CHAPTER V

HYDROSTATIC AND DEPOLARIZING STUDIES OF
ACO AND AN-TYMBENZENE

5.1 Azobenzene

5.1.1 Introduction:

Hysteresis-like hysteresis loops were reported in the azobenzene liquid phase by Williams and Heilmeyer in 1936. It melts at 62°C. Above T\textsubscript{m} azobenzene is an isotropic liquid. From the crystal structure point of view, there are two forms of azobenzene which have trans- and cis configuration of the molecule. The molecular weight is 162 and the molecular structure of trans and cis C\textsubscript{12}H\textsubscript{10}N\textsubscript{2} is given as

trans

\[
\begin{align*}
\text{trans} & \\
\text{cis} & 
\end{align*}
\]

It crystallizes sharply in alcohol into orange red monoclinic flakes. The monoclinic unit cell has the lattice parameter a = 12.2 ± 0.04 å, b = 9.77 ± 0.02 å.
c = 15.40 ± 0.04 Å and β = 114.4° with four molecules or unit cell. The space group is \( C_{2h}^{5} \) (P2\(_1\)/a) and further it has centre of molecular symmetry. The volume of the unit cell is 937 Å\(^3\). The centers of symmetry in these molecules lie at the points (000) and (001/2), while two other molecules in the (010) plane, have symmetry centres at (1/2, x, 0) and (1/2, -x, 0). The above crystal structure of the trans form of azobenzene has been determined by quantitative x-ray investigation (2). Total number of electrons per unit cell = 304. The \( N-N \) distance is 1.25 ± 0.05 Å.

The chief points of interest in azobenzene structure lie in the difference in orientation and apparently also in the structure, of the two molecules which contribute to the asymmetric unit of the crystal; and in the dimensions and valency angles concerned with \( C-N \) and \( N-N \) linkages. Considerable differences in orientations relative to the crystal axes are found for these two molecules. One is practically flat but in the other rings lie in the different planes 0.32 Å apart. In the later molecule \( N-N \) link is inclined to the plane of the ring at 15°, representing a rotation of the ring from the planar position about the \( C-N \) link of about 17°. Molecular polarizability for the \( C-N \) and \( N-N \) bond (3) has been calculated for azobenzene

\[
\alpha_{\perp} = 1.0 \times 10^{-3} \quad \alpha_{\parallel} = 1.2 \times 10^{-3}
\]
where $\chi$ is molecular polarizability tensor and $\chi_1$ being along the long molecular axis. From the measurements of the Kerr effect of azobenzene it has been estimated that (4)

$$\chi_1 = 34 \, \text{Å}^3 \quad \chi = 20 \, \text{Å}^3$$

The cooperatively study of electronic structure and spectra of cis and trans- azobenzene has been carried out by Severidge and Jaffe (5). The molecular structure of trans-azobenzene is known to be essentially planar in the solid state (6) and it is also assumed that the molecule is planar in solution as well (6). A crystal structure investigation (5) indicate that cis-azobenzene deviates somewhat from a planar conformation in the solid, and thus for the interpretation of solution spectra both planar and nonplanar conformations must be considered.

Jaffe and Severidge (5) during their electronic spectrum study of cis-azobenzene gave the most consistent interpretation that it assumes a "propeller-shaped" conformation where in the phenyl rings are rotated out of the molecular plane on a "propeller" fashion maintaining $C_2$ symmetry. The planar $C_{2v}$ conformation did not give a satisfactory interpretation of the solution spectrum. Also compounds can be converted photochemically to the cis-form under certain conditions. Only the trans-isomers of compounds have been found to be mesomorphic.
Near ultraviolet and visible absorption spectra (10) of azobenzene have been studied extensively. From electronic structure and spectra (5, 11, 12) of azobenzene, transition energies, intensities and polarization have been computed (6) and SIR study (13).

Physical properties such as elastic constant, magnetic susceptibility, refractive index and density are studied by de Jeu for the azo and azoxybenzenes (14-17) extensively.

Hysteresis loop at low frequency (8 Hz) was observed in the isotropic phase of Azobenzene by William and Hellmier (1) during the course of study of possible ferroelectric effect in nematic liquid crystals and related liquids. Then the sample is solidified there is no hysteresis loop. Their interpretation was on the line that hysteresis could probably arise due to electrical conductivity having a strongly nonlinear relation between current and voltage or by the existence of spontaneous polarization oriented uniformly throughout the specimen by wall effects and change its direction in an electric field. However, it was later on, reported (18) to be unrelated with ferroelectricity. However, Meyer (19) had outlined a piezoelectric theory which accounted for the number of such nonlinear effects as observed above and suggested that polarization can be induced externally by a mechanical stress or an electric field, thereby changing the symmetry of the
system from non-polar to polar inducing polarization by surface or wall effect.

Complete study of the ultra-violet spectra of azobenzene has been reported by Dyok and McClure. The important conclusion was that the central bond in the lowest excited triplet state has a substantial barrier to intermolecular rotation.

4.2 Azobenzene:

4.2.1 Introduction:

Ferroelectric like hysteresis loops were observed in the liquid by Williams and Heilmeier (1) in 1966. 

Azobenzene has a molecular structure \( \text{C}_6\text{H}_4\text{N}_2\text{O}_2 \)

\[
\begin{align*}
&\text{N} = \text{N} \\
&\text{O} \\
&\text{O}
\end{align*}
\]

with mol. weight 168.23. It crystallizes into dirty yellow needles \( T_{\text{melt}} = 35^\circ C \). Above \( T_{\text{melt}} \) azobenzene is an isotropic liquid. Strong dipoles are associated with the azoxy group, taken to be 1.7 \( \mu \) and the angle between the dipoles and the long axis of the molecule was estimated from the molecular structure to be 65\(^\circ\) (4).

Some work \( (20, 21) \) has been done on the dielectric properties in microwave range of azobenzene, which does not exhibit a liquid crystal phase but its structure is the same as \( \beta \)-azoxyanisole minus the \(-\text{CH}_3\) end groups.
Comparative study of Nuclear spin lattice relaxation of azobenzene and azoxybenzene has been studied by Frede (22). The proton resonance absorption of azobenzene gives a strongly coupled spectrum and the recovery rates of the single lines are very similar. At temperature 50°C, spin lattice relaxation time T1 = 3.5, 1.4, 2.5 for the nucleus C1, C2, C3, H of azobenzene are nearly the same with activation energy \( Q_{\text{act}} \) (\( \text{KCal/mol} \)) = 4.9, 4.0, 3.2 respectively. Frede and Spoel (22) assumed that the internal rotation of the phenyl ring does not contribute significantly to the carbon relaxation rate. They inferred that the proton relaxation in azobenzene is dominated by the intermolecular interaction which contributes more than 70%.

Dielectric investigation of derivatives of azo-benzene and azoxybenzene have been examined by Axmann (20,24) and Waler and Seier (25). As the molecules of the azo-benzene derivatives - in contrast to those of azoxybenzene - do not possess a permanent dipole moment localized at the central group. This fact affects a qualitative difference in the relaxation spectra of these two types of compounds with one in the relaxation spectrum of these azo compounds there is no relaxation region corresponding to the reorientation of the mol axis about the short axis. In the direction parallel and perpendicular to the axis of nematic order the microwave dielectric dispersion regions align linearly, associated with the reorientation of the terminal groups, about the para axes of the benzene ring.
The ultraviolet spectra of the electronic states of azobenzene and azoxybenzene have been discussed and assigned by Bau, e. Polarization measurements of the uniformly oriented liquid crystal compounds were used as an aid in the measurements of the absorption bands. One of the important conclusions of this study is that the central band in the lowest excited triplet state has a substantial barrier to internal rotation.

5.3 Pyroelectric Investigation of Azobenzene:

5.3.1 Experimental:

Azobenzene used for these experiments was obtained from BDH Chemicals Ltd, Poole, England. The films of azobenzene of thickness 100 μ, and area 16 mm² were investigated using transparent electrodes for poled and unpoled samples. The poling was done at 5, 6 and 8 kV/cm respectively in its isotropic phase (100°C) (Heat "0.5°C") for one hour and then it was suddenly cooled to room temperature with field still applied. The pyroelectric studies of these films were done by using dynamic current method using electrometer amplifier discussed in detail in Chapter II.

5.3.2 Results and discussion:

Measurements of pyrocurrent have been attempted from room temperature to the melting point of Azobenzene as shown in Fig. 5.1. There is no consistency in the sign
S.I.

PYROCURRENT VS. TEMPERATURE OF AZOBENZENE FILM.
of current in the heating and cooling cycle however as a
reversal in the sign of current is noticed for both cycle
at different temperatures. It will not be safe to conclude
that pyroelectricity is present in this sample for the
reason habit is non-polar in structure. However, the
poling seems to conspicuously effect the observation of
these measurements. The the opposite sign in the current
in heating and cooling cycle is observed for a larger range
of temperature. Again, it is not to be confused with true
pyroelectric behaviour which is characterized by opposite
sign of the current in heating/cooling cycle. However,
the present observation in the light of the doubtful ferro-
electric hysteresis and domain structure (1) can be under-
stood in terms of surface pyroelectricity. Such an effect
has been shown to be possible in dielectric films (26) due
to the presence of surface charges in the form of layer
near the glass plate which has temperature dependence. In
non-polar liquid crystal films and even in isotropic liquids
such an effect has been considered valid (27) due to the
strain conditions of the film and curvature strain leading
to the origin of surface charge, including surface pyro-
electricity.

3.4 Dielectric Study of Azobenzene:

3.4.1 Experimental:

A film of azobenzene of thickness 130 μm poled with
poling field 2 MV/cm were used for the dielectric studies.
These films were thoroughly examined by microscope to check
any physical faults such as air holes; shorting if any, were checked by ammeter. Sample holder (Fig. 2.4) used for the measurement is given in detail in Chapter II.

Double shielded wires were used for connections. Wayne Kerr 706 universal bridge 76-2 was used for dielectric study at different frequencies (100 kHz to 10 MHz) with microwave source and detector which again is described in detail in Chapter II.

6.4.3 Results and Discussion:

The complete dielectric studies of azobenzene in the form of film was extensively studied by us through the dielectric parameters such as dielectric constant \( \varepsilon' \) tan\( \delta \) and dielectric loss coefficient \( \varepsilon'' = \varepsilon' \tan\delta \) as a function of frequency at different temperatures (solid and isotropic phase). The dielectric constant as function of temperature dependence at fixed frequency (1.5 kHz) from room temperature to its melting point was carried out in order to understand the nature of phase transition and variation of the dielectric parameters in the two phases.

The temperature dependence of dielectric constant and tan\( \delta \) of azobenzene at fixed frequency (1.5 kHz) is shown in Fig. 5.3. The liquid phase transition of the material is clearly indicative in \( \varepsilon' \) plot at temperature 60°C. The drastic changes in the plots suggest first order phase transition. The tan\( \delta \) as shown in Fig. 5.3 increases sharply from 0.2 to 1.0 near 60°C showing the liquid phase.
FIG. 5.2. DIELECTRIC CONSTANT VS. TEMPERATURE OF AZOBENZENE FILM.
FIG 53 TAN δ VS TEMPERATURE OF AZORENZONE FILM
of the material. Though azobenzene itself does not show liquid crystal phase, the usual behaviour of first order phase transition near solid to liquid phase is observed. The transition temperature around 60°C, indicative of the trans-form of azobenzene. Since the dielectric anomaly is pronounced at the phase transition it can be inferred that this transition is associated with dielectric, mainly because in the two phases the difference in the value of ε is significant. The plot of tanδ versus temperature has also similar behaviour, that with a steep change in loss at the transition temperature as usually, the loss is higher in the liquid phase than in solid phase of azobenzene. The poling of the sample seems to decrease the value of tanδ in the liquid phase, but increases the loss in solid phase. With the increase of the temperature both the loss and dielectric constant are decreasing, it can be believed that conductance losses are predominant and are electroconductive nature.

The plot of tanδ as a function of log of frequency is shown in Fig. 5.4. The dielectric loss has been measured at 20°C (solid phase), 50°C, 75°C and 90°C (isotropic phase) for poled and unpoled samples. Azobenzene is more lossy in the isotropic phase. The dielectric loss increases with temperature and poling field showing a broad maxima.

The dielectric loss coefficient at different temperatures 20°C, 60°C, 75°C and 90°C for unpoled samples
Fig. 5.4. LOSS TANG VS. FREQUENCY AT DIFFERENT TEMPERATURE - AZORENZONE FILM.
end 20° and 75°C for poled film (2 KV/cm) is shown in Fig. 5.5. The plot clearly indicates that we are dealing exclusively with conductance loss. The loss is decreasing with increasing frequency. Therefore, the values of $\varepsilon''$ would be mainly due to a direct current conductance of space charge polarization.

The plot of $\varepsilon'$ is shown in Fig. 5.6 at two different temperatures 20° and 60°, for unpoled films and 20°, 60° and 76°C for film poled at 2 KV/cm and 3 KV/cm. The dielectric constant decreases with increasing frequency and temperature. The effect of poling is also obvious from the plot. The coie coie plot as function of $\varepsilon''$ vs $\varepsilon'$ for azobenzene film at two different temperatures 20° and 60° is given in Fig. 5.7.

5.5 Dielectric study of Azooxybenzene:

5.5.1 Experimental:

Azooxybenzene used for the dielectric study have been obtained from Merck, England. A film of azoxybenzol of thickness 20 μ sandwiched between two glass plates was deposited with transparent SnO$_2$ electrodes of area 1 cm$^2$. The above film was poled at 2, 3 and 5 KV/cm respectively by the ac electric field. Dielectric parameters such as $\tan \delta$, dielectric constant $\varepsilon'$ and dielectric loss coefficient $\varepsilon''$ at different frequencies in the range 100 KHz to 10 MHz was done by using Wayne Kerr Universal $\Delta$ bridge
FIG 5.6. DIELECTRIC CONSTANT vs FREQUENCY AT DIFFERENT TEMPERATURES OF AZOBENZENE
with Wayne Kerr Source and detector, were evaluated at different temperatures. Double shielded wire was used for the connection. Above films were thoroughly examined before the experimental studies.

5.5.2 Results and discussion:

The temperature dependence of dielectric constant and tan δ at fixed frequency (1.5 kHz) is shown in Figs.5,6 and 7. The dielectric constant and dielectric loss increased linearly with temperature and with polarizing field increasing in magnitude from 3, 4, and 5 kV/cm. The change in the slope becomes more prominent with increasing polarizing field at 30°C. The dielectric loss varies very slightly from 1.02 to 3.3 at polarizing field 4 kV/cm at 30°C to 50°C. The change in slope can be related to some different sort of molecular motion other than in solid phase. This temperature region where molecular motion drastically change, is the isotropic phase of the material. Inclination of the slope of the dielectric constant at 30°C also increases with the polarizing field which is applied perpendicular to the long molecular axis of the material which is parallel to surface of the electrodes. The strong dipole moment associated with the azoxy group (1,7,3) makes an angle of 65° with the long molecular axis of the material (4). The dispersive region can be correlated with the dielectric rotational behaviour of (1 = 0) group around its molecular axis.
FIG. 58. DIELECTRIC CONSTANT VS. TEMPERATURE OF AZOXYBENZENE FILM (POLED)
FIG. 5.9. TAN $\delta$ VS. TEMPERATURE OF AZOXYBENZENE FILM (POLED)
The dielectric constant decreases with increase of frequency as plotted in Fig. 5.10 and increases with increase of temperature and poling field. The plot shows the variation of unpoled and poled films of azoxybenzenes at two different temperatures: 18°C (solid) and 33°C (liquid) phase. The change of slope observed in ε' plot at lower frequency side,

azoxybenzene film of thickness 50 μm was poled in its isotropic phase with poling field 2, 3, and 5 kV/cm respectively. The film was suddenly cooled to its room temperature, with field still applied to the film. The film was poled for one hour. The dielectric properties such as loss tangent (tanδ), dielectric loss coefficient ε'' = ε' tanδ and dielectric constant ε' were plotted as a function of log of frequency from 100 kHz to 10 MHz at different temperatures. Fig. 5.11 shows the plot of tanδ as a function of log of frequency at two different temperatures 18°C (solid form of the sample) and 33°C (liquid form). As can be seen, there is considerable broadening of the curve of the dielectric loss at particular frequency range. tanδ increases with temperature. The material is more lossy in the isotropic phase than in the solid phase. With the increasing of the poling field from 2, 3 and 5 kV/cm, the loss increases.

The plot of dielectric loss coefficient ε'' = ε' tanδ versus log of frequency is shown in Fig. 5.12, at temperature
FIG. 5. DIELECTRIC CONSTANT vs. FREQUENCY AT DIFFERENT TEMPERATURES OF AZOXYBENZENE FILM
FIG. 5.11. LOSS TANGENT VS. FREQUENCY AT DIFFERENT TEMPERATURES OF AZOXYBENZENE FILM (POLED).
for different poling fields 1.3 and 5 kV/cm and unpoled sample film of azoxybenzene. The frequency at which the value of $\varepsilon''$ is maximum ($\omega_{\text{max}}$) increases with increasing temperature and shifts to the lower frequency side with increasing poling field. At lower frequency range (i.e., kHz), $\varepsilon''$ increases sharply with increasing frequency, but at higher frequency, decreases slowly. The minimal frequency for relaxation absorption becomes lower with increasing poling field. Relaxational absorption observed at low frequency would be due to the rotational motion of the azoxy group around the long molecular side.

The dielectric experimental study is further confirmed by plotting cole-cole diagram i.e., $\varepsilon''$ versus $\varepsilon'$ as shown in Fig. 9.13. The plot has been shown at two temperatures 15° and 33°C (for poled and unpoled samples), with poling field 5 kV/cm. The relaxation is more pronounced at higher temperature and with increasing field.
FIG. 5.12. DIELECTRIC LOSS COEFFICIENT VS. FREQUENCY AT DIFFERENT TEMPERATURE OF AZOXYBENZENE FILM.
FIG. 5.13. COLE COLE PLOT (\(\epsilon''\) Vs. \(\epsilon'\)) OF AZOXYBENZENE FILM.
REFERENCES


