

## **CHAPTER -6**

### **STRUCTURAL AND ASSOCIATIONAL ASPECTS OF DIELECTROPOLAR STRAIGHT CHAIN ALCOHOLS FROM RELAXATION PHENOMENA**

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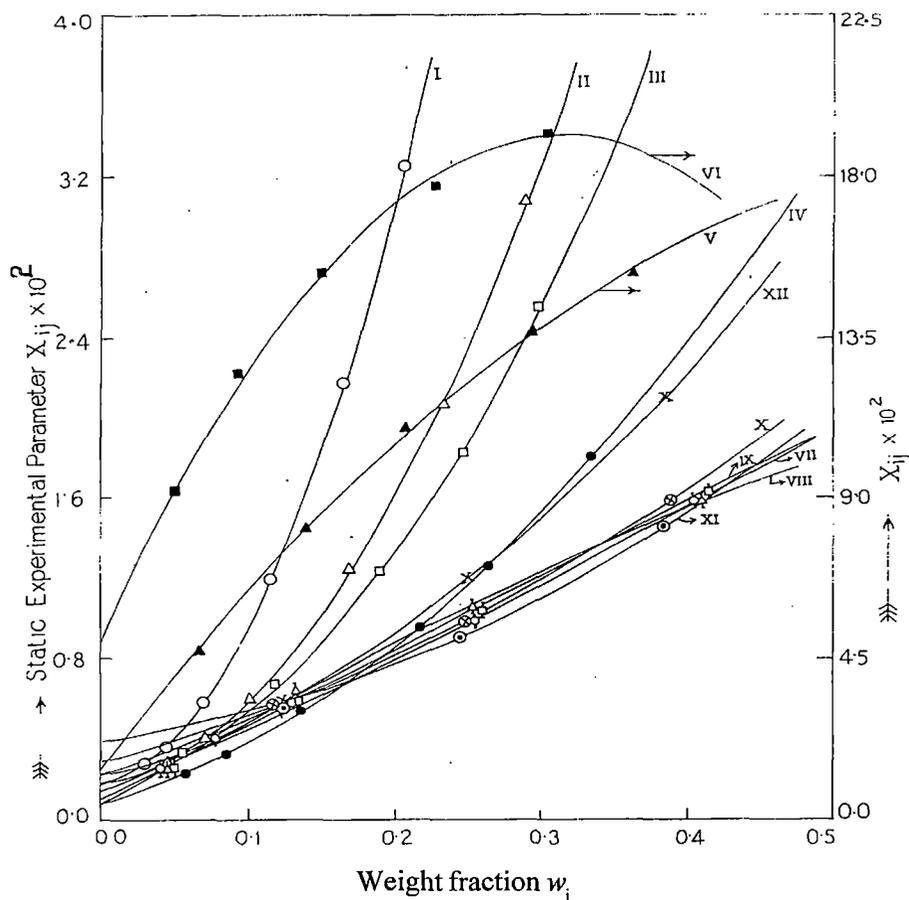
### 6.1. Introduction

The relaxation phenomena of a dielectropolar liquid in a nonpolar solvent has attracted the attention of a large number of workers [1-3] as it is a very sensitive and useful tool to ascertain the shape, size and structure of a polar molecule. The technique provides one with much information about the stability [4] of the system undergoing relaxation phenomena. It also offers valuable insight into the solute-solute i.e. dimer and solute — solvent i.e. monomer formations [4]. Structural and associational aspects of a polar liquid in a non polar solvent can, however, be gained by measured static dipole moment  $\mu_s$  and high frequency (hf) dipole moment  $\mu_j$  in terms of relaxation time  $\tau_j$  with weight fraction  $w_j$ .

Alcohols behaving like almost polymers have  $\alpha, \beta, \gamma$  etc. dispersion regions. The strong dipole of —OH group rotates about  $\equiv \text{C}-\text{O}$ —bond without disturbing  $\text{CH}_3$  or  $\text{CH}_2$  groups and thus they have possibility to exhibit intramolecular as well as intermolecular rotations. Sit and Acharyya [5] and Sit et al [6] studied the straight long chain alcohols like 1-butanol, 1-hexanol, 1-heptanol, 1-decanol in n-heptane [7] ethanol and methanol in benzene [8] (9.84 GHz) and 2-methyl —3 heptanol, 3—methyl —3heptanol, 4-methyl-3 heptanol, 5-methyl —3heptanol, 4 octanol and 2 octanol in n-heptane [9] at 25°C to observe that all the alcohols except methanol showed the double relaxation times,  $\tau_1$  and  $\tau_2$  at all the frequencies in GHz range. The alcohols were again expected to exhibit the triple relaxation phenomena [7] for different frequencies of electric field in GHz range. Such long chain liquids under investigation have wide applications in the fields of biological research, medicine and industry. Moreover, the study of alcohols in terms of modern internationally accepted units and symbols appears

to be superior for the unified, coherent and rationalised nature of the SI unit used.

The  $\mu_s$  of all the associated dielectropolar molecules under static electric field was derived from static experimental parameter  $X_{ij}$ .  $X_{ij}$  is again involved with dimensionless static and high frequency relative permittivities  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  of Table 6.1 based on Debye model [10]. The linear coefficient of the expected non-linear experimental  $X_{ij}$  curves against  $w_j$  graphically shown in Figure 6.1 of alcohols were conveniently used to estimate  $\mu_s$  at a given temperature.



**Figure 6.1 :** Variation of static experimental parameter ( $X_{ij}$ ) against weight fraction  $w_j$  of solute at 25°C under nearly 24 GHz electric field [ethanol and methanol at 9.84 GHz]

(I) 1-butanol (—○—), (II) 1-hexanol (—△—), (III) 1-heptanol (—□—), (IV) 1-decanol (—●—), (V) ethanol (—▲—), (VI) methanol (—■—), (VII) 2-methyl - 3 heptanol (—○—), (VIII) 3-methyl-3 heptanol (—△—), (IX) 4-methyl - 3 heptanol (—□—), (X) 5-methyl - 3 heptanol (—⊗—), (XI) 4-octanol (—⊕—), (XII) 2-octanol (—x—)

The  $\tau_j$  of all the alcohols were, however, estimated from the slope of linear variation of imaginary  $\sigma_{ij}''$  against real  $\sigma_{ij}'$  parts [11] of hf complex conductivity  $\sigma_{ij}^*$  for different weight fractions  $w_j$ s as seen in Figure 6.2. The hf  $\sigma_{ij}''$  did not vary linearly with hf  $\sigma_{ij}'$  at higher or even lower concentrations [12]. It is therefore, better to use the ratio of slopes of individual variations of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  both in  $\Omega^{-1} \text{m}^{-1}$  with  $w_j$ 's of Figures 6.3 and 6.4 to get the exact and accurate value of  $d\sigma_{ij}''/d\sigma_{ij}'$  in the limit  $w_j = 0$  to evaluate  $\tau_j$  [13,14].  $\tau_j$ 's thus obtained by both the methods are placed in Table 6.3 to see how far they are close in agreements.  $\tau_j$ 's of such dielectropolar alcohols were, however, estimated at 1.233 cm. for molecules like 1-butanol, 1-hexanol, 1-decanol, 2-methyl-3 heptanol, 3-methyl-3heptanol, 4-methyl-3heptanol, 5-methyl-3heptanol, 4-octanol, 2-octanol and at 1.249cm wave length electric field for 1-heptanol at which measured  $\epsilon_{ij}''$  of a given  $w_j$  of the solute when were graphically plotted against the electric field frequency "f" showed peak indicating the most effective dispersive region for such liquids.

The formulation to measure  $\mu_j$ 's of all the alcohols involves with the slopes  $\beta$ 's of the expected  $\sigma_{ij}-w_j$  non linear curves of Figure 6.5 and dimensionless parameter 'b' in terms of  $\tau_j$ 's obtained by both the methods as  $\tau_j$ 's were not found to agree excellently in Table 6.3. The  $\sigma_{ij}''$  and  $\sigma_{ij}'$  in  $\Omega^{-1} \text{m}^{-1}$  are not linear with  $w_j$  as evident from Figures 6.3 and 6.4.  $\mu_j$ 's thus obtained are finally compared with  $\mu_{\text{theo}}$ 's from available bond angles and bond moments of the substituent polar groups attached to parent ones. The slight disagreement between the measured  $\mu_j$ 's and  $\mu_s$  from  $\mu_{\text{theo}}$ 's indicates the existence of inductive and mesomeric moments of different substituent polar groups present in such dielectropolar molecules in addition to strong hydrogen bonding in them as displayed by the molecular conformation of Figure 6.6.

The solvent  $\text{C}_6\text{H}_6$  unlike n-heptane is a cyclic compound with three double bonds and six p-electrons on six carbon atoms. Hence  $\pi-\pi$  interaction or resonance effect combined with inductive effect known as mesomeric effect

is expected to play an important role in the measured  $\mu_j$  under hf electric field. A special attention is to be paid to have the conformational structures of the alcohols to evaluate  $\mu_{\text{theo}}$  as seen in Figure 6.6 and Table 6.2 from the reduction of the available bond moments [5,6] of different substituent polar groups by the ratio of  $\mu_s / \mu_{\text{theo}}$ . This takes into account of H-bonding in addition to inductive effect in them. Thus the conclusion regarding the molecular association of such long chain associated aliphatic alcohols may also be the reason to yield higher dipole moments.

## 6.2. Static Relaxation Parameter and Static dipole moment $\mu_s$

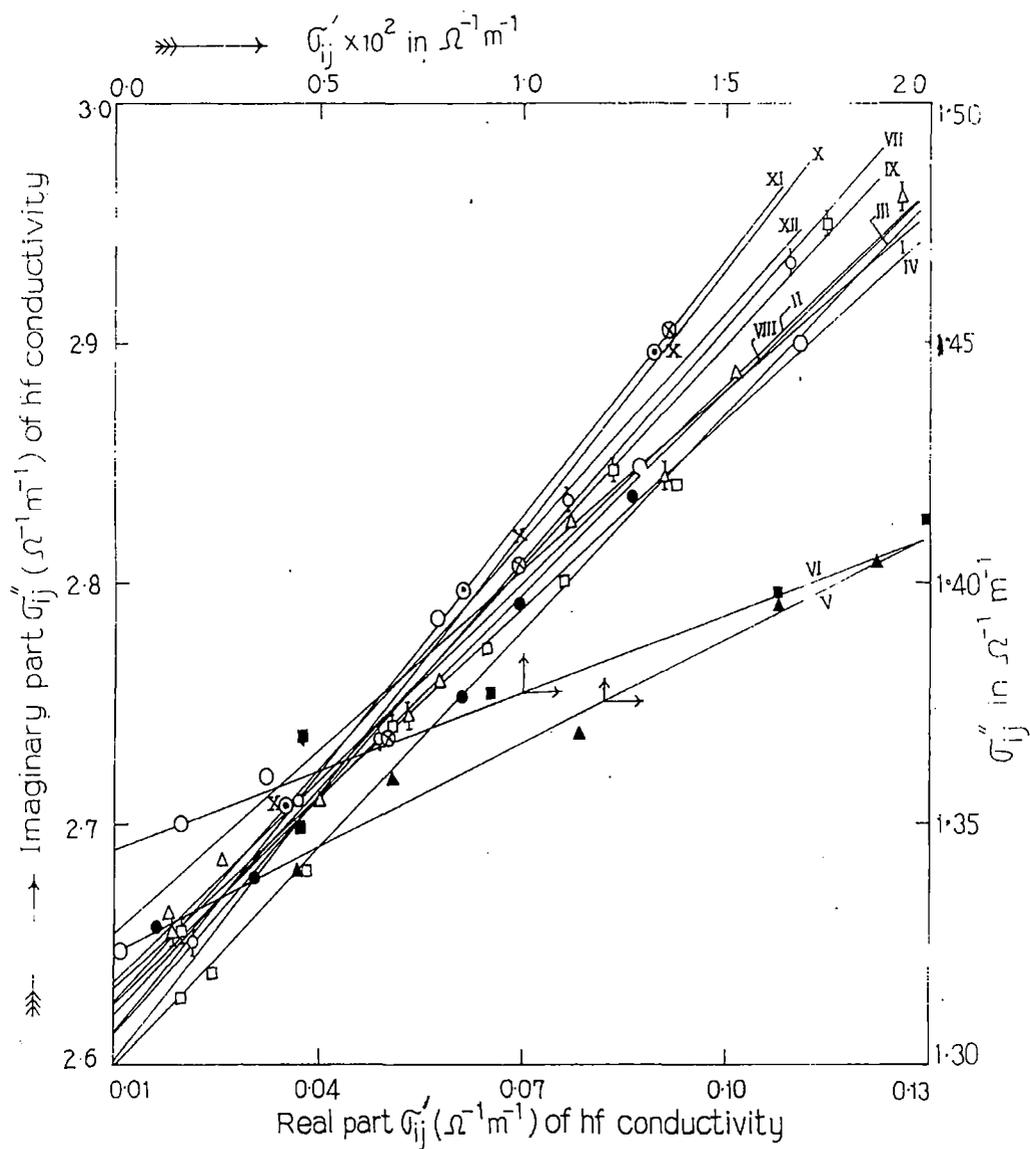
Under static electric field  $\mu_s$  of a dielectropolar molecule (j) in a non polar solvent (i) may be obtained from the following equation [10]

$$\frac{\epsilon_{\text{oj}}-1}{\epsilon_{\text{oj}}+2} - \frac{\epsilon_{\infty\text{ij}}-1}{\epsilon_{\infty\text{ij}}+2} = \frac{\epsilon_{\text{oi}}-1}{\epsilon_{\text{oi}}+2} - \frac{\epsilon_{\infty\text{i}}-1}{\epsilon_{\infty\text{i}}+2} + \frac{N\mu_s^2 c_j}{9\epsilon_0 k_B T} \quad (6.1)$$

where  $\epsilon_{\text{oj}}$  and  $\epsilon_{\infty\text{ij}}$  are the dimensionless low and infinite frequency relative permittivities of solution (ij).  $\epsilon_0$  is the permittivity of free space =  $8.854 \times 10^{-12}$  F.m<sup>-1</sup>.  $c_j$  is the molar concentration of the solute, where  $c_j = (\rho_{\text{ij}} w_j) / M_j$  and the other symbols carry usual meanings.

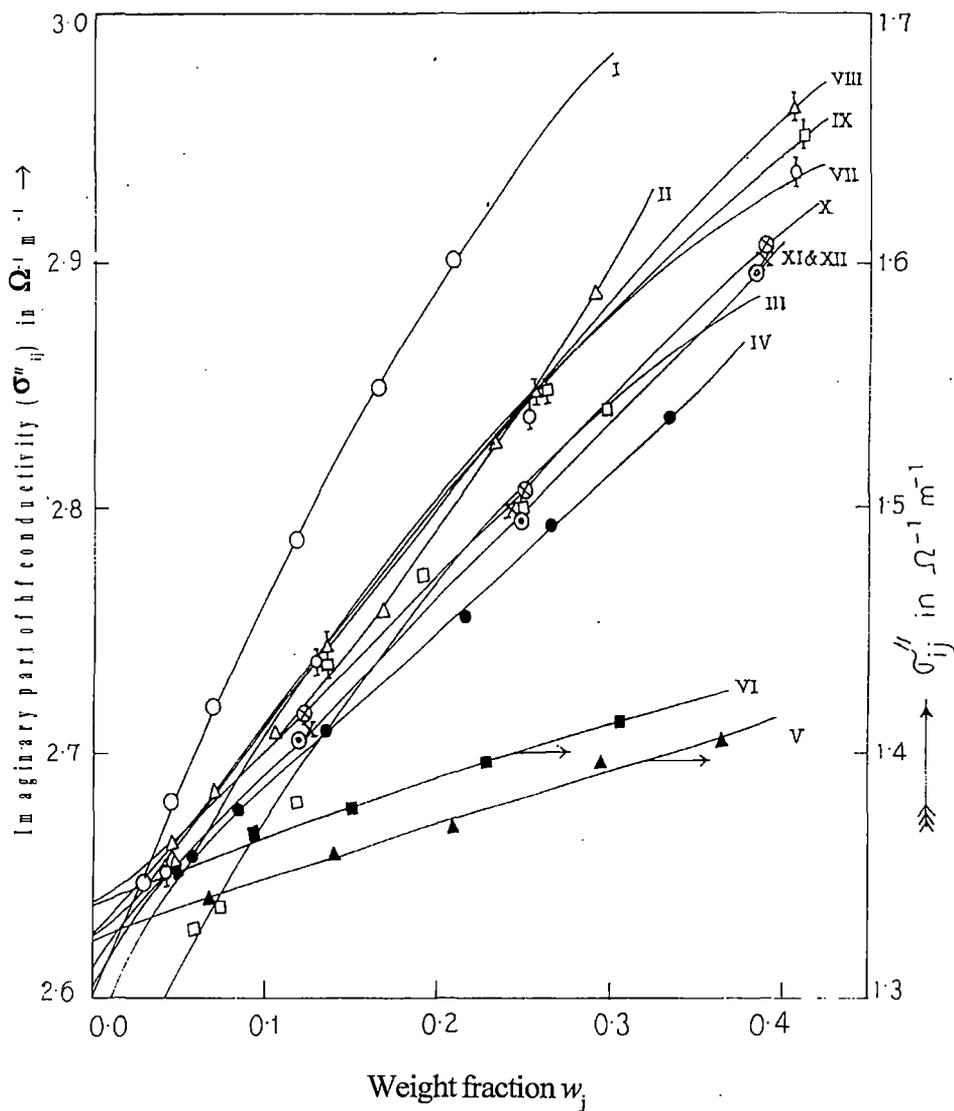
A polar liquid of weight  $W_j$  and volume  $V_j$  is mixed with a nonpolar solvent of weight  $W_i$  and volume  $V_i$  to get the solution density  $\rho_{\text{ij}}$  where

$$\begin{aligned} \rho_{\text{ij}} &= \frac{W_i + W_j}{V_i + V_j} = \frac{W_i + W_j}{W_i/\rho_i + W_j/\rho_j} \\ \rho_{\text{ij}} &= \frac{\rho_i \rho_j}{\rho_j W_i / (W_i + W_j) + \rho_i W_j / (W_i + W_j)} \\ &= \frac{\rho_i \rho_j}{\rho_j w_i + \rho_i w_j} = \rho_i (1 - \gamma w_j)^{-1} \end{aligned} \quad (6.2)$$



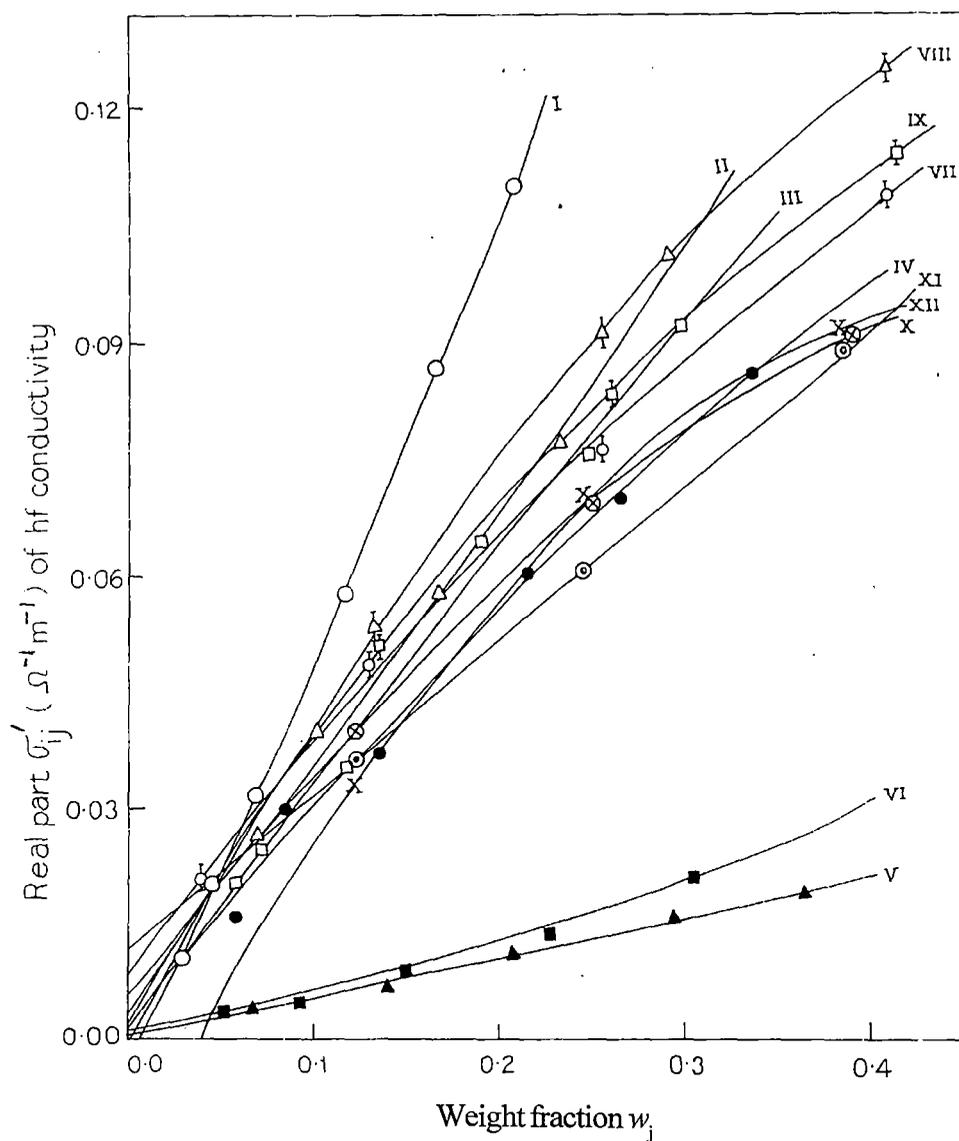
**Figure 6.2 :** Variation of imaginary part of hf conductivity ( $\sigma''_{ij}$ ) against real part ( $\sigma'_{ij}$ ) of some alcohols at 25°C under nearly 24 GHz electric field [ethanol and methanol at 9.84 GHz]

- (I) 1-butanol (—○—),
- (II) 1-hexanol (—△—),
- (III) 1-heptanol (—□—), (IV) 1-decanol (—●—),
- (V) ethanol (—▲—), (VI) methanol (—■—),
- (VII) 2-methyl-3 heptanol (—○—),
- (VIII) 3-methyl-3 heptanol (—△—),
- (IX) 4-methyl-3 heptanol (—□—),
- (X) 5-methyl-3 heptanol (—⊗—),
- (XI) 4-octanol (—⊙—),
- (XII) 2-octanol (—x—)



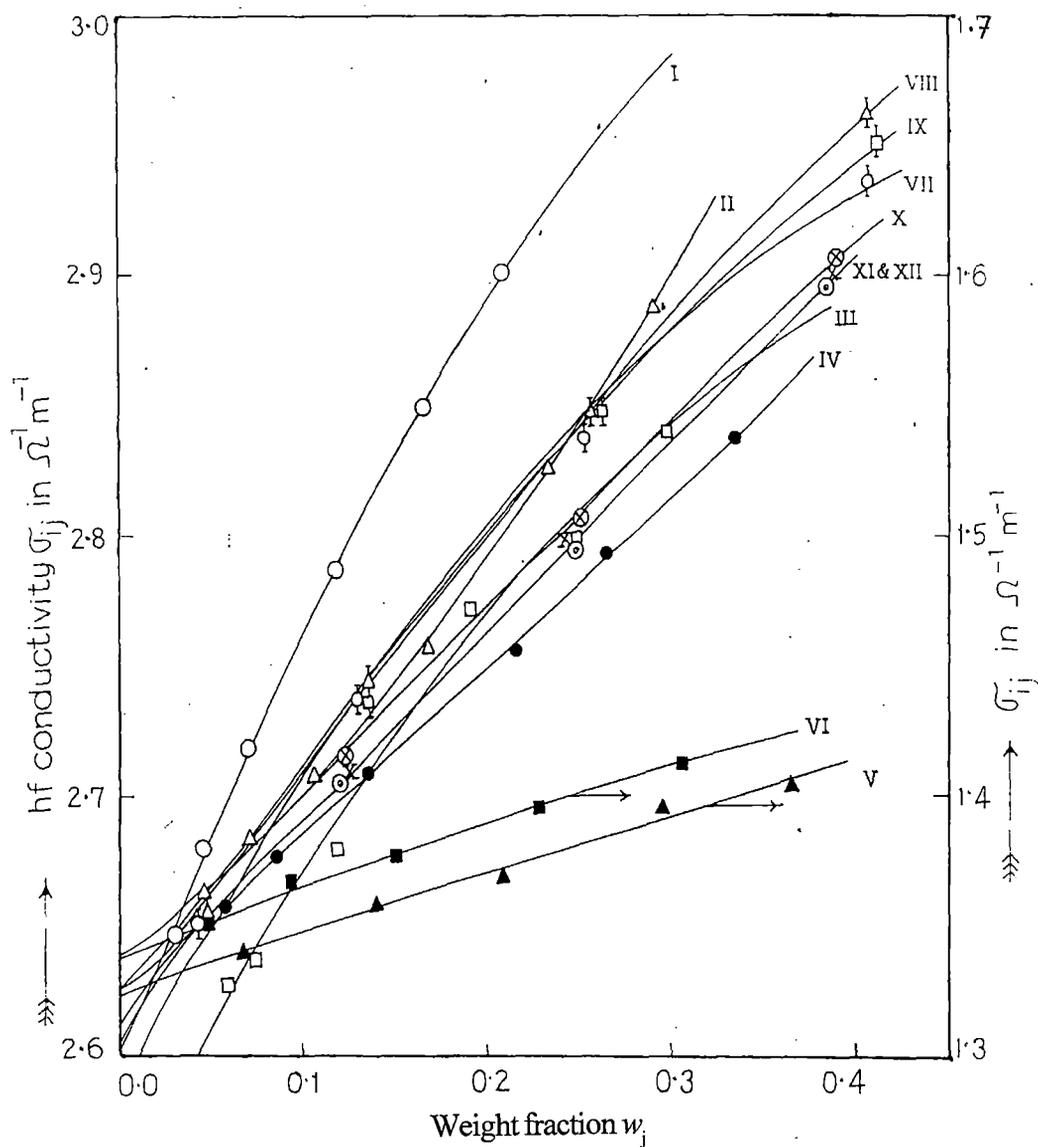
**Figure 6.3 :** Plot of imaginary part of hf conductivity ( $\sigma''_{ij}$ ) in  $\Omega^{-1} m^{-1}$  against weight fraction  $w_j$  of solute at 25°C under nearly 24 GHz electric field [ethanol and methanol at 9.84 GHz]

- (I) 1-butanol (—○—),
- (II) 1-hexanol (—△—),
- (III) 1-heptanol (—□—), (IV) 1-decanol (—●—),
- (V) ethanol (—▲—), (VI) methanol (—■—),
- (VII) 2-methyl - 3 heptanol (—⊙—),
- (VIII) 3-methyl-3 heptanol (—△—),
- (IX) 4-methyl - 3 heptanol (—□—),
- (X) 5-methyl - 3 heptanol (—⊗—),
- (XI) 4-octanol (—⊙—),
- (XII) 2-octanol (—x—)



**Figure 6.4 :** Plot of real part of hf conductivity ( $\sigma'_{ij}$ ) in  $\Omega^{-1} m^{-1}$  against weight fraction  $w_j$  of solute at  $25^\circ C$  under nearly 24 GHz electric field [ethanol and methanol at 9.84 GHz]

- (I) 1-butanol (—O—),
- (II) 1-hexanol (— $\Delta$ —),
- (III) 1-heptanol (— $\square$ —), (IV) 1-decanol (— $\bullet$ —),
- (V) ethanol (— $\blacktriangle$ —), (VI) methanol (— $\blacksquare$ —),
- (VII) 2-methyl - 3 heptanol (— $\circ$ —),
- (VIII) 3-methyl-3 heptanol (— $\triangle$ —),
- (IX) 4-methyl - 3 heptanol (— $\square$ —),
- (X) 5-methyl - 3 heptanol (— $\otimes$ —),
- (XI) 4-octanol (— $\odot$ —),
- (XII) 2-octanol (—x—)



**Figure 6.5 :** Plot of total hf conductivity ( $\sigma_{ij}$ ) in  $\Omega^{-1} \text{ m}^{-1}$  against weight fraction  $w_j$  of solute at  $25^\circ\text{C}$  under nearly 24 GHz electric field [ethanol and methanol at 9.84 GHz]

- (I) 1-butanol (—O—),
- (II) 1-hexanol (— $\Delta$ —),
- (III) 1-heptanol (— $\square$ —), (IV) 1-decanol (— $\bullet$ —),
- (V) ethanol (— $\blacktriangle$ —), (VI) methanol (— $\blacksquare$ —),
- (VII) 2-methyl-3 heptanol (— $\odot$ —),
- (VIII) 3-methyl-3 heptanol (— $\triangle$ —),
- (IX) 4-methyl-3 heptanol (— $\square$ —),
- (X) 5-methyl-3 heptanol (— $\otimes$ —),
- (XI) 4-octanol (— $\odot$ —),
- (XII) 2-octanol (—x—)

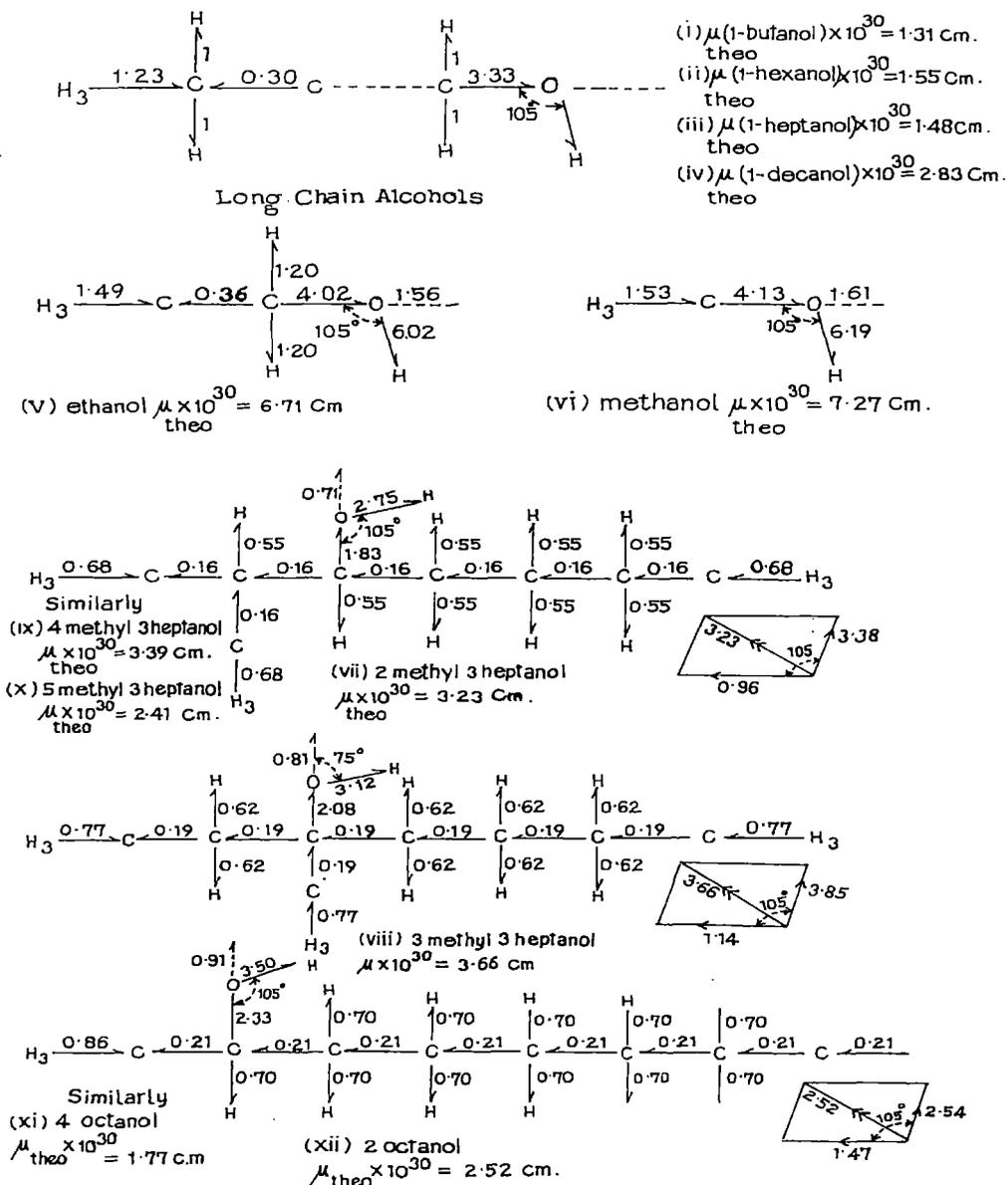


Figure 6.6 : Conformational structures of dielectropolar alcohols [ Bond moment  $\times 10^{30}$  Coulomb-metre (C.m.) given in figures]

The weight fractions  $w_j$  and  $w_i$  of solute and solvent are given by

$$w_j = \frac{W_j}{W_i + W_j} \text{ and } w_i = \frac{W_i}{W_i + W_j} \text{ such that } w_i + w_j = 1$$

and  $\gamma = (1 - \rho_i/\rho_j)$ ,  $\rho_i$  and  $\rho_j$  are densities of pure solvent and solute respectively.

Now Eq. (6.1) may be written as

$$\frac{\epsilon_{oij} - \epsilon_{\infty ij}}{(\epsilon_{oij} + 2)(\epsilon_{\infty ij} + 2)} = \frac{\epsilon_{oi} - \epsilon_{\infty i}}{(\epsilon_{oi} + 2)(\epsilon_{\infty i} + 2)} + \frac{N\rho_i\mu_s^2}{27\epsilon_0 M_j k_B T} w_j (1 - \gamma w_j)^{-1}$$

$$X_{ij} = X_i + \frac{N\rho_i\mu_s^2}{27\epsilon_0 M_j k_B T} w_j + \frac{N\rho_i\mu_s^2}{27\epsilon_0 M_j k_B T} \gamma w_j^2 + \dots \quad (6.3)$$

The right hand side of Eq. (6.3) is obviously a polynomial equation of  $w_j$  like

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 + \dots \quad (6.4)$$

Now comparing the linear coefficients of Eqs. (6.3) and (6.4) one gets  $\mu_s$  from:

$$\mu_s = \left( \frac{27\epsilon_0 M_j k_B T}{N\rho_i} a_1 \right)^{1/2} \quad (6.5)$$

where  $a_1$  is the linear coefficient of  $X_{ij}-w_j$  curve of Figure 6.1. But  $\mu_s$  from higher coefficients of Eqs. (6.3) and (6.4) are not reliable as they are involved with the various effects of solvent, relative density, solute-solute association, internal field, macroscopic viscosity etc.  $\mu_s$  from Eq. (6.5) along with  $a_1$  are placed in Table 6.2 to compare with hf  $\mu_j$ 's presented in Table 6.4.

**Table 6.1** : Measured dielectric relative permittivities  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$  of some dielectropolar alcohols in nonpolar solvent at 25°C under different weight fractions  $w_j$ .

| Systems with Sl. no. & molecular weight          | Weight fraction $w_j$ of alcohols           | Measured dielectric relative permittivities |                   |                  |                        |
|--|---|---|-------------------|------------------|------------------------|
|  |   | $\epsilon'_{ij}$                            | $\epsilon''_{ij}$ | $\epsilon_{oij}$ | $\epsilon_{\infty ij}$ |
| (i) 1-butanol in n-heptane<br>$M_j=0.074$ kg.    | 0.0291                                      | 1.957                                       | 0.0079            | 1.971            | 1.928                  |
|  | 0.0451                                      | 1.981                                       | 0.0147            | 2.000            | 1.945                  |
|  | 0.0697                                      | 2.011                                       | 0.0236            | 2.050            | 1.958                  |
|  | 0.1163                                      | 2.060                                       | 0.0425            | 2.175            | 2.978                  |
|  | 0.1652                                      | 2.105                                       | 0.0644            | 2.381            | 2.000                  |
|  | 0.2072                                      | 2.144                                       | 0.0818            | 2.621            | 2.020                  |
| (ii) 1-hexanol in n-heptane<br>$M_j=0.102$ kg.   | 0.0458                                      | 1.968                                       | 0.0131            | 1.988            | 1.944                  |
|  | 0.0703                                      | 1.984                                       | 0.0190            | 2.015            | 1.952                  |
|  | 0.1028                                      | 2.001                                       | 0.0296            | 2.064            | 1.970                  |
|  | 0.1687                                      | 2.037                                       | 0.0425            | 2.196            | 1.989                  |
|  | 0.2335                                      | 2.088                                       | 0.0569            | 2.360            | 2.002                  |
|  | 0.2901                                      | 2.134                                       | 0.0748            | 2.580            | 2.018                  |
| (iii) 1-heptanol in n-heptane<br>$M_j=0.116$ kg. | 0.0564                                      | 1.968                                       | 0.0147            | 1.985            | 1.932                  |
|  | 0.0735                                      | 1.975                                       | 0.0182            | 2.008            | 1.945                  |
|  | 0.1175                                      | 2.007                                       | 0.0265            | 2.066            | 1.957                  |
|  | 0.1909                                      | 2.076                                       | 0.0482            | 2.195            | 1.989                  |
|  | 0.2465                                      | 2.097                                       | 0.0567            | 2.315            | 2.002                  |
|  | 0.2970                                      | 2.126                                       | 0.0693            | 2.464            | 2.008                  |
| (iv) 1-decanol in n-heptane<br>$M_j=0.158$ kg.   | 0.0572                                      | 1.965                                       | 0.0120            | 1.976            | 1.940                  |
|  | 0.0857                                      | 1.979                                       | 0.0223            | 2.003            | 1.952                  |
|  | 0.1351                                      | 2.003                                       | 0.0273            | 2.050            | 1.964                  |
|  | 0.2140                                      | 2.036                                       | 0.0449            | 2.147            | 1.990                  |
|  | 0.2640                                      | 2.064                                       | 0.0513            | 2.220            | 2.008                  |
|  | 0.3353                                      | 2.097                                       | 0.0637            | 2.346            | 2.030                  |
| (v) ethanol in benzene<br>$M_j=0.046$ kg.        | 0.0664                                      | 2.450                                       | 0.0082            | 3.300            | 2.262                  |
|  | 0.1393                                      | 2.483                                       | 0.0124            | 4.300            | 2.190                  |
|  | 0.2077                                      | 2.500                                       | 0.0208            | 5.400            | 2.120                  |
|  | 0.2953                                      | 2.550                                       | 0.0297            | 7.000            | 2.062                  |
|  | 0.3638                                      | 2.567                                       | 0.0342            | 8.200            | 2.016                  |
|  | (vi) methanol in benzene<br>$M_j=0.032$ kg. | 0.0514                                      | 2.467             | 0.0082           | 4.800                  |
| 0.0930   |   | 2.500                                       | 0.0083            | 6.500            | 2.155                  |
| 0.1495   |   | 2.517                                       | 0.0168            | 8.600            | 2.085                  |
| 0.2266   |   | 2.550                                       | 0.0298            | 11.400           | 2.016                  |
| 0.3049   |   | 2.583                                       | 0.0387            | 13.700           | 1.960                  |

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| Systems with Sl. no. & molecular weight | Weight fraction $w_j$ of alcohols | Measured dielectric relative permittivities |                   |                  |                        |
|---|-----------------------------------|---|-------------------|------------------|------------------------|
|   |                                   | $\epsilon'_{ij}$                            | $\epsilon''_{ij}$ | $\epsilon_{oij}$ | $\epsilon_{\infty ij}$ |
| (vii) 2-methyl                          | 0.0437                            | 1.960                                       | 0.0156            | 1.971            | 1.930                  |
| 3-heptanol in                           | 0.1299                            | 2.022                                       | 0.0361            | 2.059            | 1.966                  |
| n-heptane                               | 0.2522                            | 2.095                                       | 0.0565            | 2.172            | 2.007                  |
| $M_j=0.130$ kg                          | 0.4081                            | 2.169                                       | 0.0809            | 2.330            | 2.054                  |
| (viii) 3-methyl                         | 0.0450                            | 1.965                                       | 0.0137            | 1.974            | 1.934                  |
| 3-heptanol in                           | 0.1334                            | 2.028                                       | 0.0393            | 2.069            | 1.966                  |
| n-heptane                               | 0.2538                            | 2.103                                       | 0.0674            | 2.180            | 2.004                  |
| $M_j=0.130$ kg                          | 0.4085                            | 2.188                                       | 0.0928            | 2.334            | 2.057                  |
| (ix) 4-methyl                           | 0.0466                            | 1.964                                       | 0.0146            | 1.976            | 1.936                  |
| 3-heptanol in                           | 0.1326                            | 2.025                                       | 0.0375            | 2.065            | 1.969                  |
| n-heptane                               | 0.2590                            | 2.104                                       | 0.0616            | 2.185            | 2.011                  |
| $M_j=0.130$ kg.                         | 0.4124                            | 2.180                                       | 0.0849            | 2.352            | 2.065                  |
| (x) 5-methyl                            | 0.1228                            | 2.008                                       | 0.0296            | 2.048            | 1.956                  |
| 3-heptanol in                           | 0.2489                            | 2.075                                       | 0.0511            | 2.168            | 2.004                  |
| n-heptane                               | 0.3898                            | 2.148                                       | 0.0676            | 2.315            | 2.040                  |
| $M_j=0.130$ kg.                         |                                   |   |                   |                  |                        |
| (xi) 4-octanol in                       | 0.1201                            | 2.000                                       | 0.0265            | 2.040            | 1.948                  |
| n-heptane                               | 0.2445                            | 2.067                                       | 0.0449            | 2.148            | 1.997                  |
| $M_j=0.130$ kg.                         | 0.3838                            | 2.140                                       | 0.0659            | 2.282            | 2.031                  |
| (xii) 2-octanol in                      | 0.1236                            | 2.001                                       | 0.0245            | 2.049            | 1.954                  |
| n-heptane                               | 0.2479                            | 2.068                                       | 0.0513            | 2.195            | 1.996                  |
| $M_j=0.130$ kg.                         | 0.3844                            | 2.141                                       | 0.0680            | 2.410            | 2.036                  |

**Table 6.2 :** Coefficients  $a_0, a_1, a_2$  of  $X_{ij} - w_j$  fitted curve of Figure 6.1, correlation coefficient (r), % of error in getting  $X_{ij}$ , static or low frequency dipole moment  $\mu_s \times 10^{30}$  Coulomb-metre, theoretical dipole moments  $\mu_{\text{theo}} \times 10^{30}$  in Coulomb-metre from reduced bond moments by  $\mu_s/\mu_{\text{theo}}$  and  $\mu_1, \mu_2$ , by double relaxation method.

| Systems with sl. no. & molecular weight $M_j$      | Coefficients $a_0, a_1$ , and $a_2$ in Eq. $X_{ij} = a_0 + a_1 w_j + a_2 w_j^2$ |                   |         | Correlation coefficient (r) | % of error in fitting technique | $\mu_s \times 10^{30}$ in Coulomb-metre from Eq. (6.5) | Corrected $\mu_{\text{theo}} \times 10^{30}$ in Coulomb-metre from bond angle & reduced bond moments | $\mu_1$ and $\mu_2$ in Coulomb-meter from double relaxation method |                                |
|--|---|-------------------|---------|-----------------------------|---------------------------------|--|--|--|--------------------------------|
|  | $a_0 \times 10^3$   | $a_1 \times 10^3$ | $a_2$   |                             |                                 |  |  | $\mu_1 \times 10^{30}$ in C.m.                                     | $\mu_2 \times 10^{30}$ in C.m. |
| (i) 1-butanol in n-heptane<br>$M_j = 0.074$ kg.    | 1.8126  | 9.6141            | 0.6665  | 0.9826                      | 0.95                            | 1.31   | 4.97x0.2636<br>=1.31   | 3.63   | 29.17                          |
| (ii) 1-hexanol in n-heptane<br>$M_j = 0.102$ kg.   | 1.7060  | 9.8358            | 0.3075  | 0.9847                      | 0.83                            | 1.55   | 4.37x0.3547<br>= 1.55  | 3.43   | 21.20                          |
| (iii) 1-heptanol in n-heptane<br>$M_j = 0.116$ kg. | 2.2603  | 7.9095            | 0.2345  | 0.9872                      | 0.70                            | 1.48   | 4.07x0.3636<br>= 1.48  | 3.73   | 27.00                          |
| (iv) 1-decanol in n-heptane<br>$M_j = 0.158$ kg.   | 0.7973  | 21.0951           | 0.0901  | 0.9922                      | 0.43                            | 2.83   | 3.17x0.8927<br>= 2.83  | 3.83   | 17.24                          |
| (v) ethanol in benzene<br>$M_j = 0.046$ kg         | 14.2833   | 524.0612          | -0.3980 | 0.9915                      | 0.51                            | 6.71   | 5.57x1.2047<br>= 6.71  | 1.70   | 490.73                         |

| Systems with sl. no. & molecular weight $M_j$                | Coefficients $a_0, a_1,$ and $a_2$ in Eq. $X_{ij} = a_0 + a_1 w_j + a_2 w_j^2$ |                   |         | Correlation coefficient (r) | % of error in fitting technique | $\mu_j \times 10^{30}$ in Coulomb-metre from Eq. (6.5) | Corrected $\mu_{\text{theo}} \times 10^{30}$ in Coulomb-metre from bond angle & reduced bond moments | $\mu_1$ and $\mu_2$ in Coulomb-metre from double relaxation method |                                |
|--|--|-------------------|---------|-----------------------------|---------------------------------|--|--|--|--------------------------------|
|  | $a_0 \times 10^3$  | $a_1 \times 10^3$ | $a_2$   |                             |                                 |  |  | $\mu_1 \times 10^{30}$ in C.m.                                     | $\mu_2 \times 10^{30}$ in C.m. |
| (vi) methanol in benzene<br>$M_j = 0.032$ kg.                | 49.8741  | 883.7091          | -1.4159 | 0.9668                      | 1.97                            | 7.27   | $5.87 \times 1.2385 = 7.27$  | —  | 293.96                         |
| (vii) 2-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg.  | 1.2160   | 33.4337           | 0.0050  | 0.9998                      | 0.01                            | 3.23   | $5.87 \times 0.5503 = 3.23$  | 3.83   | 16.00                          |
| (viii) 3-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg. | 0.7339   | 43.0349           | -0.0155 | 0.9986                      | 0.19                            | 3.66   | $5.87 \times 0.6235 = 3.66$  | 3.83   | 8.60                           |
| (ix) 4-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg.   | 0.9118   | 36.7395           | 0.0008  | 0.9996                      | 0.03                            | 3.36   | $5.87 \times 0.5775 = 3.39$  | 3.90   | 13.90                          |
| (x) 5-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg.    | 2.8971   | 18.6631           | 0.0369  | 0.9968                      | 0.25                            | 2.41   | $5.87 \times 0.4106 = 2.41$  | 3.37   | 9.50                           |
| (xi) 4-octanol in n-heptane<br>$M_j = 0.130$ kg.             | 2.5834   | 10.0231           | 0.0639  | 0.9946                      | 0.42                            | 1.77   | $3.60 \times 0.4917 = 1.77$  | 3.43   | 10.97                          |
| (xii) 2-octanol in n-heptane<br>$M_j = 0.130$ kg.            | 2.2868   | 20.4032           | 0.0737  | 0.9956                      | 0.34                            | 2.52   | $3.60 \times 0.700 = 2.52$   | 3.43   | 16.00                          |

**Table 6.3** : Intercept (c) and slope (m) of  $\sigma''_{ij} - \sigma'_{ij}$  equation (Figure 6.2), correlation coefficient (r), percentage of error, relaxation time  $\tau_j$  in p-sec from Eq. (6.10), ratio of slopes of  $\sigma''_{ij}$  and  $\sigma'_{ij}$  with  $w_j$  ( $=x/y$ ), relaxation time  $\tau_j$  in p-sec from Eq. (6.11), calculated relaxation time  $\tau_j$  in p-sec from Gopalakrishnas' method for some dielectropolar alcohols under nearly 24 GHz electric field (Q-band microwave) at 25°C.

| System with SI.No and molecular weight             | Intercept & slope of $\sigma''_{ij} - \sigma'_{ij}$ fitted equation |           | Correlation coefficient (r) | % of error | Estimated relaxation time $\tau_j$ in p-sec from Eq (6.10) | Ratio of slopes of $\sigma''_{ij}$ & $\sigma'_{ij}$ with $w_j$ $x/y = (d\sigma''_{ij}/dw_j) / (d\sigma'_{ij}/dw_j)$ | Estimated relaxation time $\tau_j$ in p-sec from Eq. (6.11) | Relaxation time $\tau_j$ in p-sec estimated from Gopalakrishnas method |
|--|---|-----------|-----------------------------|------------|--|---|---|--|
|  | Intercept (c)   | slope (m) |                             |            |  |   |   |  |
| (i) 1-butanol in n-heptane<br>$M_j = 0.074$ kg.    | 2.3624  | 2.4816    | 0.9959                      | 0.22       | 2.64   | 3.6206  | 1.81  | 2.47   |
| (ii) 1-hexanol in n-heptane<br>$M_j = 0.102$ kg.   | 2.6082  | 2.7315    | 0.9959                      | 0.22       | 2.40   | 1.7857  | 3.66  | 2.25   |
| (iii) 1-heptanol in n-heptane<br>$M_j = 0.116$ kg. | 2.5711  | 2.9898    | 0.9973                      | 0.15       | 2.22   | 4.0081  | 1.65  | 2.07   |
| (iv) 1-decanol in n-heptane<br>$M_j = 0.158$ kg.   | 2.6089  | 2.5881    | 0.9926                      | 0.41       | 2.53   | 2.0160  | 3.25  | 2.39   |
| (v) ethanol in benzene<br>$M_j = 0.046$ kg         | 1.3239  | 4.2872    | 0.9881                      | 0.72       | 3.77   | 4.5418  | 3.56  | 3.62   |

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| System with Sl.No and molecular weight                       | Intercept & slope of $\sigma''_{ij} - \sigma'_{ij}$ fitted equation |           | Correlation coefficient (r) | % of error | Estimated relaxation time $\tau_i$ in p-sec from Eq (6.10) | Ratio of slopes of $\sigma''_{ij}$ & $\sigma'_{ij}$ with $w_i x/y = (d\sigma''_{ij}/dw_i)$ | Estimated relaxation time $\tau_i$ in p-sec from Eq. (6.11) | Relaxation time $\tau_i$ in p-sec estimated from Gopalakrishnas method |
|--|---|-----------|-----------------------------|------------|--|--|---|--|
|  | Intercept (c)   | slope (m) |                             |            |  |  |   |  |
| (vi) methanol in benzene<br>$M_j = 0.032$ kg                 | 1.3448  | 3.2089    | 0.9633                      | 2.17       | 5.04   | 6.6999   | 2.41  | 4.87   |
| (vii) 2-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg.  | 2.5820  | 3.2340    | 0.9995                      | 0.04       | 2.02   | 3.3250   | 1.97  | 1.86   |
| (viii) 3-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg. | 2.5997  | 2.8021    | 0.9976                      | 0.16       | 2.34   | 2.2682   | 2.89  | 2.26   |
| (ix) 4-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg.   | 2.5901  | 3.0947    | 0.9989                      | 0.07       | 2.11   | 2.7665   | 2.37  | 1.95   |
| (x) 5-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg.    | 2.5653  | 3.6562    | 0.9949                      | 0.39       | 1.79   | 2.2437   | 2.92  | 1.63   |
| (xi) 4-octanol in n-heptane<br>$M_j = 0.130$ kg.             | 2.5791  | 3.5515    | 0.9999                      | 0.01       | 1.84   | 3.8814   | 1.69  | 1.68   |
| (xii) 2-octanol in n-heptane<br>$M_j = 0.130$ kg.            | 2.5960  | 3.1511    | 0.9875                      | 0.96       | 2.08   | 1.5636   | 4.19  | 1.93   |

**Table 6.4 :** Coefficients  $\alpha, \beta, \gamma$ , of hf  $\sigma_{ij}$  against  $w_j$  curves (Figure 6.5) correlation coefficient (r), percentage of error, dimensionless parameter b using  $\tau_j$  from Eq. (6.10) and (6.11), computed  $\mu_j \times 10^{30}$  in Coulomb metre from Eqs. (6.10) and (6.16) and Eqs. (6.11) and (6.16) estimated  $\mu_j \times 10^{30}$  in Coulomb metre from Gopalakrishna's method for some dielectropolar alcohols under nearly 24 GHz electric field (Q-band microwave) at 25°C.

| Systems with Sl. no. & molecular weight            | Coefficient of $\sigma_{ij} - w_j$ fitted equation |         |          | Correlation coefficient (r) | % of error | Dimension less parameter using $\tau_j$ from Eq. (6.10) $b=1/(1+\omega^2\tau_j^2)$ | Dimension less parameter using $\tau_j$ from Eq. (6.11) $b=1/(1+\omega^2\tau_j^2)$ | Computed $\mu_j \times 10^{30}$ in Coulomb metre |                                | Estimated $\mu_j \times 10^{30}$ in Coulomb metre from Gopalakrishna's method |
|--|--|---------|----------|-----------------------------|------------|--|--|--|--------------------------------|---|
|  | $\sigma_{ij} = \alpha + \beta w_j + \gamma w_j^2$  |         |          |                             |            |  |  | hfmethod of Eqs. (6.10)&(6.16)                   | hfmethod of Eqs. (6.11)&(6.16) |   |
|  | $\alpha$   | $\beta$ | $\gamma$ |                             |            |  |  |  |                                |   |
| (i) 1-butanol in n-heptane<br>$M_j = 0.074$ kg.    | 2.5987   | 1.8394  | -1.8413  | 0.9975                      | 0.14       | 0.8601   | 0.9290   | 4.28   | 4.16                           | 3.58  |
| (ii) 1-hexanol in n-heptane<br>$M_j = 0.102$ kg.   | 2.6391   | 0.5176  | 1.1817   | 0.9962                      | 0.21       | 0.8815   | 0.7618   | 2.63   | 2.83                           | 3.35  |
| (iii) 1-heptanol in n-heptane<br>$M_j = 0.116$ kg. | 2.5500   | 1.3385  | -1.2079  | 0.9932                      | 0.37       | 0.8992   | 0.9417   | 4.50   | 4.39                           | 3.59  |
| (iv) 1-decanol in n-heptane<br>$M_j = 0.158$ kg.   | 2.6242   | 0.6046  | 0.0962   | 0.9992                      | 0.05       | 0.8700   | 0.8022   | 3.57   | 3.71                           | 3.55  |
| (v) ethanol in benzene<br>$M_j = 0.046$ kg.        | 1.3255   | 0.2288  | -0.0206  | 0.9924                      | 0.46       | 0.9485   | 0.9538   | 1.44   | 1.43                           | 1.33  |

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| Systems with Sl. no. & molecular weight                      | Coefficient of $\sigma_{ij} - w_j$ fitted equation |         |          | Correlation coefficient (r) | % of error | Dimension less parameter using $\tau$ from Eq. (6.10) $b=1/(1+\omega^2\tau_j^2)$ | Dimension less parameter using $\tau$ from Eq. (6.11) $b=1/(1+\omega^2\tau_j^2)$ | Computed $\mu_j \times 10^{30}$ in Coulomb metre |                                 | Estimated $\mu_j \times 10^{30}$ in Coulomb metre from Gopalakrishna's method |
|--|--|---------|----------|-----------------------------|------------|--|--|--|---------------------------------|---|
|  | $\sigma_{ij} = \alpha + \beta w_j + \gamma w_j^2$  |         |          |                             |            |  |  | hf method of Eqs. (6.10)&(6.16)                  | hf method of Eqs. (6.11)&(6.16) |   |
|  | $\alpha$   | $\beta$ | $\gamma$ |                             |            |  |  |  |                                 |   |
| (vi) methanol in benzene<br>$M_j = 0.034$ kg                 | 1.3367   | 0.3049  | -0.1812  | 0.9930                      | 0.42       | 0.9116   | 0.9783   | 1.41   | 1.36                            | 1.18  |
| (vii) 2-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg.  | 2.5885   | 1.3064  | -1.1371  | 0.9958                      | 0.28       | 0.9130   | 0.9169   | 4.64   | 4.63                            | 3.42  |
| (viii) 3-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg. | 2.6133   | 1.0310  | -0.4311  | 0.9984                      | 0.10       | 0.8867   | 0.8368   | 4.18   | 4.30                            | 3.54  |
| (ix) 4-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg.   | 2.6079   | 1.0777  | -0.5929  | 0.9968                      | 0.22       | 0.9058   | 0.8841   | 4.23   | 4.28                            | 3.48  |
| (x) 5-methyl 3-heptanol in n-heptane<br>$M_j = 0.130$ kg.    | 2.6259   | 0.7479  | -0.0668  | 0.9996                      | 0.03       | 0.9304   | 0.8340   | 3.47   | 3.67                            | 3.24  |
| (xi) 4-octanol in n-heptane<br>$M_j = 0.130$ kg.             | 2.6160   | 0.7566  | -0.0677  | 0.9999                      | 0.01       | 0.9268   | 0.9375   | 3.50   | 3.48                            | 3.27  |
| (xii) 2-octanol in n-heptane<br>$M_j = 0.130$ kg.            | 2.6157   | 0.7437  | -0.0249  | 0.9999                      | 0.01       | 0.9083   | 0.7093   | 3.51   | 3.97                            | 3.32  |

### 6.3. High Frequency Dipole moment $\mu_j$ and Relaxation time $\tau_j$

Under hf electric field of GHz range the dimensionless complex dielectric relative permittivity  $\epsilon_{ij}^*$  of solution (ij) is written as

$$\epsilon_{ij}^* = \epsilon_{ij}' + j \epsilon_{ij}'' \quad (6.6)$$

where  $\epsilon_{ij}'$  and  $\epsilon_{ij}''$  are the real and imaginary parts of hf complex permittivity  $\epsilon_{ij}^*$ . The hf complex conductivity  $\sigma_{ij}^*$  of a polar-nonpolar liquid mixture [15] of weight fraction  $w_j$  is :

$$\sigma_{ij}^* = \sigma_{ij}' + j \sigma_{ij}'' \quad (6.7)$$

where  $\sigma_{ij}' = \omega \epsilon_0 \epsilon_{ij}''$  and  $\sigma_{ij}'' = \omega \epsilon_0 \epsilon_{ij}'$  are real and imaginary parts of complex conductivity  $\sigma_{ij}^*$  and  $j$  is a complex number  $= (-1)^{1/2}$ .

The total hf conductivity  $\sigma_{ij}$ , is, however, obtained from

$$\sigma_{ij} = \omega \epsilon_0 (\epsilon_{ij}'^2 + \epsilon_{ij}''^2)^{1/2} \quad (6.8)$$

$\sigma_{ij}''$  is related to  $\sigma_{ij}'$  by [11]

$$\sigma_{ij}'' = \sigma_{\infty ij} + \left( \frac{1}{\omega \tau_j} \right) \sigma_{ij}' \quad (6.9)$$

where  $\sigma_{\infty ij}$  is the constant conductivity at  $w_j \rightarrow 0$  and  $\tau_j$  is the relaxation time of a polar liquid molecule.

Eq. (6.9) on differentiation with respect to  $\sigma_{ij}'$  becomes

$$d\sigma_{ij}'' / d\sigma_{ij}' = \frac{1}{\omega \tau_j} \quad (6.10)$$

It is often better to use the ratio of slopes of individual variations of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  with  $w_j$  at  $w_j \rightarrow 0$  to avoid polar-polar interaction in a given solvent to get  $\tau_j$  from :

$$\begin{aligned} (d\sigma_{ij}''/dw_j) / (d\sigma_{ij}'/dw_j) &= 1/\omega\tau_j \\ \text{or, } x/y &= 1/\omega\tau_j \end{aligned} \quad (6.11)$$

where  $\omega = 2\pi f$ ,  $f$  being the frequency of alternating electric field.

In hf region of GHz range, it is often observed that  $\sigma_{ij}'' \simeq \sigma_{ij}$  and Eq. (6.9) becomes

$$\sigma_{ij} = \sigma_{\infty ij} + (1/\omega\tau_j) \sigma_{ij}' \quad (6.12)$$

$$\text{or} \quad \beta = (1/\omega\tau_j) (d\sigma_{ij}'/dw_j) \quad (6.13)$$

where  $\beta = (d\sigma_{ij}'/dw_j)$ , is the slope of  $\sigma_{ij} - w_j$  curve at  $w_j \rightarrow 0$

The  $\sigma_{ij}'$  of a solution of weight fraction  $w_j$  of a polar molecule at T K is given by Smyth [14,16] as :

$$\sigma_{ij}' = \frac{N\rho_i\mu_j^2}{27M_jk_B T} \left( \frac{\omega^2\tau_j}{1+\omega^2\tau_j^2} \right) (\epsilon_{ij}' + 2) w_j \quad (6.14)$$

Eq. (6.14) on differentiation with respect to  $w_j$  and at  $w_j \rightarrow 0$  yields

$$(d\sigma_{ij}'/dw_j)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27M_jk_B T} \left( \frac{\omega^2\tau_j}{1+\omega^2\tau_j^2} \right) (\epsilon_i + 2)^2 \quad (6.15)$$

Where  $N =$  Avogadro's number  $= 6.023 \times 10^{23}$

$\rho_i =$  density of solvent

$M_j =$  molecular weight of solute

$k_B =$  Boltzmann constant  $= 1.38 \times 10^{-23}$  joule mole $^{-1}$ K $^{-1}$ .

From Eqs. (6.13) and (6.15) one gets hf  $\mu_j$  as:

$$\mu_j = \left[ \frac{27M_jk_B T}{N\rho_i (\epsilon_i + 2)^2} \cdot \frac{\beta}{\omega b} \right]^{1/2} \quad (6.16)$$

$$\text{where } b = \frac{1}{1+\omega^2\tau_j^2} \quad (6.17)$$

is a dimensionless parameter involved with estimated  $\tau_j$  from Eqs. (6.10) and (6.11). All the computed hf  $\mu_j$ 's in terms of slopes  $\beta$ 's and  $b$ 's are placed in Table

6.4 in order to compare with  $\mu_{\text{theo}}$ 's,  $\mu_s$  and  $\mu_1, \mu_2$  of the flexible part and end-over-end rotation of the whole molecule [5,6] presented in Table 6.2.

## 6.4. Results and Discussion

The dimensionless real  $\epsilon'_{ij}$  and imaginary  $\epsilon''_{ij}$  parts of hf complex relative permittivity  $\epsilon^*_{ij}$  along with static and infinite frequency relative permittivities  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$  of solution (ij) for different  $w_j$  of alcohols in different solvents at 25°C are presented in Table 6.1. The static experimental solution parameter  $X_{ij}$ 's involved with  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$  of Table 6.1 are shown in Figure 6.1 for different  $w_j$  of alcohols. The nature of variation of  $X_{ij}$  with  $w_j$ 's are parabolic in nature satisfying a polynomial equation  $X_{ij} = a_0 + a_1 w_j + a_2 w_j^2$ . The coefficients of  $X_{ij}-w_j$  curves i.e.  $a_0, a_1$  and  $a_2$  are placed in 2nd, 3rd and 4th columns of Table 6.2. As evident from Figure 6.1, the  $X_{ij}-w_j$  curves for methanol, ethanol and 3 methyl 3 heptanol are convex in nature as their coefficients of quadratic terms in Table 6.2 are negative. The remaining  $X_{ij}$ 's on the other hand, showed a gradual increase with  $w_j$ 's for all the coefficients of the curves are positive as seen in Table 6.2. The anomalous behaviour of  $X_{ij}-w_j$  curves from linearity for all the alcohols in different solvents at a given temperature in °C may rouse an interesting relaxation mechanism in such long chain associated liquids. In comparison to octyl alcohols, the curves of normal alcohols in higher concentrations are highly concave having a tendency to meet at a common point on the  $X_{ij}$  axis at  $w_j \rightarrow 0$ . This sort of behaviour of  $X_{ij}-w_j$  curves of Figure 6.1 arises either due to solute-solute i.e. dimer or solute-solvent i.e. monomer formations in comparatively high concentrations. The convex shape of ethanol and methanol occurs for the probable experimental uncertainty in their  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$  measurements. The identical nature of variation of all the octyl alcohols have almost the same slope, but of different intercepts as a result of solvation effect. Their  $X_{ij}$ 's have tendency to become closer within  $0.1 \leq w_j \leq 0.2$  indicating various molecular association in them.

In case of non-associated liquids  $a_2$ 's were found to be vanishingly small in comparison to  $a_0$  and  $a_1$  to yield almost linear variation of  $X_{ij}$  against  $w_j$ . The estimated correlation coefficient ( $r$ ) and the percentage of error (%) entered in 5th and 6th columns of Table 6.2 for all the alcohols are such that one may rely on the linear terms of  $X_{ij}-w_j$  curve to compute  $\mu_s$ 's from Eq. (6.5).  $\mu_s$ 's thus computed are placed in the 7th column of Table 6.2 to compare with  $\mu_{\text{theo}}$ 's obtained from bond angles and bond moments of the substituent polar groups, as presented in Figure 6.6 and  $\mu_1$  and  $\mu_2$  of the flexible part and the whole molecule by the double relaxation method [5,6] at nearly 24 GHz electric field. The smaller and larger deviations of  $X_{ij}$ 's from linearity with  $w_j$ 's as seen in Figure 6.1 confirm the molecular association of such associated dielectropolar liquids in different solvents.

The relaxation times  $\tau_j$ 's are, however, derived from the slopes of linear [11] variation of  $\sigma_{ij}''$  with  $\sigma_{ij}'$  of Figure 6.2 for all the alcohols. Although, the experimental data, on the other hand, did not strictly fall on the fitted linear curves of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  both in  $\Omega^{-1}\text{m}^{-1}$  as drawn in Figure 6.2, the slope of  $\sigma_{ij}''$  against  $\sigma_{ij}'$  of Figure 6.2 was however, used to obtain  $\tau_j$  from Eq. (6.10). The 2nd, 3rd and 6th columns of Table 6.3 contain all the estimated intercepts and slopes together with the measured  $\tau_j$ 's. The linearity of  $\sigma_{ij}''$  against  $\sigma_{ij}'$  curves as shown graphically in Figure 6.2 is again tested by correlation coefficient  $r$ 's and % of errors. They are entered in the 4th and 5th columns of Table 6.3 only to see how far  $\sigma_{ij}''$  and  $\sigma_{ij}'$  are correlated to each other. But it is often better to use the ratio of the individual slopes of variation of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  with  $w_j$  at  $w_j \rightarrow 0$  to get  $\tau_j$ .  $\tau_j$ 's by using Eq.(6.11) are not in close agreement with those obtained from Eq.(6.10) and by freshly calculated Gopalakrishna's method as seen in Table 6.3. Figures 6.3 and 6.4 showed that both  $\sigma_{ij}''$  and  $\sigma_{ij}'$  vary nonlinearly with  $w_j$ . The nonlinear behaviour of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  as seen in Figures 6.3 and 6.4 with  $w_j$ 's invites the associational and structural aspects of such long chain dielectropolar associated molecules. The latter method to measure  $\tau_j$ 's thus

appears to be a significant improvement [12,13] over the former one [11] as it eliminates the polar-polar interaction in a given solvent.

The hf  $\mu_j$ 's from Eq. (6.16) was obtained from the slope  $\beta$  of the nonlinear variation of  $\sigma_{ij}$  in  $\Omega^{-1}\text{m}^{-1}$  with  $w_j$ 's of Figure 6.5 and dimensionless parameter 'b' of Eq. (6.17) in terms of  $\tau_j$  obtained by both the methods. The intercept  $\alpha$  and slope  $\beta$  of hf  $\sigma_{ij}$  with  $w_j$  curves of Figure 6.5 are entered in the 2nd and 3rd columns of Table 6.3. It is interesting to note that the curves of  $\sigma_{ij}-w_j$  variation of Figure 6.5 are almost identical with  $\sigma_{ij}''-w_j$  curves of Figure 6.3. This fact at once confirms the applicability of the approximation  $\sigma_{ij}'' \simeq \sigma_{ij}$  as done in Eqs. (6.9) and (6.12). The imaginary  $\sigma_{ij}''$  and total hf  $\sigma_{ij}$  in case of normal alcohols in Figures 6.3 and 6.5 decreases gradually with  $w_j$ 's of 1-butanol to methanol except ethanol. This can be explained on the basis of the fact that the polarity of the molecules decrease from 1-butanol to methanol. Both  $\sigma_{ij}''$ 's and  $\sigma_{ij}$ 's in Figures 6.3 and 6.5 of all the octyl alcohols are found to be closer only to show their nearly same polarity. The almost coincident curves of 4 octanol (— $\odot$ —) and 2-octanol (—X—) arise due to their identical polarity as estimated in Figure 6.6.

The estimated  $\mu_s$ 's and  $\mu_j$ 's in Table 6.2 and 6.4 are then compared with  $\mu_1$  and  $\mu_2$  in Table 6.2 by double relaxation method [5,6] and those by freshly calculated Gopalakrishna's method. For all the octyl alcohols  $\mu_j$ 's and  $\mu_s$ 's are in excellent agreement with Gopalakrishna's  $\mu_j$ 's (reported data) and  $\mu_1$ . The estimated  $\mu_j$ 's for normal alcohols agree with reported  $\mu$ 's and  $\mu_1$ . All these discussions made above establish the fact that a part of the molecule is rotating under GHz electric field. Slight disagreement in  $\mu$ 's and the reported ones arises due to steric hindrances of the substituent polar units of their structural configurations of Figure 6.6 and the existence of associated nature for their hydrogen bonding. Unlike methanol and ethanol  $\mu_s$ 's are always lower than  $\mu_j$ 's and  $\mu_1$ 's for all the alcohols. This at once reveals that under static electric field the possible formation of dimers which undergo to rupture into the solute solvent association i.e. monomer in the hf electric field to increase  $\mu$ 's. It is

also evident that dimer formation is favourable in octyl alcohols than normal alcohols due to existence of strong inductive effect for their –OH groups at the end of molecular chains.

The theoretical dipole moments  $\mu_{\text{theo}}$ 's of all the alcohols under study were calculated from the available bond angles and bond moments of the substituent polar groups like  $\text{H}_3\text{-C}$ ,  $\text{C-H}$ ,  $\text{C-O}$ ,  $\text{O-H}$  ( $<105^\circ$ ) and  $\text{C-C}$  of  $1.23 \times 10^{-30}$ ,  $1.0 \times 10^{-30}$ ,  $3.33 \times 10^{-30}$ ,  $1.30 \times 10^{-30}$  and  $0.3 \times 10^{-30}$  Coulomb-metre (C.m) as presented elsewhere [5,6]. The values thus estimated are then made closer with the measured static  $\mu_s$ 's or even  $\mu_j$ 's by reducing the available bond moments by a factor  $\mu_s/\mu_{\text{theo}}$  which takes into account of the inductive and mesomeric effects of the substituent polar groups as shown in Figure 6.6. An inductive effect of polar unit acts along the chain of molecular axis of the normal alcohols to make them strongly polar due to presence of –OH group at their end of the axis. The comparatively higher  $\mu_{\text{theo}}$ 's in octyl alcohols is probably due to screening effect of their –OH groups by other polar groups like  $\text{H}_3\text{-C}$ ,  $\text{C-H}$  which favour the dimer formation of these alcohols through H-bonding to make their  $\mu_s$ 's and  $\mu_j$ 's higher than the normal alcohols as seen in Figure 6.6.

## 6.5. Conclusions

The modern internationally accepted symbols of dielectric terminologies and parameters in SI units are conveniently used to obtain the static and hf dipole moments  $\mu_s$  and  $\mu_j$  in terms of relaxation time  $\tau_j$  of a polar molecule.  $\tau_j$ 's measured from the slope of imaginary  $\sigma_{ij}''$  and real  $\sigma_{ij}'$  of complex hf conductivity  $\sigma_{ij}^*$  for different  $\omega_j$  are not in agreement with those measured from the ratio of the individual slopes of  $\sigma_{ij}''-\omega_j$  and  $\sigma_{ij}'-\omega_j$  curves at  $\omega_j \rightarrow 0$  indicating the applicability of the latter method in long chain dielectropolar alcohols. This method of determination of  $\tau_j$  is a significant improvement over the previous one as it eliminates polar-polar interactions in a given solvent. The comparison of  $\mu_j$ 's and  $\mu_s$ 's with  $\mu_1$  and  $\mu_2$  of the flexible part and the whole molecule by

double relaxation method and  $\mu_{\text{theo}}$ 's from bond angles and bond moments seems to be an interesting phenomenon to have deep insight into relaxation mechanism of dielectropolar alcohols.

The results indicate that a part of the molecule is rotating under GHz electric field. The slight departure among the measured  $\mu_s$ ,  $\mu_j$  and  $\mu_{\text{theo}}$  reveals different associational aspects of dielectropolar alcohols in different solvents through the frequency dependence of relaxation parameters. It also shows the strong polar nature of normal alcohols which favour solute solvent association due to presence of  $-\text{OH}$  group at the end of their bond axis. But the comparatively higher values of  $\mu_j$ 's in octyl alcohols indicates the solute-solute association due to  $-\text{H}$  bonding supported by the fact that  $-\text{OH}$  being screened by  $-\text{CH}_3$  and a large number of  $>\text{CH}_2$  polar groups. The  $\mu_s/\mu_{\text{theo}}$ 's are almost constant for all the alcohols to take into account of all these facts in addition to their material property of the system. This study further supports the rotation of  $-\text{OH}$  group along the  $\equiv \text{C}-\text{O}-$  bond of all the alcohols under static and hf electric fields. Moreover, the methodology so far developed within the framework of Debye and Smyth model appears to be sound, simple, straightforward and useful to arrive at associational and structural aspects of alcohols which are thought to be non-Debye in relaxation behaviour.

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