

ON THE ABSORPTION MAXIMA EXHIBITED BY SOME ORGANIC LIQUIDS IN THE MICROWAVE REGION. I *

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ABSTRACT The absorption of 3.18 cm. microwaves in chloroform, ethylene chloride, ethylene bromide and glycerine at different temperatures has been studied by the direct method avoiding formation of standing waves. A maximum in the absorption-temperature curve has been exhibited by each of the four liquids. The temperatures for maximum absorption are -45°C , -10°C , 21°C and 100°C for chloroform, ethylene chloride, ethylene bromide and glycerine respectively. It is pointed out that the values of λ_m , the wave length corresponding to the maximum absorption calculated by previous workers from the Cole and Cole empirical relation on the assumption of the existence of a distribution of relaxation time do not agree with the values observed by the direct method in the present investigation. It is further pointed out that actually different discrete values of the relaxation time, more than one in number, are present in most of the liquids, instead of a continuous distribution of relaxation time assumed in Cole and Cole empirical relation.

The radius of the rotor calculated from Debye's equation comes out to be too low in all the four cases and the reasons for this discrepancy have been discussed.

INTRODUCTION

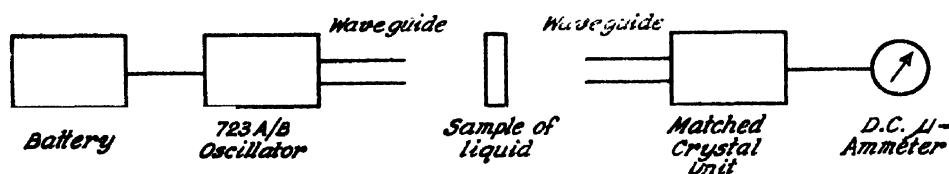
The dielectric constant of many organic liquids in solution for two different frequencies in the microwave region has been investigated by Whiffen and Thompson (1946a) and from the experimental value of $\tan \delta$, the loss tangent, the value of the relaxation time has been determined in each case with the help of the Debye equation. Whiffen and Thompson (1946b) also found out the value of $\tan \delta$ for 1.27 cm. waves in the case of pure *o*-xylene and *p*-cymene at different temperatures and also in the case of solutions of a few organic compounds in heptane at temperatures ranging from those below the freezing points of the liquids upto about their boiling points. Heston, Hennelly and Smyth (1948), on the other hand, measured the dielectric constant of a large number of organic halogen compounds for 1.27 cm. microwaves at four different temperatures and determined the value of loss tangent in each case. Hennelly, Heston and Smyth (1948) determined the values of τ_0 , the most probable relaxation time, using the Cole and Cole equation (1941) deduced empirically on the assumption of the existence of a distribution of relaxation time. It was, however, observed recently (Ghosh, 1953) that some of the liquids studied by the authors mentioned above exhibit

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absorption maxima in the range 500-920 Mc/sec at suitable temperatures, and at other temperatures the absorption was found to be negligible in this region. Also, the radius of the rotor calculated from Debye's theory indicated that the rotor in some of the cases is a dimer. These facts indicated that instead of a continuous distribution of relaxation time over wide limits only two or three discrete values are to be taken into account in these cases. This has been pointed out recently by Sirkar (1953). As the absorption due to single molecules was expected to be observed in the microwave region in the case of some liquids having simple molecules, it was thought worthwhile to determine by the optical method the temperatures at which maximum absorption of 3.18 cm. microwaves are exhibited by these liquids and to find out the value of τ and the radius of the rotor from Debye's theory. In such a method it is not necessary to use any empirical relation like the Cole and Cole equation, as has been done by the previous workers mentioned above. The preliminary results observed in the case of chloroform, ethylene chloride, ethylene bromide and glycerine are reported in this paper.

EXPERIMENTAL

A klystron oscillator of type 723 A-B was used as the source of microwaves, the power being derived from dry batteries. The frequency of oscillations used was 9415 Mc/sec and it was measured with a calibrated reaction type cavity wavemeter. The absorption of the radio waves coming out through a wave guide cut open at a distance of about 14 cm. from the tuning plunger and of cross section 2.3 cm \times 1 cm was studied by optical method. For the detection of the transmitted waves another wave guide and a matched crystal detector were used as shown in figure 1.



BLOCK DIAGRAM OF THE EXPERIMENTAL ARRANGEMENT.

FIG. 1

It was first observed that even when a thin glass plate was placed between the two wave guides after the positions of the plungers had been adjusted for maximum current in the detecting microammeter, reflection of waves at the glass plate occurred for certain distances of the plate from the open end of the transmitting wave guide, but for certain other distances full transmission of the waves through the glass plate was observed. It was also observed that the distance between successive positions of the glass plate for which the transmission was maximum was about $\lambda/2$, where λ is the wave length of the microwaves in air. It was thus evident

that when the distance between the glass plate and tuning plunger was a multiple of $\lambda/2$, stationary waves were formed and there was very little transmission through the plate in this case and for other distances equal to $n\lambda/2 + \lambda/4$ there was no reflection at the surfaces of the glass plate. When a glass cell with a distance of 1 cm between inner surfaces was placed between the two transmitting and receiving wave guides the transmission through the glass walls of the cell was not cent per cent for any position of the cell. When, however, the cell was filled with benzene, full transmission was observed for certain distance of the cell from the end of the transmitting wave guide. This arrangement was, therefore, used for observing the maximum absorption in the liquids studied in the present investigation. Incidentally, it might be pointed out that the assumption made by Whiffen and Thompson (1946) that the reflection at the mica walls of the cell used by them is identical both for the empty cell and for the cell filled with the liquid is probably not correct.

The liquids studied are chloroform, ethylene chloride, ethylene bromide and glycerine of chemically pure quality. They were purchased from U. S. A. and they were all distilled in vacuum after proper dehydration. In order to study the absorption at different temperatures the cell filled with the liquid was placed in baths at different temperatures and when the liquid attained the temperature of the bath the cell was taken out and its outer surfaces were cleaned. The cell was then placed between the wave guides and its distance from the open end of the transmitting wave guide was adjusted till maximum deflection in the detecting circuit was observed. The temperature of the liquid was measured just before starting this adjustment. The ratio of the current in the detecting circuit observed with the cell filled with the liquid placed in its position and that observed with the cell removed was noted for different temperatures of the liquid. The reflection at the glass-liquid interface was thus neglected in this method. Preliminary results obtained with chloroform and ethylene bromide at high temperatures clearly showed that reflection at glass-liquid interfaces was negligible, because there was full transmission through the liquids at certain temperatures.

RESULTS AND DISCUSSIONS

The values of apparent absorption coefficient, μ , were calculated from the relation,

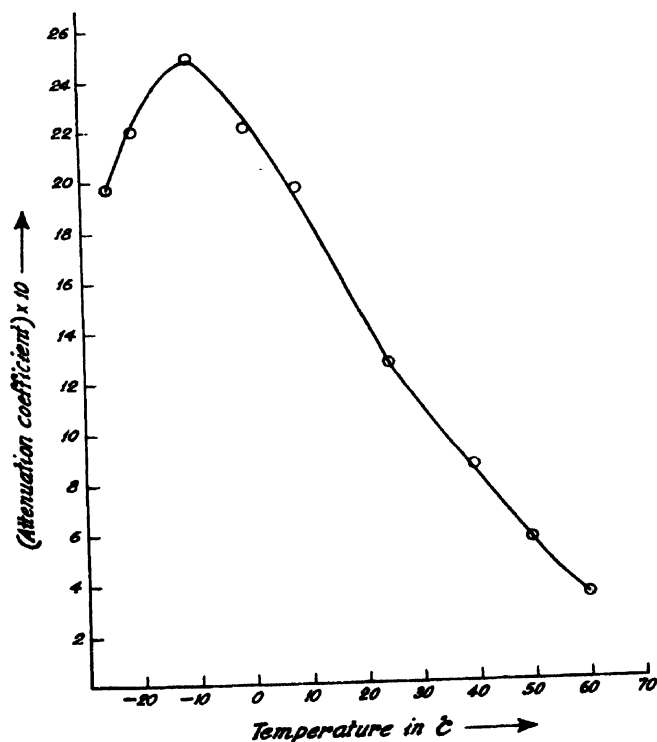
$$\mu = \frac{2.34}{x} \log_{10} \left(\frac{I_0}{I} \right)$$

where x is the thickness of the liquid, I is the observed maximum current in the microammeter in the detecting crystal circuit with the liquid absorber in its position and I_0 the current with the cell removed. The values of μ have been plotted against the temperature of the liquid in figures 2, 3 and 4. It can be seen from the figures that as the temperature of the liquid increases from a certain low value, the value of μ gradually increases and after attaining a maximum at a particular temperature, it diminishes again. In the case

of chloroform at 35°C and ethylene bromide at 70°C the transmission is cent per cent. Since dielectric constant changes from 6.12 to 4.4 in the case of chloroform with change of temperature of the liquid from -45°C to 35°C and in the case of ethylene bromide the dielectric constant is almost constant throughout the range from 21°C to 70°C, it is quite evident that the change in dielectric constant of the liquid cannot be responsible for the change in the absorption coefficient which takes place with the change of temperature of the liquid. This is further corroborated by the results obtained with glycerine. It is observed that when the temperature of pure glycerine free from water is raised from 17°C up to 200°C the value of μ gradually increases and after attaining a very large value in the range 80°C to 120°C, it diminishes again, although the value of dielectric constant gradually diminishes with the rise of temperature of the liquid. The results shown in figures 2, 3, 4 and 5 show that the value of λ_m , the wave length for maximum absorption exhibited by the liquids at the particular temperature is 3.18 cm. This wave length is thus determined directly in the present investigation. The values of τ at the respective temperatures of maximum absorption which have been calculated from Debye's theory from the relation,

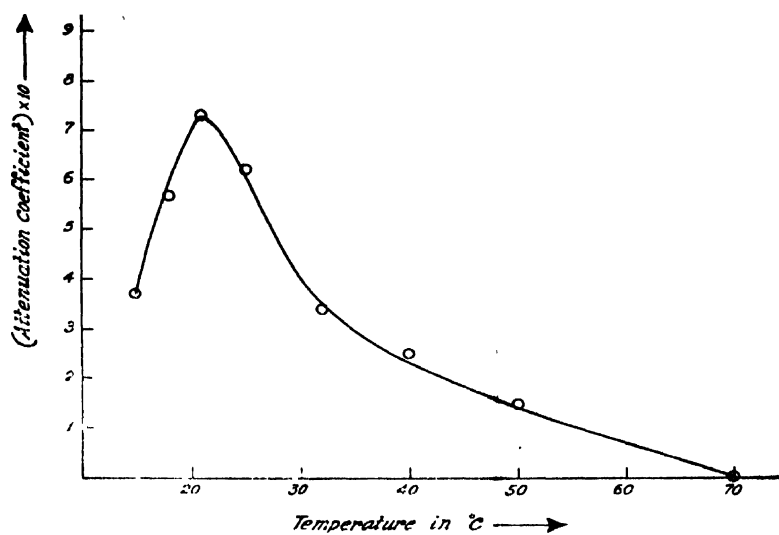
$$\omega\tau = \frac{\epsilon_0 + 2}{\epsilon_1 + 2} \sqrt{\frac{\epsilon_1}{\epsilon_0}}$$

where ω is the angular frequency at the maximum absorption, ϵ_0 and ϵ_1 are



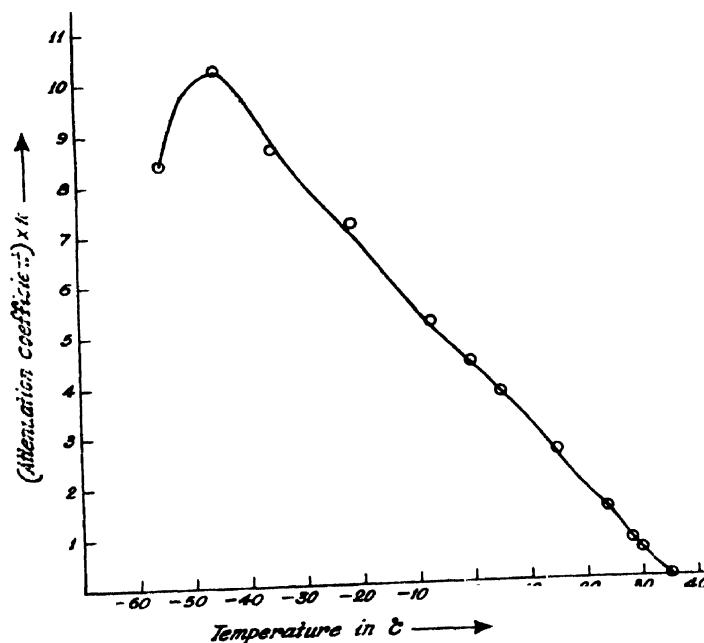
Ethylene chloride

FIG. 2



Ethylene bromide

FIG. 3



Chloroform

FIG. 4

dielectric constants for infinite frequency and zero frequency respectively, are given in Table I.

The value of η are obtained by extrapolation from the results reported in Handbook of Chemistry and Physics published by Chemical Rubber Publishing Co. The values of η for glycerine at temperatures above 30°C are taken from the results reported by Vand (1947). The value of ϵ_1 has

been obtained from the table of dielectric constant of pure liquids published by National Bureau of Standards, United States, Department of Commerce. The value of ϵ_0 has been assumed to be equal to the square of n , the refractive index at 20°C for sodium D-line, because the values of n at lower temperatures were not available. The values of radius of the rotors calculated from Debye's theory are also given in Table I.

TABLE I
 $\omega/2\pi = 9.415$ Mc/sec

Liquid	T°K for max. absorption	ϵ_1	ϵ_0	$\tau \times 10^{11}$	$\eta \times 100$	$a \times 10^8$ cm
Chloroform	228	6.12	2.094	1.455	1.12	1.478
Ethylene chloride	263	12.7	2.084	1.16	1.2	1.405
Ethylene bromide	294	4.8	2.364	1.545	1.7	1.429

Ethylene chloride and Ethylene bromide :

The values of λ_m , the wave length for maximum absorption exhibited by the liquids at the particular temperature as deduced by Hennelly, Heston and Smyth (1948) for ethylene chloride and ethylene bromide applying the empirical relation suggested by Cole and Cole (1941) on the assumption of the presence of distribution of relaxation time τ are compared with the value obtained by the optical method in the present investigation in Table II.

TABLE II

Liquid	Present author		Hennelly <i>et al</i> (1948)	
	Temperature	λ_m in cm	Temperature	λ_m in cm
Ethylene chloride	-10°C	3.18	1°C	1.83
Ethylene bromide	21°C	3.18	25°C	2.18

The value of λ_m deduced from Cole and Cole equation in the case of ethylene chloride at 1°C is 1.83 cm and this will lead to a value 2.16 cm at -10°C if the change in viscosity with temperature is taken into consideration. The value observed directly in the present investigation, however, is 3.18 cms. Similarly, in the case of ethylene bromide at 25°C the value of λ_m deduced by the previous authors is 2.18 cms and the value observed by

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the direct method in the present investigation is 3.18 cms at 21°C. Thus it is evident that the empirical relation mentioned above leads to wrong value of λ_m . Therefore, the fundamental assumption that there is a continuous distribution of τ in these liquids is not quite correct as pointed out by Sirkar (1953).

Chloroform :

In the case of chloroform solution in heptane at -45°C Whiffen and Thompson (1946) found the value of τ to be equal to 7.4×10^{-12} sec. The viscosity of heptane at this temperature, as extrapolated from the values at higher temperatures, is 0.7 centipoise and the viscosity of chloroform at this temperature is 1.12. Hence the value of τ in pure chloroform at -45°C deduced from the values of the solution in heptane at the same temperature is 1.18×10^{-11} sec. This does not differ much from the value 1.45×10^{-11} sec obtained in the present investigation.

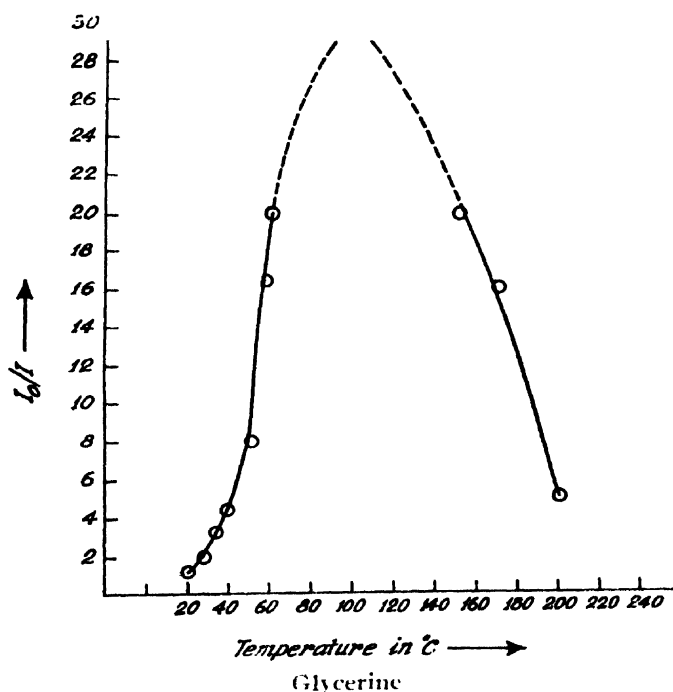


FIG. 5

Glycerine :

It can be seen from figure 5 that the value of I_0/I increases with temperature till it reaches enormously high values beyond 80°C and it begins to diminish again beyond about 100°C . Thus the value of λ_m for glycerine at about 100°C is 3.18 cm. Previous authors (Mizushima, 1928, Sirkar and Sen, 1949) observed that glycerine at about 31°C shows absorption peak at about 60 cms. Since the viscosity of glycerine at 31°C is very high, being 620 centipoise the value of the radius of the rotor calculated from these data from

Debye equation comes out to be of the order of 0.4×10^{-8} cms. The value is obviously too small to correspond to even a small part of the molecule. The radius of the rotor calculated similarly with the help of η for 100°C observed in the present investigation is about 0.6×10^{-8} cms. This value also is too low. The high value of viscosity is evidently responsible for these discrepancies because as the viscosity decreases to one tenth of its value with the change from 31°C to 100°C the discrepancy also is reduced to some extent. The cause for this discrepancy has been discussed by Sirkar (1953) in another paper.

It is thus quite evident from the facts mentioned above that although the method adopted in the present investigation is the simplest of all the methods used so far the measurement of maximum absorption, the results obtained regarding the value of λ_m at particular temperature of the liquid are quite accurate and they show that such results deduced from Cole and Cole empirical relations are not quite correct in some cases. These results further show the hypothesis of the presence of continuous distribution of τ in the range from 0 to ∞ in the case of all the liquids is not quite correct, because in the case of three of the four liquids studied in the present investigation, discrete absorption peaks have been observed. These maxima in the present case seem to be due to single molecules. Peaks at lower frequencies may be observed at low temperatures and those peaks will be due to dimers, because such peaks due to dimers have been observed in other cases (Ghosh, 1953).

The value of a , the radius of the rotor calculated from the Debye's equation $\tau = \frac{4\pi\eta a^3}{kT}$ is almost the same for all the three liquids—chloroform, ethylene chloride and ethylene bromide, and it is less than the C-Cl distance. Even in the case of chloroform the value is too small to lead to the correct volume of the molecule deduced from the density of the liquid. This discrepancy may be due to the presence of dimers in the liquid which has not been taken into account in the calculation, as pointed by Sirkar (1953).

The fact that the value of a is almost the same in ethylene chloride or ethylene bromide as in chloroform may indicate that only the C-Cl or C-Br group orientates along the impressed field due to the freedom of rotation about the C-C bond. This can happen only when the other half of the molecule is held rigidly in the liquid, which means that the molecules may be associated with the neighbouring molecules so that the freedom of motions of the portion of the molecules directly linked to each other is very much restricted. At higher temperatures the associated molecules are expected to break up into single molecules and the whole molecule is expected to orientate along the impressed field. Further investigations with other liquids are in progress.

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