ABSORPTION OF 3.18 CM MICROWAVES IN SOME AROMATIC AND ALIPHATIC COMPOUNDS IN THE LIQUID STATE*

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ABSTRACT. The absorption of 3.18 cm microwaves in o-cresol, m-cresol and 3-chloropropene has been studied by the direct optical method avoiding formation of stationary waves. Maximum absorption of 3.18 cm microwaves has been exhibited by o-cresol, m-cresol and 3-chloropropene at temperatures 50°C, 80°C and —80°C respectively. In the case of cresols these are assumed to be due to rotation of the OH group about the diameters of the molecule passing through the carbon atoms to which the OH group is attached. In the case of 3-chloropropene probably the rotor is rotating around the length of the molecule. It has been observed that toluene, o-bromotoluene and xylenes do not exhibit any absorption in the 3 18 cm microwave region which corroborates views expressed in the previous papers of the author that the absorption in the microwave region is due to the rotational freedom of the group containing permanent electric moment about an axis of the molecule. Toluene and o-bromotoluene also do not exhibit any absorption in the U.H.F. region 250—900 Mc/sec. This may be due to the fact that the permanent electric moment in the case of toluene is very small and that the moment of inertia of o-bromotoluene is very high.

INTRODUCTION

It has been reported recently (Ghosh, 1954) that some substituted benzenes exhibit absorption maxima at the 3.18 cm microwave region and that the radii of the rotors calculated from Debye's theory are found to be too small to be that of the molecule and they are equal to the projections of the lengths of the substituent groups on a diameter of the benzene ring passing through the point of substitution. This shows that in the case of these substituted benzenes the time of relaxation has different discrete values in each case and the occurrence of "effective time of relaxation" owing to freedom of rotation of the substituent group about a diameter of the molecules postulated by Fischer (1949) is corroborated by these results. The presence of rotational freedom of some groups in substituted benzenes was inferred by Fischer (1949) from the values of dielectric loss observed in the solution of some substituted benzenes in the metre wavelength region. In the method employed by the present author, the frequencies of absorption peak are actually observed in the case of pure liquids for wavelengths shorter than 1 metre and the radius of the rotor is calculated from Debye's theory.

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It was observed that the pure liquids such as benzyl alcohol, benzyl chloride, benzyl amine, ethylene chloride, ethylene bromide and chloroform exhibit maximum absorption of 3.18 cm microwaves at suitable temperatures. In the case of the substituted benzenes mentioned above the substituent groups were assumed to have rotational freedom in explaining the observed absorption. It would be interesting, however, to find out whether substituted benzenes in which there is no such group with rotational freedom also exhibit absorption in the 3.18 cm microwave region. In the present investigation the absorption of 3.18 cm microwave as well as of U.H.F. radiowaves of frequency ranging from 250 Mc/sec to 900 Mc/sec in a few more liquids has, therefore, been studied for different temperatures of the liquids and attempts have been made to calculate the radii of the rotors from Debye's theory.

EXPERIMENTAL

The liquids studied in the present investigation are toluene, o-bromo-toluene, o-xylene, m-xylene, o-cresol, m-cresol and 3-chloropropene. The experimental arrangement used in the present investigation was the same as that reported previously (Ghosh, 1953a, 1953b, 1954). The liquids studied were of chemically pure quality. They were all distilled in vacuum after proper dehydration. The liquids were supplied by Fisher Scientific Company, New York. Ortho and meta cresol were supplied by B.D.H.

RESULTS

The values of a^3 and τ calculated from Debye's theory and the different constants involved in this calculation are shown in Table I.

TABLE I

$\omega/2\pi = 9415$ Mc/sec.

Liquid	$T°K$ for max. abs.	ϵ_0	ϵ_1	$\eta \times 100$	$\tau \times 10^{11}$	$a \times 10^8$ c.c.
o-Cresol	323	2.393	6.3	2.5	1.518	1.28
m-Cresol	353	2.372	5.5	1.8	1.458	1.46
3-Chloropropene	193	2	10.6	75	1.235	1 51

Toluene and o-bromotoluene showed no absorption at all in the range 250-900 Mc/sec and also in the 3.18 cm microwave region when the liquid was heated nearly up to the boiling point and cooled up to the freezing point.

Ortho-xylene and *m*-xylene showed no absorption in the 3.18 cm microwave region. Absorption by *o*-xylene and *m*-xylene in the U.H.F. region was reported by Ghosh (1953a). Absorption by *o*-cresol and *m*-cresol in the U.H.F. region was studied by Kastha (1952) and the absorption in the microwave region has been plotted in figures 1 and 2 respectively.
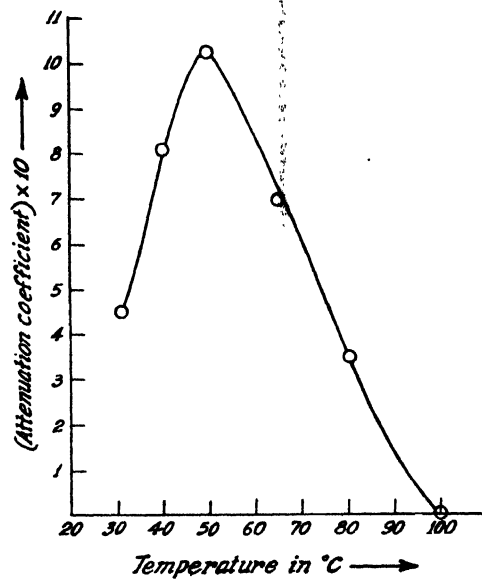

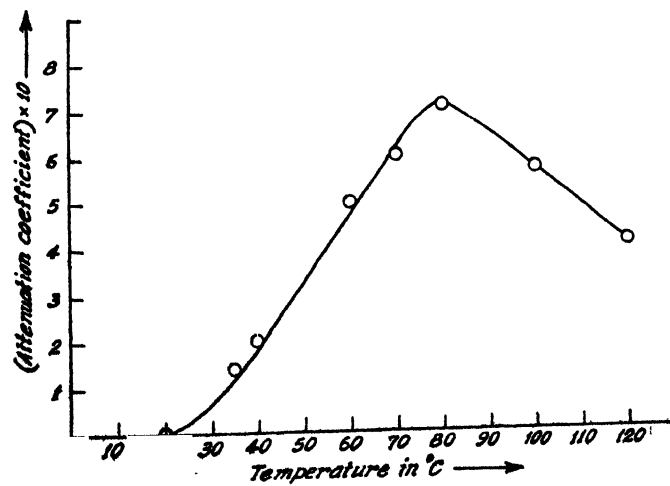Fig. 1. *o*-Cresol
f=9415 Mc/sec thickness of liquid=1cm.

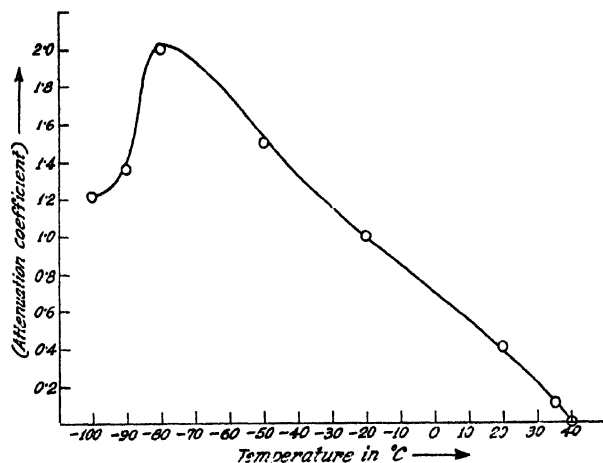Fig. 2. *m*-Cresol.
f=9415 Mc/sec, thickness of the liquid=1 cm.

FIG. 3. 3-Chloropropene

f=9415 Mc/sec, thickness of the liquid=1.5 cm

It has been observed that 3-chloropropene shows no absorption in the U.H.F. region in the range 250-900 Mc/sec even when cooled upto the freezing point of the liquid. The absorption in the microwave region has been plotted in figure 3.

The values of η are obtained from the results reported in the International Critical Tables. The values of ϵ_1 have been obtained from the table of dielectric constants of pure liquids published by National Bureau of Standards, United States Department of Commerce and also from the International Critical Tables. The results at very low and high temperatures have been obtained by extrapolation. The values of ϵ_0 have been assumed to be equal to square of n, the refractive index at 20°C for sodium D-line.

DISCUSSION

It can be seen from the Table I that the radii of the rotor in all the three liquids are much smaller than that of the single molecule. So, in the case of cresols probably the OH group rotates about the diameter of the molecule passing through the carbon atoms to which the OH group is attached. Since the values of viscosity were obtained from the International Critical Table, they are quite reliable. Therefore, the difference in the values of a for the m-cresol molecule and that for the o-cresol molecule may not be due to any uncertainty regarding the accuracy of the data used in the calculation, but it may be a genuine difference. If that be the case, it can be inferred that the angle COH between C and OH bonds is smaller in the case of o-cresol than in the case of m-cresol. This may be due to the proximity of the CH_3 group in the case of o-cresol.

In the case of 3-chloropropene the rotation of the molecules about an axis perpendicular to the length of the molecule would require a large volume and the radii also would be much larger than 1.51 Å calculated from observed absorption. Probably, in the particular case the rotor is rotating around the length of the molecule. In that case the projection of the radius of the rotor would be of the order of 1.51 Å shown in the Table I. Such a value was also observed in the case of ethylene chloride and ethylene bromide. Now the absence of absorption in the region 250 - 900 Mc/sec indicates that the frequency of absorption corresponding to the rotation of the molecule about an axis at right angles to the length of the molecule is much lower than the lowest frequency used in the present investigation.

It is well known that in the case of toluene, o-bromotoluene and xylenes the rotational group does not change the orientation of the permanent electric moment and it is not surprising that these liquids do not exhibit any absorption in the 3.18 cm microwaves region. Toluene and bromotoluene do not show any absorption also in the range 250 - 900 Mc/sec. This may be due to the fact that in the case of toluene the permanent electric moment is much smaller. It the case of bromotoluene the moment of inertia is very high and the absorption may be in a region of much lower frequency. The results thus fully corroborate the views expressed in the previous papers (Ghosh, 1954) that the absorption in the microwave region is due to the rotational freedom of the group containing permanent electric moment about an axis of the molecule. These results also demonstrate the fact that the molecules in the liquid state of these type exhibit more than one absorption maximum due to the orientation of the whole molecule as well as of part of it as postulated by previous workers.

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