High frequency and static relaxation parameters of some polar monosubstituted anilines in benzene

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The use of slopes of individual variation of the imaginary \( \sigma''_{ij} \) and real \( \sigma'_{ij} \) parts of high frequency (hf) conductivity \( \sigma^*_{ij} \) with the weight fractions \( W_j \)'s of a solution is employed to determine relaxation times \( \tau_j \)'s of some monosubstituted anilines in \( C_6H_6 \). The dipole moments \( \mu_j \)'s of such polar molecules in terms of estimated \( \tau_j \)'s are calculated and compared with those by using the existing methods for \( \tau_j \) (Murthy et al. 1989). Excellent agreement of \( \mu_j \)'s in most cases except \( m \)-toluidine indicates the applicability of both the methods. The hf \( \mu_j \) as well as static \( \mu_j \) differ from \( \mu_{\text{calc}} \)'s as obtained from the available bond angles and bond moments. The reduced bond moments are, however, calculated from the estimated \( \mu_j \)'s to yield the exact \( \mu_j \)'s in close agreement with \( \mu_j \) and \( \mu_{\text{calc}} \) only to establish the presence of inductive and mesomeric moments of the substituent groups, in addition to solute-solute or solute-solvent molecular associations among the molecules in the solution. The \( \mu_j \)'s being little affected by the frequency of the electric field, are finally compared with \( \mu_j \) and \( \mu_{\text{calc}} \) (Sit and Acharyya, 1996) due to rotations of the whole and a part of the molecules. They are very close to \( \mu_j \) indicating the fact that a part of the molecule is rotating under the electric field of 10 GHz.

1 Introduction

The dielectric relaxation behaviour of disubstituted benzenes and anilines in a nonpolar solvent is very interesting, because they usually show the double relaxation phenomena under high frequency (hf) electric fields. Monosubstituted anilines, on the other hand, possess either single or double relaxation times \( (\tau_j) \)'s at three different hf electric fields of Giga hertz (GHz) range. But they always showed double relaxation times at 9.945 GHz electric field, which seems to be the most effective dispersive region for such polar molecules. They were also found to obey the symmetric relaxation behaviour under such electric field.

An attempt is, therefore, made to get the dimensionless dielectric relaxation parameters like real \( \kappa'_{ij} \), imaginary \( \kappa''_{ij} \), and parts of complex dielectric constant \( \kappa^*_{ij} \) as well as static and infinite frequency-dielectric constants \( \kappa_{\text{static}} \) and \( \kappa_{\text{inf}} \) of solution \( (ij) \) as shown in Table 1, from the measured permittivities of \( \varepsilon'_{ij} \), \( \varepsilon''_{ij} \), \( \varepsilon_{\text{ij}} \) and \( \varepsilon_{\text{inf}} \) respectively, of three isomers of anisidines and toluidines at 35°C under 9.945 GHz electric field at different weight fractions \( W_j \)'s of solute \( (j) \). The purpose of such consideration is to get static dipole moment \( \mu_j \) at any stage of dilution as well as the relaxation times \( (\tau_j) \)'s and hence hf dipole moments \( (\mu_j) \)'s derived from hf conductivities \( \sigma^*_{ij} \)'s as functions of \( \kappa^*_{ij} \) and \( \kappa''_{ij} \) at different \( W_j \)'s.

The ratio of individual slopes of the concentration variation of the imaginary \( \sigma''_{ij} \) and the real \( \sigma'_{ij} \) parts of complex hf conductivity \( \sigma^*_{ij} \) as well as the slope of linear variation of \( \sigma''_{ij} \) with \( \sigma'_{ij} \) were simultaneously used to estimate \( \tau_j \)'s of a polar liquid. The \( \tau_j \) obtained by the former method provides a significant improvement over the latter one, as it eliminates the polar-polar interaction in the solution. It is better to use the ratio of slopes of concentration variations of \( \kappa'_{ij} \) and \( \kappa''_{ij} \) instead of \( \sigma''_{ij} \rightarrow W_j \) and \( \sigma'_{ij} \rightarrow W_j \) curves to get \( \tau_j \), because \( \kappa'_{ij} \) and \( \kappa''_{ij} \) can be obtained directly from experimental measurements of \( \varepsilon'_{ij} \) and \( \varepsilon''_{ij} \).

But, the variation of \( \kappa''_{ij} \) with \( W_j \) is not always linear with a constant intercept. In this paper, a comparison of static \( \mu_j \) from the slope of \( \chi_0-W_j \) curve and hf \( \mu_j \) in terms of \( \tau_j \) using hf conductivities of solution under 9.945 GHz electric field is also made with \( \mu_j \) and \( \mu_{\text{calc}} \) due to rotations of the whole as well as the flexible part attached to the parent ring of the molecule from the dielectric relaxation parameters of Table 1 obtained by careful graphical interpolation of measured data used earlier. The comparison of all these seems to be an interesting phenomenon only to see how far they agree.
Table 1 — Experimental dielectric relaxation parameters of three isomers of anisidines and toluidines at 35°C under 9.945 GHz electric field for different weight fractions Wj's of solutes

<table>
<thead>
<tr>
<th>System with Sl. No and molecular wt.</th>
<th>Weight fraction of solutes</th>
<th>Real part of permittivity (εr)</th>
<th>Dielectric loss factor (εm)</th>
<th>Static permittivity (εs)</th>
<th>Infinite frequency permittivity (ε∞)</th>
<th>Dimensionless dielectric constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mj, kg</td>
<td>Wj</td>
<td>(εr) F.m⁻¹</td>
<td>(εm) F.m⁻¹</td>
<td>(εs) F.m⁻¹</td>
<td>(ε∞) F.m⁻¹</td>
<td>k'ij x 10⁻¹²</td>
</tr>
<tr>
<td>1. o-anisidine in C₆H₆ Mj = 0.123 kg</td>
<td>0.0326</td>
<td>2.3106</td>
<td>0.0148</td>
<td>2.336</td>
<td>2.239</td>
<td>0.2609</td>
</tr>
<tr>
<td>2. m-anisidine in C₆H₆ Mj = 0.123 kg</td>
<td>0.0604</td>
<td>2.3520</td>
<td>0.0244</td>
<td>2.404</td>
<td>2.247</td>
<td>0.2656</td>
</tr>
<tr>
<td>3. p-anisidine in C₆H₆ Mj = 0.123 kg</td>
<td>0.0884</td>
<td>2.4064</td>
<td>0.0340</td>
<td>2.459</td>
<td>2.255</td>
<td>0.2718</td>
</tr>
<tr>
<td>4. o-toluidine in C₆H₆ Mj = 0.107 kg</td>
<td>0.1135</td>
<td>2.4416</td>
<td>0.0400</td>
<td>2.538</td>
<td>2.262</td>
<td>0.2758</td>
</tr>
<tr>
<td>5. m-toluidine in C₆H₆ Mj = 0.107 kg</td>
<td>0.1361</td>
<td>2.4672</td>
<td>0.0512</td>
<td>2.588</td>
<td>2.267</td>
<td>0.2786</td>
</tr>
<tr>
<td>6. p-toluidine in C₆H₆ Mj = 0.107 kg</td>
<td>0.0160</td>
<td>2.2720</td>
<td>0.0234</td>
<td>2.315</td>
<td>2.235</td>
<td>0.2566</td>
</tr>
</tbody>
</table>

with μ₂ and μ₁ as obtained elsewhere. This study further observes the effect of inductive and mesomorphic moments of polar groups of the molecules as well as the frequency of the alternating electric field on μ₁'s in comparison to μ₂. Moreover, the present method of study in terms of modern internationally accepted units and symbols appears to be superior because of its unified, coherent and rationalized nature.

As is evident from Table 2, hfμ₁'s of the polar liquids were computed in terms of τ, and the slopes (b's) of σ'' - Wj curves of Fig. 1 under 9.945 GHz electric field at 35°C. τ being an important parameter for obtaining μ₁ of polar liquid estimated from the ratio of slopes of individual variation of σ'' and σ' with Wj. The nature of variations of σ'' - Wj and σ' - Wj curves are presented in Figs 2 and 3, respectively. In place of using τ,
from the ratio of the slopes of $\sigma''_j - W_j$ and $\sigma'_j - W_j$ curves, one may use the linear slope of $\sigma''_j - \alpha'_j$ curve to get $\tau_j$ and hence $\mu_j$ as suggested by Murthy et al.5. All the $\mu_j$'s and $\tau_j$'s from both the methods are reported in Table 2.

The static dipole moment $\mu_j$ under static or low frequency electric field was also calculated from the linear coefficient of $X_j - W_j$ curve of Fig. 4 for each polar-nonpolar liquid mixture. The correlation coefficient $r$ of the linear curve as well as the % error are presented in Table 3 alongwith $\mu_j$ and coefficients $a_0, a_1$ of $X_j - W_j$ curve. The theoretical dipole moment $\mu_{\text{theo}}$'s from available bond angles and bond moments are found to be deviated from static $\mu_j$'s and $\text{hf} \mu_j$'s, because of the existence of the inductive and mesomeric moments of the different polar groups in them. As the variation of $\mu_j$ compared to $\mu_i$ is very little, conformational structures of the polar molecules are predicted by $\mu_{\text{cal}}$ values, which are in agreement with $\mu_j$ from the reduced bond moments of the substituent groups by a factor $\mu_j / \mu_{\text{theo}}$ presented in Table 3 and illustrated in Fig. 5.

![Figure 1](image-url)
Table 2 — Reports ratio slopes of \((\sigma'_{ij} - W)\) and \((\sigma_{ij} - W)\) curves at \(W \to 0\), linear slope of \((\sigma_{ij} - \sigma_{ij})\) curve, computed relaxation time \(\tau\) and hence \(\tau_{ij}\) for both the methods and reported \(\mu_2\) and \(\mu_1\) in C.m from double relaxation method.

<table>
<thead>
<tr>
<th>System with</th>
<th>Ratio of slopes</th>
<th>Slope Correlation</th>
<th>% of</th>
<th>Estimated (\tau)</th>
<th>Slope (\beta \times 10^{-12}) in (\Omega^{-1}\text{m}^{-1}) of</th>
<th>Computed (\mu_2 \times 10^{30}) in C.m from</th>
<th>Reported (\mu_1 \times 10^{30}) in C.m</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI.No and</td>
<td>(\frac{\sigma'<em>{ij} - W}{\sigma</em>{ij} - W} \to 0)</td>
<td>(\frac{\sigma_{ij} - \sigma_{ij}}{\sigma_{ij} - W} \to 0)</td>
<td>(r)</td>
<td>Eq. (5)</td>
<td>Eq. (6)</td>
<td>Eq. (5) &amp; Eq. (11)</td>
<td>Eq. (11)</td>
</tr>
<tr>
<td>M&lt;sub&gt;j&lt;/sub&gt; in kg(solutes)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. o-anisidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>(1.3024 \times 10^{10}) (1.7179 \times 10^{10})</td>
<td>4.5290 0.988</td>
<td>0.71</td>
<td>2.11 3.53</td>
<td>0.1302</td>
<td>5.38 5.38</td>
<td>31.11 6.40</td>
</tr>
<tr>
<td>2. m-anisidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>(1.7305 \times 10^{10}) (5.2415 \times 10^{10})</td>
<td>3.3521 0.993</td>
<td>0.40</td>
<td>4.85 4.77</td>
<td>0.1732</td>
<td>6.33 6.33</td>
<td>24.57 7.55</td>
</tr>
<tr>
<td>3. p-anisidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>(2.6210 \times 10^{10}) (4.7768 \times 10^{10})</td>
<td>3.8143 0.983</td>
<td>0.99</td>
<td>2.92 4.20</td>
<td>0.2621</td>
<td>7.58 7.71</td>
<td>52.74 9.00</td>
</tr>
<tr>
<td>4. o-toluidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>(1.4076 \times 10^{10}) (5.0973 \times 10^{10})</td>
<td>3.5123 0.997</td>
<td>0.31</td>
<td>5.45 4.56</td>
<td>0.1500</td>
<td>5.44 5.47</td>
<td>29.87 7.70</td>
</tr>
<tr>
<td>5. m-toluidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>(7.3263 \times 10^{10}) (3.7452 \times 10^{10})</td>
<td>2.9025 0.783</td>
<td>11.69</td>
<td>8.18 5.51</td>
<td>0.0732</td>
<td>4.13 3.89</td>
<td>17.07 5.20</td>
</tr>
<tr>
<td>6. p-toluidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>(4.3247 \times 10^{10}) (4.2379 \times 10^{10})</td>
<td>4.4801 0.929</td>
<td>4.12</td>
<td>1.57 3.57</td>
<td>0.0428</td>
<td>2.82 2.88</td>
<td>18.54 4.03</td>
</tr>
</tbody>
</table>

Table 3 — Coefficients \(a_0, a_1\), in the equation \(X_{ij} = a_0 + a_1 W\), correlation coefficient \(r\), % of error in fitting technique, static dipole moment \(\mu_0\) in coulomb-metre, theoretical dipole moment \(\mu_{theo}\) from bond angles and bond moments, reduced bond moments of substituent groups, \(\mu_{cal}\) from reduced bond moments of anisidines and toluidines under static electric field at 35°C.

<table>
<thead>
<tr>
<th>Systems with SI.No and</th>
<th>Intercepts and slopes of (\beta_{ij} - W) Eq.</th>
<th>Correlation % of error in fitting technique</th>
<th>(\mu_{theo} \times 10^{30}) of</th>
<th>Reduced bond moments (\times 10^{30}) of (\mu_{cal} \times 10^{30}) in C.m</th>
</tr>
</thead>
<tbody>
<tr>
<td>M&lt;sub&gt;i&lt;/sub&gt; in kg. solutes</td>
<td>(a_0 \times 10^{10}) (a_1 \times 10^{10})</td>
<td>(\beta_{ij} \times 10^{10}) in C.m</td>
<td>(\text{OCH}_2\text{(C.m)})</td>
<td>(-\text{CH}_3\text{(C.m)})</td>
</tr>
<tr>
<td>1. o-anisidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.0193 1.2196</td>
<td>0.9976 0.14</td>
<td>2.94 3.40</td>
<td>2.07</td>
</tr>
<tr>
<td>2. m-anisidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.0211 1.9208</td>
<td>0.9988 0.07</td>
<td>3.69 5.50</td>
<td>1.61</td>
</tr>
<tr>
<td>3. p-anisidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.0219 1.7353</td>
<td>0.9977 0.14</td>
<td>3.51 6.30</td>
<td>1.33</td>
</tr>
<tr>
<td>4. o-toluidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.0158 1.5942</td>
<td>0.9981 0.13</td>
<td>3.13 4.63</td>
<td>-</td>
</tr>
<tr>
<td>5. m-toluidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.0240 1.3430</td>
<td>0.9988 0.08</td>
<td>2.88 3.43</td>
<td>-</td>
</tr>
<tr>
<td>6. p-toluidine in C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.0230 1.2393</td>
<td>0.9996 0.02</td>
<td>2.76 5.13</td>
<td>-</td>
</tr>
</tbody>
</table>
2 Theoretical Formulation to Estimate hf Dielectric Relaxation Parameters

Under hf electric field of GHz range the dimensionless complex dielectric constant $\kappa_{ij}^*$ is written as

$$\kappa_{ij}^* = \kappa_{ij}' - j\kappa_{ij}''$$  \hspace{1cm} (1)

where $\kappa_{ij}' = \varepsilon_{ij}' / \varepsilon_0 = \text{real part of dielectric constant}$ and $\kappa_{ij}'' = \varepsilon_{ij}'' / \varepsilon_0 = \text{dielectric loss factor}$, respectively. $\varepsilon_{ij}'$ and $\varepsilon_{ij}''$ are the real and imaginary parts of complex permittivity $\varepsilon_{ij}^*$ having dimension of Farad meter$^{-1}$ ($\text{F.m}^{-1}$) and $\varepsilon_0 = \text{permittivity of free space} = 8.854 \times 10^{-12} \text{F.m}^{-1}$. Hence, Murphy-Morgan relation for the complex hf conductivity $\sigma_{ij}^*$ of a solution of $W_j$ is given by

$$\sigma_{ij}^* = \omega \varepsilon_0 \kappa_{ij}'' + j\omega \varepsilon_0 \kappa_{ij}'$$  \hspace{1cm} (2)

where $\sigma_{ij}' = \omega \varepsilon_0 \kappa_{ij}''$ and $\sigma_{ij}'' = \omega \varepsilon_0 \kappa_{ij}'$ are the real and imaginary parts of complex conductivity, and $j$ is a complex number $= \sqrt{-1}$.

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

$$\sigma_{ij} = \frac{\omega \varepsilon_0}{\omega} \sqrt{\kappa_{ij}''^2 + \kappa_{ij}'^2}$$  \hspace{1cm} (3)

Again, the imaginary part of hf conductivity $\sigma_{ij}''$ related to the real part of hf conductivity $\sigma_{ij}'$ by

$$\sigma_{ij}'' = \sigma_{oij} + (1/\omega \tau) \sigma_{ij}'$$  \hspace{1cm} (4)

where $\sigma_{oij}$ is the constant conductivity in the limit of $W_j = 0$ and $\tau$ is the relaxation time of a polar unit.

Differentiating Eq. (4) with respect to $\sigma_{ij}'$ one gets

$$d\sigma_{ij}'' / d\sigma_{ij}' = 1 / \omega \tau$$  \hspace{1cm} (5)

In higher concentration region, the variation of the individual $\sigma_{ij}''$ and $\sigma_{ij}'$ with $W_j$ may not be linear due to
polar-polar interactions, it is better to use the following relation to get $\tau_j$ as:

$$(\frac{d\sigma''_y}{dW_j})_{W_j\to 0} / (\frac{d\sigma''_y}{dW_j})_{W_j\to 0} = 1 / \omega \tau_j$$

or $x/y = 1 / \omega \tau_j$

Under hf alternating electric field, it is also observed experimentally that $\sigma''_y \equiv \sigma_y$

Hence Eq. (4) becomes

$$\sigma_y = \sigma_{eq} + (1 / \omega \tau_j) \sigma''_y$$

or $\beta = \frac{1}{\omega \tau_j} \left( \frac{d\sigma''_y}{dW_j} \right)_{W_j\to 0}$

where $\beta = $ slope of $\sigma_y - W_j$ curve at $W_j \to 0$, i.e. $\frac{d\sigma''_y}{dW_j} \to 0$ as presented in Table 2 for all the liquids under investigation. The real part of hf conductivity $\sigma'_y$ at $T$, $K$ is related with imaginary part of dielectric constant or dielectric loss\(^{10}\) of a given solution of $W_j$ by

$$\sigma'_y = \frac{N \rho_i \mu_i^2}{27 \varepsilon_0 k_B T M_i} \left( \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) (\varepsilon_0 \kappa_{eq} + 2) (\varepsilon_0 \kappa_{eq} + 1) W_j$$

which on differentiation with respect to $W_j$ and at $W_j \to 0$ yields

$$\left( \frac{d\sigma'_y}{dW_j} \right)_{W_j\to 0} = \frac{N \rho_i \mu_i^2}{3 \varepsilon_0 k_B T M_i} \left( \frac{\varepsilon_i + 2}{3} \right) \left( \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right)$$

Here, $N = $ Avogadro's number, $\rho_i = $ density of solvent, $\varepsilon_i = $ dielectric permittivity of the solvent, $M_i = $ molecular weight of solute and $k_B = $ Boltzmann constant. All the parameters are, however, expressed in S.I. Units. From Eqs (8) and (10) one gets hf dipole moment $\mu_i$ from

$$\mu_i = \left( \frac{27 \varepsilon_0 k_B T M_i \beta}{N \rho_i (\varepsilon_i + 2)^2 c \mu_b} \right)^{1/2}$$

in terms of $b$, which is a dimensionless parameter, given by

$$b = \frac{1}{1 + \omega^2 \tau^2}$$

All the $\mu_i$'s in terms of $\beta$'s and $b$'s involved with $\tau_j$'s are, however, placed in Table 2, in order to compare with the static $\mu_i$ as presented in Table 3.
3 Static Relaxation Parameters

Under static or low frequency electric field, $\mu_0$, of a polar liquid (j) in a non-polar solvent (i) may be written from Debye's equation as

$$\frac{(\varepsilon_0 \kappa_{ij} - 1)}{(\varepsilon_0 \kappa_{ij} + 2)} = \frac{(\varepsilon_0 \kappa_{ii} - 1)}{(\varepsilon_0 \kappa_{ii} + 2)} + \frac{N \mu_i^2}{3 \varepsilon_0 k_b T} c_i$$

where $\kappa_{ij}$ and $\kappa_{ii}$ are the dimensionless static and infinite frequency dielectric constants of solution. $c_i$ is the molar concentration given by

$$c_i = \frac{\rho_j W_j}{M_j}$$

A polar liquid of weight $W_j$ and of volume $V_j$ is mixed with a non-polar solvent of weight $W_i$ and of volume $V_i$ to get the solution density $\rho_y$ where

$$\rho_y = \frac{\rho_i \rho_j}{\rho_j W_j + \rho_i W_i} = \rho_i (1 - \gamma W_j)^{-1}$$

Here, weight fractions $W_j$ and $W_i$ of solute and solvent are given by $W_j = W_{ij} W_j$ and $W_i = W_{ii} W_i$, such that

$$W_j + W_i = 1, \gamma = \left(1 - \frac{\rho_j}{\rho_i}\right)$$

and $\rho_i$ and $\rho_j$ are densities of pure solvent and solute, respectively.

Now Eq. (13) may be written as

$$\frac{(\varepsilon_0 \kappa_{ij} - 1)}{(\varepsilon_0 \kappa_{ij} + 2)} = \frac{(\varepsilon_0 \kappa_{ii} - 1)}{(\varepsilon_0 \kappa_{ii} + 2)} + \frac{N \rho_i \mu_i^2}{9 \varepsilon_0^2 M_i k_b T} W_j (1 - \gamma W_j)^{-1}$$

or

$$X_j = X_i + \frac{N \rho_i \mu_i^2}{9 \varepsilon_0^2 M_i k_b T} W_j + \frac{N \rho_j \mu_j^2}{9 \varepsilon_0^2 M_j k_b T} \gamma W_j^2$$

Since, the left hand side of Eq. (15) is a function of $X_j$, the usual variation of $X_j$ with $W_j$ can, however, be represented by

$$X_j = a_0 + a_1 W_j + a_2 W_j^2$$
Comparing the linear coefficients of $W_j$ of Eqs (15) and (16) one gets $\mu_i$ from

$$\mu_i = \left( \frac{9 \varepsilon_0^2 M_j k_B T}{N \rho_i} \times a_i \right)^{1/2}$$  \hspace{1cm} (17)

where $a_i$ is the slope of $X_i - W_j$ curve. But $\mu_i$ from higher coefficients of Eqs (15) or (16), which are involved with different factors like solvent effect, relative density effect, solute-solute associations, etc. are not reliable. The estimated $\mu_i$ along with the slope $a_i$ are placed in Table 3 in order to compare with hf $\mu_i$'s presented in Table 2.

4 Results and Discussion

The hf dipole moments $\mu_i$'s of all the isomers of anisidines and toluidines at different $W_j$'s of solutes from the measured data of Table 1 are calculated in terms of slope $\beta$ of $\sigma_i - W_j$ curve and $\tau_j$ estimated from Eqs (5) and (6) of the methods suggested. The variation of $\sigma_i$ with $W_j$'s of solutes are parabolic, having almost same intercept and slope as seen in Fig.1. This is probably due to same polarity of the molecules as observed earlier. They also meet at a point within $0.02 \leq W_j \leq 0.045$ indicating solute-solute (dimer) or solute-solvent (monomer) molecular associations under 9.945 GHz electric field. $\tau_j$'s of polar liquids were, estimated from the linear slope of $\sigma''_{ij} - \sigma'_{ij}$ curve as well as the ratio of slopes of individual variations of $\sigma''_{ij} - W_j$ and $\sigma'_{ij} - W_j$ curves of Figs 2 and 3. Both $\sigma''_{ij}$ and $\sigma'_{ij}$ are functions of $W_j$. Their variations with $W_j$'s were not linear as shown in Figs 2 and 3. The latter method appears to be a significant improvement over the other, as it eliminates polar-polar interactions at $W_j \to 0$. The correlation coefficients ($r$'s) and the % errors in measurement of $\tau_j$'s from Eq. (4) were calculated and presented in Table 2. $\tau_j$'s are found to agree well for both the methods and the % error involved in them are very low except m-toluidine, perhaps due to experimental uncertainty in the measurement of the relaxation parameters. It is interesting to note that unlike $\sigma''_{ij} - W_j$ curve, the variation of $\sigma''_{ij}$ with $W_j$ is identical with $\sigma_i - W_j$ curve. This fact suggests the applicability of the approximation of $\sigma'' \cong \sigma_i$ in Eq.
They are seen to increase from 232 INDIAN very little influenced by the frequency of the applied solution s. The -NH2 groups, which make angles 57°, alternating electric field of GHz range.

The theoretical dipole moments µ' of the polar molecules are calculated assuming their planar structures, from the vector addition of available bond moments of 4.40 x 10^-30, 1.25 x 10^-30, 4.93 x 10^-30 in Coulomb-meter(C.m) for respective OCH3, -CH3 and -NH2 groups, which make angles 57°, 180° and 142° with the C-atoms of parent benzene ring as placed in Table 3. µ' is found to differ from µ probably due
to existence of inductive and mesomeric moments of the substituent polar groups arising out of difference in electron affinity of two adjacent atoms. For all the polar compounds as referred to Tables 1 - 3 are planar ones and have the property of cyclic delocalized π-electrons on each carbon atom of the rings. The solvent C6H6 is also a cyclic and planar compound and has three double bonds and six p-electrons on its six carbon atoms. Hence due to their aromaticity, the resonance effect combined with inductive effect known as mesomeric effect are playing an important role among the substituent polar groups attached to the parent ring under static and hf electric field. The so called mesomeric moment is, however, caused by the permanent polarization of different substituent groups acting as pusher or puller of electrons towards or away from p-electrons of C-atoms attached to the parent rings. Thus a special attention is to be paid to get the conformational structures of the molecules of Fig.5 by µµ in terms of reduced bond moments by a factor µ'/µ's in agreement with µ to take into account of the mesomeric effects in them. Similar effects may also be observed in those molecules in the hf electric field. They are not calculated because they were found not to depend strongly on the frequency (f) of the alternating hf electric field of 10 GHz.

5 Conclusions
A convenient method for the determination of τ, of a polar liquid from the ratio of slopes of the individual variations of imaginary σ'' with W' with W's of solutes in a non-polar solvent is suggested in terms of measured data to avoid polar-polar interactions. The estimated τ when compared with the existing method using the slope of σ'' with σ' for different W's reveals the soundness of the method suggested. τ's are reliable and claimed to be accurate up to ± 10%. The computed µs (± 5%) in terms of the slopes β's of σ'W curves and τ's are found to agree with the static µ excellently. The static µ, as calculated from X - W curves are used to test the accuracies of permittivities of ε and µ measured in the static or low frequency electric field. The curves of X with W vary linearly and have a tendency to meet at a common point in the ordinate axis at W = 0, signifying the accuracy of the measured relaxation data once again. The % errors in terms of correlation coefficients r's of σ - W and X - W curves are very easy, simple and straightforward to compute. The deviations of the static µ and hf µ, from µ's as obtained from the available bond moments and bond angles of the substituent polar groups attached to the parent molecule imply
the existence of mesomeric and inductive moments in
the molecules. The comparison of $\mu_1$ with $\mu_2$ and $\mu_3$
on obtained from double relaxation method provides an
important information, that under the 10GHz electric
field only a part of the molecule is rotating. Thus the
present method of study in terms of measured dimensionless dielectric constants of Table 1 seems to give a
new insight of the molecular interactions in relaxation
phenomena.

References