

CHAPTER IIIMICROWAVE CONDUCTIVITY AND DIPOLE MOMENT OF POLAR  
DIELECTRICSIntroduction:

One of the main application of the dielectric theory in physics and chemistry is still the determination of permanent dipole moment of molecules. These values can be of great use, in both organic and inorganic chemistry for the elucidation of molecular structures and also in the study of the chemical bond. In view of the importance of the permanent dipole moment of molecules we have tried to determine the dipole moment of the polar molecule in non polar solvent at different temperatures.

The temperature dependence of dipole moment of a polar liquid is not a new concept, (Ras and Bordewijk, 1971) yet it is found to occur when the polar - nonpolar liquid mixture is subjected to an alternating microwave electric field. There are several methods (Gopala Krishna, 1957, Sen et al 1972) to compute the dipole relaxation time  $\tau_s$  of polar liquid dissolved in nonpolar solvent under the application of radio - frequency and microwave alternating electric field.

Gopala Krishna's concentration variation method in the microwave region and Sen's graphical method in the r.f. region always invite a slight personal judgement to locate the exact and accurate value of  $\tau_s$  within a certain considerable range. In order to avoid this difficulty we, in the process of derivation of the dipole moment  $\mu_j$  of polar liquids in nonpolar solvent from the conductivity data in h.f. region devised a simple procedure (Ghosh et al, 1980, Datta et al 1981) to obtain the relaxation times  $\tau_s$  of polar liquids from the microwave and radiofrequency conductivity data based on sound mathematical foundation. When the frequency of the impressed field exceeds a certain critical value, the permanent dipoles of solute molecules cannot follow the exact alternation of the applied field. This measurable lag is commonly known as dielectric relaxation, and the relaxation time of a solute is defined as the lag in response of polar solute with the forces to which it is subjected. Using the slope of concentration variation of total microwave conductivity  $K_{ij}$  at infinite dilution we attempted to obtain the relaxation time at different temperatures with the single  $\mu_j$  value as obtain from literature. We found that the single value of  $\mu_j$  could not yield the magnitude

of  $\tau_s$  though it gave the relative temperature dependence of computed  $\tau_s$  only. This fact at once indicates that in the h.f. region  $\mu_j$  is not a fixed quantity, but most probably it slightly varies with temperature to ascertain the actual magnitude of  $\tau_s$ .

Theory:-

According to Murphy and Morgan (1939) the h.f. conductivity is a complex quantity  $K^*$ , where

$$K^* = K' + jK'' \quad \dots 3.1$$

In the case of polar nonpolar liquid mixture the high frequency conductivity can be represented as

$$K_{ij} = K'_{ij} + jK''_{ij} \quad \dots 3.2$$

where  $K'_{ij}$  is the real part of the conductivity

$\left[ K'_{ij} = \frac{\omega \epsilon''_{ij}}{4\pi} \right]$  and  $K''_{ij}$  is the imaginary part of the conductivity  $\left[ K''_{ij} = \frac{\omega \epsilon'_{ij}}{4\pi} \right]$

of the solution.

Now the magnitude of the total high frequency conductivity can be written as

$$K_{ij} = \left( K'^2_{ij} + K''^2_{ij} \right)^{1/2} \quad \dots 3.3$$

but the magnitude of  $K_{ij}$  is usually calculated from the relation

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon''_{ij}{}^2 + \epsilon'_{ij}{}^2)^{1/2} \quad \dots 3.4$$

But in the microwave region  $\epsilon'_{ij}$  of the solution is very small and equals to the optical dielectric constant, but still  $\epsilon'_{ij} \gg \epsilon''_{ij}$  and  $\epsilon''_{ij}$  is responsible for the absorption of electrical energy to yield to polarisation.

Now from the eq. (3.4) the total conductivity should be

$$K_{ij} = \frac{\omega \epsilon''_{ij}}{4\pi} = K''_{ij} \quad \dots 3.5$$

Thus the total conductivity of the solution equals to the imaginary part of the conductivity in the microwave frequency.

But for high frequency it can be shown by using Debye equations

$$\epsilon' = \left( \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau^2} \right) \quad \text{and} \quad \epsilon'' = \frac{(\epsilon_s - \epsilon_{\infty}) \omega \tau}{1 + \omega^2 \tau^2}$$

the h.f. dielectric constant,

$$\epsilon'_{ij} = \epsilon_{ij\infty} + \epsilon''_{ij} / \omega \tau_s$$

or,

$$\frac{\omega \epsilon'_{ij}}{4\pi} = \frac{\omega \epsilon_{ij\infty}}{4\pi} + \frac{\omega \epsilon''_{ij}}{4\pi \omega \tau_s}$$

$$\therefore K_{ij} = K_{\infty} + K'_{ij}/\omega \tau_s \quad \dots 3.6$$

where  $\epsilon_{ij\infty}$  is the optical dielectric constant of the solution and  $K_{\infty}$  is a constant and  $\tau_s$  is the relaxation time of the solute molecule in solution.

Now, the real part of h.f. conductivity  $K'_{ij}$  of polar nonpolar solution is obtained from eqn. (1.72) as

$$K'_{ij} = \left( \frac{\epsilon_{ij} + 2}{3} \right)^2 \frac{N C_j \mu_j^2}{3kT} \frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \quad \dots 3.7$$

Smyth (1955) introduced the idea of weight fraction  $W_j$  and replaced the molar concentration of solute  $C_j$  by  $C_j = \rho_{ij} W_j / M_j$  where  $\rho_{ij}$  is the density of the solution,  $M_j$  is the molecular weight of the solute. Hence from eq. (3.7) we get

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3 M_j k T} \cdot \frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} W_j \quad \dots 3.8$$

where  $\mu_j$  is the dipole moment of polar solute,  $N$  is the Avogadro number,  $k$  is the Boltzmann constant and

$$F_{ij} = \left( \frac{\epsilon_{ij} + 2}{3} \right)^2$$

is the local field.

Since  $K_{ij}$  is a function of  $W_j$ , so we have from eq. (3.6)

$$\left( \frac{dK_{ij}}{dW_j} \right)_{W_j \rightarrow 0} = \frac{1}{\omega \tau_s} \left( \frac{dK'_{ij}}{dW_j} \right)_{W_j \rightarrow 0}$$

or

$$\left( \frac{dK'_{ij}}{dW_j} \right)_{W_j \rightarrow 0} = \omega \tau_s \left( \frac{dK_{ij}}{dW_j} \right)_{W_j \rightarrow 0} = \omega \tau_s \beta \quad \dots 3.9$$

where  $\beta$  is the slope of  $K_{ij}$  vs  $W_j$  curve at

$W_j \rightarrow 0$  the density  $\rho_{ij}$  of the solution becomes  $\rho_i$  the density of the solvent and the local field  $F_{ij}$

of the solution is  $F_i =$  the local field of the

solvent  $= \left[ (\epsilon_i + 2)/3 \right]^2$

Under the circumstances, eq.(3.8) on being differentiated with respect to  $W_j$  and as  $W_j \rightarrow 0$  takes the form

$$\left( \frac{dK'_{ij}}{dW_j} \right)_{W_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3 M_j k T} \left( \frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \right) \quad \dots 3.10$$

From eq. (3.9) and eq. (3.10) we get

$$\omega \tau_s \beta = \frac{\mu_j^2 N \rho_i F_i}{3 M_j k T} \cdot \frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2}$$

or,

$$\frac{1}{1 + \omega^2 \tau_s^2} = \beta / \left( \frac{\mu_j^2 N \rho_i F_i}{3 M_j k T} \cdot \omega \right) = b \text{ (say)} \quad \dots 3.11$$

or,

$$\tau_s = \frac{1}{\omega} \sqrt{\frac{1}{b} - 1}$$

or,

$$\tau_s = \frac{1}{2\pi f} \sqrt{\frac{1}{b} - 1}$$

when  $\omega = 2\pi f$  is the frequency of the applied field. When  $f = c/\lambda$

$c$  is the velocity of electromagnetic radiation

$\lambda$  is the wave length.

$$\therefore \tau_s = \frac{\lambda \times 10^{-10}}{18.84} \sqrt{\frac{1}{b} - 1} \quad \dots 3.12$$

Now from eq. (3.11) the dipole moment of the solute can be written in the form

$$\mu_j = \left( \frac{3 M_j k T}{N \rho_i F_i} \cdot \frac{\beta}{\omega b} \right)^{1/2} \quad \dots 3.13$$

The eq. (3.12) is used to compute  $b$  from reported  $\tau_s$  data and hence the dipole moment of polar solute  $\mu_j$  when it is dissolved in a nonpolar solvent.

### Results and Discussions:

The radiofrequency and high frequency conductivity (Sen and Ghosh, 1972) of polar nonpolar liquid mixture is comparatively easy to measure down to very low concentration by the help of Hartley and Klystron valve oscillator in the laboratory. But as the experimental conductivity data under radio frequency and microwave electric fields are very scanty, it is therefore, used the available concentration, variation experimental data for  $\epsilon''_{ij}$  and  $\epsilon'_{ij}$  of seven systems in benzene such as: 2-5 dichloronitrobenzene and 2-5 dibromonitrobenzene under 3.13 cm. wavelength electric field (Pant et al, 1977) and 3-nitro-O-anisidine, 2-chloro-p-nitroaniline, p-phenetidine, O-nitroaniline and p-anisidine under 3.17 cms. wavelength electric field (Some Vanshi et al 1978) to obtain the corresponding experimental microwave conductivity  $K_{ij}$  values from the eq. (3.4) which is the extended relation of Murphy and Morgan

$$K_{ij} = \frac{\omega}{4\pi} \sqrt{\epsilon''_{ij}{}^2 + \epsilon'_{ij}{}^2}$$



at various temperatures 20°C, 30°C and 40°C. The  $K_{ij}$  values of the above mentioned solutes in benzene solution are plotted against weight fraction ( $W_j$ ) at different temperatures are shown in fig. (3.1) and Fig. (3.2).

The temperature dependence of  $K_{ij}$  for each system is vividly exposed in the plot. But at the lower concentration region the conductivity  $K_{ij}$  varies almost linearly with  $W_j$ . As the weight fraction  $W_j$  approaches to zero, it is assumed that the solvent benzene possesses a constant value of conductivity which is independent of experimental temperature. It is considered because of the fact that the quantity ( $\rho_{ij} F_{ij} / T$ ) in eq.(3.8) approaches nearly a fixed value which is in the neighbourhood of 0.006. Consequently, at  $W_j = 0$ , the conductivity of a given system at all temperature remain the same. Nevertheless, at  $W_j = 0$  the  $K_{ij}$  values of different systems are different. This is due to solvation effect (Datta et al 1981).

From Fig. (3.1, 3.2) it is clear that at  $W_j = 0$  i.e. at infinite dilution where the solute molecules immersed in macroscopic amount of solvent and meeting of the curves at a point indicate that there are no effect of temperature on  $K_{ij}$ , therefore the change

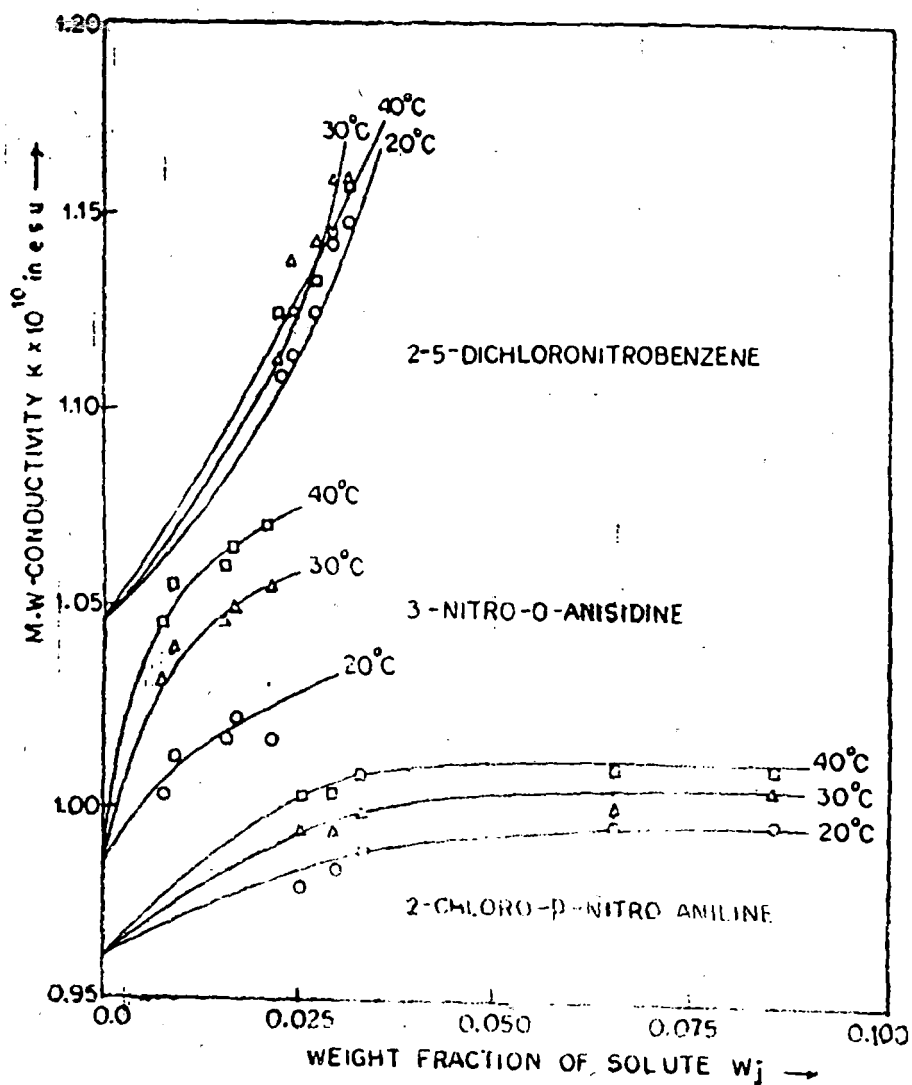


Figure 51-Microwave conductivity  $K$  is plotted against weight fraction  $w_j$  at 20°C, 30°C and 40°C.

○ ————— ○ ————— at 20°C,  
 Δ ————— Δ ————— at 30°C,  
 □ ————— □ ————— at 40°C.

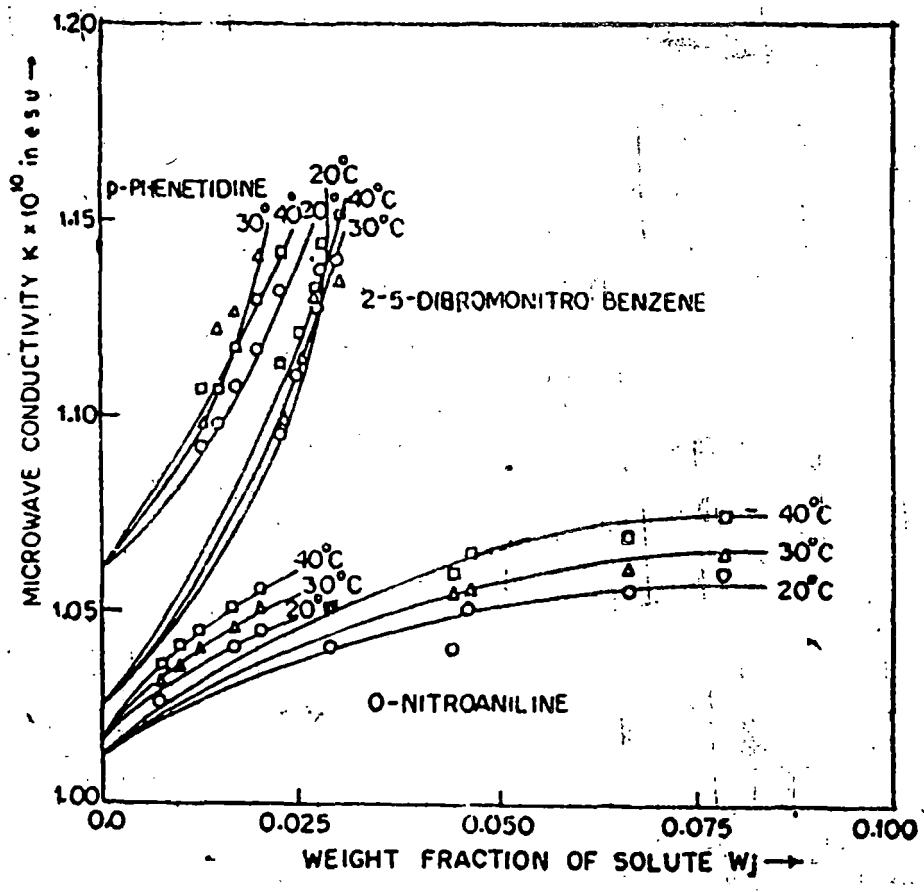


Figure 3.2 Microwave conductivity  $K$  is plotted against weight fraction  $w_j$  at 20°C, 30°C and 40°C.

○ ————— ○ ————— at 20°C,  
 △ ————— △ ————— at 30°C,  
 □ ————— □ ————— at 40°C.

in  $K_{ij}$  values at  $W_j = 0$  may be considered due to solvation effect, which is independent of temperature over a large temperature range (Böttcher and Bordewijk, 1978).

For each systems in the lower concentration region there is a regularity in increase of slopes of the curves with temperature. At any experimental temperature the variation of  $K_{ij}$  with  $W_j$  is excellent to suggest that h.f. conductivity can be represented by a fitted formula

$$K_{ij} = \alpha + \beta W_j + \gamma W_j^2 \quad \dots 3.15$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are arbitrary constants depending upon the nature of the respective solution of polar nonpolar liquid mixture of which  $\beta$  plays a very important role in estimating dipole moment  $\mu_j$ . Of course we have tried for determining the numerical values of  $\alpha$ ,  $\beta$  and  $\gamma$  by least square fitting technique. But unfortunately the process was abandoned because the available data are not smooth enough for the said technique. However, at linear portion the slope  $\beta$  of  $K_{ij}$  against  $W_j$  curve at  $W_j \rightarrow 0$  was estimated by drawing a tangent to each curve at  $W_j \rightarrow 0$  as demanded by the relation (3.9).

Though errors due (a) experimental uncertainty and (b) theoretical approximation done in obtaining eq.(3.9) may be expected to accumulate in determined  $\mu_j$  by this method yet we have adopted this method because the (i) conductivity data are very scanty in the lower concentration region and (ii) the error due to theoretical approximation is negligibly small in the h.f. region.

Using eq. (3.12) the values of 'b' were determined with the reported relaxation time  $\tau_s$  value for each systems at temperature  $20^\circ$ ,  $30^\circ$  and  $40^\circ\text{C}$  and are placed in table (3.1). The corresponding  $\mu_j$  values for all the chosen systems were also calculated from eq. (3.13) at those temperatures and are placed in table(3.1) along with the reported and theoretical ones for comparison. The dipole moment  $\mu_j$  values thus obtained were found to satisfy the following empirical formulae:

(i) 2-5 dichloronitrobenzene:

$$\mu_j = 3.1729 - 3.143 \times 10^{-3} t + 4.51 \times 10^{-4} t^2$$

(ii) 2-5 dibromonitrobenzene:

$$\mu_j = 5.2209 + 2.7966 \times 10^{-2} t - 1.423 \times 10^{-4} t^2$$

(iii) 3-nitro-0-anisidine:

$$\mu_j = 2.154 + 1.8412 \times 10^{-2} t + 3.5226 \times 10^{-3} t^2$$

(iv) 2-chloro-p-nitroaniline:

$$\mu_j = 0.22158 + 0.11997 t - 1.221 \times 10^{-3} t^2$$

(v) p-phenetidine:

$$\mu_j = 1.8453 + 6.3216 \times 10^{-2} t - 7.22 \times 10^{-4} t^2$$

(vi) O-nitroaniline:

$$\mu_j = 1.1532 + 4.873 \times 10^{-2} t - 2.616 \times 10^{-4} t^2$$

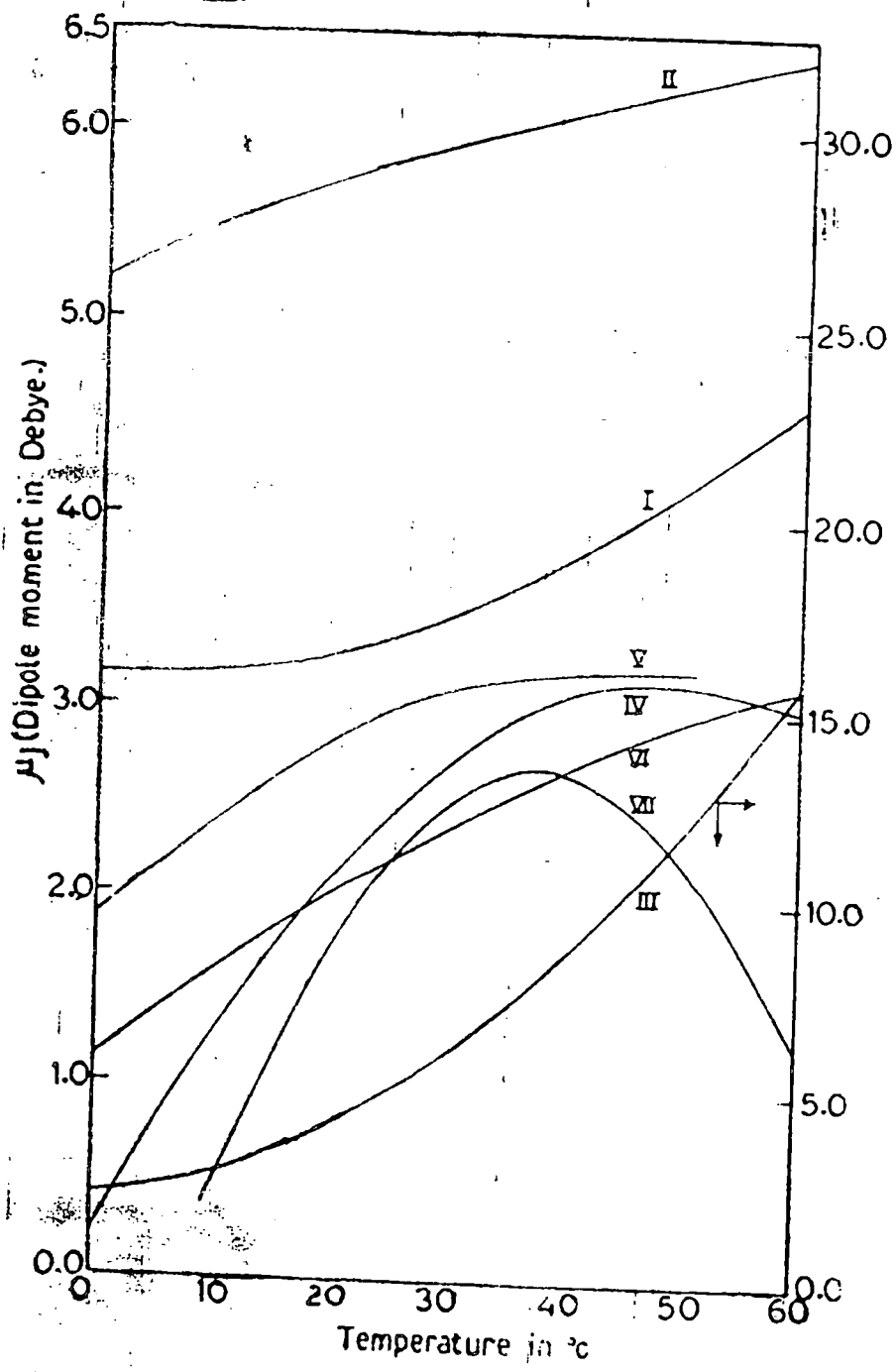
and

(vii) p-anisidine:

$$\mu_j = -1.4232 + 2.2068 \times 10^{-1} t - 2.958 \times 10^{-3} t^2$$

for different systems with temperature  $t$  in  $^{\circ}\text{C}$ . The value of variation of the computed dipole moment  $\mu_j$  of polar liquids against temperature in  $^{\circ}\text{C}$  are shown graphically by the fitted lines in Fig. (3.3).

From table (3.1) it is obvious that  $\mu_j$  in all the cases increases with experimental temperatures as observed by other workers (Ras et al, 1971) showed that dipole moments of some liquid compounds such as glycerol triacetate, glycerol tributriate etc. increase with temperature both in the pure form and in solution with benzene under the microwave alternating electric field though the values of pure compounds differ upto 7 percent from those determined in benzene. So far as the magnitude is concerned, the dipole moments of our



**Figure 3.3**—Computed dipole moments  $\mu_j$  of seven polar liquids are plotted against temperature in  $^{\circ}\text{C}$ .  
 For system II I :  $\mu_j$  (0–15D) is shown on the right side of the graph while for other six systems :  $\mu_j$  (0–6.5 D) on the left side of the graph.

systems computed from eq. (3.13) are in excellent agreement with the reported ones based on Gopala Krishna's (1957) method and those theoretically calculated from vector atom model (Datta et al, 1981). However, for the system: 3-nitro-0-anisidine(III) the values at 20°C is very close to the reported data, but at 30°C and 40°C they are abnormally high. This could not be explained at present. Though the reported data of 2-5 dibromonitrobenzene (II) and 2-5 dichloronitrobenzene (I) are not available, the dipole moments as obtained from eq. (3.13) of the former is always greater than those of the latter. This indicates that the bulky molecule possesses a greater dipole moment to yield high  $\tau_s$  values than those of lighter ones. Hence the size and shape of the molecules are important to locate the magnitudes of both relaxation time and dipole moment. The greater values of the dipole moments which are very close to the theoretical ones for 2-5 dibromonitrobenzene (II) undoubtedly confirms our methods to be a correct one. In fig. (3.3) the computed experimental  $\mu_j$  of seven polar liquids are plotted against the temperature in °C in the range of 0 to 60°C. At present we are not interested to study to below and above this range of the said organic compounds.



It is observed that in all these cases that the dipole moment  $\mu_j$  increases with temperatures in accordance to the mathematical relation given by

$$\mu_j = a' + b't + c't^2 \quad \dots (3.16)$$

where  $a'$ ,  $b'$  and  $c'$  are the arbitrary constants depending upon the nature of the respective solute molecule in benzene under the h.f. alternating electric field and  $t$  is the temperature in degree centigrade.

The  $a'$  terms of all the systems are positive except the last one i.e. p-anisidine (VII) for which it is negative. For 2-5 dichloronitrobenzene (I) dipole moment increases monotonically with temperature producing a slight concave nature of the curve because the  $b'$  term of eq. (3.16) is negative while  $c'$  is positive. For 3-nitro-O-anisidine (III)  $a'$ ,  $b'$ , and  $c'$  terms of eq. (3.16) are positive. As a result, the dipole moment of this compound becomes very high at comparatively higher temperatures, still, it agrees with the reported  $\mu_j$  at 20°C. The most interesting system is p-anisidine (VII) for which  $a'$  and  $c'$  are negative, nevertheless, its dipole moment within the experimental range of temperature is finite which

agrees fairly well with both the experimental and theoretical values. Beyond the experimental range of temperatures its dipole moment becomes zero at  $7.1^{\circ}\text{C}$  and at  $67.5^{\circ}\text{C}$  as observed from the curve (VII) of fig. (3.3) as well as from its empirical relation. This fact is also corroborated with the reported data which could also satisfy an empirical relation

$$\mu_j^{\text{rept}} = -7.46 + 6.49 \times 10^{-1} t + 9.90 \times 10^{-3} t^2 \dots 3.17$$

giving zero value of  $\mu_j$  at  $14.9^{\circ}\text{C}$  and at  $50.7^{\circ}\text{C}$ . This trend is also visualised in curves (IV) and (V) of 2-chloro-p-nitroaniline and p-phenetidine respectively of fig. (3.3). We therefore, conclude that para molecules of organic polar liquids must show the zero value of dipole moment at lower and higher temperatures most probably due to association of polar units as well as due to the solvation effect, occurred due to specific interactions between solute molecule and the solvent molecule and also to the bulk properties of the solvent especially the dielectric constant.

Table 3.1

Computed dipole moment  $\mu_j$  (compt), rept. dipole moment  $\mu_j$  (rept), relaxation times  $\tau_s$ ; and b at temperature 20°, 30° and 40°C.

System	Temp °C	b comp.	$\tau_s \times 10^{12}$ rep.in sec.	$\mu_j$ (compt.) in D	$\mu_j$ (rept.) in D	$\mu_j$ (theor.) in D
1) 2-5 dichloro- nitrobenzene	20	0.6620	11.87**	3.29		
	30	0.7060	10.72	3.48		4.23***
	40	0.7477	9.65	3.77		
2) 2-5 dibro- monitro- benzene	20	0.3736	21.51**	5.72		
	30	0.4090	19.97	5.93		4.23***
	40	0.4369	18.86	6.11		
3) 3-nitro-O- anisidine	20	0.6165	13.27*	3.93	2.76	
	30	0.6793	11.56	5.88	3.11	4.93***
	40	0.7282	10.28	8.53	3.76	
4) 2-chloro-p- nitroani- line.	20	0.7170	10.57*	2.13	2.44	
	30	0.7432	9.89	2.72	3.28	2.39***
	40	0.7706	9.18	3.07	3.93	
5) p-phene- tidine	20	0.6975	11.08*	2.82	2.24	
	30	0.7147	10.63	3.09	2.78	1.53***
	40	0.7409	9.95	3.22	3.14	
6) O-nitro- aniline	20	0.7648	9.33*	2.02	3.95	
	30	0.7779	8.99	2.38	2.19	4.25***
	40	0.8050	8.28	2.68	2.24	
7) p-anisi- dine	20	0.9493	3.89**	1.81	1.56	
	30	0.9546	3.67	2.51	3.10	1.87***
	40	0.9657	3.17	2.67	2.66	

\* Somevanshi et al (1978), \*\* Pant et al (1977),

\*\*\* Calculated from the vector model assuming molecule to be planar.

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## Microwave conductivity and dipole moment of polar dielectrics

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**Abstract:** The slope of the concentration variation of high frequency conductivity of polar-nonpolar liquid mixture at infinite dilution has been employed to estimate the dipole moment of polar solute at different temperatures. The calculations showed that in the microwave electric field the dipole moment of a polar unit is not fixed, but varies uniformly with temperature.

### 1. Introduction

The variation of dipole moment of a polar liquid with temperature is not a new concept (Ras and Bordewijk 1971) but it really occurs when the polar-nonpolar liquid mixture is subjected to the alternating microwave electric field. There are several methods (Gopala Krishna 1957; Sen *et al* 1972) to compute the relaxation times  $\tau$ , of polar liquid dissolved in nonpolar solvent under the application of radio frequency and microwave alternating electric field. Gopala Krishna's concentration variation method in the microwave region and Sen's graphical method in r.f. region always invite a slight personal judgement to locate the exact and accurate value of  $\tau$ , within a certain considerable range. In order to avoid this difficulty we, in the process of derivation of the dipole moment  $\mu_j$  of polar liquids in solvent from the conductivity data (Ghosh and Acharyya 1977) in h.f. region, devised a simple procedure (Ghosh *et al* 1980, Datta *et al* 1981) to obtain the relaxation times  $\tau$ , of polar liquids from the m.w and r.f. conductivity data based on sound mathematical foundation. When the frequency of the impressed field exceeds a certain critical value, the permanent dipoles of solute molecules cannot follow the exact alternation of the applied field. This measurable lag is commonly known as dielectric relaxation, and the relaxation time of a solute is defined as the lag in response of polar solute with the forces to which it is subjected. Using the slope of concentration variation of total conductivity  $K$  at infinite dilution we attempted to obtain the relaxation time

at different temperatures with the single  $\mu_j$  value as obtained from literature. We found that the single value of  $\mu_j$  could not yield the magnitude of  $\tau$ , though it gave the relative temperature dependence of computed  $\tau$ , only. This fact at once indicates that in the h.f. region  $\mu_j$  is not a fixed quantity, but most probably varies with temperature to ascertain the actual magnitude of  $\tau_j$ .

All these points put us in a sound position to utilise the concentration variation of conductivity data to evaluate  $\mu_j$  at different temperatures for the following seven systems of interest.  $\mu_j$  values thus obtained were found to satisfy the following empirical formulae :

- (i) 2-5 dichloronitrobenzene :  $\mu_j = 3.1729 - 3.143 \times 10^{-3}t + 4.51 \times 10^{-4}t^2$ .
- (ii) 2-5 dibromonitrobenzene :  $\mu_j = 5.2209 + 2.7966 \times 10^{-2}t - 1.423 \times 10^{-4}t^2$ .
- (iii) 3 nitro-*o*-anisidine :  $\mu_j = 2.154 + 1.8412 \times 10^{-2}t + 3.5226 \times 10^{-3}t^2$ .
- (iv) 2-chloro-*p*-nitroaniline :  $\mu_j = 0.22158 + 0.11997t - 1.221 \times 10^{-3}t^2$ .
- (v) *p*-phenetidine :  $\mu_j = 1.8453 + 6.3216 \times 10^{-2}t - 7.22 \times 10^{-4}t^2$ .
- (vi) *o*-nitroaniline :  $\mu_j = 1.1532 + 4.873 \times 10^{-2}t - 2.616 \times 10^{-4}t^2$ . and
- (vii) *p*-anisidine :  $\mu_j = -1.4232 + 2.2068 \times 10^{-1}t - 2.958 \times 10^{-3}t^2$ .

for different systems with temperature in °C.

## 2. Theory

According to Murphy and Morgan (1939) the high frequency conductivity of a polar-nonpolar liquid mixture is given by  $K = K' + jK''$ , where  $K'$  = the real part of the conductivity  $= \frac{\omega \epsilon''_{ij}}{4\pi}$ , and  $K''$  = the imaginary part of the conductivity  $= \frac{\omega \epsilon'_{ij}}{4\pi}$ . Now the magnitude of the total h.f. conductivity is usually calculated by the relation

$$K = \frac{\omega}{4\pi} [\epsilon''_{ij} + \epsilon'_{ij}]^{1/2} \quad (1)$$

But, in practice, as  $\epsilon'_{ij}$  decreases with frequency and eventually equals the optical dielectric constant in the h.f. region, and  $\epsilon''_{ij}$  increases with frequency to attain a maximum value at  $\omega = \frac{1}{\tau}$  and then begins to decrease, the real part  $K'$  of h.f. conductivity of polar-nonpolar liquid mixture of weight fraction  $w_j$  of polar solute at any temperature T°K is given by

$$K' = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j kT} \left( \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) w_j \quad (2)$$

where  $\mu_j$  is the dipole moment of polar solute of molecular weight  $M_j$ ,  $N$  is the Avogadro number,  $k$  is the Boltzman constant and  $F_{ij} = \left( \frac{\epsilon_{ij} + 2}{3} \right)^3$  is the

local field. This  $\epsilon_{ij}$  however, is the complex dielectric constant of the solution of density  $\rho_{ij}$  and is expressed as  $\epsilon_{ij} = \epsilon'_{ij} - j\epsilon''_{ij}$  of which the emaginary part  $\epsilon''_{ij}$  is responsible for the absorption of electrical energy to yield resistance to polarization. Now for microwave electric field  $\epsilon'_{ij} \gg \epsilon''_{ij}$  and the conductivity of the solution becomes

$$K = \frac{\omega \epsilon''_{ij}}{4\pi} \quad (3)$$

But for h-f region it can be shown that

$$\epsilon''_{ij} = \epsilon_{ij, \infty} + \epsilon''_{ij}/\omega\tau \quad (4)$$

where  $\epsilon_{ij, \infty}$  is the optical dielectric constant of the solution. From eqs. (3) and (4) the total h-f conductivity of the solution takes the form

$$K = K_{\infty} + K'/\omega\tau, \quad (5)$$

where  $K_{\infty}$  is a constant and  $\tau_s$  is the relaxation time of the solute molecule in solution. As  $K$  is a function of  $\omega_j$ , we have from eq. (5)

$$\left(\frac{dK'}{d\omega_j}\right)_{\omega_j \rightarrow 0} = \omega\tau_s \left(\frac{dK}{d\omega_j}\right)_{\omega_j \rightarrow 0} = \omega\tau_s \beta \quad (6)$$

where  $\beta$  is the slope of  $K-\omega_j$  curve at  $\omega_j \rightarrow 0$ . When  $\omega_j$  approaches zero, the density  $\rho_{ij}$  of the solution becomes  $\rho_i$  the density of the solvent, and local field  $F_{ij}$  of the solution is  $F_i =$  the local field of the solvent  $= \left(\frac{\epsilon_i + 2}{3}\right)^2$ . Under the circumstances, eq. (2) on being differentiated w.r. to  $\omega_j$  as  $\omega_j \rightarrow 0$  takes the form :

$$\left(\frac{dK'}{d\omega_j}\right)_{\omega_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT} \left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2}\right) \quad (7)$$

Taking

$$b = \beta / \left(\frac{\mu_j^2 N \rho_i F_i}{3M_j kT} \cdot \omega\right) \quad (8)$$

we have from eqs. (6) and (7)

$$b = \frac{1}{1 + \omega^2 \tau_s^2} \text{ and whence} \\ \tau_s = \frac{\lambda}{2\pi C} \sqrt{\frac{1}{b} - 1} = \frac{\lambda \times 10^{-10}}{18.84} \sqrt{\frac{1}{b} - 1} \quad (9)$$

Now from eq. (8) the dipole moment of the solute molecule can be written in the form

$$\mu_j = \left(\frac{3M_j kT}{N \rho_i F_i} \cdot \frac{\beta}{\omega b}\right)^{\frac{1}{2}} \quad (10)$$

With reported values of  $\tau_s$  at experimental temperatures  $b$  may be calculated from eq. (9). With a knowledge of the slope  $\beta$  from  $K-\omega_j$  curve at  $\omega_j \rightarrow 0$  and corresponding  $b$  it is easy to calculate  $\mu_j$  of the solute molecule from eq. (10) because all other quantities of the solvent benzene are known. Further, it is clear from eq. (9) that for a given frequency  $\omega$  of the applied field the relaxation time  $\tau_s$  depends upon the magnitude of  $b$  which in turn depends on  $\mu_j$ . As  $\tau_s$  changes with temperature,  $\mu_j$  should change with temperature in order to localise the magnitude of  $\tau_s$  in the microwave region because the change of the factor  $\beta/\rho_i F_i$  with temperature of eq. (8) alone cannot cope with the pace of change of  $\tau_s$  with temperature.

### 3. Results and discussions

The h.f. conductivity (Sen and Ghosh 1972) of polar-nonpolar liquid mixture is comparatively easy to measure down to very low concentration by Hartley oscillator and klystron valve in the laboratory. But the expt. conductivity data under radio-frequency and microwave electric fields are very scanty. We, therefore, used the available concentration variation expt. data for  $\epsilon''_{ij}$  and  $\epsilon'_{ij}$  of seven systems in benzene: 2-5 dichloronitrobenzene and 2-5 dibromonitrobenzene under 3.13 cm wavelength electric field (Pant *et al* 1977), and 3-nitro-*o*-anisidine, 2-chloro-*p*-nitroaniline, *p*-phenetidine, *o*-nitroaniline and *p*-anisidine under 3.17 cm wavelength electric field (Somevanshi *et al* 1978) to obtain corresponding experimental  $K$  values from Murphy-Morgan relation  $K = \frac{\omega}{4\pi} \sqrt{\epsilon''_{ij} + \epsilon'_{ij}}$  at 20°, 30° and 40°C. The values of  $K$  thus obtained are shown graphically in Figures 1 and 2 for every stage of dilution for seven systems.

The temperature dependence of  $K$  for each system is vivid.  $K$  varies almost linearly with  $\omega_j$  in the lower concentration region. As  $\omega_j$  approaches zero, the solvent benzene assumes a constant value of conductivity independent of experimental temperature. This is because of the fact that the quantity  $\rho_{ij} F_{ij} / T$  in eq. (2) assumes nearly a fixed value which is in the neighbourhood of 0.006. Consequently, at  $\omega_j = 0$  the conductivity of a given system at all temperatures remains the same. Nevertheless, at  $\omega_j = 0$  the  $K$  values of different systems are different. This is due to solvation effect (Datta *et al* 1981).

For each system in the lower concentration region there is a regularity in increase of slopes of the curves with temperature. At any experimental temperature the variation of  $K$  with  $\omega_j$  is excellent to suggest that h.f. conductivity can be represented by a fitted formula  $K = \alpha + \beta\omega_j + \gamma\omega_j^2$ , where  $\alpha$ ,  $\beta$  and  $\gamma$  are arbitrary constants depending upon the nature of the respective solution of polar-nonpolar liquid mixture of which  $\beta$  plays a very important role in estimating  $\mu_j$ . Of course we tried for numerical values of  $\alpha$ ,  $\beta$  and  $\gamma$  by fitting technique. But the process was abandoned because available data are



not smooth enough for the said technique. However, the slope  $\beta$  of  $K-\omega_j$  curve at  $\omega_j \rightarrow 0$  was estimated by drawing a tangent to each curve at  $\omega_j \rightarrow 0$  as demanded by the relation (6).

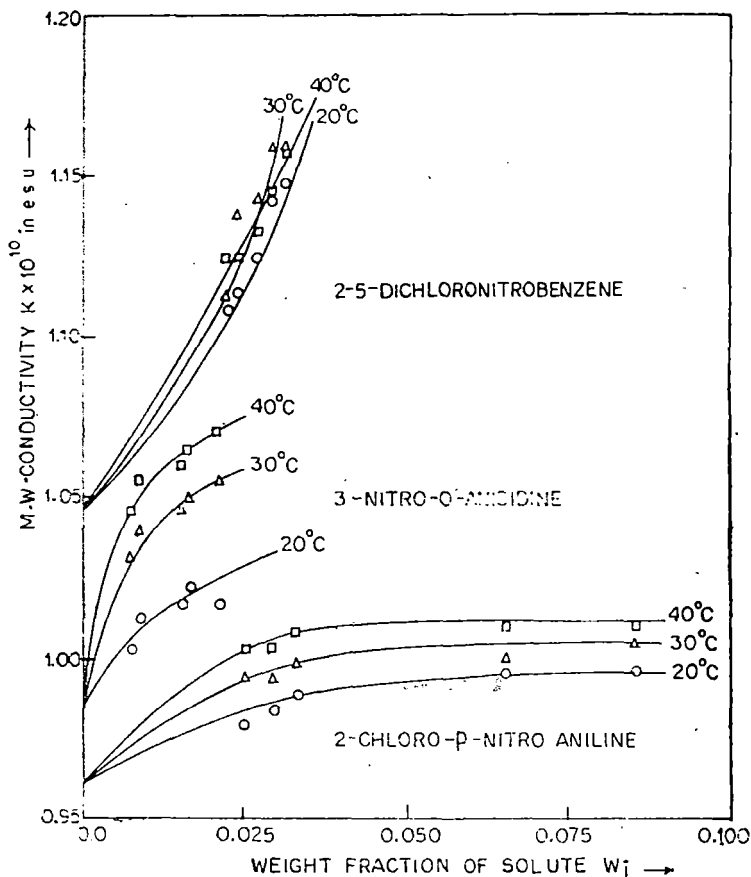


Figure 1. Microwave conductivity  $K$  is plotted against weight fraction  $w_j$  at 20°C, 30°C and 40°C.

—○—○—○— at 20°C,  
 —△—△—△— at 30°C,  
 —□—□—□— at 40°C.

Though errors due to (1) experimental uncertainty and (2) theoretical approximation done in obtaining eq. (6) may be accumulated in  $\mu_j$  determined by this method. still we have adopted it because (i) conductivity data are very scanty in the lower concentration region and (ii) the error due to theoretical approximation is negligibly small in the h.f. region. Further, the uncertainty in drawing  $K-\omega_j$  graph drawn with available  $\epsilon'_{ij}$  data for different concentrations. is very small.

Using eq. (9) values of  $b$  were determined with reported  $\tau$ , for each system at 20°, 30° and 40°C and are placed in Table 1. The corresponding  $\mu_j$  values for all the chosen systems were also calculated from eq. (10) at these temperatures and are placed in Table 1, along with the reported and

Table 1. Computed dipole moment  $\mu_j$  *compt.*, rept. dipole moment  $\mu_j$  *rept.*, relaxation times  $\tau_s$  and  $b$  at temperatures: 20°, 30° and 40°C.

System	Temp. °C	$b$ compt.	$\tau_s \times 10^{12}$ rept in sec.	$\mu_j$ <i>compt.</i> in D	$\mu_j$ <i>rept.</i> in D	$\mu_j$ <i>theor.</i> in D
(i) 2-5 dichloroni- trobenzene	20	0.6620	11.87**	3.29		
	30	0.7060	10.72	3.48		4.23***
	40	0.7477	9.65	3.77		
(ii) 2-5 dibromoni- trobenzene	20	0.3736	21.51**	5.72		
	30	0.4090	19.97	5.93		4.23***
	40	0.4369	18.86	6.11		
(iii) 3-nitro- <i>o</i> -ani- sidine	20	0.6165	13.27*	3.93	2.76	
	30	0.6793	11.56	5.88	3.11	4.93***
	40	0.7282	10.28	8.53	3.76	
(iv) 2-chloro- <i>p</i> -nitro- aniline	20	0.7170	10.57*	2.13	2.44	
	30	0.7432	9.89	2.72	3.28	2.99***
	40	0.7706	9.18	3.07	3.93	
(v) <i>p</i> -phenetidine	20	0.6975	11.08*	2.82	2.24	
	30	0.7147	10.63	3.09	2.78	1.53***
	40	0.7409	9.95	3.22	3.14	
(vi) <i>o</i> -nitroaniline	20	0.7648	9.33*	2.02	3.95	
	30	0.7779	8.99	2.38	2.19	4.25***
	40	0.8050	8.28	2.68	2.24	
(vii) <i>p</i> -anisidine	20	0.9493	3.89**	1.81	1.56	
	30	0.9546	3.67	2.54	3.10	1.87***
	40	0.9657	3.17	2.67	2.66	

\* Somevanshi *et al* (1978)

\*\* Pant *et al* (1977)

\*\*\* Calculated from the vector model assuming molecule to be planar.

theoretical ones for comparison. The  $\mu_j^s$  thus obtained are also shown graphically by fitted lines in Figure 3.

From Table 1, it is obvious that  $\mu_j$  in all the cases increases with experimental temperatures as observed by other workers (Ras *et al* 1971) who showed that dipole moments of some lipid compounds such as glycerol triacetate, glycerol tributriate etc. increase with temperature both in the pure form and in solution with benzene under the microwave alternating electric field though the values of pure compounds differ by up to 7% from those determined in

benzene. So far as the magnitude is concerned, the dipole moments of our systems computed from eq. (10) are in excellent agreement with the reported

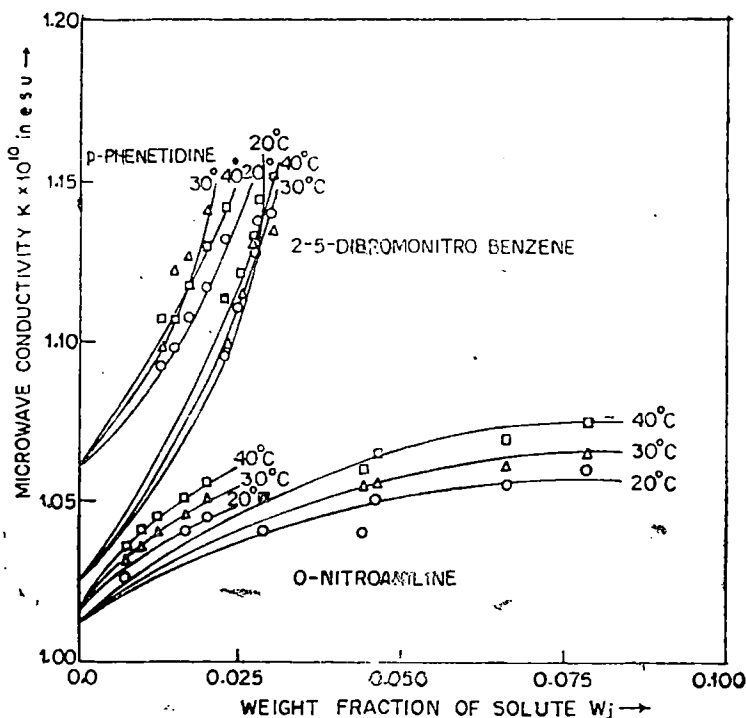


Figure 2. Microwave conductivity  $K$  is plotted against weight fraction  $w_j$ ; at 20°C, 30°C and 40°C.

—○—○—○— at 20°C,  
 —△—△—△— at 30°C,  
 —□—□—□— at 40°C.

ones based on Gopala Krishna's (1957) method and those theoretically calculated from vector atom model (Datta *et al* 1981). However, for the system : 3 nitro-*o*-anisidine (III) the values at 20°C is very close to the reported data, but at 30°C and 40°C they are abnormally high. This could not be explained at present. Though the reported data of 2-5 dibromonitrobenzene (II) and 2-5 dichloronitrobenzene (I) are not available, the dipole moments as obtained from eq. (10) of the former is always greater than those of the latter. This indicates that the bulky molecule possesses a greater dipole moment to yield high  $\tau$ , values than those of lighter ones. Hence the size and shape of the molecule are important to locate the magnitudes of both relaxation time and dipole moment. The greater values of the dipole moments which are very close to the theoretical ones for 2-5 dibromonitrobenzene (II) undoubtedly confirms our method to be a correct

one. In Figure 3, the computed experimental  $\mu_j$  of seven polar liquids are plotted against the temperature in  $^{\circ}\text{C}$  in the range of 0 to  $60^{\circ}\text{C}$ . Below and above

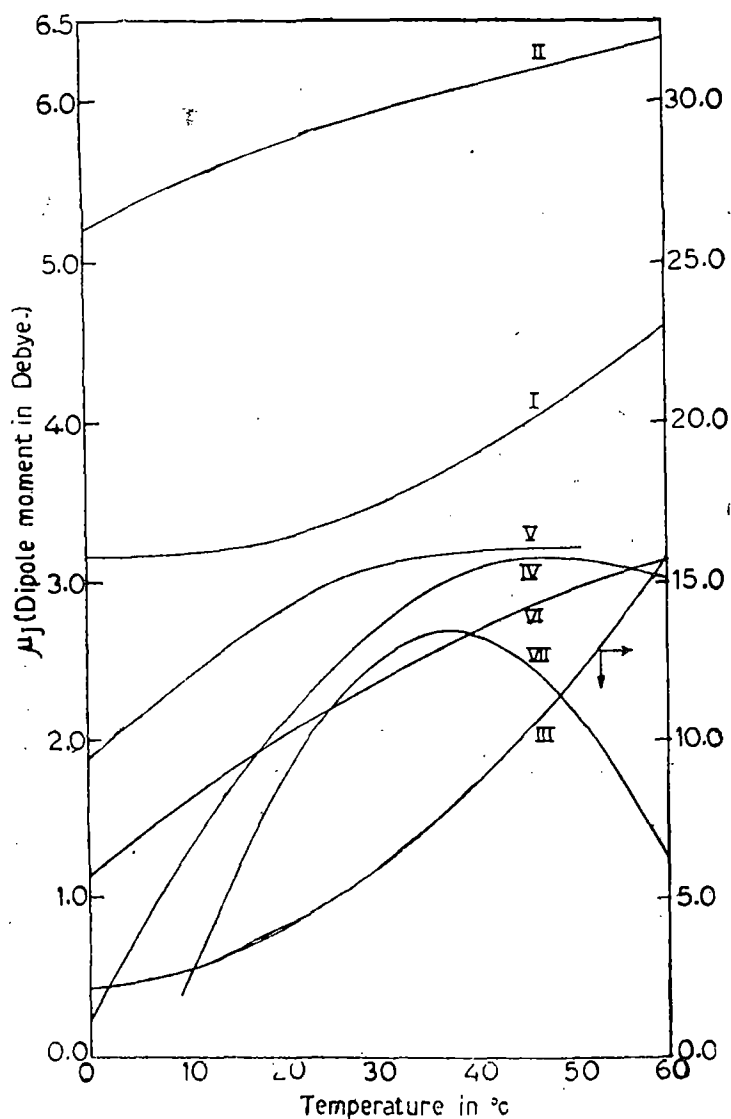


Figure 3. Computed dipole moments  $\mu_j$  of seven polar liquids are plotted against temperature in  $^{\circ}\text{C}$ .

For system II I:  $\mu_j$  (0-15D) is shown on the right side of the graph while for other six systems:  $\mu_j$  (0-6.5 D) on the left side of the graph.

this range we are not interested because the liquids are organic compounds. However, in all these cases, dipole moment increases in the fashion

$$\mu_j = a' + b't + C't^2 \quad (11)$$

with temperature in °C, where  $a'$ ,  $b'$  and  $c'$  are the arbitrary constants depending upon the nature of the respective solute molecule in benzene under the h.f. alternating electric field.

The  $a'$  terms of all the systems are positive except the last one i.e. *p*-anisidine (VII) for which it is negative. For 2-5 dichloronitrobenzene (I) dipole moment increases monotonically with temperature producing a slight concave nature of the curve because the  $b'$  term of eq. (11) is negative while  $c'$  is positive. For 3-nitro-*o*-anisidine (III)  $a'$ ,  $b'$  and  $c'$  terms of eq. (11) are positive. As a result, the dipole moment of this compound becomes very high at comparatively higher temperatures, still, it agrees with the reported  $\mu_j$  at 20°C. The most interesting system is *p*-anisidine (VII) for which both  $a'$  and  $c'$  are negative; nevertheless, its dipole moment within the experimental range of temperature is finite which agrees fairly well with both the experimental and theoretical values. Beyond the experimental range of temperatures its dipole moment becomes zero at 7.1°C and at 67.5°C as observed from the curve (VII) of Figure 3 as well as from its empirical relation. This fact is also corroborated with the reported data which could also satisfy an empirical relation :

$$\mu_j^{*pt} = -7.46 + 6.49 \times 10^{-1}t - 9.90 \times 10^{-3}t^2 \quad (12)$$

giving zero value of  $\mu_j$  at 14.9°C and at 50.7°C. This trend is also visualised in curves (IV) and (V) of 2-chloro-*p*-nitroaniline and *p*-phenetidine respectively of Figure 3. We, therefore, conclude that para molecules of organic polar liquids must show the zero value of dipole moment at lower and higher temperatures most probably due to association of polar units as well as solvation effect.

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