CHAPTER VII

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

Introduction:

Considerable amount of work has been carried out by different workers in an endeavour to clarify the dielectric behaviour of liquid-water under the alternating electric stress. Despite its apparent complex molecular structure, liquid-water closely follows a simple Debye type relaxation ($\tau = 4\pi\eta d^3/kT$) Sexton and Lane (1946) described measurements of the dielectric properties of water at microwave frequency range and at different temperatures. After that Collie et al (1948) established that, the dispersion observed in water seems to be explicable in terms of single relaxation time, They calculated the value of $\tau = 0.85 \times 10^{-11}$ secs. from Debye equation at a given temperature.

Lane and Sexton (1952) gave a very accurate method for measuring the refractive index and absorption coefficient of water and showed that the dielectric properties of water can be expressed in terms of only one relaxation time at any given temperature.

It has been further observed that the associated mixture which contain group of molecules of both kinds also shows a single relaxation time. Dalbert et al (1949), compared the various available measured values for τ of water and aliphatic alcohols and concluded that it is difficult to get reliable values for relaxation time from dielectric measurements.

Considering the above mentioned facts, we have paid special attention in our present experiment to study the temperature dependence of relaxation time (τ), the thermodynamical parameters (ΔH_τ , ΔS_τ , ΔF_τ), the dipole moment (μ) and correlation factor (g) of water in the radio frequency field.

Experimental Arrangement:

The schematic diagram of the experimental arrangement and the method of determining the r.f. conductivity of the mixture has been described in detail in the chapter II section 2.1. The oscillator frequency was fixed at 5 MHz. The dielectric cell was made up of a pyrex glass tube of diameter 2.5 cm., fitted with one pair of stainless steel circular electrodes of diameter 1.5 cms. and separated by a distance of 1 cm. Analar grade glycerine supplied by M/s. British Drug House (London) was used without further purification and highly pure distilled water (H_2O) was used for this experiment.

The viscosity of the experimental water was measured with Ostwald viscometer at different temperatures. The temperature variation was regulated by a good thermostat whose accuracy is better than ± 1°C. All the measurements were accurate upto ± 2 percent.

Results and Discussion:

The dielectric phenomena with which we are principally concerned and most conveniently discussed in electrostatic units, in which the complex dielectric constant ϵ^* represent by

$$\epsilon^* = \epsilon' - j\epsilon'' \qquad \ldots 7.1$$

The dielectric loss ϵ'' is a parameter, which describes the motion of electric charge, i.e. the electrical conduction phenomenon. Certain dielectrics are found to display conduction which arises not from the effect of polarization on the displacement current, but from the actual charge transport just like ionic conduction in electrolytes. Such conduction would normally be described by volume conductivity K' $\text{ohm}^{-1}\text{cm}^{-1}$. The effect of conductivity is an additional term of the dielectric loss. Therefore, the conductivity term K' can be expressed as $K' = \frac{\omega\epsilon''}{4\pi}$ where ω is the angular frequency.

A mathematical expression connecting radio frequency conductivity K' and the macroscopic viscosity η of the dielectric liquid given by Sen and Ghosh (1974) as

$$K' = A + \frac{B}{\eta} \qquad \ldots\ 7.2$$

where A and B are constants. The detail deduction of the equation (7.2) is given in chapter I, section 1.9. The constant B gives the ion density 'n' of the liquid mixture. Using the eq. (7.2) the average number of ion density has been obtained from the slope B is of the order of 1.7×10^{18} ions/c.c.

The radio frequency conductivity of the glycerine + water mixture at 50 percent concentration to down to unit mole fraction of water has been measured at 5 MHz over the temperature range 20°C to 60°C. The measured conductivities at different temperatures and concentrations are accurate upto ± 2 percent.

In the present paper an attempt has been taken to calculate the time of relaxation τ of the mixture at various concentrations and temperatures using the given relation deduced by Ghosh et al (1980).

$$\tau_s = \frac{2}{3}\,\frac{a^2 e}{v k T} \qquad \ldots\ 7.3.$$

where 'a' is the radius of the molecule, 'e' is the electronic charge, v is the mobility of the free ions obtained from the equation $K' = nev$, k is the Boltzmann's constant and T is the absolute temperature. The time of relaxation values (τ_s) thus calculated are placed in the table (7.1). The fig. (7.1) shows the plot of exponential variation of relaxation time (τ_s) with mole fraction 'f' of mixture. It is observed that at a particular temperature the increase of water concentration is accompanied by exponential decrease of relaxation time which eventually become the time of relaxation of water (τ_0) at unit mole fraction of water at pure state. The time of relaxation τ_0 determined from extrapolation curve at unit mole fraction of water at different temperatures are placed in table (7.2). The observed τ_0 values obtain from r.f. conductivity measurements are little greater than the values obtained by Mason et al (Von Hipple, 1954) from microwave data of pure water at different temperatures. Von Hipple (1954) had calculated the value of $\tau_0 = 0.25 \times 10^{-10}$ sec. at room temperature, considering the radius of the molecule 'a' = 2Å and viscosity η = 10 m poise. He showed graphically that τ_0 for water is located near the wavelength λ = 1 cm. It may be ascribed that slight high value of τ_0 for water at the present experiment may be due to the presence of certain minute quantity of glycerine

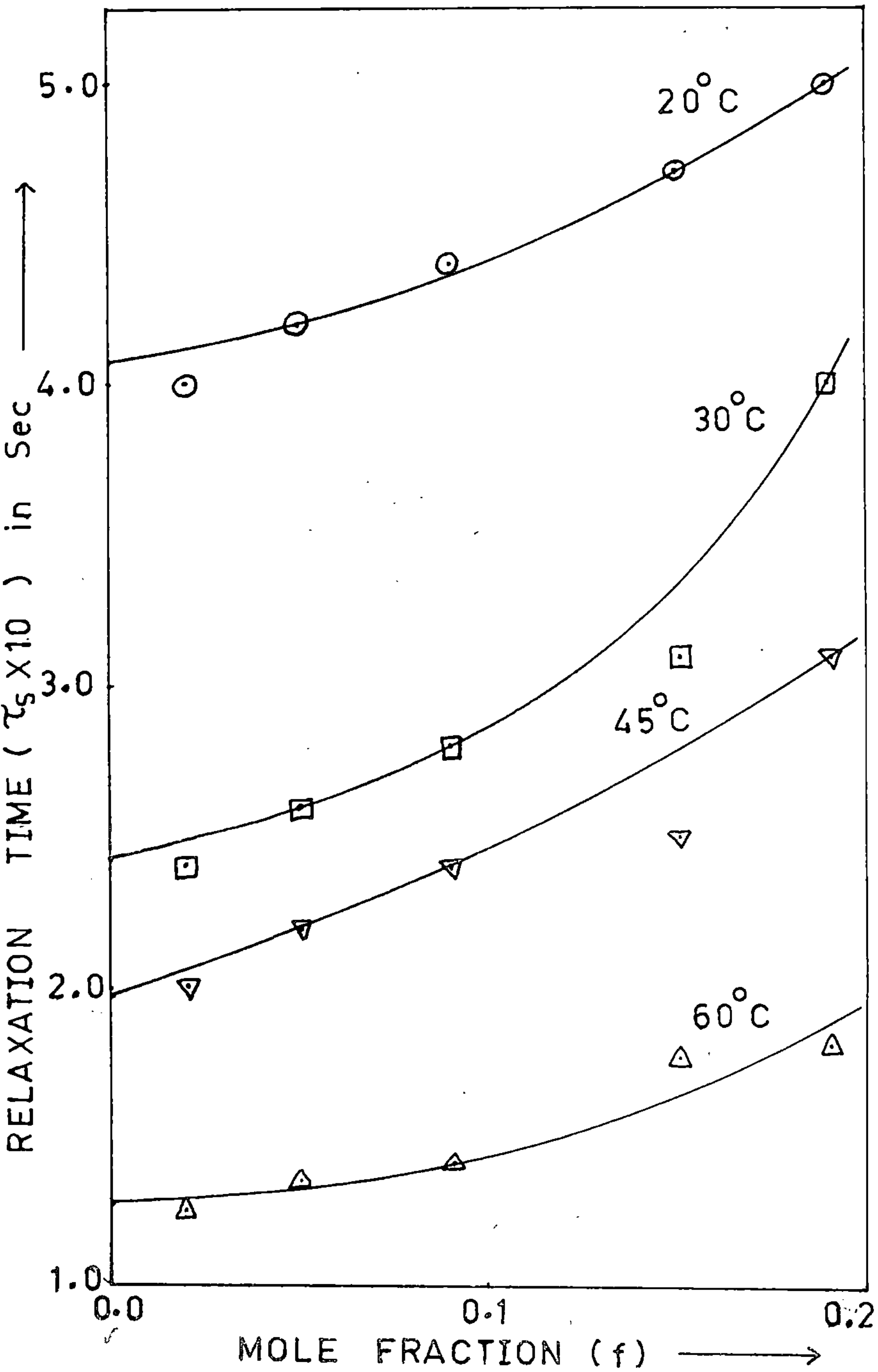

Fig-7.1 Relaxation time (τ_s) is plotted against Mole fraction(f) at different temperatures.

as an impurity, which increases the hydrogen bonding between water molecules with the impurity molecules. Thus the existance of the organic molecule increase the relaxation time for water. Generally it is observed that the τ_0 decreases with temperature. A number of studies revealed that the neutral molecules especially alcohol group increase the value of relaxation time for water. The decrease of τ_0 value for water with temperature has been suggested by Oster (1946), may be due to breaking of hydrogen bond with rise of temperature. Powles (1953) equation

$$\tau_0' = \frac{2\epsilon_s + \epsilon_\infty}{3\epsilon_s}\tau_0 \qquad \ldots 7.3a$$

has been applied for calculating the molecular relaxation time τ_0'. The different values of τ_0' at various temperatures are tabulated in Table 7.2.

Determination of molar enthalpy of activation ΔH_{τ_0}.

It is possible to treat the dipole relaxation process as analogous to a chemical rate process (Glasstone et al, 1941). The theory of rate process applied to the temperature variation of single relaxation time yields the equation

$$\tau_0 = \frac{h}{kT}\exp\left(\frac{\Delta F_{\tau_0}}{RT}\right) \qquad \ldots 7.4a$$

or,

$$\tau_o = \frac{h}{kT} \exp\left(\frac{-\Delta S_{\tau_o}}{R}\right) \exp\left(\frac{\Delta H_{\tau_o}}{RT}\right) \qquad \ldots 7.4b$$

where ΔS_{τ_o} is the molar entropy of activation, ΔH_{τ_o} is the molar enthalpy of activation and ΔF_{τ_o} is the free energy of activation. From the equation (7.4a) it follows that a graph of $\log_e(\tau_o T)$ against $1/T$ should be rectilinear and from the slope of the graph shown in Fig. (7.2), the molar enthalpy of activation ΔH_{τ_o} has been calculated. The order of magnitude of the enthalpy ΔH_{τ_o} clearly shows some involvement of molecular energy in the dipole relaxation process of water. An individual water molecules may require one, two, three or four (OH-O) bonds in all, in order to build a tetrahedral structure. Again the reorientation of dipole due to the effect of external applied field involves in breaking of typical (OH-O) hydrogen bond which give the principal relaxation time for water. The amount of enthalpy of activation energy ΔH_{τ_o} needed to rapture such bond in water is generally of the order of 4.5 Kcal/mole (Hasted,1973). in our present experiment we obtained $\Delta H_{\tau_o} = 4.8$ Kcal/mole which agrees very well with the literature value.

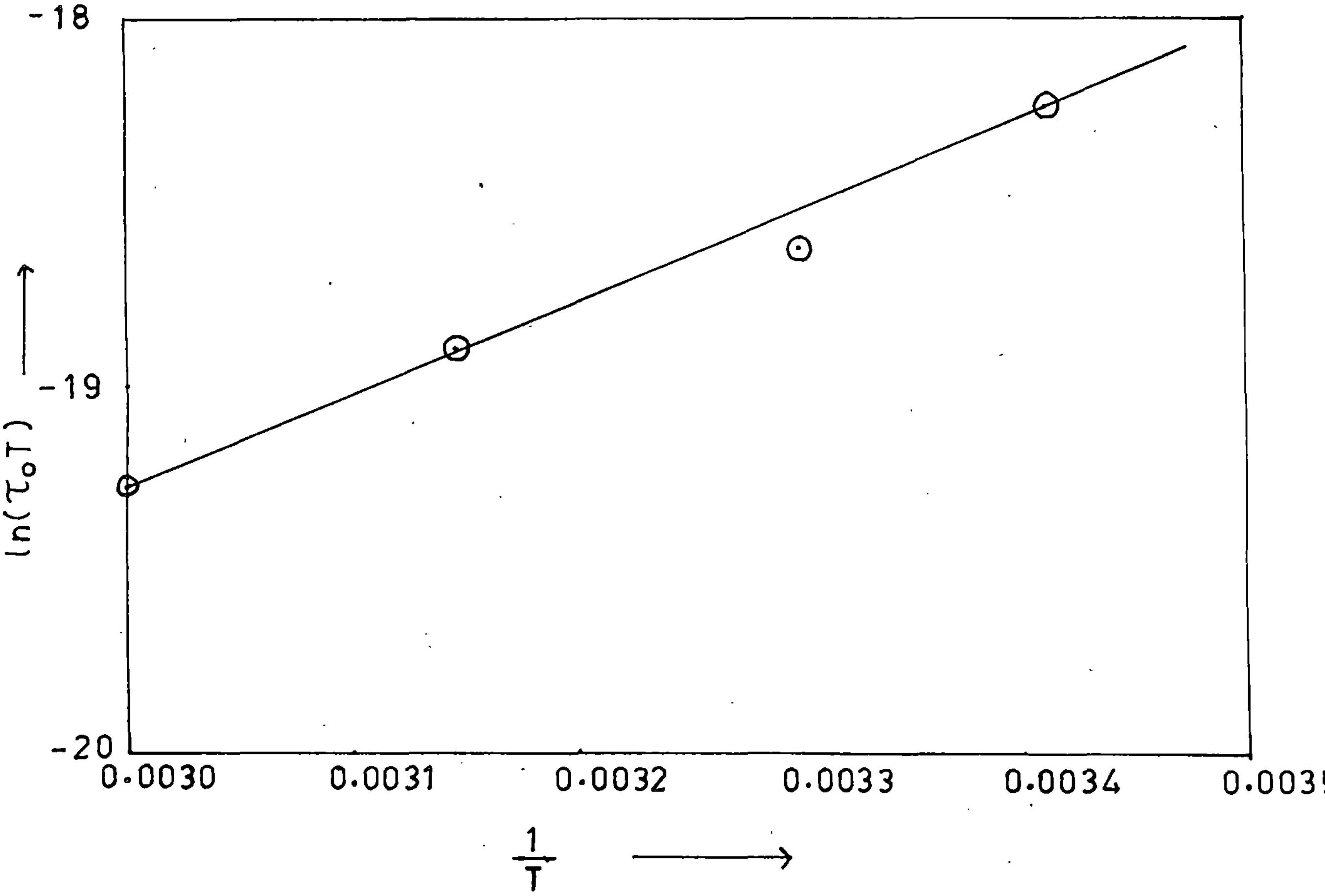

Fig → 7.2 Value of $\ln(\tau_o T)$ is plotted against reciprocal value of absolute temperature (T^{-1}) .

The values of free energy of activation ΔF_{τ_0} enthalpy of activation ΔH_{τ_0} and entropy of activation ΔS_{τ_0} at different temperatures are placed in Table (7.2).

If we consider ΔH_{τ_0} to be of the same order of magnitude of dipole-dipole interaction energy then it gives us an opportunity to calculate the apparent dipole moment of water by applying Debye-Keesom (Ketelaar, 1953) expression.

Determination of Correlation Parameter 'g' and Apparent Dipole Moment μ_{app}.

Polar liquid such as water posses its own static dielectric constant, dipole moment, relaxation time and correlation factor 'g'. The correlation parameter 'g' is a measure of the local ordering in the material. The structure of water has been the subject of such study till today. Kirwood assumed a single structure similar to that suggested by Bernal and Fowler (1933) in order to calculate the correlation parameters g. The Kirkwood (Smyth, 1955) correlation parameter 'g' can be determined by using the equation

$$\mu_{app}^2 = g\mu_{Vapour}^2 \qquad \ldots 7.5$$

where μ_{app} is the apparent dipole moment of the water and μ_{Vapour} is the dipole moment of water at gaseous state. Assuming the enthalpy of activation ΔH_{τ_o} = 4.8 Kcal/mole is of the same order of magnitude as the dipole-dipole interaction energy, the apparent dipole moment value μ_{app} at different temperature has been calculated from the Debye-Keesom (Ketelaar,1953) expression

$$\Delta H_{\tau_o} = \frac{2}{3} \cdot \frac{\mu_{app}^4}{a^6 k T} \qquad \ldots\ 7.6$$

where a = 1.48 Å is the average intermolecular distance. The μ_{app} thus calculated from equation (7.6) are placed in Table (7.2) and found that the values of $\mu_{app} > \mu_{Vapour}$ has tendency to increase slowly with rise of temperature. It may be interpreted as, with the rise of temperature, the rotational vibration of the molecules increases, which causes the slight increase of dipole moment. It is observed that the correlation parameter is large in associated or associated - associated liquid (Bordewijk et al,1978) because the material possesses high degree of correlation between dipoles. In liquid water the local forces between dipole molecules are very large. So, it could be expected that 'g' value should differ appreciably from unity. Here also we found that the 'g' values thus calculated from the relation $g = \left(\mu_{app} / \mu_{Vapour}\right)^2$

are greater than unit. But the variation of g values is small, that can be taken as constant within our experimental range of temperatures, and the values are given in Table (7.2).

After the work of Bernal and Fowler (1933), almost all the theories adopted a tetrahedrally arranged hydrogen bonded model of water. Haggis et al (1952) modified the model further and proposed that each water molecule may be hydrogen - bonded to four other water molecules. In the case of water Kirkwood (Smyth,1955) gave a relation

$$g = 1 + Z \cos^2 \frac{\theta}{2} \qquad \ldots\ 7.7$$

where θ is the angle of (H-O-H) bond taken as 104° and Z = 4, is the number of nearest neighbour molecules, which surround each water molecules. The bond angles have been calculated at various temperatures using equation (7.7) and the values are listed in Table (7.2). Thus we may conclude that the correlation parameter of water $g > 1$, suggest that the structure of water has appreciable effect on dipolar polarization which causes $\mu_{app} > \mu_{Vapour}$ and the rise of temperature results in bending of hydrogen bond.

Table 7.1

Values of conductivities (K'), mobilities (ν) and relaxation times (τ_s) of the solution at different temperatures (t) and mole fractions (f):

Temp. in °C	20°C			30°C			45°C			60°C		
Mole fraction f	$K' \times 10^5$ mho/cm	$\nu \times 10^4$ $cm^2V^{-1}Sec^{-1}$	$\tau_s \times 10^{11}$ secs.	$K' \times 10^5$ mho/cm	$\nu \times 10^4$ $cm^2V^{-1}sec^{-1}$	$\tau_s \times 10^{11}$ sec.	$K' \times 10^5$ mho/cm	$\nu \times 10^4$ $cm^2V^{-1}sec^{-1}$	$\tau_s \times 10^{11}$ secs.	$K' \times 10^5$ mho/cm	$\nu \times 10^4$ $cm^2V^{-1}sec^{-1}$	$\tau_s \times 10^{11}$ secs.
0.19	3.699	1.156	5.0	4.458	1.393	4.01	5.494	1.717	3.10	9.04	2.825	1.80
0.15	3.933	1.229	4.7	5.770	1.803	3.10	6.815	2.1297	2.50	9.245	2.889	1.76
0.09	4.202	1.313	4.4	6.387	1.996	2.80	7.098	2.218	2.40	11.622	3.632	1.40
0.05	4.403	1.376	4.2	6.877	2.149	2.60	7.744	2.420	2.20	12.051	3.766	1.35
0.02	4.624	1.445	4.0	7.45	2.328	2.40	8.518	2.662	2.00	13.018	4.068	1.25

Table 7.2

Values of relaxation time (τ_0), molar relaxation time (τ_0'), viscosity (η), enthalpy of activation (ΔH_{τ_0}), entropy of activation (ΔS_{τ_0}), free energy of activation (ΔF_{τ_0}), apparent dipole moments (μ_{app}), dipole moment in vapour state (μ_{Vapour}), correlation factors (g), bond angle (θ) of water and radius of the molecule 'a' at different temperatures.

Temp. in ^{o}C	$\tau_0 \times 10^{11}$ secs.	$\tau_0' \times 10^{11}$ secs	η mpoise	ΔH_{τ_0} Kcal/mole	ΔS_{τ_0} Cal/mole	ΔF_{τ_0} Kcal/mole	μ_{app} in D	μ_{Vapour} in D	'g'	θ^{o}	a in Å
20	4.075	2.72	10.01		5.358	3.230	2.83		2.47	105.36	2.3
30	2.425	1.62	8.0	4.80	5.788	3.046	2.86	1.8	2.52	103.9	2.16
45	1.963	1.32	6.05		5.366	3.094	2.89		2.58	102.1	2.25
60	1.275	0.85	4.77		5.457	2.983	2.92		2.63	100.7	2.14

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