

CHAPTER 11

SUMMARY OF THE RESULTS AND CONCLUSIONS

In Chapter 3, the dielectric absorption data in the case of three halothiophenols in the liquid state have been reported. The data were analysed in terms of molecular and intramolecular relaxation processes by the method of least squares, avoiding the trial and error method used by other workers. The molecular and group relaxation times of the halothiophenols were compared with the corresponding values of halophenols in dilute solution.

From a comparison of the -SH group relaxation time in the halothiophenols in the liquid state with the SH group relaxation time in naphthalenethiol in dilute solution, and the OH group relaxation in halophenols in dilute solution, it is concluded that the intermolecular hydrogen bonding S-H...S is absent in halothiophenols even in the liquid state, where OH group relaxation time is lengthened very much due to intermolecular hydrogen bonding O-H...O in chlorophenols even in dilute solution.

The experimentally obtained value of the weight factor C_1 for molecular orientation in the halothiophenols compares well with the value of C_1 calculated from bond moments. Similarly the dipole moment obtained experimentally, tallies well with the moment calculated from bond moment and bond angles.

In Chapter 4, the results of dielectric absorption in ortho- and para bromoanisoles and β -bromophenetole in the liquid state have been presented and discussed. Molecular and group relaxation times have been obtained for the three molecules and compared with the corresponding values in the case of similar molecules in dilute solution. In all the three molecules, molecular reorientation ($C_1 \approx .65 - .8$) is found to be the major relaxation process. Theoretically calculated value of the weight factor $C_2 = .30$ in o-bromoanisole compares well with the experimentally obtained value of $C_2 \approx .37$. The similarity in the values of C_1 and C_2 in p-bromoanisole in the liquid state and in dilute solution reported by Farmer and Walker, shows that dipole-dipole interaction is not effective even in the liquid state.

This is also supported by the similar values of activation energy for molecular orientation ($\Delta H_{c1} = 2.1$ Kcal/mole) in liquid para bromoanisole and the activation energy ($\Delta H_{c1} = 2.07$ Kcal/mole) in para bromoanisole in dilute solution. The energy barrier to group rotation in all the three molecules is of similar magnitude as the energy barrier to molecular orientation.

In Chapter 5, the dielectric studies of thioanisole in the liquid state have been discussed. The dielectric data were analysed in terms of molecular and group relaxation times. The molecular and group relaxation times in thioanisole were compared with the corresponding values in anisole and thiophenol all in the

liquid state. Though the molecular and group relaxation time were found comparable in the three molecules in the liquid state, the weight factor G_2 for group rotation (.2) in anisole in the liquid state was found to be much smaller than the G_2 -values in thioanisole and thiophenol (.6 - .7) in the liquid state. This suggests that the SCH_3 group rotation like thiophenol is almost free to rotate unlike the OCH_3 group in anisole in the liquid state. This is also supported by the fact that the activation energy for $S-CH_3$ group rotation ($\Delta H_{c_2} = .7$ Kcal/mole) is much lower than that for the rotation of the OCH_3 group ($\Delta H_{c_2} = 1.5$ Kcal/mole).

The calculated value of the weight factor G_2 from bond angles and bond moments agrees well with the experimentally obtained G_2 -value in thioanisole.

In Chapter 6, the dielectric studies of some aromatic molecules containing multibonded polar groups such as $-NCO$, $-NCS$, $-NSO$ have been reported. The fact that the dielectric data in all these molecules could be analysed in terms of molecular and group rotations by the least square method suggests that the group $-NCO$ and $-NCS$ are not collinear with the $C_1 - C_4$ axis of the phenyl ring, but inclined to it by a certain angle.

From consideration of the dipole moment of the molecule and the weight factor G_1 for molecular orientation, it is concluded that the angle of inclination of the $-NCO$ group with the $C-N$ axis is about 33° .

From the analysis of the results it is also concluded that the structure of the group $-NCO$ and $-NCS$ in the molecules phenylisocyanate and phenylisothiocyanate are $-\overset{+}{N} \equiv C - \overset{-}{O}$ and $-\overset{+}{N} \equiv C - \overset{-}{S}$ respectively.

The energy barrier to internal rotation is found to be less than 1 Kcal/mole in all the three molecules and this is much smaller than the energy barrier to molecular orientation ($\Delta H_{c_1} = 2$ Kcal/mole). The experimentally obtained values of dipole moment in each case agrees with the literature values.

In Chapter 7, the results of absorption of microwaves in 1-phenylpropylbromide, 1-phenylpropyl mercaptan and 1-phenylpropylamine have been presented and discussed.

The data were analysed in terms of two relaxation processes by the method of least square and the molecular relaxation time τ_1 the group relaxation time τ_2 and the weight factor for the molecular orientation C_1 were determined. From the comparison of the shorter relaxation times in 1-phenylpropylbromide, 1-phenylpropyl mercaptan and 1-phenylpropylamine with those in benzyl bromide, benzyl mercaptan and benzyl amine respectively, it was concluded that group rotation occurs in each of the above molecule by the rotation of the end group $-\text{CH}_2\text{Br}$, CH_2SH and $-\text{CH}_2\text{NH}_2$ respectively and not by the rotation of group $\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$ ($\text{X} = \text{Br}, \text{SH}, \text{NH}_2$) as a whole.

The weight factor C_1 for molecular orientation is the major relaxation process in each of these molecules. This is unlike the case in benzyl mercaptan and benzylamine where group rotation is the major relaxation process. An explanation has been given for the lowering of C_2 in the present molecules.

The barrier to group rotation in phenylpropylbromide and phenylpropyl mercaptan ($\Delta H_{C_2} = 1$ Kcal/mole) is half as much as the energy barrier to molecular orientation in the respective cases.

The energy barrier to group rotation in phenylpropyl amine is only 120 cal/mole, which means that there is almost free rotation of $-CH_2NH_2$ group in this liquid.

In Chapter 8, the results of measurements of dielectric absorption in 1,3-propanedithiol and 1,2,3-tribromopropane in the liquid state have been presented and a discussion of the result is given. The most probable relaxation times in both the molecules were determined from the Cole-Cole arc plots. The relaxation time of 1,3-propanedithiol was found to be comparable with that of 1,2-propanedithiol, indicating the two molecules are of similar sizes. The reduced relaxation time (τ/η) of 1,2,3-tribromopropane is found to be little bit larger than that of the 1,2-dibromopropane suggesting that the 1,2,3-tribromopropane is a little larger in size than the 1,2-dibromopropane molecule. The distribution parameter α in 1,3-propanedithiol

is found to increase with the increase of temperature, while in 1,2,3-tribromopropane the distribution decreases as observed in other liquids.

The increase in the distribution parameter α in 1,3-propanedithiol is explained as follows.

Spectroscopic studies have shown that 1,3-propanedithiol have three conformers GG, TG and TT. The moments of three forms, TG ($\mu = 1.4$ D) and GG ($\mu = 1.14$ D) calculated from bond angles and bond moments are much less than that of TT ($\mu = 2.06$ D). The observed apparent moment was found to increase with increase of temperature, suggesting the increase in proportion of TT at higher temperature.

The TT form being more extended than the GG or TG form, should have a larger relaxation time which causes the distribution parameter α to increase at higher temperature.

In the 1,2,3-tribromopropane only two conformers are reported from spectroscopic studies. The moments of the two conformers calculated from bond angles and bond moments are found to be same, not likely to be affected by change of temperature. This is supported by the observed moment being independent of temperature. The size of the two conformers being similar, the distribution parameter α does not increase with increase of temperature.

In Chapter 9, the results of the dielectric relaxation studies of a few α, ω dicyanoalkanes in benzene solution have been reported. The results could be analysed in terms of two relaxation processes. The larger relaxation time τ_1 was attributed to the end-on-end rotation of the molecule as a whole and the shorter relaxation time τ_2 is assigned to the rotation of the end-group $-\text{CH}_2\text{CN}$ about ^{the} adjacent ~~to~~ ~~the~~ C-C bond. The shorter relaxation time τ_2 in all the dicyanoalkanes compares fairly well with the τ -value of acetonitril (CH_3CN) in benzene solution in literature. Therefore it was concluded that the shorter relaxation time was due to the $-\text{CH}_2\text{CN}$ group rotation. The distribution parameter α at any temperature is in the increasing order from 1,2-dicyano- to 1,4-dicyanoalkanes. This is explained as the number of segmental oscillations about the various C-C bonds increases with the increase in the number of such bonds.

The distribution parameter α in 1,2- and 1,4-dicyano alkane decreases with the increase of temperature as is generally observed in polar liquids. But in 1,3-dicyanopropane, the distribution α increases with increase of temperature. This can be explained in the following way.

Spectroscopic studies have shown that in 1,3-dicyano propane in the liquid state three conformers GG, TG and TT are present, the former two are in comparable proportion, while the

TT form is present in minute proportion. From bond moments and bond angles calculations the dipole moment of GG ($\mu = 3.8$ D) and TG ($\mu = 4.0$ D) are nearly equal, while the moment for TT ($\mu = 4.5$ D) is appreciably higher. The increase in the observed apparent moment with increase of temperature, indicates that the proportion of TT form increases at higher temperature. The TT conformer being more extended than the TG or GG, has a larger relaxation time which causes the distribution parameter to increase at higher temperatures. The behaviour of 1,3-dicyano propane is similar to 1,3-propanedithiol discussed in the previous chapter.

In Chapter 10, the results of dielectric absorption in six halogenated aliphatic esters viz. ethyl-2-chloropropionate, methyl-2-chloropropionate, methyl-2-bromopropionate, methyl-3-bromopropionate, ethyl-3-chloropropionate and methyl-4-chloro butyrate have been discussed. The dielectric data could be analysed in terms of molecular and intramolecular relaxation times. The molecular relaxation times were consistent with their sizes. The shorter relaxation time was attributed to CH_2X ($\text{X} = \text{Cl}$ or Br) group rotation in 3-halopropionates and 4-chloro butyrate and CH_3CHX ($\text{X} = \text{Cl}$ or Br .) in 2-halopropionates.

In all the esters the molecular reorientation was found to be the major relaxation mechanism.

From comparison of the observed moments and the calculated moments (from bond moments and bond angles) for probable conformers in each ester, the conformers actually present in each ester have been indicated.

It was concluded that in ethyl-3-chloropropionate and methyl-3-bromopropionates, TC, TG and TT conformers are present. In methyl-4-chlorobutyrate the conformers ^{GTG}TTG_A and TGG are present.

In methyl-2-halopropionates the conformers Cis and Gauche I are the major constituents.