl alcohol	0.92	0.35

equation, the value of  $v$  has to be found from Eq. (13) in the usual manner and then both  $u$  and  $v$  are substituted in Eq. (11). Table I gives the values of  $\omega\tau$  so calculated. It will be seen how good is Cole's approximation, since, as his parameter is  $\omega\tau$ , this implies that at the midpoint,  $\omega\tau$  is unity. Table I shows the divergence between the two theories, but it is difficult to interpret numerical deductions from it. If Debye's equation for  $\tau$  is used, namely,

$$\tau = 3\eta v/kT,$$

then the volume of the molecule is

$$v = (kT/3\eta)\tau,$$

$\eta$  is the coefficient of "inner" viscosity generally taken to be the macroscopic viscosity. The values of  $\tau$  are given by  $\omega\tau$  for the midpoint of the dispersion region at the air wave-length  $\lambda_s$ .

$$v = (\lambda_s kT/6\pi c\eta) \cdot \omega\tau, \quad (14)$$

where  $c$  is the velocity of light. It is customary to compare values of  $v$  found from dielectric measurements with those from van der Waals' equation. Table II gives the values of  $v$  calculated from the van der Waals  $b$  coefficient and from Debye and Onsager's theories, using Table I and Eq. (14). It has been assumed that  $b$  is  $4 \times$  (volume of molecules in 1 cc). The unit of  $v$  is  $10^{-24}$  cc. No value of  $\lambda_s$  for tertiary butyl alcohol was found in the literature. The observations of B  z<sup>9</sup> and Slevogt<sup>10</sup> cover the major part of the dispersion region of ethyl alcohol.

Any deduction based on Debye's equation for  $\tau$  cannot be very valuable. The two weaknesses

TABLE II.

	$\lambda_s$ (cm)	Authority	$v$ from		
			Onsager	Debye	van der Waals
Water	1.5	Abadie <sup>a</sup>	12	0.6	14
Ethyl alcohol	28.9	B��z, <sup>b</sup> Slevogt <sup>c</sup>	160	23	35

<sup>a</sup> P. Abadie, J. Faraday Soc. (1947).

<sup>b</sup> G. B  z, Physik. Zeits. 40, 394 (1939).

<sup>c</sup> K. E. Slevogt, Ann der Physik 36, 141 (1939).

inherent in the equation are that the molecule is assumed to be spherical and that the viscosity coefficient entering into the damping of the rotation of the molecule is simply the macroscopic viscosity coefficient.

There is no need to assume Onsager's internal field to show that the locus of  $(\epsilon', \epsilon'')$  is a circle with parameter  $\omega\tau$  because, as Fr  hlich<sup>11</sup> has suggested, for some substances the internal field acting on each dipole may be just the electric field due to the potential distribution, no contribution being given by the volume polarization of the medium in such a case. Fr  hlich showed that the Debye circle was given as before with the one difference that the parameter was

$$x = \omega\tau.$$

Again,  $x=1$  at the midpoint of the semicircle. The extension made by Kirkwood<sup>6</sup> to Onsager's equation was to multiply  $\beta$  in Eq. (3) by a factor which was calculated from the "structure" of the liquid. As  $\beta$  does not appear explicitly in the equation for  $(u, v)$  neither will any multiplying factor, and the resulting analysis is unaffected. (The factor  $q$  introduced by Cole affects only the value of  $\tau$  deduced from the circle.) It is perhaps best to leave  $\tau$  as a time and not attempt to deduce anything from it. Too wide an application should not be expected for any one theory, and the internal field on an individual dipole in all probability varies according to the substance considered.

<sup>9</sup> See reference b to Table II.

<sup>10</sup> See reference c to Table II.

<sup>11</sup> H. Fr  hlich, J. Inst. Elec. Eng. 91, 456 (1944).