A. Dielectric absorption of polar liquids.

It is well known that a phenomenon of absorption of energy is always associated with the phenomenon of dispersion of dielectric constant observed in the case when a polar dielectric medium is subjected to a high frequency alternating field.

It was Debye (1929) who first correlated this phenomenon of absorption of energy with the phenomenon of dielectric dispersion.

From a complex distribution function for the polar molecules under the influence of a high frequency alternating field he obtained the following expression for the complex dielectric constant:

\[
\frac{\varepsilon^* - 1}{\varepsilon^* + 2} \cdot \frac{M}{\rho} = \mathcal{P}(\omega) = \frac{4\pi N}{3} \left( \mu + \frac{\mu^2}{3K_T} \cdot \frac{1}{1 + i\omega \tau} \right)
\]

where \( \varepsilon^* \) = the complex dielectric constant of medium at the absolute temperature \( T^0 \)K under a field of angular frequency \( \omega \) = the molecular polarisibility, \( \mu \) = permanent dipole moment of the molecule, \( K \) = the Boltzmann constant, \( N \) = number of molecules per cc., \( \rho \) = density of the fluid, \( M \) = molecular weight, \( \tau \) = the relaxation time of the rotor which can be the whole molecule or a part of it. This relaxation time can be defined as the time in which after the removal of the external field the polarisation induced by the applied field is reduced to 1/e th of its original value, 'e' being the natural
Fig. 1.
The intimate connection between the phenomenon of absorption and the phenomenon of dielectric dispersion will be evident if we can establish the relation between the real and imaginary parts of the complex dielectric constant.

Let us assume the quantity $\varepsilon_x(\omega)$ to be given by

$$\varepsilon_x(\omega) = 1 + \int_0^\infty f(u) e^{i\omega u} du \ldots \ldots (4)$$

where $u$ is a function of time and of the properties of the medium. This equation shows single valuedness of $\varepsilon_x(\omega)$ in the complex $\omega$-plane. Kramer and Kronig (1927) obtained the following equations:

$$\varepsilon'(\omega) - 1 = \frac{1}{\pi} \text{P} \int_{-\infty}^{+\infty} \frac{\varepsilon''(\omega)}{\omega - \omega_0} d\omega \ldots \ldots (5-1)$$

$$\varepsilon''(\omega) - 1 = \frac{1}{\pi} \text{P} \int_{-\infty}^{+\infty} \frac{\varepsilon'(\omega)}{\omega - \omega_0} d\omega \ldots \ldots (5-2)$$

where $\text{P}$ denotes the principal value of the integral.

These equations show the relation between the real and imaginary parts of the function $\varepsilon_x(\omega)$ and thus show that the intimate connection between the phenomenon of absorption and the phenomenon of dispersion. Thus phenomenon of absorption associated with the dispersion gives the dielectric constant a complex characteristics and we can write

$$\varepsilon^x = \varepsilon' - i \varepsilon'' \ldots \ldots (6)$$

This means that in an ideal condenser of capacity $C$ placed in a rapidly varying field $E = E^0 e^{i\omega t}$ the capacitative
current \( E_0 \omega \epsilon' C \) is always associated with an ohmic or loss current \( E_0 \omega \epsilon'' C \) the phase difference between the two currents being \( \pi \) as is indicated by the introduction of 'i' in equation (6). Hence the total current due to the effect of the loss current measuring the absorption, makes an angle \( \delta \) with the capacitative current as shown in Fig. 1 and greater the value of this loss current greater the magnitude of this angle \( \delta \). Thus the value of the tangent of this angle \( \delta \) gives the measure of the absorption. Hence the condition of maximum \( \tan \delta \) gives the condition of maximum absorption.

Now from the equation
\[
\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + i/\beta \tau} \quad \ldots \quad (2)
\]
by rationalising the denominator and separating the real and imaginary parts we get
\[
\epsilon'(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \beta^2 \omega^2 \tau^2} \quad \ldots \quad (2.1)
\]
and
\[
\epsilon''(\omega) = \frac{(\epsilon_0 - \epsilon_\infty) \beta \omega \tau}{1 + \beta^2 \omega^2 \tau^2} \quad \ldots \quad (2.2)
\]

This gives the value of \( \tan \delta \) as
\[
\tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{(\epsilon_0 - \epsilon_\infty) \beta \omega \tau}{\epsilon_0 + \beta^2 \omega^2 \tau^2} \quad \ldots \quad (2.3)
\]
Equation (2.3) gives the following condition for maximum value of \( \tan \delta \) or the condition for maximum absorption
\[
\frac{\epsilon_0}{\beta \omega \tau} = \beta \omega \tau \epsilon_\infty
\]
Thus the frequency at which the maximum absorption occurs is given by

$$\omega_{max} \tau = \frac{1}{\beta} \frac{\sqrt{\varepsilon_0}}{\sqrt{\varepsilon_0 + 2}} = \frac{\varepsilon_0 + 2}{\varepsilon_0 + 2} \sqrt{\varepsilon_0} \quad \ldots (7)$$

The condition for $\varepsilon''(\omega)$ to attain the maximum value is

$$\omega \tau = \frac{1}{\beta} = \frac{\varepsilon_0 + 2}{\varepsilon_0 + 2} \quad \ldots (7.1)$$

The coefficient of maximum absorption is given as

$$k_{max} = \frac{\sqrt{\varepsilon_0} - \sqrt{\varepsilon_\infty}}{\sqrt{\varepsilon_0} + \sqrt{\varepsilon_\infty}} \quad \ldots \ldots (8)$$

It is thus evident that the phenomenon of absorption indicates a time lag between the polarisation and the applied field which means that the molecules do not come back to their original state of distribution immediately after the field is removed. Treating these molecules as spheres rotating in a viscous medium and applying Stokes Law, Debye derived the following equation connecting the relaxation time $\tau$ of the molecules with $\gamma$ the coefficient of viscosity of the liquid and 'a' the radius of the rotor:

$$\alpha = \frac{K T}{4 \pi \gamma \tau} \quad \ldots (9)$$

where $T$ is the absolute temperature at which the maximum absorption takes place and $K$ is the Boltzman constant.

B. Validity of Debye's equation.

It is well known that due to the introduction of Mossotti's hypothesis Debye's equation for static dielectric
constant does not give the correct value of the dielectric constant and dipole moment of a liquid of considerable polarity.

Now it is noticed that Debye's equation for complex dielectric constant given in equation (1) is almost the same as that given by him (Debye, 1912) in the case of static dielectric constant.

\[
\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \cdot \frac{M}{\rho} = \frac{4\pi N}{3} \left( \alpha_0 + \frac{\mu^2}{3kT} \right) \quad (10)
\]

The only difference between the two expressions being the factor \( \frac{1}{1 + \varepsilon \omega^2} \) which arises out of the fact that in the case of rapidly alternating field there is an observable lag in the response of the system to the changes in forces to which it is subjected.

The similarity between the equation (1) and equation (10) suggests that the limitations of Debye's theory on static dielectric constant also exist in the case of his theory on complex dielectric constant.

Modifications of Debye's equations have been suggested by different authors from time to time.

Cole (1938) extended Onsagar's (1936) equation for static dielectric constant to the case of a rapidly oscillating
field which may be reduced to
\[ \varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega \tau_0} \]  
\[ \text{(11)} \]
when \( \varepsilon_0 \) the static dielectric constant is so large that
\[ \frac{3 \varepsilon_0}{2 \varepsilon_0 + \varepsilon_\infty} \]
may be taken as \[ \frac{3}{2} \]
\[ \text{ i.e., } \frac{3 \varepsilon_0}{2 \varepsilon_0 + \varepsilon_\infty} = \frac{3}{2} \]

Separating the real and imaginary parts of equation (11) by rationalising the denominator we get
\[ \varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau_0^2} \]
\[ \text{(11.1)} \]

and
\[ \varepsilon' = \frac{(\varepsilon_0 - \varepsilon_\infty) \omega \tau_0}{1 + \omega^2 \tau_0^2} \]
\[ \text{(11.2)} \]

The maximum value of \( \varepsilon'' \) occurs when
\[ \omega \tau_0 = 1 \]
\[ \text{(11.3)} \]
and maximum absorption takes place when \( \tan \phi \) is maximum condition for which is
\[ \omega \tau_0 = \sqrt{\frac{\varepsilon_0}{\varepsilon_\infty}} \]
\[ \text{(11.4)} \]

Frolich (1949) obtained the equations (11), (11.1), (11.2), (11.3) and (11.4) from a macroscopic viewpoint.

Smyth (1955) has, however, suggested that equation (11.3) i.e., \( \omega \tau = 1 \) given by Cole and Frolich should be taken as the condition of \( \varepsilon''(\omega) \) to be maximum instead of Debye’s equation
\[ \omega \tau = \frac{\varepsilon_\infty + 2}{\varepsilon_0 + \omega} \]
This question has been discussed recently by Ghosh (1961) and he has pointed out that the condition for maximum absorption is the condition for maximum $\tan \delta$ and not of maximum $\varepsilon''$ and according to Cole-Frolich equation the condition for $\tan \delta$ to attain its maximum value is:

$$\omega_{\text{max}} \tau_0 = \frac{\varepsilon_0}{\varepsilon_\infty}$$

For pure liquids as $\frac{\varepsilon_0}{\varepsilon_\infty}$ is much larger than unity we can not take $\omega \tau_0 = 1$ as the condition for maximum absorption. But in the case of dilute solutions when $\frac{\varepsilon_0}{\varepsilon_\infty}$ is nearly equal to unity equation (11.3) can be taken as the condition for maximum absorption as has been done by previous workers (Whiffen and Thompson, 1946). He has pointed out further that Debye's condition for maximum absorption i.e., the equation:

$$\omega_{\text{max}} \tau = \frac{\varepsilon_\infty + 2}{\varepsilon_0 + 2} \frac{\varepsilon_0}{\varepsilon_\infty} \ldots (7)$$

gives relaxation time not much different from that given by equation (11.3) even in the case of pure liquids.

Bolton (1948) using the method of Cole-Cole-plot has shown that experimental results for liquids like water, tertbutyl alcohol and ethyl alcohol shows better agreement with the Debye's theory than with the Onsagar's theory without approximation.

Hence Debye's equations have been used in the present investigations which have been restricted to the liquids
like alcohols, substituted phenols, anilines and substituted anilines.

The absorption in these compounds was studied by using optical method which has been discussed in latter chapter of this Section.

A few ternary mixtures of chloroform and benzophenone in heptane and binary mixtures of chlorobenzene in nujol and bromobenzene in nujol were also studied. The real and imaginary parts $\varepsilon'$ and $\varepsilon''$ of these compounds were measured by a method developed by W. Surber which has been discussed in Section C.

C. Review of past work and the object of the present work.

Since the molecular interpretation of the behaviour of dielectrics in high frequency field was put forward by Debye (1913) many workers have tried to apply the theory to find out the radius of the rotor from the observed values of $\tau$ the time of relaxation. Mizushima (1927, 1928) was the first to report some experimental results for this purpose. He measured the dielectric constants and the coefficients of absorption of several alcohols at wavelengths 3.08 metres, 9.5 metres, 50 metres and 58 cms. in the temperature range -68°C to 65°C. He found in the case of lower alcohols the molecules themselves oriented with the field and the radius of the rotor calculated on Debye's theory corroborated this conclusion. In the case of glycol he however
found that the value of the radius of the rotor was only 0.1 of what it should be according to the known atomic dimensions.

Following Mizushima many other workers reported evidences of agreement between the values of the rotors derived from the experimental results with the help of Debye's equations and approximate radii of the respective molecules.

A qualitative agreement with Debye's theory was reported by Symanowski (1933) in the cases of higher alcohols and chlorobenzene. He used waves of 1.82 meter length in his investigation.

Jackson and Powell (1946) measured the dielectric loss in the case of a number of polar molecules such as benzophenone, nitrobenzene, bromobenzene, chloroform and acetone in solutions in benzene at the frequency of about $10^4$ Mc/sec. They found that in each of these cases there exists only one absorption region agreeing with the requirements of Debye's theory. They also found that the variation of $\tan \delta$ with frequency conform to the Debye's formula.

Besides the afore mentioned investigations in which cases agreement with the Debye's theory were reported many workers have found discrepancies between the experimental results and the results expected from Debye's theory.

White and Morgan (1932) reported evidences of distribution of relaxation times in propylene, glycol, trimethylene glycol and 2-methylpentadiol-2,4.
Luthi (1933), Girard and Abadie (1946), Hafelin (1946) and Cole and Davidson (1952) reported the existence of more than one dispersion region in different alcohols. They worked in meters and decimeters regions.

Whiffen and Thompson (1946) investigated the absorption of microwaves in the centimetre region in o-xylene, p-cymene and solutions in heptane of chloroform, methyl benzoate and bromo naphthalene. He showed that a linear relationship exists between the logarithm of the relaxation time and the reciprocal of the absolute temperature as required by Debye’s theory. He however used the Frolich’s condition for maximum as the condition for maximum absorption.

Heston, Hennelly, Laquer, Branin and Smyth (1948) measured the dielectric constant and loss factors using radiations of wavelengths 1.27 cm, 3.22 cm and 10.00 cm, of twenty seven organic halides in the liquid state using Cole-Cole plot (Cole and Cole, 1941). They investigated distribution of relaxation times in these liquids. They found that at high temperatures the relaxation time is single valued and the molecules behave in accordance with the Debye’s equation, but they do not do so at lower temperatures.

Most of the previous workers observed the orientation of the whole molecule along the electric field of the incident radiation. Ghosh (1954a,b; 1955a,b and c) investigated the absorption of microwaves in 3 cm region in some organic liquids with molecules containing small groups like the OH and found the
radius of the rotor calculated from Debye’s equation to be of value appropriate for the orientation of the group along the C-C bond in the molecule. He was also able to throw much light on the intermolecular field on the polar group. He however restricted his investigations to the case of pure liquids.

In dilute solutions of these polar liquids in some non-polar solvents we can expect a large number of associated molecules to be broken up in single molecules in which substituent group is free to rotate about the C-C bond. Hence the study of absorption of microwaves in solutions of these polar liquids the molecules of which contain the OH group and NH₂ group which exhibit the phenomenon of hydrogen bonding may help us in estimating the percentage of such dimers in the liquid and the change in the number of the dimers with the change of temperature of the liquid.

The object of the present work was also to get the above information in the cases of some molecules containing OH, NH₂ and OCH₃ groups by studying the absorption of 3.18 cm microwaves in the respective liquids at different temperatures.

References

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