PART I

REVIEW OF LITERATURE IN DIELECTRIC STUDIES
CHAPTER 1

A Brief Review Of Literature In Dielectric Study Of Liquids And Solutions

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CHAPTER-1

A BRIEF REVIEW OF LITERATURE IN DIELECTRIC STUDY OF LIQUIDS AND SOLUTIONS

1.1 INTRODUCTION

The space around us is filled with a kind of never ending activities. These whole restless activities create an inherent urge to know and understand the mystery of nature. The natural phenomenon involves the interaction between matter and energy. Out of the three states of matter, the liquid state offers a peculiar compromise and is latent with more potential. After the society's successful discussion on liquids and liquid mixtures, many people, perhaps, drew the conclusions that the major quantitative experimental works on liquids offer direct effective information about the molecular interactions.

The nature and strength of molecular interactions in liquids have been established as the cause for the behavioural change in chemical compounds. The extent of recognition of the most suitable and strongly proven structures involving certain chemical bonds and interactions are based on quite a number of qualitative and quantitative test utilising independent physical methods. IR, NMR, Ultrasonic and Dielectric Spectroscopy are a few among them.

Dielectric Spectroscopy is a powerful tool for investigating the transient species that occurs as intermediates in chemical and physical processes. In particular, vital information could be obtained from microwave dielectric studies. The present work deals with dielectric studies employing Frequency Domain and Time Domain techniques. The present chapter provides a survey of the principles, practice, and results of the study of molecular
systems by dielectric methods. Dielectric method is the non quantal response of
the material to the electric field ranging from the static field to those of
microwave.

Associated mixtures are defined as those in which there is
chemical evidence for the association of particles of at least one of the
components either with each other (self-association) or with those of another
component (mutual association). The study of mixtures is most interesting. It is
possible to approach the description of such mixtures in terms of the properties
of the components in a formal thermodynamic manner or with respect to the
molecular interaction.

The state of aggregation of molecule in a continuum depends on
the type of chemical bond, molecular geometry, mutual effect between atomic
groups, nature of complexes etc. A system of electrically charged molecules
involves the process of molecular interaction. The spatial arrangement of
electrically charged atoms and molecules in the system is perturbed by the
influence of existing physical conditions.

The dielectric properties of a substance such as dielectric
constant, dielectric loss, relaxation time have provided an insight into the
structure of the molecules of the system. In liquids, the molecule has rotational
freedom and its dispersion occurs at microwave frequency. Hence studying the
dielectric properties at microwave frequency will reveal the dielectric
relaxation of polar molecules and its variation with respect to the interaction
with the neighbouring polar as well as non polar molecules.

1.2 POLARIZATION AND DIPOLE MOMENT STUDIES

The spectroscopic studies give a clear picture about the formation
and strength of molecular interaction. The nature and structure of the liquid
mixtures can be better understood by the dipole moment determination. Many authors (2-9) applied successfully the determination of dipole moment of the hydrogen bonded complexes to have a clear understanding of the nature of the interactions. From the dielectric studies and molecular dipole moment data, one can determine the group moments of organic molecules. Price et al. (10) have consolidated the group moments of organic polar liquids and identified the structure of functional groups. A comparison between linear H-C = N and substituted aliphatic cyanides show i) lowering or ii) incrementing of moments presumably due to (a) dipole formed at farther points or (b) induction and analogous polar structures.

In the case of aromatic compounds, the charge distribution in the ring is influenced by the substituents towards ortho and para positions when the aryl-alkyl moment difference is positive, otherwise the direction is to the meta position (11). The formation of complex modifies the charge distribution of the participants. The extent of this modification may be understood from dipole moment increment or enhancement. Sabesan et al. (12) have explained the enhancement values calculated on the basis of the tautomeric equilibrium existing in the system p-chlorophenol and ethyl acetate.

Huyskens et al. (13) have determined the dipole moment values for forty complexes between substituted phenols and substituted pyridines. The dipole moment studies of different functional groups indicate the changes in the moment values, which have been utilised to assess the molecular configuration of the functional groups. (14,15)

Brink et al. (16) have studied the dipole moment of 2, 3, 4 trimethyl-3-pentanol in solution. The dielectric properties of 2, 4 methyl-cyclohexanols have been studied (17) and the molecular geometric dependence of the dielectric properties of alcohols are elucidated through the linear correlation factors.
Srivastava and Sinha \(^{(18)}\) have determined and compared the electric dipole moment of o-chlorophenol along with some alcohols. Gough and Price \(^{(19)}\) have analysed dielectric properties of some cryptophenols in p-dioxane and their effect on the values of dipole moment. Electric dipole moments of some amines and anilines have been evaluated. The dipole moment is found to be higher in p-dioxane than in benzene, p-xylene and cyclohexane \(^{(18)}\). This behaviour has been attributed to the hydrogen bonding and mesomeric effects in amines and anilines.

Seigal et al. \(^{(20)}\) have studied co-operative proton jump in hydrogen bonded chains between phenols and amines in benzene. For p-chlorophenol the larger \(< \mu^2 >\) in the absence of amines is explained in terms of co-operative protons jump, which is governed by the principle of random walk. A detailed study by Sabesan et al. \(^{(21)}\) on benzaldehyde, phenol mixture in carbon tetrachloride and carboxylic acid, amine mixture in benzene, discussed about the nature of hydrogen bonding and charge transfer interaction.

In contrast to the complete transfer of proton in an acid-base equilibrium, some authors \(^{(22)}\) have suggested that the charge delocalisation is responsible for the increment in dipole moment. This point has been strengthened with the fact that the properties of hydrogen bonded systems depend upon the ionisation potential of electron donor molecule \(^{(23-25)}\) or upon the acidity and basicity of the components which are in some way related to the election affinity and ionisation potential of these components. Hence the determination of dipole moment of the adducts may give more information regarding the nature and structure of these complexes.

Besides the structural analysis of molecular group from the studies on dipole moments, the study of dielectric loss and relaxation processes throws more light on the functional groups and overall structural aspect of molecules.
1.3 DIELECTRIC ABSORPTION AND RELAXATION STUDIES - MICROWAVE FIELD

Dielectric relaxation behaviour of liquids and solutions in the microwave region provides meaningful information about the self association, solute-solvent and solute-solute type of molecular association among polar molecules. Relaxation mechanism associated with the absorption of energy consequently involves the reorientation of different groups in a molecule. Researchers have applied both Frequency Domain and Time Domain Techniques to the study of relaxation behaviour.

1.3.1 FREQUENCY DOMAIN TECHNIQUE

The method of Gopalakrishna subsequent modified by Vij et al. is popularly known as the dielectric constant study at single frequency and concentration variation method. About twenty seven liquid organic halides in dilute solutions in a variety of solvents had been investigated at different frequencies by Heston et al. Branin and Smyth have systematically investigated about twenty five liquid organic halides at 10 cm microwave and have discussed the distribution of relaxation time. The process of dipole orientation and viscous flow has been compared on the basis of absolute rate theory. Madan have studied microwave absorption and relaxation processes of some aliphatic molecule, mono substituted benzenes and binary mixtures of mono substituted benzenes in dilute solutions. The effect of temperature variation on the dielectric and viscous relaxation processes and thermodynamic properties for the activated states have been analysed.

Keniti Higasi and Higasi et al. have done pioneering works on dielectric relaxation and molecular structure of liquids. Sharma and Gandhi have analysed certain binary mixtures of non-rigid molecules in
benzene solution at 3 cm microwave and at different temperatures using the principles of Higasi et al. (38)

C. K Mishra et al. (43) have studied the dielectric relaxation time of ortho, meta, para tolualdehyde and cuminaldehyde at different temperatures in benzenes. They have reported that the molecules relax by molecular as well as intramolecular rotations and the dipole relaxation is a co-operative process. They also have suggested that the solid rotator phase exists on solidification. Mehrotra et al. (44) have investigated anisaldehyde, salisaldehyde and o-chlorobenzaldehyde for their dielectric behaviour by Gopalakrishna method (26). Desphande et al. (45), Walker et al. (46) and Vij and Singh (47-48) have made a similar study on different aldehydes and have analysed the results in terms of molecular relaxation time and intra-molecular relaxation time.

Sharma et al. (49) have studied the temperature dependence of dielectric relaxation of acetophenone, pyridine and their mixture in benzene, while dielectric measurements on aromatic ketones have been made by various workers (50, 51). Madan et al. (52) have studied the dielectric absorption of dilute solutions of rigid molecule pyridine, quinoline, isoquinoline and their mixture in benzene. They have found that in the mixture, the order of degree of polarization decays exponentially just as it does with single component system.

The present study has a direct correlation with the works of Saxena et al. (53-56) Direct measurements have been carried out in 1:1 mixtures of i) some acetates and phenols in carbon tetrachloride ii) pyridine and phenols, quinoline and phenol iii) p-halophenol etc in non polar solvent of different concentration at 9.8 GHz. In all such cases, the nature of relaxation and associative structural aspects of N---OH bond have been analysed. Vir Singh Rangra and Sharma (57) have attempted to study the solute-solvent type of interaction with the mixture of N, N-dimethylacetamide with acetone.
The dielectric studies at microwave frequencies reveal two dispersion regions for mixtures of two polar liquids in dilute solution of non-polar solvents, which are clearly exhibited by Cole-Cole plot. This hypothesis has been supported by the recent works of Sharma and Gandhi \(^{(41, 43, 58)}\) and Nour et al. \(^{(59)}\) However, Vyas et al. \(^{(60-62)}\) and Madan have reported the presence of only one relaxation process in dilute solution of two polar liquids in non-polar solvents. Sharma et al. \(^{(63-68)}\) studied concentration dependence of the dielectric relaxation in the mixture of a number of dipolar liquids. Madhurima et al. \(^{(69)}\) have studied the binary mixture of methanol with ketones and nitriles in benzene at different microwave frequencies and have found interactive association between two species of the molecules.

Magee and Walker \(^{(70, 71)}\) have investigated phenol in a number of non-polar solvents and found that even at the lowest concentration the relaxation time of phenol is substantially lengthened by intermolecular association due either to solute-solute interaction or solute-solvent interaction. They have also investigated p-chlorophenol along with other substituted phenols for their dielectric behaviour. The dielectric relaxation times of chlorophenol and cresol have been studied by Ghosh \(^{(72)}\) in pure liquid state. Deogoankar et al. \(^{(73)}\) reported the experimental findings on the formation of molecular complexes through hydrogen bonding between each of β-picoline, quinoline, aniline and N, N, Dimethylaniline with o-chlorophenol.

Relaxation studies on phenyl acetonitrile and its para substituted has been carried out by Saxena et al. \(^{(74)}\) in different temperature ranges at 9.8 GHz and it has been reported that the addition of chloro, nitro groups at para position does not show any appreciable influence on the values of τ. On investigating the dielectric behaviour of some alkyl cyanides, Krishnaji and Mansingh \(^{(75,76)}\) have found that the distribution parameter decreased with chain length and becomes zero for n-propyl and n-butyl cyanides in the temperature range 30-60°C. Dielectric measurements on phenyl cyanide by
Poley \(^{(77)}\) yielded the distribution parameter \(\alpha = 0\) indicating the rigid nature of the molecule. Studies of Firman et al. \(^{(76)}\) on the permittivity and dielectric relaxation of benzonitrile, acetonitrile, and their mixtures in carbon tetrachloride have primarily evinced interest for the study of substituted benzonitrile.

The group moment of \(\text{C} \equiv \text{N}\) group in aromatic compounds has been investigated as 3.9 D, while group moment of acetonitrile \(-\text{CH}_2\text{CN}\) has been obtained as 3.5 D indicating the influence of sandwiching \(\text{CH}_2\) between carbon atom and \(-\text{CN}\) group. In an attempt to investigate systematically the influence of sandwiching \(\text{CH}_2\) between \(\text{C}\) atom and \(-\text{CN}\) on dielectric properties Frost and Smyth \(^{(79)}\) have studied phenyl acetonitrile and 1-naphthalene acetonitrile in dilute solution of benzene. They found that phenyl acetonitrile relaxed by molecular and intramolecular \(-\text{CH}_2\text{CN}\) group orientation and 1-naphthalene acetonitrile shows no evidence of group relaxation confirming the steric blocking \(-\text{CH}_2\text{CN}\) group. Hassan et al. \(^{(80)}\) analysed absorption of phenyl acetonitrile in pure liquid state and noticed the occurrence of molecular and intramolecular processes.

Rastogi et al. \(^{(81,82)}\) recorded the vibrational spectra of anthranilonitrile molecule and amino benzonitrile in different phases. Vibrational spectra of mono and di substituted benzonitriles have been studied in detail by many workers. Ultra-Violet absorption spectra of benzonitrile and substituted benzonitrile have been reported. \(^{(83)}\)

1.3.2 TIME DOMAIN REFLECTOMETRY

Using TDR dielectric properties in frequency range 10 MHz to 10 GHz over temperature range 0 to 15°C on nitriles have been studied by Mehrotra et al. \(^{(84)}\) Comparative dielectric study of mono-, di- and trihydric alcohols have been studied by R.J. Sengwa \(^{(85)}\) by TDR techniques. He has
analysed the intramolecular group rotation due to the breaking and the reforming of hydrogen bonds by considering the observed values and the corresponding dielectric dispersion models of the liquids containing different member of hydroxyl groups in their molecular structure.

Choudhari et al. (86) have used TDR in reflection mode to determine the complex reflection co-efficient for ethanol-ethylene glycol mixtures at different temperatures in frequency range 10 MHz - 10 GHz and found dielectric parameters that show a systematic change with concentration and temperature.

Puranik et al. (87) have studied t-butyl alcohol using TDR at different temperature in the range 30°C to 40°C. They have suggested that polymeric structure is more dominant and the hydrogen bonding is about 40% stronger in n-alcohol. In the study of dielectric relaxation parameters, the Kirkwood correlation factor of polar-polar liquid mixtures has a considerable significance in providing valuable information about solute-solvent interaction, especially when one component is parallel and the other antiparallel to the electric dipoles. The dielectric relaxation studies of a series of n-nitriles and water-methanol mixtures have been made using TDR. (88)

Kumbharkhane et al. (89) have investigated acetophenone-ethanol mixtures at various temperatures to understand the molecular interaction in the mixture by means of dielectric parameters. Temperatures and frequency dependent dielectric studies of p-fluorophenyl acetonitrile (FPA), methanol mixture using TDR have been made by Hosamani et al. (90). They have analysed it in terms of the Kirkwood correlation factor of pure FPA. Though FPA is highly polar, the value 0.4 for the correlation factor suggests antiparallel orientation of its dielectric dipoles. Addition of methanol to FPA is found to break the antiparallel orientation effectively leaving behind monomers and causing positive excess permittivity.
Sanjay et al. (91) have studied the complex dielectric spectra in the frequency range 10 MHz-10 GHz and have determined using the TDR technique the complex permittivity at various temperatures for DMSO-water mixtures and have attempted to explain the dielectric behaviour of this mixture by the hydrogen bonding model as suggested by Luzar. (92) N, N, dimethylacetamide (DMA) and water mixture are studied by Puranik et al. (93). They have reported the excess dielectric properties as a function of concentration of water, suggesting that the disappearance of dimmers or timers and leaving behind monomers is due to addition of water in DMA.

Dielectric properties of aqueous solution of acetonitrile in the temperature range 0 to 40°C have been studied by Helambe et al. (94). The excess permittivity activation energy, Kirkwood correlation factor of acetonitrile-water mixture is evaluated. The complex permittivity of aniline-methanol mixture for various temperatures as a function of frequency has been studied by Desphande and Mehortra. (95) They have found a strong interaction between solute-solvent molecules at low methanol concentration through hydrogen bonding.

Fornies et al. (96, 97) have studied the mechanisms of dielectric relaxation of ten primary amines at different frequencies. The influence of the chain length and the behaviour of the NH₂ group in the relaxation process are shown and their behaviour is compared with that of analogous alcohols.

Bertolini et al. (98) carried out a systematic study of dielectric properties of alcohol with water and alcohol with alcohol solution in the frequency range 10 MHz up to 10 GHz. The data obtained are discussed in terms of the strength and the associating effect of the hydrogen bond. He introduced a model based on the hydrogen bond dynamics, originally intended
to study the dielectric relaxation of pure liquids. It was tentatively extended to binary solutions.

Many other workers (99-104) have analysed rigid and non rigid branched organic polar liquids in mixtures, which though not having direct implication with the present work and systems, have also been surveyed to account for the accuracy and reliability of measuring techniques.

CONCLUSION

Perusal of Chapter I have shown a great variety of molecular behaviour remains to be adequately explored.
CHAPTER 2

An Overview Of Relevant Dielectric Theories Of Liquids And Solutions

2.1 Introduction

2.2 Theoretical consideration of static permittivity of liquids
   2.2.1 Debye's theory for static dielectric constant
   2.2.2 Onsager's theory for static dielectric constant
   2.2.3 Kirkwood's theory on static dielectric constant
   2.2.4 Association in liquids and Kirkwood's correlation factor
   2.2.5 Other theories relating dielectric constant and dipole moment
   2.2.6 Static dielectric constants of liquid mixture in solutions

2.3 Theoretical consideration of dynamic permittivity of liquids
   2.3.1 Theory of statistical dielectric relaxation
   2.3.2 Molecular interpretation of the dielectric relaxation times of associated liquids

2.4 Conclusion
CHAPTER 2

AN OVERVIEW OF RELEVANT DIELECTRIC THEORIES OF LIQUIDS AND SOLUTIONS

2.1 INTRODUCTION

Properties of dielectric materials are of interest to Scientists in various branches of Physics, Chemistry, Electrical Engineering and Biology. The interests of concern are of different aspects. An electrical engineer will require the dependence of dielectric loss on frequency and temperature in order to find substances, which are loss free in certain range. Physicists and Chemists on the other hand can use their knowledge to draw conclusion on the properties of molecules. For these, and for many other purposes, it is imperative to have a theory of dielectrics. The present Chapter is intended to give a systematic overview of the theories of the Dielectric Studies.

A large part of theoretical research in dielectric has been concerned with the effect of molecular interactions upon the dielectric behaviour. Mostly, the dielectric behaviour is described in terms of the dielectric permittivity and molecular dipole moments of the substances in local and non local fields. The calculation of dipole moments from the measured dielectric constant of the bulk material depends upon the molecular interaction with its neighbours and hence it gives the geometrical structure of the molecules, the polarities of their bonds, and significant shifts of electric charge in them.

The dielectric constant depends upon how polarizable a material is and the frequency of the applied field. The fall of polarizability is related to the decrease of dielectric constant and occurrence of absorption of electrical energy constituting dielectric dispersion. This behaviour is shown by the
frequency dependent dielectric loss. The static and dynamic dielectric mechanisms govern the behaviour of dipolar liquids and liquid mixtures. Debye \(^{(105)}\) elucidated the phenomenon of dielectric dispersion occurring in liquids containing polar molecules.

### 2.2 THEORETICAL CONSIDERATIONS OF STATIC PERMITTIVITY OF LIQUIDS

In general, the aim of the proposed theoretical models is to describe the dielectric behaviour of liquids by assessing the electric dipole moments and tracing their origin. The dipole moments either permanent or induced do depend on the external field and atomic and molecular structure of the dielectric substance. The dipole moment of liquids is a characteristic parameter of atomic and molecular polarization. The polarization is found to maintain equilibrium for a constant and for a very slowly varying external field. The dielectric constants appropriate themselves to such kind of time independent fields are termed as “static dielectric constants” with zero or negligible dielectric losses.

#### 2.2.1 DEBYE’S THEORY FOR STATIC DIELECTRIC CONSTANT

The Debye’s theory for the Static Dielectric Constant and dipole moment incorporates the Langevin method of finding mean moment and Boltzmann law of distribution of moments about an applied field. A basic relation for the static dielectric constant with the usual notations is given as

\[
\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{4\pi N}{3V} \left( \alpha_0 + \frac{\mu^2}{3kT} \right) 
\]

2.1

This relation, when \( \mu = 0 \), is reduced to the well-known Clausius-Mosotti equation for the optical refraction

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N \alpha_0}{3V} \text{ for non-polar materials.}
\]
A little difference, if any between $\frac{\varepsilon - 1}{\varepsilon + 2}$ and $\frac{n^2 - 1}{n^2 + 2}$ is due to the atomic polarization. This equation is extremely valid for gases, non-polar liquids and solids but not for dense liquids as it fails to reproduce the static dielectric constants. However, the dipole moment calculations from the static dielectric data show that the Debye equation holds good approximately to dilute solutions but not so to polar liquids. The inadequacy of equation 2.1 for polar liquids is due to the neglect of Lorentz inner field and local directional forces exerted by the neighbouring molecules. In order to overcome the inadequacy Lars Onsager suggested a better approximation by taking into account the internal field, due to long range interactions and improved the treatment.

### 2.2.2 ONSAGER'S THEORY FOR STATIC DIELECTRIC CONSTANT

This theory is restricted to polar liquids. A molecule of species is considered as a polarizable point dipole of moment $m_i$ at the centre of a spherical cavity of radius $a_i$ defined by $(4/3) \pi a_i^3 N = 1$ for the Avogadro Number $N$. The presence of spherical cavity in a homogenous medium of a static dielectric constant $\varepsilon_i$ limits the validity of the theory to liquids in which no strong forces are present. The internal field in the cavity is made up of two parts (i) the field in the empty cavity to be produced by the external applied field and (ii) the reaction field set up in the cavity by polarization through induced dipoles in its surroundings. The reaction field $R$ is assumed to be proportional to the total electric moment and dependent on instantaneous orientation of the molecule. The phenomenological generalization of the reaction field factor adds a polarizability term and renormalizes the dipole moment by introducing the optical dielectric constant ($\varepsilon_o$).

On the basis of the above assumptions, Onsager finally arrived at the following expression for the static dielectric constant,
\[
\left( \varepsilon_2 - \varepsilon_\infty \right) \left( 2\varepsilon_2 + \varepsilon_\infty \right) \varepsilon_2 \left( 2\varepsilon_2 + \varepsilon_\infty \right) = \frac{4\pi N P_i^2}{9 kT} \quad 2.2
\]

\( P_i \) - becomes the effective dipole moment of \( i \)th molecule in the gaseous state. For dense liquids, this expression is found to be more suitable than that of Debye's in predicting the static dielectric constant. In a convenient form, the resultant equation can be written as

\[
\frac{(\varepsilon_2 - 1)}{(\varepsilon_2 + 2)} \frac{(\varepsilon_\infty - 1)}{(\varepsilon_\infty + 2)} = \frac{3\varepsilon_2 (\varepsilon_\infty + 2)}{(2\varepsilon_2 + \varepsilon_\infty)(\varepsilon_2 + 2)} \frac{4\pi N P_i^2}{9 kT} \quad 2.3
\]

which differs from Debye's equation by a factor

\[
\frac{3\varepsilon_2 (\varepsilon_\infty + 2)}{(2\varepsilon_2 + \varepsilon_\infty)(\varepsilon_2 + 2)} \quad 2.4
\]

when \( \varepsilon_2 \) tends to \( \varepsilon_\infty \), this factor turns to be unity, reducing the expression 2.3 to the original form. Also on careful examination, the expression shows that when \( P_i = 0 \), it becomes Clausius Mosotti relation. Further, Onsager has extended the treatment \(^{(107)}\) and obtained an expression for the dilute solutions for a polar substance in a non-polar solvent. The static dielectric constant is then given as

\[
\varepsilon = \varepsilon_\infty + \frac{4\pi n_2 \mu_2^2}{3kT} \left( \frac{\varepsilon_2 (\varepsilon_\infty + 2)}{2\varepsilon_2 + \varepsilon_\infty} \right)^2 \quad 2.5
\]

The suffixes 2 and 1 denote the polar substance and non-polar solvent respectively. The mole fraction of polar solute molecule in a non-polar solvent is denoted as \( n_2 \) and other notations have the usual meaning.

Though inadequacies of the Onsager explanation as applied to non-associated liquids have been found to arise from the assumption of a
spherical shape for the molecules, it is possible to calculate the effect of size on polarization of the dipole molecules by considering them as ellipsoidal ones.

In spite of some set backs as stated above, the Onsager method of calculating dipole moment in many cases agrees with experimental values. The disagreement in some cases has been analyzed by Hoye and Stell \(^{(108)}\) and Chandler \(^{(109)}\) expressing the dielectric constant in terms of site-site distribution function. Frenkel \(^{(110)}\) also pointed out the disagreement between the dielectric constants calculated by equation 2.5 and the observed constants.

2.2.3 KIRKWOOD'S THEORY ON STATIC DIELECTRIC CONSTANT

Kirkwood \(^{(111)}\) pointed out that hindered rotation must play a part in the dielectric polarization of polar liquids. It must be responsible for large departures from the Lorentz field and that it should be introduced not to supplement but to correct Lorentz field. He further generalized the Onsager theory by eliminating the approximation of uniform local dielectric constant identical with the macroscopic dielectric constant of the medium by obtaining, the following equation

\[
\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} \frac{M}{d} = \frac{4\pi N}{3} \left[ \alpha_0 + \frac{\mu \bar{n}}{3kT} \right]
\]

where \(\mu\) is the molecular dipole moment in the liquid and \(\bar{n}\) is the average sum of the molecular dipole moment and the moment induced as the result of the hindered rotation in the spherical region surrounding the molecule.

Considering a microscopic cavity of volume \(V\) containing \(N\) number of molecules, and if \(E_0\) is the mean macroscopic field due to electric charges situated outside the volume under consideration, the average dipole moment by adding the moments of all the \(N\) molecules is given as,
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\[ M = \sum_{i=1}^{N} \left( \mu_i + \alpha \left( E_o - \sum_{k=1}^{N} T_{ik} m_k \right) \right) \]

2.7

where \( \mu_i \) is the dipole moment of the isolated molecule, \( \alpha \) is the polarizability inclusive of both atomic and electronic deformation polarization \( T_{ik} m_k \) is the tensor product in the first approximation representing the field created by the \( k^{th} \) molecule in the region occupied by the \( i^{th} \) molecule.

The above procedure is used to modify the Onsager equation with \( \mu^2 \) replaced by \( g\mu^2 \) as,

\[ \frac{(\varepsilon_r - 1)(2\varepsilon_r + 1)}{3\varepsilon_r} = \frac{4\pi N}{3KT} \left( g\mu^2 \right) \]

2.8

When both the atomic and electronic polarizations are incorporated, the above equation gets modified as,

\[ \frac{(\varepsilon_r - 1)(2\varepsilon_r + 1)}{3\varepsilon_r} = \frac{4\pi N}{3KTV} \left( g\mu^2 \right) + \frac{4\pi N}{3V} \alpha \]

2.9

In spite of the semi-empirical formulation with statistical deformation effects exerted upon each molecule by its nearest neighbours, there exist certain difficulties in specifying the boundary conditions. The problem in specifying the boundary condition was overcome by Frohlich (112) by treating the deformation polarization as a macroscopic phenomenon. Hence the molecules may be regarded as a set of non deformable point dipoles of moment \( p' \) placed in the continuous medium of dielectric constant (\( \varepsilon_{\infty} \)). Hence the moment of the spherical molecule becomes
therefore the Kirkwood equation then becomes

\[
\frac{(\varepsilon_s - \varepsilon_m)(2\varepsilon_s + \varepsilon_m)}{3\varepsilon_s} = \frac{4\pi N}{3kTV}\langle P'M^* \rangle
\]

where \( M^* \) is the moment of spherical cavity placed in a continuous dielectric moment defined by \( P' \). Further treating the fundamental unit as a molecule itself the moment can be written as

\[
\langle P'M^* \rangle = \langle \mu M^* \rangle = \langle g \mu^2 \rangle = \frac{9kTV}{4\pi N} \left( \frac{\varepsilon_s - \varepsilon_m}{\varepsilon_s(\varepsilon_m + 2)^3} \right)
\]

where "\( g \)" estimates the average mutual orientation correlation between the representative dipolar molecule and its neighbours and the volume \( V = M/\rho \), \( M \) being molecular weight and \( \rho \) the density of the medium.

The phenomenological generalization of Kirkwood formula has been refined subsequently by many workers \(^{(10)}\). Though some more modifications have been suggested, the final expression becomes essentially true for polarizable species. Cole \(^{(11)}\) has also deduced the same expression using different method of distortion polarization, applicable even for alternating fields. Using yet another method, Harris and Alder \(^{(113)}\) obtained a formula which is applicable to all liquids.

\[
\frac{(\varepsilon_s - 1)}{(\varepsilon_s + 2)} = \frac{4\pi N\alpha}{3} + \frac{4\pi N}{3} \frac{g\mu^2}{kT} \frac{9\varepsilon_s}{(2\varepsilon_s + 1)(\varepsilon_s + 2)}
\]

\[
p' = \frac{(\varepsilon_m + 2)}{3} \mu
\]
where the parameters have their usual meanings and “g” resembles the same as in Kirkwood equation. Kosower (114) has given a detailed view in this regard.

2.2.4 ASSOCIATION IN LIQUIDS AND KIRKWOOD’S CORRELATION FACTOR

The orientational ordering of molecules in a liquid through the angular correlation of the neighbouring dipoles is described precisely by the factor “g”. This factor very well establishes a relationship with the static dielectric constant and its measurement provides information about the structure. A method has been proposed by Oster (115) and Oster and Kirkwood (116) to predict the structure of the associated liquids from the “g” factor. An extensive review in this regard has been given by Botcher (117) and latter by Tjia (118).

The influence of temperature, concentration, chain length of functional groups and occurrence of double or triple bond are also related to the variation of “g”. The extent of association or contra-association of molecules in a liquid is understood using g>1 or g<1. Tjia (118) and Bordewijk et al. (119) stressed that g = 1 was not an indication in itself for the absence of association between the molecules of the system. Hence one has to look for yet another approach to test the molecular association.

2.2.5 OTHER THEORIES RELATING DIELECTRIC CONSTANT AND DIPOLE-MOMENT

The static dielectric constant calculated by using the Debye equation 2.1 from molecular polarizability and permanent dipole moment is not applicable to polar liquids but the Onsager equation 2.2 provides the approximate relation between the dielectric constant of a normal polar liquid and molecular dipole moment. The dipole moment value calculated by it from
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the dielectric constant of the pure liquid is only a little more approximate than the uncorrected Debye solution values. The Kirkwood equation is more exact than the Onsager equation in that it encounters a factor to take into account the restriction of molecular orientation by neighbouring molecules.

Raman and Krishnan \(^{(120)}\) treated the molecule as both optically and electrically anisotropic. They deviated from the treatment of a molecule as a sphere with dipole at the centre and derived a complicated equation, which was criticized by Hans Mueller \(^{(121)}\) and by Jenkins and Bauer \(^{(122)}\).

Scholte \(^{(123)}\) and Abbott and Bolton \(^{(124)}\) also have extended the Onsager treatment to ellipsoidal molecules, obtaining somewhat better agreement with gas moment values for a few substances than that obtained by means of Onsager equation for a spherical model.

Frood and Dekker \(^{(125)}\) concluded that the Onsager equation holds not only for a mathematical dipole at the centre of spherical molecule but also for extended dipoles of arbitrary position and direction in a spherical molecule.

The effect of optical anisotropy was introduced by Wilson \(^{(126)}\) into the Onsager equation. He assumed that the optical polarizability \(\alpha_1\) along the dipole axis of the molecule was different from the polarizability \(\alpha_0\) averaged over all directions, the quantity used in the Debye and Onsager equations and obtained an equation as follows,

\[
\frac{\varepsilon - 1}{\varepsilon} \frac{3(\varepsilon_\infty - 1)}{2\varepsilon + \varepsilon_\infty} = \frac{4\pi N\mu^2}{9KT} \left(\frac{2\varepsilon + 1)(\varepsilon_1 + 2)}{(2\varepsilon + \varepsilon_1)^2}
\]

\[\text{2.14}\]

where \(\varepsilon_1\) is the value of the optical dielectric constant \(\varepsilon_\infty\) corresponding to the polarizability along the molecular axis in which the dipole moment lies.
In an apparently empirical approach, Syrkin \(^{(127)}\) has proposed an equation which may be written as,

\[
\frac{(\varepsilon - 1 - \varepsilon - 1)}{(\varepsilon + 2 - 2)} \frac{M}{d} = 4\pi N\mu^2 \frac{9K}{T} \tag{2.15}
\]

Using the square of the refractive index for sodium D line, instead of \(\varepsilon\) in equation 2.15 he has calculated a large number of dipole moments from the dielectric constants of the pure polar liquids.

Syrkin also proposed without demonstration of its accuracy, an equation for mixtures of polar components indicated as suffixes 1 and 2 where \(R\) is the molar refraction.

\[
\frac{(\varepsilon - 1)}{(\varepsilon + 2)} \frac{C_1M_1 + C_2M_2}{d} - C_1R_1 - C_2R_2 \frac{4\pi N}{9K} (C_1\mu_1^2 + C_2\mu_2^2) \tag{2.16}
\]

Jaffe \(^{(128)}\) has extended Onsager treatment and has obtained an equation somewhat similar to that of Kirkwood.

### 2.2.6 Static Dielectric Constant of Liquid Mixture in Solution

Onsager and Frohlich have considered the case of liquid mixtures by taking unit volume constituted by the mixtures in a manner different from domain theory. When there are \(i\) types of molecules per unit volume containing \(N_i\) molecules, for each component \(i\) containing a polarizable point dipole of
permanent moment $\mu_i$ and polarizability $\alpha_i$, the internal refractive index is defined by

$$\frac{n_i^2 - 1}{n_i^2 + 1} = \frac{\alpha_i}{a_i^3}$$

where $a_i$ is the radius of the $i^{th}$ type molecule. Assuming $\theta_i = \frac{4\pi N_i a_i^3}{3}$, so that the available space is completely filled by the molecule and $\sum \theta_i$ becomes unity. In this manner the Onsager equation is generalized as,

$$\varepsilon_i - 1 = g \sum \left(\frac{4\pi N_i \alpha_i}{1 - r \frac{\alpha_i}{a_i^3}} + \frac{4\pi N_i}{1 - r \frac{\alpha_i}{a_i^3}} \frac{\mu_i^2}{3KT}\right)$$

where $r$ is the degree of polymerization, $g$ and $\varepsilon_i$ refer to the mixture as defined earlier under the condition that $\sum \theta_i = 1$. Thus the expression gets reduced to

$$\sum \theta_i \left(\frac{\varepsilon_i - n_i^2}{2\varepsilon_i + n_i^2}\right) = \left(\frac{\varepsilon_i \left(n_i^2 + 2\right)^2}{3\left(2\varepsilon_i + n_i^2\right)}\right) \left(\frac{4\pi N_i \mu_i^2}{3KT}\right)$$

or

$$\sum \theta_i \frac{3e_i \left(\varepsilon_i - n_i^2\right)}{2\varepsilon_i + n_i^2} = \sum \left(\frac{4\pi N_i \mu_i^2}{3KT}\right)$$

where

$$\mu'_i = \frac{\varepsilon_i \left(n_i^2 + 2\right)^2}{3\left(2\varepsilon_i + n_i^2\right)} \mu_i$$

Usually a polar solute $B$ in dilute solution in a non-polar solvent $A$ is taken so that $\theta_B > (1 - \theta_A) = \theta_A$ and $\varepsilon_{ss} - \varepsilon_{SA} = (\varepsilon_{ss} - n_A^2) < \varepsilon_{ss}$ where $\varepsilon_{ss}$
and $\varepsilon_{sA}$ are the static dielectric constants of the solution and solvent and $n_A$ is the internal refractive index of the solvent. In this limitation, the Onsager's equation becomes

$$\theta_A \frac{\varepsilon_{ss} - n_A^2}{2\varepsilon_{ss} + n_A^2} + \theta_B \left[ \frac{\varepsilon_{ss} - n_B^2}{2\varepsilon_{ss} + n_B^2} - \frac{\varepsilon_{ss} - n_A^2}{2\varepsilon_{ss} + n_A^2} \right] = \frac{4\pi N_B \mu_B^2}{3\varepsilon_{ss} 3kT}$$  \hspace{1cm} 2.21

or in a simple form

$$\varepsilon_{ss} - n^2 = \frac{2\varepsilon_{ss} + n_A^2}{3\varepsilon_{ss}} \frac{4\pi N_B \mu_B^2}{3kT}$$  \hspace{1cm} 2.22

where

$$n^2 = n_A^2 - \theta_B \frac{3\varepsilon_{ss} (n_B^2 - n_A^2)}{2\varepsilon_{ss} + n_B^2} \hspace{1cm} 2.23$$

since $\varepsilon_{ss} - n_A^2 << n_A^2$, equation 2.21 becomes

$$\varepsilon_{ss} - n^2 = \frac{4\pi N_B \mu_B^2}{3kT}$$  \hspace{1cm} 2.24

Under the same limitations, the Clausius – Mosotti equation becomes

$$\varepsilon_{ss} - n^2 = 4\pi N_B \left( \frac{\varepsilon_{ss} + 2}{3} \right) \left( \frac{\mu^2}{3kT} \right)$$  \hspace{1cm} 2.25

where

$$n^2 = n_A^2 - \theta_B \frac{\left( n_A^2 - n_B^2 \right) (\varepsilon_{ss} + 2)}{(n_B^2 + 2)} \hspace{1cm} 2.26$$

Therefore, if the dipole moment is deduced on the assumption that the Clausius – Mosotti equation holds true, an apparent moment $\mu_{app}$ becomes
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\[
\mu_{\text{app}} = \frac{3\varepsilon_{s}n_{g}^{2}+2}{(\varepsilon_{s}+2)(2\varepsilon_{s}+n_{g}^{2})}\mu_{g} \tag{2.27}
\]

In dilute solution, the dipoles are sufficiently separated so that the correlation parameter tends to unity, which is also seen from the Frohlich equation,

\[
\mu_{\text{app}} = (1 - \gamma)\mu_{g} \tag{2.28}
\]

where \[\gamma = \frac{2(\varepsilon_{s}-1)(\varepsilon_{s}-n_{g}^{2})}{(2\varepsilon_{s}+n_{g}^{2})(\varepsilon_{s}+2)}\]

|\gamma| is usually much less than unity, but because of the term \((\varepsilon_{s}-n_{g}^{2})\), \(\gamma\) sometimes takes either positive or negative value.

This is the reason for taking dilute solutions to determine the dipole moments and more particularly the solvent as of non-polar nature. The theories are always in conjunction with Clausius-Mosotti equation, governing the static dielectric behaviour in the limit of low concentration. The dipole moments measured in this way are found to differ slightly from those measured in the gas phase. This difference of very small order might be due to the nature of solvent.

2.3 THEORETICAL CONSIDERATIONS OF DYNAMIC PERMITTIVITY OF LIQUIDS

The dynamic behaviour of dielectrics predicts about the kinetic properties of molecules. When compared to the static theories, it is more complexed and complicated due to certain anomalous behaviour. The static dielectric theories deal with the dipoles and their orientations only in the applied fields of low frequency. The increase in the external field frequency
makes the permanent dipoles to change their orientations in order to follow the applied field. At high frequencies, it is not so easy to attain equilibrium with the alternating electric field. The faster the field is varied, the more rapid is the motion required from the dipole. The lag in the attainment of the equilibrium in an electric field at very high frequency is known as the lag in the response of a system to change with the forces to which it is subjected. The oriented dipoles undergo a process known as dielectric relaxation leading to an anomalous dispersion of dielectric constants.

According to Debye's\(^{(105)}\) theory, the phenomenon of dielectric relaxation is the lag in dipole orientation behind an alternating electric field. The polar molecules of a system tend to rotate towards the equilibrium distribution in molecular orientation retaining the dielectric polarization. The same can also be regarded as the re-orientation against the viscous forces of its surroundings. While the static dielectric constants relate the microscopic parameters through equilibrium positions of the molecular dipoles, the dielectric relaxation is understood from the nature of relationship between them.

### 2.3.1 Theory of Statistical Dielectric Relaxation

The equation for the average dipole moment for the time dependent field is given by a most general relation

\[
\langle M_\varepsilon(t) \rangle = C \int M_\varepsilon(t) f(X, E_\omega, t) \, dx
\]

where \(f(X, E_\omega, t)\) is the distribution function which depends on time \(t\) through \(E_\omega\). The distribution function must be such that \(E_\omega = 0, \langle M_\varepsilon(t) \rangle = 0\) for a static field, then the dipole moment.


\[ \langle M_k \rangle = C' E_o \int M_k f_o(X) f_1(X) \, dx \]  \hspace{1cm} 2.30

where

\[ f(X, E_o) = f_o(X)(1 + f_1(X)E_o \ldots \ldots \ldots ) \]  \hspace{1cm} 2.31

and for a periodic field it can be written in analogy as

\[ f(X, E_o, t) = f_o(X) \left[ 1 + f_{1,\omega}(X) E_o e^{j\omega t} + \ldots + \ldots \right] \]  \hspace{1cm} 2.32

The expression for \( f_{1,\omega}(X) \) can be obtained using a macroscopic method, describing the relaxation time \( \tau \) of macroscopic polarization as the rate at which the orientation polarization disappears. It is represented by a decay function \( \phi(t) \), which follows the exponential law

\[ \phi(t) = e^{(-t/\tau)} \]  \hspace{1cm} 2.33

so that the distribution function at an instant of time becomes

\[ f(X, E_o, t) = f_o(X) \left[ 1 + f_1(X) \int_0^t \phi(x)e^{j\omega t} E_o e^{j\omega x} \, dx + \ldots + \ldots \right] \]  \hspace{1cm} 2.34

On evaluation this leads to the relation,

\[ \varepsilon' - \varepsilon_o = \frac{\varepsilon_s - \varepsilon_o}{1 + \omega^2 \tau^2} - j \frac{\varepsilon_s - \varepsilon_o}{1 + \omega^2 \tau^2} \]  \hspace{1cm} 2.35

where \( \varepsilon' \) is the dielectric constant at angular frequency \( \omega \). The imaginary part is the dielectric loss factor \( \varepsilon'' \) given by
\[ \varepsilon^* = \frac{(\varepsilon_s - \varepsilon_m) \omega \tau}{1 + \omega^2 \tau^2} \]  

is the energy dissipated in the dielectric. This treatment has introduced the complex dielectric constant as

\[ \varepsilon^* = \varepsilon' - j \varepsilon'' \]  

Cole and Cole {\textsuperscript{(129)}} have shown

\[ \left( \varepsilon' - \frac{(\varepsilon_s + \varepsilon_m)}{2} \right)^2 + \varepsilon''^2 = \left( \frac{(\varepsilon_s - \varepsilon_m)}{2} \right)^2 \]  

representing a semicircle as all the values in the equation are positive with \( \varepsilon'' \) as the ordinate and \( \varepsilon' \) as the abscissa, the diameter lies along the abscissa. Any dielectric substance showing this characteristic variation of \( \varepsilon' \) and \( \varepsilon'' \) is then said to have the Debye behaviour. The dielectric loss factor \( \varepsilon'' \) is smaller and its maximum value is found to be less than \( \frac{(\varepsilon_s - \varepsilon_m)}{2} \) as predicted by the theory.

The discrepancies exhibited for the dielectrics are explained due to the existence of a range of relaxation times. The equation 2.37 and 2.38 are accordingly changed as

\[ \varepsilon' - \varepsilon_m = \int_0^\infty \frac{F(\tau) d\tau}{1 + \omega^2 \tau^2} \]  

To account for the dynamic behaviour of associated dielectric liquids Cole and Cole {\textsuperscript{(129)}} have treated the distribution of relaxation time in an empirical manner. The semi - empirical formula is
This convenient graphical method introduces an empirical constant $\alpha$ which varies from zero to one. $\tau_0$ is regarded as the most probable relaxation time corresponding to the maximum frequency $f_{\text{max}}$ at which $\varepsilon''$ has its maximum value. The circle which cuts the abscissa at $\varepsilon_{\infty}$ makes an angle $\alpha \pi/2$ with the abscissa. This theoretical approach leads to a depressed semicircle, where $\varepsilon''$ are plotted as ordinates against $\varepsilon'$ abscissa (figure 2.1) but in the actual case, the plot in the complex plane shows a right skewed arc (figure 2.2), which is represented by the relation

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_{\infty} + \frac{(\varepsilon_s - \varepsilon_{\infty})}{(1 + j\omega \tau_0)^{1-\alpha}}$$

Figure 2.1 Complex plane showing depressed circular arc

Figure 2.2 Skewed arc representation in the complex plane

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_{\infty} + \frac{(\varepsilon_s - \varepsilon_{\infty})}{(1 + j\omega \tau_0)^{1-\alpha}}$$
where $\beta$ is also an empirical constant with a value between 0 and 1. When $\alpha_0 = 0$ in equation 2.40 or $\beta = 1$ in equation 2.41 the equations reduce to 2.42

$$\varepsilon^* = \varepsilon_{\infty} + \frac{(\varepsilon_i - \varepsilon_{\infty})}{(1 + j\omega\tau_0)}$$  

2.42

The latter method has some advantage in that the frequency appears explicitly. This method often fits the experimental data successfully combining this procedure with the state dielectric properties, the molecular dipole moment of any substance in dilute solution in a non-polar solvent or of a slightly polar substance in the pure liquid state can be determined using the equation

$$\tan \delta = \left(\frac{\varepsilon' + 2}{\varepsilon'}\right)^2 \frac{4\pi CN}{27KT} \frac{\mu^2}{\omega \tau} \frac{\omega \tau}{1 + \omega^2 \tau^2}$$  

2.43

where $C$ is the concentration of polar solute in mole per cubic centimeter.

A large variety of function for the distribution of relaxation time has been proposed on empirical basis (110, 130), when two or more relaxation processes occur. The absorption regions for the two processes overlap with appreciable $\alpha$ values.

### 2.3.2 MOLECULAR INTERPRETATION OF THE DIELECTRIC RELAXATION TIMES OF ASSOCIATED LIQUIDS

Based on Eyring’s model (130), Kaufmann (131) considered the dielectric relaxation as a chemical rate process activated by environmental fluctuations. Debye treated the dielectric relaxation as a Brownian motion of the spherical polar molecules rotating in a continuous viscous medium and related the microscopic relaxation time to that of a single polar unit. The
relaxation time $\tau$ as a function of shear viscosity $\eta_s$ of the liquid is given by the equation.

$$\tau = \frac{4\pi\eta_s a^3}{kT}$$

where "a" is radius of the spherical polar molecule. Both theories describe the behaviour of dielectric relaxation in almost all the associated and interacting molecules. In this connection, the review articles of Hill et al. \(^{(10)}\) and Grant et al. \(^{(132)}\) show the trend of single relaxation time for associated liquids. The works of Smyth are also extensively reviewed \(^{(107)}\) so as to describe the methods of evaluating relaxation times. Higasi’s work on dielectric relaxation which forms a theoretical basis for the occurrence of more than one relaxation time succeeds, in the interpretation of observed difference in relaxation processes. The relaxation times observed for a particular system of liquids are thus informative in sensing the group and overall molecular structures.

2.4 CONCLUSION

Based on some theoretical concepts on liquids, experimental studies are of great use in knowing the nature and strength of molecular interactions in liquids and their mixtures. In the present work, an attempt has been made to study the dielectric properties of some organic liquids and their mixtures.
CHAPTER 3

Selection Of Materials

3.1 Introduction
3.2 The present study
3.3 Choice of chemical compounds
3.4 Aim and objectives
3.5 Purification of chemicals
3.6 Sample preparation
CHAPTER 3

SELECTION OF MATERIALS

3.1 INTRODUCTION

On the basis of survey of the available literature reveals that the dielectric parameters get changed, when there are possibilities of molecular interactions. The excess dipole moment describes the relative displacements of the nuclei and the electrons at the H-bonding site and this could conveniently be used to characterize the nature of H-bond. Thermodynamic effect in the mixtures, variation of viscous forces and the dielectric relaxation times are aimed to identify the molecular interactions which pave ways to structural analysis. Selections of chemicals for this study are based on literature survey. The present Chapter gives the details of the compound selected, their purification and sample preparation.

3.2 THE PRESENT STUDY

The literature survey indicates that nitriles and phenols had been subjected to various Physico-Chemical studies and the results suggest an intimate relation between the data obtained and the changes in the state of hybridization of bond orbital, molecular association solvent effect of different kinds, rotational isomerism etc. Firman et al. (78) have studied the permittivity and dielectric relaxation of benzonitrile, acetonitrile and their mixtures in carbon tetrachloride. Spectroscopic studies (133) of mixtures of benzonitriles and phenols have revealed information on hydrogen bonding as a function of concentration and temperature. Also, the study on acetonitrile and phenol mixture has provided evidence for molecular interaction. A D Vyas (134) and Madan (135) have respectively studied the interaction of benzonitrile with aniline and with nitrobenzene. These studies have primarily evinced interest for the study of substituted benzonitriles and substituted phenols. Further,
dimethylsulphoxide has been widely explored by different techniques. It has given interesting results when studied in mixture with acetone \(^{(64)}\) and N, N dimethylformamide \(^{(65)}\) in carbon tetrachloride. An investigation to have more information about the molecular interaction between nitriles, phenols and dimethylsulphoxide has been undertaken, as there is only relatively meagre amount of information available on the dipolar interactions and dielectric relaxation behaviour.

### 3.3 CHOICE OF THE CHEMICAL COMPOUNDS

The compounds chosen for the present study are:

i) Benzonitrile; its para substituted (Cl, NH\(_2\), and OCH\(_3\)) compounds,

ii) Phenol; its ortho substituted (Cl, NO\(_2\)) compounds

and iii) Dimethylsulphoxide (DMSO).

Some of their available standard physical and chemical properties \(^{(136, 137, 138)}\) are listed in table 3.1. Some data are provided by the manufacture of the chemicals.

### 3.4 AIM AND OBJECTIVES

It is aimed at furthering the knowledge about the interaction between the

i) Nitriles and phenols,

ii) Nitriles and DMSO

and iii) Phenols and DMSO. For this

1. It has been planned to determine the static, microwave and optical dielectric constants at different temperatures by varying the concentration of selected chemicals and their complexes in dilute solution of benzene,

2. to determine density and viscosity of the prepared solutions of various concentration at different temperatures,
3. to evaluate dipole moments, related dielectric parameters, relaxation times and assess their changes for the molecules dissolved in the pure and complexed forms in non-polar solvents,

4. to calculate the free energies of the thermodynamically activated states from the dipolar and viscous forces,

5. to carry out the same with Time Domain Technique with the view of correlating the interactions and

6. to analyse and discuss the consolidated results to arrive at the conclusions regarding molecular interactions.

3.5 PURIFICATION

AR/GR/EXCELAR grade chemicals are procured from the suppliers. All the substances are used after purifications. The prepared compounds have been tested for their purity adopting standard assay methods. The purity has been confirmed by the measurement of boiling point, densities and refractive indices in the case of liquids and melting points in the case of solids.

Phenol

Phenol is distilled and collected at 182°C in 50 ml flasks. The colourless phenol crystallized immediately at room temperature.

Chlorophenol

Pink coloured chlorophenol is purified by distillation under reduced pressure and the colourless liquid is collected at the boiling temperature of 220°C in small air tight flasks.
### TABLE 3.1 PHYSICAL AND CHEMICAL PROPERTIES

#### 1. BENZONITRILE (C₆H₅CN)

- **Molecular weight**: 103.12
- **Density**: 1.005 g/cc (20°C)
- **Melting point**: -13.1°C
- **Boiling point**: 190.7°C (760 mm Hg)
- **Refractive index**: 1.5289 (20°C)
- **Solubility**: alc, eth, ace, bz, chl
- **Physical nature, toxicity & Precautions**: Colourless oil, almond like odor, sharp taste, high toxicity, absorbed by skin.
- **CAS. No**: 100-47-0.

#### 2. P-AMINO BENZONITRILE (4-NH₂C₆H₅CN)

- **Molecular weight**: 118.14
- **Density**: -
- **Melting point**: 86°C
- **Boiling point**: dec
- **Refractive index**: -
- **Solubility**: alc, eth, bz, chl
- **Physical nature, toxicity & Precautions**: solid, high toxicity
- **CAS. No**: -

#### 3. P-CHLORO BENZONITRILE (4-ClC₆H₅CN)

- **Molecular weight**: 137.57
- **Density**: -
- **Melting point**: 94 - 6°C
- **Boiling point**: 223°C (760 mm Hg)
- **Refractive index**: -
- **Solubility**: alc, eth, bz, chl
- **Physical nature, Toxity & Precautions**: Toxic, harmful if swallowed, irritating to eyes.
- **CAS. No**: 710-765-4
4. P-METHOXY BENZONITRILE
(4-CH$_3$OCH$_2$CN)

- Molecular weight: 133.15
- Density: 1.302
- Melting point: 57-59°C
- Boiling point: 256-257°C (760 mm Hg)
- Refractive index: 1.5476
- Solubility: alc, eth, bz
- Physical nature: Solid, toxic
- Precautions: 
- CAS No: 67-548-EEC

5. PHENOL (C$_6$H$_5$OH)

- Molecular weight: 94.11
- Density: 1.071 g/cm$^3$ (20°C)
- Melting point: 42-43°C
- Boiling point: 182°C (760 mm Hg)
- Refractive index: 1.5408 (20°C)
- Solubility: alc, eth, chl, ace, bz
- Physical nature: White crystalline mass, distinctive odor, sharp burning taste, toxic by ingestion, inhalation and skin absorption
- Precautions: strong irritant to tissue.
- CAS No: 108-95-2

6. O-CHLORO PHENOL (2-CIC$_6$H$_5$OH)

- Molecular weight: 128.56
- Density: 1.241 g/cm$^3$ (20°C)
- Melting point: 9.3°C
- Boiling point: 175°C (760 mm Hg)
- Refractive index: 1.5582 (20°C)
- Solubility: alc, eth, bz
- Physical nature: Colourless to yellow – brown liquid unpleasant penetrating odor, toxic by ingestion, inhalation and skin absorption
- Precautions: strong irritant to tissue.
- CAS No: 95-57-8
7. O- NITRO PHENOL (2-NO₂C₆H₄OH)

- Molecular weight: 139.11
- Density: 1.479 g/cc (20°C)
- Melting point: 44-45°C
- Boiling point: 216°C (760 mm Hg)
- Refractive index: 1.5723 (20°C)
- Solubility: alc, eth, ace, bz, chl
- Physical nature: Yellow crystals, toxic by ingestion, harmful by inhalation
  Precautions
- CAS No: 88-75-5

8. DIMETHYL SULPHOXIDE (CH₃)₂SO

- Molecular weight: 78.13
- Density: 1.101 g/cc (20°C)
- Melting point: 18.5°C
- Boiling point: 189°C (760 mm Hg)
- Refractive index: 1.4713 (20°C)
- Solubility: alc, bz, ace, chl, eth
- Physical nature: Colourless, hygroscopic liquid nearly odorless, slightly bitter taste, combustible, readily penetrates skin and other tissues
  Precautions
- CAS No: 67-68-5

9. BENZENE (C₆H₆)

- Molecular weight: 78.11
- Density: 0.8740 g/cc (20°C)
- Melting point: 5.53°C
- Boiling point: 80.1°C (760 mm Hg)
- Refractive index: 1.5011 (20°C)
- Solubility: eth, ace, CCl₄
- Physical nature: Colourless liquid with petroleum like odor, a carcinogen, highly toxic
  Precautions
- CAS No: 71-43-2
Chapter - 3

Benzene

Benzene is allowed to stand on anhydrous calcium chloride for two days and then filtered. Then the filtered benzene is refluxed with phosphorous pentoxide for six hours and distilled. Sodium is drawn in the form of wires in the distillate and is redistilled. Then benzene is collected at its boiling point of 80 °C and is stored in dark bottles.

Dimethylsulphoxide (DMSO)

DMSO is stirred over CaH₂ and distilled “in vacuo” (Distillation at atmospheric pressure will cause decomposition of the solvent) and the fraction boiling in the range 83 – 86 °C at the pressure of 12 mm Hg is collected and is used immediately.

Benzonitrile

Benzonitrile is washed with a little Na₂CO₃ solution, then with water and is dried over anhydrous MgSO₄. It is then distilled under atmospheric pressure and the product distilling at 188 - 189 °C is collected.

3.6 SAMPLE PREPARATION

The liquid systems of different desired concentration for the study have been prepared by weight at laboratory temperature. The method of investigation in the present dielectric study involves concentration variation of dilute solutions, over a suitable range of solute concentration in a polar solvent from 0.004 to 0.024 w\w. A top pan electronic digital balance (Anamad series Max 7000, Sensitivity ±0.001gms) has been used. Suitable concentration in steps of 0.004 is preferred for all the systems. The complexes in dilute
solutions also have been prepared by weight so as to have the same set of concentrations.

For time domain, the solutions have been prepared suitably in the volume fraction. Polar solutes have been dissolved in non-polar solvent benzene to their maximum solubility and then they are mixed in volume fraction ranging from 0 to 100 % in steps of 25 %.