Absorption in Polar Liquids with the Help of Dispersion Relation

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The working out of ϵ'', i.e. the absorbtive part of the complex dielectric constant for polar liquids, is effected through the use of dispersion relation. A simple analytic form of the complex dielectric constant not only displays the Cole-Cole curve but is tractable for Hilbert transforms also. The method gives a calculated value of ϵ'' which is very close to the value of ϵ'' for N,N-dimethylamine in cyclohexane determined at 9·313 GHz and 25°.

THE relaxation process in polar organic liquid has been studied theoretically and experimentally. Cole[1] and Drude[2] measured the dielectric constants of polar liquids at various radio frequencies and provided evidence of anomalous dispersion of dielectric constant in these liquids. The theory was first given by Debye[3] and later by Froelich[4] and Kauzmann[5]. The following empirical expression represents the complex dielectric constant as a function of the frequency of the oscillating electric field,

$$\epsilon^*(\omega) \equiv \epsilon'(\omega) - i\epsilon''(\omega)$$

$$= \epsilon_\infty + \frac{\epsilon_0 - \epsilon}{1 + iw\tau} \qquad \ldots(1)$$

This gives a semicircular plot in the ϵ', ϵ'' plane. Further experimental results of Cole and Cole[6], Froelich[7], Lane and Saxton[8], Davidson and Cole[9], etc., were analysed by Kauzmann[10], Cole[11] and Higasi[12]. A definite departure from the Debye type relation (1) was proposed by Cole and Cole[13]. Their much used empirical relation is represented by Eq. 2.

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + (i\omega\tau)^{1-\alpha}} \qquad \ldots(2)$$

where α is an empirical parameter and $0 \leqslant \alpha \leqslant 1$. This Cole-Cole also gives a circular plot in the ϵ', ϵ'' plane with the centre below the ϵ' axis.

Now, the complex dielectric constant as a function of the real frequency must satisfy the Kramer-Kronig[14] type of dispersion relation. The condition, that the real and imaginary parts be connected by the Hilbert transforms[15], heavily restricts the nature of the functions, i.e. their analytic characters. From this point of view, Eq. (1) is acceptable but Eq. (2) presents difficulties as it violates causality.

Theory

If, instead of relation (2), we assume a general expression for ϵ^* as given by Eq. 3,

$$\epsilon^*(\omega) = a + \frac{U(\omega)}{V(\omega) + iW(\omega)} \qquad \ldots(3)$$

where a is a real constant and $U(\omega)$, $V(\omega)$, $W(\omega)$ are real polynomials of ω, we can surmount the difficulty.

The fact that ϵ^* must become real constant when $\omega = \infty$ and $\omega = 0$ makes $W = 0$ and

$$\underset{\omega \to \infty}{Lt} \frac{U(\omega)}{V(\omega) + iW(\omega)} \text{ a real constant} \qquad \ldots(4)$$

So far, we have discussed the physical requirements of Eq. (3) which satisfies the dispersion relation, or more correctly, the subtracted dispersion relation depending on the asymptotic behaviour of $\epsilon^*(\omega)$. Now we stipulate that $U(\omega)$, $V(\omega)$ and $W(\omega)$ be connected by a linear relation (5),

$$C_1 U(\omega) + C_2 V(\omega) + C_3 W(\omega) = 0 \qquad \ldots(5)$$

where C_1, C_2, C_3 are constants. The $\epsilon^*(\omega)$ so obtained, has the property of depicting exactly the Cole-Cole plot in the ϵ'—ϵ'' plane. In order to demonstrate this, we note that because of Eq. (3),

$$(\epsilon' - a) + i\epsilon'' = \frac{U}{V + iW} \text{ or } \frac{\epsilon'}{(\epsilon' - a)^2 + \epsilon''^2} = \frac{V}{U}$$

and

$$\frac{\epsilon''}{\epsilon''^2 + (\epsilon' - a)^2} = \frac{W}{U}$$

From Eq. 5,

$$C_1 + \frac{C_2 \epsilon'}{(\epsilon' - a)^2 + \epsilon''^2} + \frac{C_3 \epsilon''}{(\epsilon' - a)^2 + \epsilon''^2} = 0$$

i.e. $(\epsilon' - a)^2 + \epsilon''^2 - g\epsilon' - h\epsilon'' = 0 \qquad \ldots(6)$

which is similar to a Cole-Cole curve.

It may be noted that the dispersion-theoretic method can vastly improve the accuracy of the experimental determination of dielectric loss. In fact, the determination of ϵ'' involves a lot of errors and is much less precise than the determination of its counterpart $\epsilon'(\omega)$. ϵ' can be determined quite accurately for various values of ω. In fact, nowadays, with the development of microwave techniques, ϵ' can be obtained for very small to reasonably large values of frequencies. Thus one has a fair knowledge of $\epsilon'(\omega)$ from $\omega = 0$ to $\omega = \infty$. This may be used in the dispersion intergal to obtain $\epsilon''(\omega)$ for any particular frequency. This integration has to be performed numerically.

Results and Discussion

As an application we have redetermined the value of ϵ'' at a wavelength of 3 cm for N,N-di-

methylamine in cyclohexane at 25°, taking standard precautions. The value of $\epsilon''(\omega)$ so obtained is ϵ'' (9·313 GHz) = 0·0606.

The values of $\epsilon'(\omega)$ for various values of ω have been taken from published work. The values of $\epsilon'(\omega)$ being known for some known values of ω, a curve of best fit was obtained, which asymptotically lead to the constant value and which at $\omega = 0$ is the constant ϵ_0. The values of ϵ' at intermediate values of ω were then read off from the interpolated curve[16]. These values were numerically integrated using relation (7) to obtain the value of ϵ'' for the given wavelength.

$$\epsilon''(\omega) = \frac{\omega}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon'(\omega')d\omega'}{\omega'(\omega'-\omega)} \qquad ...(7)$$

This is the subtracted dispersion formula. We used the relation $\epsilon''(\infty) = 0*$. The condition $\epsilon''(0) = 0$ is obtained automatically. For calculating the values of $\epsilon'(\omega)$ for negative values of ω, we have assumed $\epsilon'(-\omega) = \epsilon'(\omega)$.

The values of $\epsilon'(\omega)$ for N,N-dimethylamine in cyclohexane at 25° for various values of ω (ref. 17) are given below:

ω' (GHz)	ϵ'	ω' (GHz)	ϵ'
0	2·1881		
9·313	2·13	34·86	2·071
16·2	2·102	70·01	2·066
23·98	2·081	∞	2·062

For the purpose of integration, a change of variable is made to avoid the infinite range. We used the relation

$$\omega = \frac{a(1+Z)}{(1-Z)}$$

where $a = 30$, so that Eq. (7) is transformed to Eq. (8).

$$\epsilon''(Z) = \frac{2a(1+Z)}{\pi} P \int_{-1}^{1} \frac{\epsilon'(Z')dZ'}{(1+Z')(Z'-Z)} \qquad ...(8)$$

$\epsilon'(Z')$ is the sort of $\epsilon'(\omega')$ and $\epsilon'(\omega)$ normalized to 0 at $\omega = 0$.

The values of $\epsilon'(\omega)$ for intermediate values of ω were obtained by parabolic interpolation. Finally,

a computer calculation of the right hand side of Eq. (8) gave the value of ϵ''. This computed value is $\epsilon'' = 0·0607$ which agrees well with the experimental measured value, $\epsilon'' = 0·0606$ as given earlier.

The experimental set up is shown in Fig. 1. The dielectric loss was calculated by the method of Altschuler[17].

In order to illustrate the method we shall calculate $\epsilon''(\omega)$ which, in the Debye[3] formula, is

$$\epsilon''(\omega) = (\epsilon_0-\epsilon_\infty)\omega\tau[1+\omega^2\tau^2]^{-1} \qquad ...(9)$$

From Debye expression (10) for $\epsilon'(\omega)$,

$$\epsilon'(\omega) = \epsilon_\infty + \frac{(\epsilon_0-\epsilon)}{1+\omega^2\tau^2} \qquad ...(10)$$

The one subtracted dispersion relations is, obtained (Eq. 11).

$$-\epsilon''(\omega) = \frac{\omega}{\pi} P \int_{-\infty}^{\infty} \frac{[\epsilon'(\omega')-\epsilon'(\infty)]d\omega}{\omega'(\omega'-\omega)} \qquad ...(11)$$

$$= \frac{\omega}{\pi} P \int_{-\infty}^{\infty} \frac{bd\omega'}{\omega'(\omega'-\omega)(1+\omega'^2\tau^2)}$$

where $b = \epsilon_0-\epsilon_\infty$.

In order to evaluate this integral (11) we took recourse to contour integration using Eqs. (9) and (10). The integrals on the contours Γ_+ and Γ_- were evaluated separately and then subtracted to obtain the principal value. Γ_+ is the contour bounded by the real axis and the infinite semicircle on the upper half plane and Γ_- is the one bounded by the real axis and the infinite semicircle in the lower half plane, with indentations. The final integral expressions are

$$\int_{\Gamma_+} = \frac{b}{\tau^2} 2\pi i \left[-\frac{\tau^2}{\omega} + \frac{\tau^2}{\omega(1+\omega^2\tau^2)} - \frac{\tau^3}{2(i-\omega\tau)} \right]$$

$$\int_{\Gamma_-} = \frac{b}{\tau^2} 2\pi i \left[\frac{\tau^2}{\omega} + \frac{\tau^2}{\omega(1+\omega^2\tau^2)} + \frac{\tau^3}{2(i+\omega\tau)} \right]$$

$$\therefore P \int_{-\infty}^{\infty} = -\pi b\tau[1+\omega^2\tau^2]^{-1} \qquad ...(12)$$
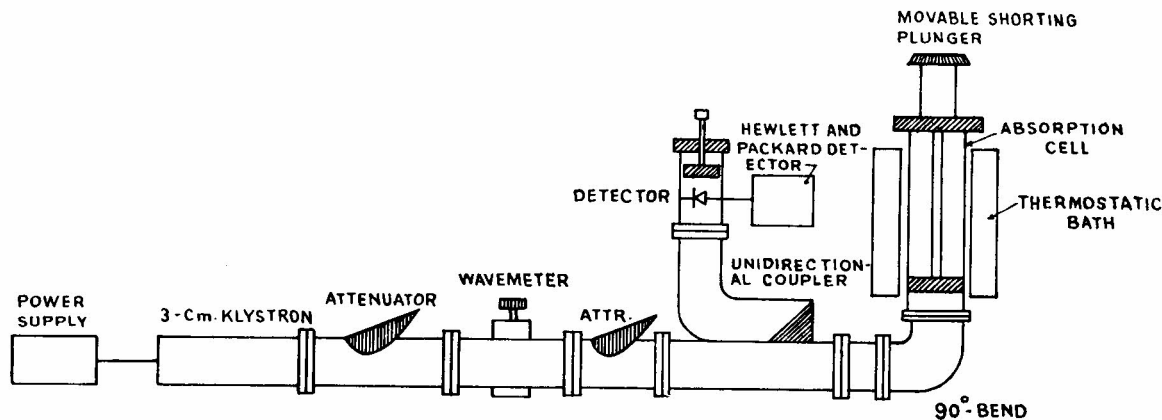
These expressions are in conformity with the results.

Fig. 1 — The experimental set up for measuring dielectric constant

*$\epsilon''(\infty) = 0$ follows from Eq. (7) since $\epsilon'(\omega)$ is an even function.

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