

ON THE RELAXATION TIME OF POLAR MOLECULES IN THE LIQUID STATE

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(Received for publication September, 11, 1953)

ABSTRACT. It is pointed out that the values of λ_m , deduced by previous workers from Cole and Cole equation do not agree with the values actually observed by some recent workers in the case of a few polar liquids. Debye's theory is extended to the case of a liquid containing a mixture of monomeric and dimeric molecules and an expression for the complex dielectric constant has been deduced. It is found that the expression is too complicated to yield a simple condition for maximum absorption.

The various causes for the discrepancy between the actual molecular volume and the volume of the rotor calculated from Debye's theory observed in certain cases have been discussed.

I N T R O D U C T I O N

It is well known that the value of the permanent electric moment, μ of the molecule in the liquid state calculated from the Debye equation from the observed values of ϵ_0 and ϵ_∞ , the dielectric constant of the liquid for fields of zero and infinite frequencies respectively, do not generally agree with the values observed in the case of the respective vapours. Attempts have been made by Onsagar (1936) and Kirkwood (1939) to modify the Debye equation, taking into account the influence of intermolecular field so that the values of μ calculated from the modified equations may agree with those observed for the vapour. In the region of very high frequencies certain polar liquids exhibit absorption and the dielectric constant ϵ^* is complex due to the presence of a relaxation time τ which should be given by the Debye equation

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + iB\omega\tau}, \quad \dots (1)$$

where

$$B = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2}$$

Actually, however, it is observed that in the case of many liquids equation (1) cannot explain the complex dielectric constant for different frequencies if a suitable fixed value of τ is assumed in equation (1). To overcome this difficulty existence of a distribution in the relaxation time in such cases has been assumed. In order to take into account the distribution

of relaxation time Cole and Cole (1941) suggested the following empirical expression for the complex dielectric constant

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 + \epsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}} \quad \dots (2)$$

where τ_0 is the most probable relaxation time corresponding to a frequency at which the absorption is maximum and α is the empirical constant with values between 0 and 1.

Hennelly, Heston and Smyth (1948) observed that in the case of certain alkyl bromides such as octyl bromide etc., there is a distribution of relaxation time, α being greater than zero. Franklin *et al* (1950) have discussed the values of α for certain alkyl halides dissolved in different solvents and have shown that α has a value different from zero in the case of solutions in certain solvents, but in some other cases α is zero.

Branin and Smyth (1952) have pointed out that in the arc plot with $(\epsilon' - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty)$ as abscissa and $\epsilon''/(\epsilon_0 - \epsilon_\infty)$ as the ordinate, where ϵ' and ϵ'' are defined by the equation $\epsilon^* = \epsilon' - i\epsilon''$, the following expressions can be assumed to take account of the distribution of relaxation time

$$\begin{aligned} \frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} &= \int_0^\infty \frac{G(\tau) d\tau}{1 + \omega^2\tau^2} \\ \frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} &= \int_0^\infty \frac{\omega\tau G(\tau) d\tau}{1 + \omega^2\tau^2} \end{aligned} \quad (3)$$

where $G(\tau)$ is a function of τ . Two forms of the function, the Cole and Cole function (1941) and the Wagner-Yager (1936) function have been discussed and compared with experimental results by these authors.

It is the object of the present paper to point out that results of investigations on the absorption of U. H. F. and microwaves reported by Sen (1950, 1951), Kastha (1952) and Ghosh (1953a, 1953b) indicate the presence of several discrete values of τ in the case of some of the liquids studied by them and that in calculating the complex dielectric constant in such cases these discrete values of τ should be taken into account instead of a distribution given by the G -function. It has also been pointed out by Ghosh (1953) that new absorption maxima due to dimers appear in some cases only when the liquids are cooled down to low temperatures. In such cases, therefore, a single value of τ should explain the observed dielectric constant for different frequencies at higher temperatures. This is corroborated by the results reported by Hennelly, Heston and Smyth (1948) who observed that the value of α in Cole and Cole equation is small in the case of certain liquids and it diminishes almost to zero with rise of temperature of the liquids. Some of these liquids are *i*-propyl bromide, *i*-butyl bromide, chlorobenzene, bromobenzene, ethylene chloride etc. These facts clearly indicate that the agents which are responsible for the

deviation from Debye equation at lower temperatures tend to disappear at higher temperatures. These agents are evidently dimers which are present in the liquid in considerable proportions at lower temperatures and gradually break up into monomers at higher temperatures, as observed in the case of many liquids by Sen (1950, 1951), Kastha (1952) and Ghosh (1953a).

DIFFICULTIES WITH DISTRIBUTION OF
RELAXATION TIME THEORY

The Cole and Cole empirical relation would explain the observed facts satisfactorily if a distribution of relaxation time dependent only on temperature and consequently on the viscosity of the liquid were present in the liquid. As pointed out above, actually, more than one discrete relaxation time, instead of a continuous distribution, are observed in many cases at any particular temperature. Hence although the empirical equation can explain the dielectric constant of the liquid for different frequencies with a suitably adjusted value of α for each temperature, the value of λ_m , the wave length showing maximum absorption at each temperature, deduced from the Cole and Cole equation may not agree with the actual value observed by the method of direct determination of absorption coefficient of the liquid for different frequencies. It can be seen from a comparison of the two sets of values given in Table I that such a discrepancy actually occurs in some cases.

TABLE I

Liquid	Temperature	λ_m deduced from Cole and Cole equation (Hennelly <i>et al.</i> , 1948)	λ_m actually observed by direct method (Ghosh, 1953a)
Chlorobenzene	25°C	1.94 cm	36.5 cm
Bromobenzene	1°C	4.53 cm	34.5 cm

The absorption peak at 36.5 cm observed by Ghosh (1953a) is assumed by him to be due to dimers and that due to monomers should, of course, be at a smaller wave length, but the consistent value of λ_m due to the monomer deduced from that for the dimer is about 28 cm, and it cannot be so small as 1.94 cm deduced from Cole and Cole equation. In the case of bromobenzene at 0°C the peak observed at 34.5 cm (Ghosh, 1953a) has been assumed to be due to a monomer. So the value 4.53 cm deduced by Hennelly *et al.* (1948) from Cole and Cole equation is much too low. It has further been observed by Ghosh (1953c) that bromobenzene does not show any absorption maximum for the wave length 3.18 cm in the temperature range 0°–80°C, and therefore, the λ_m deduced by Hennelly *et al.* (1948) from Cole and Cole equation is not actually observed. Similar discrepancies have also been observed in the case of ethylene chloride and ethylene bromide by Ghosh (1953b).

APPLICABILITY OF DEBYE'S THEORY IN PRESENCE
OF BOTH MONOMERS AND DIMERS IN THE
LIQUID

It has to be pointed out that the values of the radius of the rotor have been calculated so far by previous authors from Debye's theory on the assumption that there is only one type of rotor in the liquid. As actually both monomers and dimers are present in the liquid, it is not possible to obtain the accurate value of τ from the relation

$$\omega\tau = \frac{\epsilon_0 + 2}{\epsilon_0 + 2} \sqrt{\frac{\epsilon_0}{\epsilon_\infty}} \quad \dots (4)$$

unless the relative concentration of the monomers and dimers and their contributions to ϵ_0 and ϵ_∞ are known and equation (4) is suitably modified to take into account these contributions. If f_1 and f_2 be the mole fractions of the single and double molecules respectively the equation for the complex dielectric constant ϵ given by Debye (1929) can be modified in the case of a mixture assuming Mosotti's hypothesis to hold. The modified equation for the mixture becomes

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{Mf_1 + M'f_2}{\rho} = P_1(\omega)f_1 + P_2(\omega)f_2 \quad \dots (5)$$

where

$$P_1(\omega) = \frac{4\pi N}{3} \left[\alpha_0 + \frac{\mu^2}{3kT} \cdot \frac{1}{1 + i\omega\tau} \right],$$

$$P_2(\omega) = \frac{4\pi N}{3} \left[\alpha'_0 + \frac{\mu'^2}{3kT} \cdot \frac{1}{1 + i\omega\tau'} \right],$$

α_0 , μ , M and τ are respectively the polarisability, permanent electric moment, molecular weight and relaxation time of the single molecule and α'_0 , μ' , M' and τ' are the corresponding quantities for the dimer. Let the quantities ϵ_0 , ϵ_∞ , ϵ'_0 and ϵ'_∞ for the monomeric and dimeric molecules respectively be defined as follows according to Debye (1929) :—

$$\begin{aligned} \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \cdot \frac{M}{\rho} &= \frac{4\pi N}{3} \left(\alpha_0 + \frac{\mu^2}{3kT} \right) \\ \frac{\epsilon'_0 - 1}{\epsilon'_0 + 2} \cdot \frac{M'}{\rho'} &= \frac{4\pi N}{3} \left(\alpha'_0 + \frac{\mu'^2}{3kT} \right) \\ \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \cdot \frac{M}{\rho} &= 4\pi N \alpha_0 \\ \frac{\epsilon'_\infty - 1}{\epsilon'_\infty + 2} \cdot \frac{M'}{\rho'} &= \pi N \alpha'_0 \end{aligned} \quad (6)$$

Here ϵ_0 and ϵ_∞ are the dielectric constants of the liquid containing only monomeric molecules, for frequencies zero and infinity respectively and ϵ'_0 and ϵ'_∞ are the corresponding quantities for the liquid containing only

dimeric molecules, and ρ and ρ' are the corresponding densities of the liquids.

Then from (5) and (6) we get,

$$f_1 P_1(\omega) + f_2 P_2(\omega) = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \cdot \frac{f_1 M}{\rho} + \frac{\epsilon_\infty' - 1}{\epsilon_\infty' + 2} \cdot \frac{f_2 M'}{\rho'}$$

$$+ \frac{M f_1}{\rho} \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right) \frac{1}{1 + i\omega\tau} + \frac{M' f_2}{\rho'} \left(\frac{\epsilon_0' - 1}{\epsilon_0' + 2} - \frac{\epsilon_\infty' - 1}{\epsilon_\infty' + 2} \right) \frac{1}{1 + i\omega\tau'} \quad \dots (7)$$

If it is now assumed that $\epsilon_\infty = \epsilon_\infty' = n^2$, where n is the refractive index of the actual liquid containing both monomeric and dimeric molecules and that $\rho = \rho'$, we get,

$$f_1 P_1(\omega) + f_2 P_2(\omega) = \frac{1}{\rho} \cdot \frac{n^2 - 1}{n^2 + 2} (M f_1 + M' f_2) + \frac{M f_1}{\rho} \cdot \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{1 + i\omega\tau}$$

$$+ \frac{M' f_2}{\rho} \cdot \left(\frac{\epsilon_0' - 1}{\epsilon_0' + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{1 + i\omega\tau'} \quad \dots (8)$$

From (5) we get,

$$\epsilon = \frac{1 + \frac{2\rho}{M f_1 + M' f_2} \{P_1(\omega) f_1 + P_2(\omega) f_2\}}{1 - \frac{\rho}{M f_1 + M' f_2} \{P_1(\omega) f_1 + P_2(\omega) f_2\}} \quad \dots (9)$$

From (8) and (9) we get,

$$1 + \frac{2(n^2 - 1)}{n^2 + 2} + \frac{2M f_1}{M f_1 + M' f_2} \cdot \frac{1}{(1 + i\omega\tau)} \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$

$$+ \frac{2M' f_2}{M f_1 + M' f_2} \cdot \frac{1}{(1 + i\omega\tau')} \left(\frac{\epsilon_0' - 1}{\epsilon_0' + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$

$$1 - \frac{n^2 - 1}{n^2 + 2} - \frac{M f_1}{M f_1 + M' f_2} \cdot \frac{1}{(1 + i\omega\tau)} \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$

$$- \frac{M' f_2}{M f_1 + M' f_2} \cdot \frac{1}{(1 + i\omega\tau')} \left(\frac{\epsilon_0' - 1}{\epsilon_0' + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$

$$\frac{\epsilon_0}{\epsilon_0 + 2} + \frac{M' f_2}{M f_1} \cdot \frac{(1 + \omega^2 \tau \tau')}{(1 + \omega^2 \tau'^2)} \left\{ \frac{\epsilon_0'}{\epsilon_0' + 2} - \frac{\omega^2 \tau' (\tau - \tau') n^2}{n^2 + 2} \right\}$$

$$+ i\omega \left[\frac{n^2}{n^2 + 2} \cdot \tau + \frac{M' f_2}{M f_1 (1 + \omega^2 \tau'^2)} \right] \left\{ \frac{(1 + \omega^2 \tau \tau') \tau' n^2}{n^2 + 2} + \frac{\epsilon_0' (\tau - \tau')}{\epsilon_0' + 2} \right\}$$

$$\frac{1}{\epsilon_0 + 2} + \frac{M' f_2 (1 + \omega^2 \tau \tau')}{M f_1 (1 + \omega^2 \tau'^2)} \left\{ \frac{1}{\epsilon_0' + 2} - \frac{\omega^2 \tau' (\tau - \tau')}{n^2 + 2} \right\}$$

$$+ i\omega \left[\frac{\tau}{n^2 + 2} + \frac{M' f_2}{M f_1 (1 + \omega^2 \tau'^2)} \right] \left\{ \frac{\tau' (1 + \omega^2 \tau \tau')}{n^2 + 2} + \frac{\tau - \tau'}{\epsilon_0' + 2} \right\} \quad \dots (10)$$

When $M=M'$, $f_1=f_2$ and $\tau=\tau$, equation (10) reduces to the following form:

$$\epsilon = \frac{\epsilon_0}{\epsilon_0 + 2} + \frac{\epsilon_\infty}{\epsilon_\infty + 2} i\omega\tau \quad \dots (11)$$

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_0 + 2} + \frac{1}{\epsilon_\infty + 2} i\omega\tau$$

Equation (11) is the well known Debye equation for the dielectric constant of the liquid having only one type of molecules. The condition for maximum absorption deduced by Debye (1929) from (11) is given by the relation

$$\omega\tau = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \sqrt{\frac{\epsilon_0}{\epsilon_\infty}} \quad \dots (12)$$

As equation (10) is more complicated than equation (11), the simple condition for the maximum absorption given in (12) cannot be deduced from (10). Hence it is clear that the value of τ deduced from (12) in the case of a mixture of monomeric and dimeric molecules cannot be accurate. In certain cases, however, it is found that equation (12) gives some values of τ which lead to values of volume of the rotors agreeing with those of the dimers calculated from the density. Chlorobenzene, *o*-xylene and *m*-xylene are such substances. As reported by Ghosh (1953a), the absorption peaks due to the dimers in these cases are exhibited in the range 500–900 Mc/sec at different temperatures and those due to the single molecules may be observed at still higher frequencies.

It is unlikely that all the molecules in any of these liquids are dimers. The validity of equation (12) in these cases probably indicates that the absorption coefficient in the neighbourhood of the frequency of maximum absorption is determined predominantly by that frequency of maximum absorption, the influence of the other frequency of maximum absorption due to single molecules being negligible. Also, the values of ϵ_0 for the two types of molecules should not differ widely from each other if we want to get any reliable value of τ from equation (12). This condition may be satisfied in the case of all the three molecules mentioned above, because the dielectric constant being low in all these cases, the contribution of the permanent electric moment to the dielectric constant is not very great and it may not change very much with the formation of dimers.

VISCOUS FORCES ACTING ON THE MOLECULES IN POLAR LIQUIDS

It has been pointed out by many previous authors that the volume of the rotor calculated from the relation $\tau = 4\pi\eta a^3/kT$, where η is the viscosity of the liquid, does not agree in many cases with the volume of the molecule calculated from the density of the liquid. For instance, Whiffen and

Thompson (1946) observed that in the case of solution of chloroform in heptane the volume calculated from Debye's equation is too small. The results obtained recently by Ghosh (1953*b*) in the case of pure chloroform, ethylene chloride and glycerine in the liquid state also lead to the same conclusion. Whiffen and Thompson suggested that the discrepancy is due to the fact that internal viscosity acting on the polar molecule is different from the macroscopic viscosity. It has to be pointed out, however, that the macroscopic viscosity leads to correct value of the volume of the molecule in many pure liquids such as chlorobenzene, bromobenzene etc., (Ghosh, 1953*a*). The discrepancy is actually enormous in the case of liquids having high macroscopic viscosity, such as glycerine. This may be due to the fact that in such liquids there is strong association among neighbouring molecules. Each group of associated molecules being large in volume, the macroscopic viscosity is large, as the rate of flow is determined predominantly by the flow of the large groups. There may be, however, many single molecules in the liquid not strongly associated with their neighbours and these may orient freely along external electric field. The viscous forces acting on these molecules during the orientation are much smaller owing to want of association with neighbouring molecules. As the volume of the rotor is inversely proportional to η according to Debye's equation, the volume calculated with the smaller value of η will be much larger than that calculated taking the macroscopic viscosity in place of η .

In the case of other liquids having smaller coefficient of viscosity the discrepancy between the calculated value of the volume of the rotor and the actual volume of the molecule, deduced from density, may be due to two causes. As pointed out earlier, if the liquid contains both monomeric and dimeric molecules, the value of τ calculated from Debye's equation is not correct and so the volume of the rotor deduced from the value of τ cannot be correct. In the case of solution, presence of dimers is ruled out and the discrepancy is obviously due to the difference between the actual viscous force acting on the molecule during orientation and the macroscopic viscosity. The viscosity of heptane, for instance, is determined by the viscous forces acting on the long heptane molecule when it moves in the liquid. The chloroform molecule being almost spherical and much smaller, the viscous forces acting on it during its orientation when it is dissolved in heptane are much smaller than the macroscopic viscosity of pure heptane. If this smaller viscous force be taken into account in calculating the volume of the rotor, the volume will come out much larger than that deduced by Whiffen and Thompson (1946) assuming η to be equal to the macroscopic viscosity of heptane. It is difficult, however, to measure the actual viscous forces acting on the chloroform molecule when it is dissolved in heptane. In the case of such a solution of simple molecules in liquids of low viscosity if the value of τ and the volume of the molecule calculated from its density are taken in calculating the value of η from Debye's equation probably the

'internal' viscous forces acting on the dissolved molecule can be roughly estimated.

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