CHAPTER IX

SUMMARY OF THE RESULTS OF PRESENT WORK AND CONCLUSION

The result and discussions of the present investigation have been described in detail in Chapter III to VIII. Here a chapterwise summary of the results are given below.

Chapter III

MICROWAVE CONDUCTIVITY AND DIPOLE MOMENT OF

POLAR DIELECTRICS.

The high frequency conductivity of the seven systems in benzene, such as (i) 2-5dichloronitrobenzene, (ii) 2-5 dibromonitrobenzene, (iii) 3-nitro-o-anisidine (iv) 2-chloro-p-nitroaniline (v) p-phenitidine, (vi) O-nitroaniline, (vii) p-anisidine have been calculated from the relation

$$K_{ij} = \frac{\omega}{4\pi} \sqrt{\epsilon_{ij}'^2 + \epsilon_{ij}''^2} \qquad \text{where} \quad \epsilon_{ij}''$$

is the dielectric loss and ϵ_{ij}' is the dielectric constant at various temperatures. The computed conductivity K_{ij} for each systems varies almost linearly with weight fraction W_j ; specially in the lower concentration region. The slope of the concentration variation of h.f. conductivity of polar - nonpolar

liquid mixture at infinite dilution has been employed to estimate the dipole moment $\mathcal{M}_j$ of polar solute at different temperatures by using the relation $\mathcal{M}_j = \left[\dfrac{3M_j kT\beta}{N\rho_i F_i \omega b}\right]^{1/2}$ where β is the slope of the curve, ρ_i is the density, F_i is the local field and $b = \dfrac{1}{1+\omega^2 \tau^2}$.
It is further observed that in all the systems, the increase of dipole moment can be expressed by the relation $\mathcal{M}_j = a' + b't + c't^2$ where a', b' and c' are the least square fits constants which depends upon the nature of the respective molecules in benzene under the high frequency alternating electric field. It is observed from the computed values of dipole moment at different temperatures that, in microwave electric field the dipole moment of a polar unit is not fixed, but varies uniformly with temperature.

Chapter IV

MICROWAVE CONDUCTIVITY AND DIPOLE MOMENT OF SOME SUBSTITUTED BENZENE

This chapter reported the measurement of permanent dipole moment and bond moment of the following dielectric liquids -

(a) m-Aminobenzotrifluoride, (b) O-Nitrobenzotrifluoride
(c) m-Nitrobenzotrifluoride (d) O-Chlorobenzotrifluoride
(e) O-chloronitrobenzene (f) 4-chloro-3-nitrobenzo trifluoride (g) 4-chloro-3-nitrotoluene.

The theory and method of determination of dipole moment (μ_j) from the microwave conductivity method in the 3 cms. wavelength range is same as previous chapter. The data of dipole moment at higher and lower concentration explain the formation of dimer and monomer. The μ_j values have also been computed from the bond moment and bond angles, assuming that the benzene molecules is a planer one. It has been considered that the variation of μ_j for the substituted molecules in benzene may be due to the difference in values of group moment and the inductive effect.

Chapter V

ULTRA HIGH FREQUENCY CONDUCTIVITY OF
POLAR - NONPOLAR LIQUID MIXTURES

The UHF conductivity of nitromethyl acetamide (NMA) in benzene and in dioxane solvent in the lower as well as higher concentration region of polar solute have been determined from dielectric absorption data in the temperature range of $25^{\circ}C$ to $55^{\circ}C$. It is observed that at lower concentration region the UHF conductivity data varies linearly with the weight fraction of the solute, but differ radically at weight fraction $W_j \rightarrow 0$, which has been considered due to the solute solvent

association effect. At the higher concentration the above mentioned effect was not detected in the case of NMA but found in p-bromonitrobenzene (P-BNB). From the slope of the curve of UHF conductivity against concentration of solute molecules at infinite dilution, the dipole moment have been estimated for above mentioned liquids at various temperatures using the equation given in chapter III. It has been suggested that in the case of NMA in benzene and dioxane, the higher (computed) values of dipole moment are due to the formation of monomer and slightly lower estimated values may be due to the formation of dimer.

Chapter VI

CONDUCTIVITY, RELAXATION TIME AND ENERGY
OF ACTIVATION OF SOME ALCOHOL + BENZENE
MIXTURE AT RADIO FREQUENCY FIELD

A study has been made on the nature of variation of dipolar relaxation time (τ) for three normal alcohols such as, methyl alcohol, ethyl alcohol and 1-propyl alcohol at very dilute solution in nonpolar solvent benzene and at various temperatures. The time of relaxation has been determined from radiofrequency conductivity measurements at 1 MHz. The radio frequency conductivities of the three systems at various dilute solution and at different temperatures have been

computed from least square fit equation

$$K' = \alpha + \beta W_j + \sqrt{W_j^2}$$

and the time of relaxation τ_S determined from the relation given in chapter III. The relaxation time of dipole at infinite dilution (τ_∞) at various temperatures ($30^\circ C$ to $60^\circ C$) were computed from the relation $\tau_\infty = (2/3)\tau_S$ and also the changes due to solvent effect were estimated. It has been concluded that the lower values of τ_∞ compared to τ_S indicates that at infinite dilution the rotation of a molecule is not hindered by the interaction with other molecules, which suggests that rotational orientation occured due to (-OH) group of a molecule.

The temperature dependence of relaxation time has been utilised for determining the molecular free energy of activation ΔF_{τ_∞} , enthalpy of activation energy ΔH_{τ_∞} and entropy of activation energy ΔS_{τ_∞} for the dipole orientation of polar alcohols in nonpolar solvent. It is observed that ΔH_{τ_∞} and activation energy for viscosity ΔH_η are almost same for two systems where as it differ widely in the case of propanol. It has been considered that slightly higher value of ΔH_{τ_∞} for propanol compared to ΔH_η may be due to the energy concentration for its higher chain length.

Chapter VII

ENERGY OF ACTIVATION, DIPOLE MOMENT AND CORRELATION PARAMETER OF WATER.

In this chapter the radio frequency conductivity K' of water and glycerine mixture at 50% concentration down to unit mole fraction of water has been determined at 5 MHz over the temperature range $20^{\circ}C$ to $60^{\circ}C$. The relaxation time τ_s for the mixture at various temperatures and concentration have been calculated from the relation $\tau_s = \frac{2}{3} \cdot \frac{a^2 e}{v k T}$, where a is the radius of the molecule, e is the electronic charge and v is the mobility of the free ions calculated from the relation $K' = Nev$. The time of relaxation of water τ_o at various temperatures have been determined from the extrapolation curve at unit molefraction of water. It has been thought that the little high value of τ_o may be due to the presence of minute quantity of glycerine as impurity, which increases the hydrogen bonding between water molecules with the impurity molecules. The decrease of τ_o value with the rise of temperature suggested due to the breaking of the hydrogen bond.

The theory of rate process has been used to the temperature variation of single relaxation time in order to calculate the thermodynamical parameters

ΔF_{τ_o} , ΔH_{τ_o} and ΔS_{τ_o}) .

for water. Assuming the ΔH_{τ_o} = 4.8 Kcal/mole is of the same order of magnitude as the dipole-dipole inte- raction energy, the apparent dipole moment for water has been calculated from the Debye-Keesom relation

$$\Delta H_{\tau_o} = \frac{2}{3} \frac{\mu_{app}^4}{a^6 kT} ,$$

where $a = 1.48$ Å is the average intermole- cular distance. The correlation parameter for water $g = \left(\mu_{app}/\mu_{gas}\right)^2$ was calculated and found greater than unity ($g > 1$) The bond angle θ of (H-OH) has been calculated at various temperatures from Kirkwood relation $g = 1 + Z \cos^2\frac{\theta}{2}$.

Analysing the results a conclusion has been drawn that, the structure of water has an appreciable effect on dipolar polarisation which causes $\mu_{app} > \mu_{gas}$ and the bending of hydrogen bond with the rise of temperature.

Chapter VIII

ELECTRICAL CONDUCTIVITY ANOMALY IN BINARY
LIQUID MIXTURES NEAR THE CRITICAL POINT

In this chapter a study has been made on the electrical conductivity anomaly of three critical binary liquid mixtures at the critical temperature region. The elect- rical conductivities of the three binary liquid mixtures

such as, (a) Methyl alcohol + carbondisulphide,

(b) Nitrobenzene + n-Hexane, (c) Aniline + cyclohexane

have been determined at various temperature starting

from one phase region to down to T_c at 400 KHz. The

conductivity (K') data fitted against reduced tempe-

rature (ϵ) for three systems indicated the

asymptotic behaviour of derivative of conductivity

and existence of conductivity anomaly near critical

temperature T_c.

As the percolation theory is applicable only

to temperature variation of conductivity rather than

resistivity R(T) near T_c, so it has been tried to

fit the reduced conductivity data $K'_R = \dfrac{K' - K'_c}{K'_c}$

at the reduced temperature range $10^{-4} \leqslant \epsilon \leqslant 10^{-2}$

in the least square fit equation $K'_R = A \epsilon^{\Theta} + B_1 \epsilon + B_2 \epsilon^2$

where A, B_1 and B_2 are the least square fit parameters and

Θ is the critical exponent, which is the slope of the

linear plot $\log_{10} K'_R$ against $\log_{10} \epsilon$. The linear plot

further proved that the validity of the above mentioned

fit equation, when the calculated fitted data points

run smoothly through the experimental data points.

The striking observation made in this studies that

apart from the shape of the conductivity curves of

the three systems, the critical exponent θ for

the three different systems are almost have the

same value $\theta = 0.71$. Therefore it has been sugges-

ted that in the one phase region, the conductivity

of the binary liquid mixture near critical tempe-

rature must contain the term of the form $K'_{\text{singular}} = A \epsilon^{\theta = 2\beta}$,

. with $\theta = 0.71$ and $\beta = 0.35$

which is an universal value for the temperature

variation of the order parameter in critical

phenomena.