CHAPTER IX

SUMMARY OF THE PRESENT WORK

The absorption of 3.18 cm microwaves in some organic liquids the molecules of which contain the OH, NH₂ or OCH₃ group and in the solutions of the substances in some suitable non-polar solvents has been studied at different temperatures.

**Molecules containing the OH group.**

Ten liquids in which the molecules contains the OH group as substituent were selected for studying the absorption of this 3.18 cm microwaves. These liquids are o-chlorophenol, cyclohexanol, cyclopentanol, n-propyl alcohol, n-butyl alcohol, isopropyl alcohol, isobutyl alcohol, n-heptyl alcohol, n-octyl alcohol and ethylene chlorhydrin.

The absorption of the microwaves in solutions of these substances in a few solvents at different temperatures has also been investigated. Maxima have been observed in the temperature-attenuation curves in the cases of solutions of o-chlorophenol in CCl₄, cyclohexanol, cyclopentanol and their solutions in heptane solutions, of n-propyl, n-butyl, isopropyl, isobutyl, heptyl and octyl alcohol in hexane and CCl₄ and of the pure heptyl and octyl alcohol. Solution of ethylene chlorhydrin in CCl₄ was found to exhibit a maximum. The relaxation time has been determined in each case. The viscosity, the dielectric constant under static field, and refractive index have also been determined in each case in order to calculate the radius of the rotor with the help of Debye's
theory. The value of the radius calculated in this way is about 1.4 Å in the cases of o-chlorophenol, cyclohexanol and cyclopentanol while it is about 1.8 Å in the cases of the aliphatic alcohols. It is concluded that in the cases of the three aromatic compounds the rotor is the OH group which rotates about the C-O bond and in the other cases this OH group rotates about C-C bond.

In the cases of pure ethylene chlorhydrin and its solution in methyl cyclohexane the absorption increases continuously with the rise of temperature without showing tendency to attain a maximum value all through the range of temperature -70°C to 115°C. Similar results were also obtained in cases of lower alcohols. The CCl₄ solutions of cyclohexanol and cyclopentanol show no absorption at all.

The aggregate absorptions in all cases has been found to increase with the lowering of concentration giving evidences of breaking up of dimers formed through OH... hydrogen bonds into single molecules.

The results obtained in the cases of different liquids and their solutions in different solvents have been discussed in the light of those obtained in the investigations on the infrared, Raman and electronic spectra of the liquids reported by previous workers.

It has been concluded in the case of o-chlorophenol that in dilute solutions the OH group in most of the molecules
are in trans-position with respect to the chlorine atom.

In the case of ethylene chlorhydrin that the pure liquid has been assumed to contain two types of dimers formed through intermolecular OH...O and OH...Cl hydrogen bonds while in solutions of the substance in carbon tetrachloride OH group of solute molecule has been assumed to form OH...Cl bond with the chlorine atom of solvent CCl₄ molecule. Formation of such intermolecular OH...Cl hydrogen bond between the solute and the solvent molecule has been postulated in the case of the solutions of cyclohexanol and cyclopentanol in CCl₄ to explain the absence of absorption in these cases.

The results obtained in the cases of alcohols has been explained by assuming that most of the molecules in the lower alcohols in the pure state are in the form of dimers which break up in solutions into single molecules. The higher alcohol molecules being larger some of the molecules do not form such dimers and remain as single molecules.

The effective radius of O-H rotor in the case of aliphatic alcohols was found to be 1.9 Å larger than that obtained in the case of aromatic compound. This has been explained by assuming that the O-H bond-length is less inclined to the C-C axis which is the axis of rotation in aliphatic compound, than it is to C-O axis, i.e. axis of rotation of OH group in aromatic compound.

Molecules containing the NH₂ group.

The absorption of microwaves of 3.18 cm was also found in aniline, o- and p-chloroaniline, and o-, m- and p-toluidine in
liquid state and in solutions in diphenyl ether at different
temperatures. The radius of the rotor in each case has been found
to be 1.1 Å approximately and the rotor has been identified with
the NH₂ group rotating about the C-N bond.

It has been concluded that NH₃ group retains its
pyramidal structure even when one of its hydrogen atoms is
substituted by the benzene C₆H₆ group.

Molecules containing the OCH₃ group.

Anisole, o- and p-chloroanisole and o-nitroanisole and
their solution in carbon tetrachloride and hexane were chosen to
find out whether the OCH₃ group in these molecules have freedom
of rotation. Maxima in the temperature-attenuation curves have
been observed in these cases.

The radius of the rotor calculated in the cases of
anisole, o-chloroanisole and p-chloroanisole has been found to be
about 1.6 Å. It has been concluded that the rotor of these cases
is the OCH₃ group. In the case of n-nitroanisole the OCH₃ rotor
has been found to have the same value.

It has been suggested that the molecules in o-chloro
anisole have their OCH₃ group in trans-position with respect to
the chlorine atom.