9.1 DIELECTRIC BEHAVIOUR OF THE 1:1 COMPLEX

Mixtures of phenols and alcohols with acrylates in a non-polar solvent certainly show a specific interaction, characterised by the modification observed in the hydroxyl as well as carbonyl spectrum. A linear association is a straight forward assumption which is quite valid in this type of complexes, since a bent configuration leads to a large destabilization of energy and highly unfavoured. Further, such a bent configuration also leads to the possibility that the two H-bonding molecules do not lie in the same plane, in which case the total dipole moment of the complex, will be high. This would result in

\[ \mu_{ab}^{\text{Experimental}} < \mu_{ab}^{\text{Theoretical}} \]

which is not the case in our studies. There is another possibility that in some cases the H-bond might be formed at yet another site of the molecules outside the carbonyl group. However, such H-bonds formed are generally very weak than those formed with lone pairs of electrons as proton acceptors\(^1\). In liquid phase complexes, the possibilities
of mutual orientations of the partners are often more numerous than in the solid phase and hence Huyskens\textsuperscript{2} suggested a statistical dipolar method for finding the most probable structure. For different assumed structures, the dipolar increments $\Delta \mu$ are calculated. The most probable structure is that wherein one obtains the most coherent evolution of $\Delta \mu$ values with similar characteristics of the complexes like H-bond enthalpy. Such calculations, for the systems studied here, favour the structure dictated by generalised hybridization model namely along the $sp^2$ lone pair direction of the carbonyl group. Further, this is in agreement with the calculations of Schuster\textsuperscript{3} who showed that the potential energy is minimum when the H-bond is directed along the lone pair direction (within 1 kcal. limit). The change in the dipole moment during the rotation of the hydroxyl molecule as a whole around the carbonyl oxygen calculated by the method of Pople and Segal\textsuperscript{4} showed that in structures with some orientation of the functional groups forming the H-bond, the arrangement with the smallest dipole moment has the lower energy. Hence if there is no steric hindrance to the free rotation of the molecules around the
H-bond, then it is the position of the dipoles that dictates the stable configuration. The dipole moment of the 1:1 complex of the systems studied were calculated for the most stable configuration (Fig. 9.1).

If \( \mu_a \) and \( \mu_b \) are the dipole moments of the proton donor and the proton acceptor determined in the solvent, \( \mu_{ab} \) is the dipole moment of the 1:1 complex. \( \theta_a \) and \( \theta_b \) are the angles made by the \( O-H\cdots O \) axis with the dipole vectors \( \mu_a \) and \( \mu_b \) respectively, then the dipolar increment \( \Delta \mu \) is

\[
\Delta \mu = \left[ (\mu_{ab})^2_{\text{expt}} - (\mu_b \sin \theta_b - \mu_a \sin \theta_a)^2 \right]^{1/2} - \mu_b \cos \theta_b - \mu_a \cos \theta_a
\]

Table 9.1 gives the values of \( \theta_a, \theta_b, \mu_a, \mu_b, \mu_{ab} \) and \( \Delta \mu \) for all the systems studied.

Dipolar increment for 1:1 complexes. Phenols (alcohols) + Methyl acrylate.

<table>
<thead>
<tr>
<th>System</th>
<th>( \mu_a )</th>
<th>( \theta_a )</th>
<th>( \mu_{ab} )</th>
<th>( \Delta \mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl acrylate +</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) p-cresol</td>
<td>1.73</td>
<td>42°</td>
<td>2.6485</td>
<td>0.4003</td>
</tr>
<tr>
<td>2) p-Chlorophenol</td>
<td>2.25</td>
<td>20°</td>
<td>3.4240</td>
<td>0.2511</td>
</tr>
<tr>
<td>3) Pentan-1-ol</td>
<td>1.78</td>
<td>42°</td>
<td>2.6029</td>
<td>0.3603</td>
</tr>
<tr>
<td>4) Propan-2-ol</td>
<td>1.72</td>
<td>42°</td>
<td>2.4556</td>
<td>0.1732</td>
</tr>
<tr>
<td>Ethyl acrylate* + p-Fluorophenol</td>
<td>2.15</td>
<td>20°</td>
<td>3.4399</td>
<td>0.4195</td>
</tr>
</tbody>
</table>

\( \mu_a = 1.80; \theta_b = 60° \)
Fig 9.1 1:1 Complex model for evaluating $\Delta P$ of carbonyl + phenol (alcohol) system.
Table 9.1 shows that for all the systems, the values of dipolar increment is $0.1 < \Delta \mu_a < 0.5$. Comparison of these values with those obtained by Sundaresan et al.\textsuperscript{5} and Varadarajan et al.\textsuperscript{6} for ester + phenol systems, shows that, $\Delta \mu$ is less by more than 50%. This dipolar behaviour could now be analysed from the theoretical point of view. A rough estimate of the value of the contribution of the displacement of the proton in the dipole moment of a complex made by Huyskens and Hernandez\textsuperscript{7} from the bond distance relationship with the frequency shift of the $A$–$H$ bond yields a remarkable conclusion, namely that 50% of the dipolar increment is contributed by the proton displacement ($\Delta \mu_H$) and the balance by the transfer of electronic charges. Mulliken's charge transfer theory, predicts a compensation of $\Delta \mu_H$ by the electron displacement of $\sigma_{O-H}$ bond and hence this entire $\Delta \mu$ could be attributed to charge transfer ($\Delta \mu_{CT}$) only. This concept was further developed by Ratajczak\textsuperscript{8,9} and evidences for charge transfer complex formation were found in as much as the relation between the change in the transition moment of the $O$–$H$ stretching vibration and the dipolar increment due to H-bond is concerned. As discussed earlier, in the introduction, this seemed to be a good
experimental justification of invoking Mulliken's theory for such complexes. However, Shanmugasundaram and Mohan\(^1\) failed to observe the characteristic absorption band in the ultraviolet region in such complexes. Further, the mutual polarization of the bonding atoms would give a component of dipolar increment along the direction of proton displacement. By treating the polarizability of a bond as the polarization occurring at the meeting point of the X-ray radius of the bonding atoms in the line joining the two atoms, it is possible to calculate the approximately the mutual polarization\(^1\)\(^1\). This works out around 0.1D which is more or less than that obtained as \(\Delta\mu\) presently. This only indicates that though the charge transfer is highly unlikely the anion field leads to an increased dielectric polarization. This should have a profound effect on the IR spectrum.

### 9.2 IR BEHAVIOUR OF 1:1 COMPLEXES OF PHENOLS + ETHYL (METHYL) ACRYLATE

In a non-polar solvent like benzene or carbon tetrachloride, it has been found that only 1:1 complex dominates. The 1:2 complex is either absent or appears rather weakly only when the proton donor concentration is high. With the knowledge of the relative concentration of the free acrylate the
C=O absorption of the free carbonyl in each solution was calculated and subtracted from the measured spectrum of solutions. The remainder spectrum represents the absorption of the 1:1 complex in solution, of course, when the higher order complexes are considered negligible. The values of absorbance were calculated at several frequencies and plotted to give the calculated spectrum (Fig. 9.2) (representative sample for chlorophenol alone is given). It is found that the half-width of the 1:1 complex is larger compared to the free carbonyl spectra and there is a large increase in the intensity of the complexed carbonyl band. Assuming that the vibration is a pure stretching mode, the bond moment derivative is obtained as

\[
\frac{d\mu}{dr} = \frac{1}{m_C} + \frac{1}{m_O} \left( \frac{d\mu}{dQ} \right)^{-1/2}
\]

and

\[
\frac{d\mu}{dQ} = + \frac{3 C \cdot 1000 \text{ A}}{N_A \pi} 1/2
\]

where \( m_C \) and \( m_O \) are the masses of carbon and oxygen atoms. \( A \) is the observed intensity in litre mol\(^{-1}\). \( C \) is the velocity of light and \( Q \) is the normal coordinate.
Fig. 9.2 Calculated carbonyl spectra of Methyl Acrylate in para chlorophenol + carbon tetrachloride.
The intensity increase ratio is given by

\[
I_R = \frac{\frac{\langle d\mu \rangle}{dr}}{\left( \frac{\langle d\mu \rangle}{dr} \left. \right|_{C=O} \right)_\text{free}}^{2}
\]

A value of \( I_R > 2 \) is found in all systems studied here. This increase in intensity could be explained on the basis of the pulsed cloud charge model of Boobyer and Orville Thomas\(^\text{12}\). The induced moment of the O–H bond on the lone pair charge cloud of the carbonyl is a maximum on linear hydrogen bond formation which enhances the IR intensity. The equilibrium geometry of the O–H…O=C bond calculated by the PCILO method\(^\text{13}\) yielded a value of \( R_{\ldots}O = 0.271 \) nm. This value along with \( \frac{\langle d\mu \rangle}{dr} \), the dipolar increment due to polarization works out to be around 0.2D in such cases. Further, the dipole moment of the complex phenol + acetone, calculated by the PCILO method\(^\text{14}\) is 3.63D which again yields a dipolar increment of 0.25D only and the charge migration from the proton acceptor to proton donor in such complexes was calculated to be around 5 per cent. These evidences support our earlier conclusion that only polarization interaction is predominant in such type of complexes.
9.3 CONTINUOUS SPECTRA AND POLARIZABILITY

The theoretical studies of Pfeiffer et al.\textsuperscript{15} showed that the distribution of electric fields in solution polarizes the easily polarizable H-bonds and causes an IR continuum. Further, the symmetry of the H-bond is found to be decisively determined by the induced field and bond transition moments. The reaction field always favours the structure with greater dipole moment. In our studies, it is found that the polarity of the environment influences the polarizable H-bonds and causes an intense continuous absorption spectra in the region of 1000 cm\textsuperscript{-1} to 1200 cm\textsuperscript{-1} (Figs. 9.3 and 9.4). Hayd et al.\textsuperscript{16} calculated the continuum for different O—O bond lengths and showed that for a mean field strength of 5x10\textsuperscript{6} V/m and for a distance of 2.6 Å, a continuum is expected around 1000 cm\textsuperscript{-1}. As indicated earlier, the \( R_{O-O} \) is calculated for our systems as 2.6 Å. Hence the calculated continuous absorption is in very good agreement with our experiment. The continuum observed by Pawlak and Sobczyk\textsuperscript{17} with carboxylic acid in the region of 1500–800 cm\textsuperscript{-1} also confirms the existence of the polarizable H-bonds in such systems. It could further be seen that if chloroform is used as the solvent, instead of benzene, the same continuous absorption
Fig. 9.3 Continuous absorption spectrum of para nitrophenol + Ethyl Acrylate system.
Fig. 9.4 Continuous absorption spectrum of para fluorophenol + Ethyl Acrylate system.
Fig. 9.5 Continuous absorption spectrum of para nitrophenol
Ethyl Acrylate system in Benzene and chloroform.
band intensities, the characteristic frequency at 1700 cm\(^{-1}\) for the 1:1 complex is no more sharp but the carbonyl band is alone broadened (Fig. 9.5) in systems with phenols and acrylate. This is obvious since the reaction field of the solvent chloroform, rather increases the polarizability of the H-bond, while inhibiting the formation of a specific complex. It is expected that if the H-bond becomes stronger and a partial proton-transfer takes place, this continuous absorption should shift to higher wave numbers.

To conclude, it has been demonstrated from our experiments with dielectric polarization and IR studies that systems of \(\text{O}---\text{H}---\text{O} \equiv \text{C}\) are not of the charge transfer type, but only polarization interaction takes place.
REFERENCES

8. Ratajczak, H., J. Physics, 76, 3000 (1975),