Dipole moment and Dielectric Relaxation Behaviour of Some Anilines and Phenol from Different Methods: An Experimental Approach

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Abstract

The study of dielectric relaxation behaviour of polar molecules and their mixtures in the pure liquid state or their dilute solutions in non-polar solvents in the microwave region has been the subject of interesting research for many years. The important molecular parameters associated with these studies are mainly electric dipole moment (μ) and relaxation time (τ). The studies related to dipole moment and relaxation time are useful in understanding the structure, size, shape of the orienting dipole unit, nature of the relaxation process involved and they also give information about inter and intra molecular forces etc.

The dielectric relaxation behaviour of four polar molecules namely 2-Nitroaniline, 4-Bromoaniline, 4-Chloroaniline and 4-Chlorophenol were studied in dilute solutions of benzene using microwave bench at 9.59 GHz frequency. The different parameters like, dielectric constant (ε'), dielectric loss (ε''), static dielectric constant (ε_0) and optical permittivity (ε_∞) have been determined. Further from these values, dipole moment (μ) and relaxation time (τ) were calculated for all the molecules using Gopalkrishna, microwave conductivity and Higasi method. The dipole moment for all the molecules were also estimated theoretically from *ab initio* computations by using Density Functional Theory (DFT) calculations with the help of Gaussian 09W software. Dipole moments determined experimentally and through DFT computations are in good agreement with the dipole moments estimated by taking vector sum of group moments of Aniline, Nitrobenzene, Bromobenzene, Chlorobenzene and Phenol by neglecting interaction between pendant groups.

The experimentally determined relaxation times were analysed in terms of Stokes-Einstein-Debye (SED) theory and the results are compared with molecular radii estimated from DFT and Edward's atomic increment methods. Our experimental findings suggest that, 2-Nitroaniline exhibits simple Debye type relaxation behaviour while the other three samples exhibit the Higasi's distribution of relaxation times which may be due to both overall and intra-molecular rotation of the molecules.

Keywords: Dipole moment, relaxation time, Gopalkrishna method, Higasi method.

I. INTRODUCTION:

The dielectric studies of polar molecules and their mixtures in the pure liquid state and in their dilute form in non-polar solvents in the microwave region has been the subject of interest for many years. The understanding of dielectric properties and the study of molecular interactions provide useful information regarding conduction mechanism, interfacial polarization, molecular dynamics and they also contribute to a greater extent in fields like transport, chemical industries, etc. The important molecular parameters associated with these studies are mainly electric dipole moment (μ) and relaxation time (τ). The studies related to dipole moment and relaxation time are useful in understanding the structure, size, shape of the molecules, inter and intra molecular forces etc. The two important factors which affect the relaxation time are temperature and viscosity. It is possible to study the variation of relaxation time with temperature by performing experiments on pure liquid state at different frequencies. However from these studies, it is not possible to study the variation of relaxation time (τ) with viscosity, for which purpose one has to again perform dielectric experiments using dilute solutions only. Therefore the dielectric measurements based on dilute solutions have some additional advantages and the dielectric measurements on the single set of these dilute solutions permit one to determine the two important molecular parameters, the dipole moment (μ) and relaxation time (τ). Further, the studies related to the effect of temperature on relaxation time provide valuable information regarding the nature of the relaxation process involved and helps to calculate the thermodynamical parameters like change in activation energy (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*), which are useful in understanding the state of orderliness of the dielectric system. The studies related to the effect of viscosity on relaxation time helps in drawing certain quantitative conclusions regarding molecular motion and inter molecular forces in liquids, liquid mixtures, dilute solutions and multi component polar solutes in dilute solutions. The molecular dynamics of polar liquids and their mixtures in dilute solutions can be studied using different methods like dielectric, spectroscopic, ultrasonic, nuclear magnetic resonance, etc.

The two parameters dipole moment (μ) and relaxation time (τ) can be determined by measuring the dielectric parameters like dielectric constant (ε'), dielectric loss (ε''), static dielectric constant (ε_0) and optical permittivity (ε_∞) of polar molecules and their mixtures in pure liquid form or diluted in a non-polar solvent like benzene using different techniques. There are several methods available in the literature for determining (μ) and (τ) from dilute solution measurements and they have been classified into two categories viz., i) Frequency variation at single concentration.

ii) Concentration variation at single frequency. Gopalkrishna, Microwave conductivity and Higasi methods are the most commonly used methods for the determination of dipole moment and relaxation time using dilute solutions and are based on variation of concentration at single frequency.

A. THEOROTICAL BACKGROUND:

A dielectric material is an electrically non conducting material such as glass, porcelain, wood, rubber, waxed paper, etc., which provides electrical insulation between two media which are at different potentials and serve as an electrical charge storage aid under certain circumstances. If its main purpose is to provide just the insulation, then they are referred as insulating materials, but if they are employed for charge storage, then the name dielectric is used. Dielectric materials may be gases, solids or liquids and they interact with electric, magnetic and electromagnetic fields. They have the ability of storing/dissipating electric and magnetic energy and are used in electrical devices, in different industries and have many important applications.

The studies related to the dielectric properties have become an important tool in understanding the study of the structure of matter. The results obtained from the study of molecular systems can be understood by the dielectric methods, namely by the non-quantal response of dielectric materials to electric fields ranging from static to those of frequencies up to 10^{12} Hz. The phenomenological electric properties of matter can be described in terms of different properties like polarization, magnetization and conduction and it is possible to interpret these results from the stand-point of molecular theory. Further, a connection can be obtained between the macroscopic constants of the dielectric and its molecular parameters like electric dipole moment, magnetic dipole moment etc., by using this molecular theory. In order to understand the molecular processes, one has to examine the molecular causes of dielectric dispersion from dielectric measurements in the dispersion region. It is observed that, these molecular processes vary with the mechanism by means of which these molecules rotate under the influence of the applied field.

In case of insulators, there are no free electrons as all the electrons are bound very strongly to their respective nuclei of the parent molecules. Since negative and positive charges in each part of the material are centered at the same point, the conductivity is not possible in these materials. It is observed that, at ordinary temperatures, these materials can be dislodged either by thermal vibrations or with ordinary electric fields. However, it is found that the centers of positive charges are slightly displaced in the direction of the electric field and negative charges are slightly displaced in the opposite direction when an electric field is applied to these materials. The displacement of charges in the atoms or molecules of a dielectric under the action of an applied field, leading to the development of dipole moment is called polarization of the dielectric and the charges appearing separated are known as polarization charges.

In case of polar molecules the effective centre of positive charges and effective centre of negative charges do not coincide with each other and hence they have permanent electric dipole moment and their dipole moments are much larger than the dipole moments induced by an external electric field. When there is no electric filed applied, it is observed that the permanent dipoles present in case of polar molecules are randomly oriented and such randomly oriented assembly of polar molecules does not exhibit any polarization as the net dipole moment is zero. When these dipoles viz., molecules, ions, atomic nuclei and electrons are placed in an external varying field, the motions of these dipoles need characteristic times to build an equilibrium polarization. If the applied electric field varies sufficiently fast, then the polarization lags behind the applied field. Hence, it is observed that, the dielectric properties of the materials in a varying field are found to change characteristically from the corresponding equilibrium properties in steady states. The total polarization of a dielectric is contributed by various polarization mechanisms like electronic, atomic, orientation and space charge or interfacial polarization. The electronic polarization is due to the relative displacement of electrons relative to the nucleus in each atom. The atomic polarization is due to the relative displacement of the atomic nuclei to one another. The orientation polarization is due to the orientation of the permanent dipoles with the applied electric field. The interfacial polarization is due to the field distortion brought about by moving charge carriers.

At low frequencies, all the four polarization mechanisms are found to be in phase with the external applied field and as a result there are no losses. However, at very high frequencies, the electronic and atomic polarization mechanisms continue to be in phase with the applied field but the rotatory motion of the molecules are not sufficiently rapid to cope up with the applied field. As a result, the polarization acquires a component out of phase with the field, which leads to the thermal dissipation of energy or dielectric loss which results in the absorption of energy from the applied field. By applying these various polarization mechanisms to molecules in the gaseous or liquid state, it is possible to obtain the knowledge about the structures of molecules.

At frequencies greater than 10^{12} Hz, the general type of response of gases to an alternating electric field is that, they gives rise to a sequence of resonance states and leads to a resonance spectra like Electronic and Vibrational spectra. Thus electronic and atomic polarizations lead to dispersion and absorption phenomena in the IR, Visible, UV and X-ray regions of the electromagnetic spectrum. However in case of condensed phase of the matter i.e. in case of liquids and solids, the origin of electronic and vibrational resonance spectra are found to be characteristic of the condensed phase but not of the individual molecules. In other words the sharp spectral lines of gases are greatly broadened in case of condensed phase and the rotational states are entirely altered because of the closeness of the rotational levels with respect to the thermal energy. In the condensed phase, the rotational motions of dipole molecules or molecular groups are not free as in the case of gaseous phase. Therefore, the associated polarization mechanism viz., orientation polarization gives rise to the phenomenon of dielectric relaxation spectra instead of quantized rotation spectra. In case of liquids and solids, the characteristic times involved in the relaxation process are normally greater than 10^{-12} sec and hence microwave signals in the giga Hertz range can be conveniently used for measurements leading to the evaluation of relaxation time.

According to Maxwell, a dielectric medium may be specified in terms of dielectric constant (ε'), permeability and an effective mobility (σ). For all dielectric materials except ferromagnetic materials, the permeability will in general be equal to (μ_0) i.e. permeability of the free space. When such a dielectric is placed in a periodic electromagnetic field given by $e = E.e^{j\omega t}$, it carries an electric current density given by

$$I = \sigma . e + \frac{\varepsilon\, \partial e}{\partial t}$$

$$= (\sigma + j\omega t) E e^{j\omega t} \qquad (1)$$

In the above equation, the first term represents a conduction current in time phase with the applied field and the second term represents a displacement current density in phase quadrature. The resultant current density leads E by an angle ϕ and cosϕ is known as the power factor of the dielectric and the complement of the phase angle ϕ is usually denoted by an angle δ known as the loss angle and tanδ = (σ/ωε') is taken as loss tangent. The loss tangent (tanδ) is indistinguishable from the power factor for small values of δ. The resultant current (I) is expressed in the form

$$I = (\sigma + j\omega\varepsilon)\, Ee^{j\varepsilon t}$$

$$= j\omega\left(\varepsilon + \frac{\sigma}{j\omega}\right) Ee^{j\omega t}$$

$$= j\omega\left(\varepsilon - j\frac{\sigma}{\omega}\right) Ee^{j\omega t}$$

$$= j\omega(\varepsilon' - j\varepsilon")Ee^{j\omega t}$$

$$= j\omega\varepsilon^{*}Ee^{j\omega t} \qquad (2)$$

Here (ε*) may be taken as an equivalent dielectric constant of the conducting medium and loss tangent tanδ = (σ/ωε') = ε"/ε', where both the quantities dielectric constant (ε') and dielectric loss (ε") are functions of frequency.

Debye was the first to contribute towards the molecular aspects of the theory of dielectric polarization and his concepts are still used in interpreting the experimental results. Debye's treatment for the motion of dipoles in condensed phases subjected to an alternating electric field deals with the fact that, the polar molecules rotate in a medium of friction. He introduced a molecular parameter known as relaxation time (τ). According to this theory, the dielectric behaviour of the medium is described in terms of the complex dielectric constant (ε*). This complex dielectric constant (ε^*) is in turn related to the two macroscopic parameters, the static dielectric constant (ε_0) and optical permittivity (ε_∞) by the following Eq. (3)

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \qquad (3)$$

where (ω) is the angular frequency of the applied alternating field. The quantity optical permittivity (ε_∞) corresponds to the electronic and resonance polarization of the dielectric. This deformation polarization contributes constant induced moments in the low frequency range of the relaxation polarization. The parameter static dielectric constant (ε_0) contains in addition, the full contribution resulting from the orientation of the permanent dipole moments. The permanent dipole moments contribute only an average dipole moment because they cannot align themselves in the field direction as a result of the randomising thermal agitation, opposing forces and the torque due to the applied electric field. The space charge or interfacial polarization which arises only in heterogeneous media will be significant at very low frequencies and is usually negligible.

The dielectric medium is supposed to be acted by the local field, the applied field itself or by the Mosotti field in the case of gases and vapours at low pressures and the complex dielectric permittivity (ε^*) is related with the microscopic molecular parameters, namely the electronic polarizability (α_e) and atomic polarizability (α_a), the electric dipole moment (μ) and the relaxation time (τ) of the molecules of the dielectric and is given by the relation

$$P^* = \frac{4\pi N_A}{3}\left[\alpha_e + \alpha_a + \frac{\mu^2}{3KT}\frac{1}{1 + j\omega\tau}\right] \qquad (4)$$

Where (P^*) is the complex molar polarization, N_A is the Avogadro’s number, K is the Boltzmann's constant and T is the absolute temperature.

According to Debye, the relaxation time (τ) is given as,

$$\tau = \frac{4\pi\eta a^3}{KT} \tag{5}$$

where (η) is the macroscopic viscosity of the medium and ‘a’ is the radius of the molecule. Relaxation time (τ) determined by assuming the molecules of the medium to be spherical is usually of the order of picoseconds.

From Eq. (3) it is seen that the real part (ε') of complex permittivity (ε*) and imaginary part (ε") of complex permittivity (ε*) and the loss tangent (tanδ) can be expressed as,

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1+\omega^2\tau^2} \tag{6}$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{(1+\omega^2\tau^2)} \tag{7}$$

$$tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{8}$$

These relations shows that if dielectric loss factor (ε") is plotted against (ωτ), the loss factor (ε") is maximum when ωτ =1. Similarly a graph between the dielectric conductivity σ (=ωε") versus (ωτ) also gives a dispersion curve as above but is a mirror image of it.

In particular for a dielectric medium like gas or dilute solution to which Debye equation is valid, the loss tangent (tanδ), as a fair approximation can be expressed by the following equation

$$tan\delta = A\frac{\omega\tau}{(1+\omega^2\tau^2)} \tag{9}$$

Where A is given by

$$\frac{(\varepsilon' + 2)^2}{\varepsilon'} \frac{4\pi N_A W d \mu^2}{27KTM}$$

where W, d, M represent weight fraction, density, and molecular weight.

This equation in comparison with Debye equation for $\tau = (4\pi\eta a^3/KT)$ suggests that, if dielectric measurements are carried out on a liquid or on a random concentration of it in a non-polar medium as a function of i) frequency ii) temperature and iii) viscosity, the loss tangent (tanδ) reaches maximum for $\omega\tau = 1$, so that relaxation time (τ) and dipole moment (μ) can be determined with a pre knowledge of other quantities appearing in these equations.

For the frequency response of a number of dielectrics, particularly of dilute solutions of polar molecules in non-polar solvents, the assumption of a single relaxation time fits satisfactorily. But it has been observed that, the actual relaxation spectra of liquids and polymers are frequently characterised by a distribution of relaxation times spread around a most probable value and this indicates coupling of the dipole moments to their surroundings. Instead of smoothly rotating spheres, one has to visualize the dipoles as statistically jumping over the potential wells, whenever the activation energy becomes available. However, in general the permanent electric dipoles are completely immobilised in crystals as for as any individual rotation is concerned.

Von Schweidler, Wager and Yager gave a theory for the distribution of relaxation times for the first time. In Yager's theory in order to explain the observed experimental curves, the expressions for the distribution of relaxation times are based on Gaussian distribution. Kirkwood and Fuoss obtained a formula for the distribution function for long-chain polymers which is found to be in general agreement with experimental results. Fuoss and Kirkwood showed how to derive the distribution function giving the best experimental fit with the given loss factor versus log frequency curve. However, there is no satisfactory general theory for the dependence of dielectric constant (ε') and dielectric loss (ε") on frequency, as well as for the distribution function. Therefore in dealing dielectric dispersion data on polar liquids, usually two empirical approaches are used. According to Cole-Cole approach, if the medium is characterised with a single relaxation time (τ), then the complex plane locus obtained by plotting dielectric loss (ε") versus dielectric constant (ε') is a semicircle with radius $(\varepsilon_0-\varepsilon_\infty)/2$ and center at $(\varepsilon_o + \varepsilon_\infty)/2$ on the ε'-axis. On the other hand, if there is a distribution of relaxation times, the locus is generally a circular arc with center depressed below the ε'-axis. This implies that the Debye equation for the complex dielectric constant (ε*) must be modified to

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0-\varepsilon_\infty}{(1+j\omega\tau_0)^{1-\alpha}} \qquad (10)$$

Where (α) is known as distribution parameter and this would be equal to zero in the case of a single relaxation time. If there is a distribution of relaxation times, then (α) varies between 0 and 1 and for such cases the most probable relaxation time is given by (τ_0). It is observed that, this relation is found to be valid in case of many simple molecules. But the usual circular shape of the Cole-Cole plot is found to deviate in the case of certain other dielectric systems such as associated liquids like glycerol, alcohols, for non-spherical molecular media, etc. In such dielectrics the dispersion is found to be not symmetric but it is represented by a skewed arc. Further, these results were interpreted by Davidson and Cole by means of an empirical expression for the complex dielectric constant (ε*) as a function of the frequency and is given by the following Eq. (11)

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega\tau')^b} \qquad (11)$$

Where the quantity (b) may assume a value between 0 and 1 and (τ') is the relaxation time different from most probable relaxation time (τ_0) of Eq. (10).

A different empirical relation is suggested by Fuoss and Kirkwood approach and by using this approach the experimental data could be analysed in the light of the empirical relation given by the Eq. (12)

$$\varepsilon'' = \varepsilon''_{max} Sech\beta \log\left(\frac{\omega}{\omega_{max}}\right) \qquad (12)$$

Where β is a parameter and its value varies from 0 to 1 for an infinitely broad dispersion to that of Debye dispersion. However no general expression has been given by them for the variation of ε' versus logω, but they have computed analytical expressions for two specific values of the parameter β. Later Macdonald found analytical expressions for (ε'') and these expressions will provide a method for a complete comparison with experiment and for any value of β from 0 to1, they enable the determination of the dependence of (ε') on frequencies.

From all these discussions made above, it is observed that the Debye's dielectric relaxation model is too simple particularly because of the reason that the relaxation time depends strongly on the temperature as indicated by the equation ($\tau = 4\pi\eta a^3/KT$) and this indicates that in the relaxation process at some stage, to overcome a potential barrier a molecule requires a certain amount of energy like activation energy in excess of that of the average thermal energy. This suggests that the dielectric relaxation process being treated like viscosity as a rate process, as has been done by Eyring.

This interpretation of dielectric relaxation implies that the conversion of chemical energy into heat during a chemical reaction is similar to that of the accompanying conversion of electrical energy into heat in a dielectric relaxation, whereas in the Debye's theory it would be a result of inner friction. The expression obtained for the relaxation time based on these interpretations by Eyring is given by the following Eq. (13)

$$\tau = \frac{h}{KT}\exp(\Delta G_{\tau}^{*}/RT) \tag{13}$$

The above equation is similar to the expression for viscosity treated also as rate process and is given by

$$\eta = \frac{hN_A}{V}\exp(\Delta G_{\eta}^{*}/RT) \tag{14}$$

Where

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*} \tag{15}$$

Where ΔG* is the molar free energy of activation, ΔH* is the molar enthalpy of activation and ΔS* is the molar entropy of activation and the suffixes τ, η corresponds to relaxation process and viscous flow process. It is to be noted that, the activation energies required for the two phenomena are different and the activation energy required for dielectric relaxation is less as it involves only rotational motion whereas the activation energy required for viscosity is more as it involves in addition to rotational motion, the translational motion of the molecules also.

It is to be noted that, the relaxation time of a molecule in the pure liquid state is found to be larger than that in the solution of the same viscosity. According to Smyth, Higasi and their collaborators, the difference in the relaxation times is due to the hindrance experienced by the molecular rotation by dipole-dipole interaction which is present in the pure liquid state and largely absent in dilute solutions. Thus, the dielectric studies both in dilute solutions and in the pure liquid state in conjunction with Eyring's rate process would give considerable information about the dielectric behaviour of the medium.

In order to understand whether a dielectric medium is characterized by a single relaxation time or a distribution of it, one has to perform dielectric measurements in the pure liquid state at different frequencies. But such studies do not give any information regarding the other important molecular parameter dipole moment (μ), the determination of which requires another separate set of dielectric measurements. This is because of the fact that, no theory using the right internal field such as Onsager's internal field for D.C. applied fields, has yet been available at the high frequencies as far as the author is aware and because of which, consequently there is no method available yet. Unlike in the case of pure liquids, for dilute solutions a well-tested Debye's theory which deals with dielectric dispersion, absorption and according to which a dilute solution of a polar solute in a non-polar solvent characterized by a single relaxation time is available.

It is observed from the above discussions that, by using the phenomenon of dielectric relaxation, it is possible to determine the two important molecular parameters the dipole moment (μ) and relaxation time (τ) from the experimentally determined real and imaginary parts (ε', ε'') of the complex dielectric permittivity (ε^*) from the dielectric measurements carried out on dilute solutions of polar solutes in non-polar solvents for which the Debye's theory which assumes a single relaxation time is applicable. Further, by carrying out the experiments on pure liquid state at different frequencies for which the Cole-Cole approach is applicable, the single relaxation time (τ) for which the distribution parameter (α) will be equal to zero or the distribution of relaxation times for which the distribution parameter (α) may vary from 0 to 1 may be obtained. However by using a method suggested by Higasi, a crude estimation of the distribution of relaxation time (τ) can be obtained from the experiments carried out on the dilute solutions at single frequency in the microwave region. The dipole moment (μ) in the pure liquid state can be determined by using the experimentally determined parameter like static dielectric constant (ε_0), density (d) and optical permittivity ($\varepsilon_\infty = n_D^2$) by using several methods reported in the literature. Therefore the dielectric studies based on pure liquid state and on dilute solution measurements have proved to be very useful techniques in understanding the dielectric behaviour of polar molecules in terms of the molecular structure, size, shape of the molecules, inter and intra molecular forces, to calculate the thermo dynamical parameters like change in activation energy (ΔG*), enthalpy of activation (ΔH*) and entropy of activation (ΔS*) which are useful in understanding the state of orderliness of the dielectric system, to draw certain quantitative conclusions regarding molecular motion and inter molecular forces in liquids, liquid mixtures, dilute solutions and multi component polar solutes in dilute solutions, etc. It is observed that one can find the results of such measurements on a variety of polar molecules extensively discussed and reported in the literature.

II. Determination of dipole moment and relaxation time by different methods:

The dipole moment and relaxation time of all the four samples were determined by using Gopalkrishna, Microwave conductivity and Higasi method and the corresponding theoretical background for all these methods is described again here in brief for the convenience of the reader.

A. Gopalkrishna’s method (G.K. Method):

Gopalkrishna method is the most frequently used method for the determination of dipole moment and relaxation time. In this method, the dielectric measurements are carried out at a single frequency on dilute solutions of different concentrations of polar solute molecules in non-polar solvent. For each concentration, X and Y parameters are calculated using the following equations.

$$X = \frac{\varepsilon'^2 + \varepsilon''^2 + \varepsilon' - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad (16) \qquad\qquad Y = \frac{3\,\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad (17)$$

Where ε' and ε'' represents dielectric constant and dielectric loss respectively.

The relaxation time (τ) is given by the equation

$$\tau = \frac{1}{\omega \times slope\ of\ X\ vs. Y} \qquad (18)$$

The dipole moment is given by

$$\mu = \sqrt{\frac{9KTM(1+\omega^2\tau^2)\times n}{4\pi N d}} \qquad (19)$$

Where K, T, M, ω, d, and N are Boltzmann’s constant, absolute temperature, molecular weight of solute, angular frequency, density of solvent and Avogadro’s number respectively. n is the slope of X vs. W (weight fraction of solute molecule) plot.

B. Microwave conductivity method:

Dipole moment (μ) and relaxation time (τ) can also be determined by the microwave conductivity method proposed by Murthy M.B.R. et al. The two parameters K' and K'' are given as

$K^{'} = \frac{\omega\varepsilon^{"}}{4\pi}$ (20) and $K^{"} = \frac{\omega\varepsilon^{'}}{4\pi}$ (21)

The relaxation time (τ) is given by the equation

$$\tau = \frac{1}{\omega \times slope of K^{"} vs.\ K^{'}} \tag{22}$$

The dipole moment is given by

$$\mu = \left(\frac{27KTM(1+\omega^2\tau^2) \times slope of K^{'} vs.\ W}{\omega^2 Nd(\varepsilon_0+2)^2\tau}\right)^{1/2} \tag{23}$$

C. Higasi's method:

The two important molecular parameters dipole moment (μ) and most probable relaxation time (τ_0) can also be determined by the single frequency method proposed by Higasi. Using this method, it is possible to examine whether the system under study is of Debye type or not. According to this method, the most probable relaxation time (τ_0) is given by the following equation

$$\tau_0 = \frac{1}{\omega}\left[\frac{A^2+B^2}{C^2}\right]^{\frac{1}{2(1-\alpha)}} \tag{24}$$

Where $1 - \alpha = \frac{2}{\pi}\tan^{-1}\left(\frac{A}{B}\right)$ (25)

$A = a^{"}(a_0 - a_\infty)$, $B = (a_0 - a^{'})(a^{'} - a_\infty) - a^{"}$ and $C = (a^{'} - a_\infty)^2 + a^{"2}$

(26)

Here α is the distribution parameter. The parameters a_0, $a^{'}$, $a^{"}$and a_∞ corresponds to the slopes obtained from the linear graphs of ε_0 , $\varepsilon^{'}$, $\varepsilon^{"}$ and ε_∞ vs. W respectively.

The dipole moment (μ) is given by

$$\mu = B \times (a_0 - a_\infty)^{\frac{1}{2}} \tag{27}$$

Where $B = \frac{1}{2(\varepsilon_0+2)}\left[\frac{27MKT}{\pi Nd}\right]$ (28)

III. EXPERIMENTAL:

A. Measurement of dielectric constant (ε') and dielectric loss factor (ε"):

The experimental set-up used for the measurement of dielectric constant (ε') and dielectric loss factor (ε") and hence electric dipole moment (μ) and relaxation time (τ) and other related parameters by using an X- band microwave setup at frequencies ranging from 8.5 GHz to 11.5 GHz is shown in Fig.1.

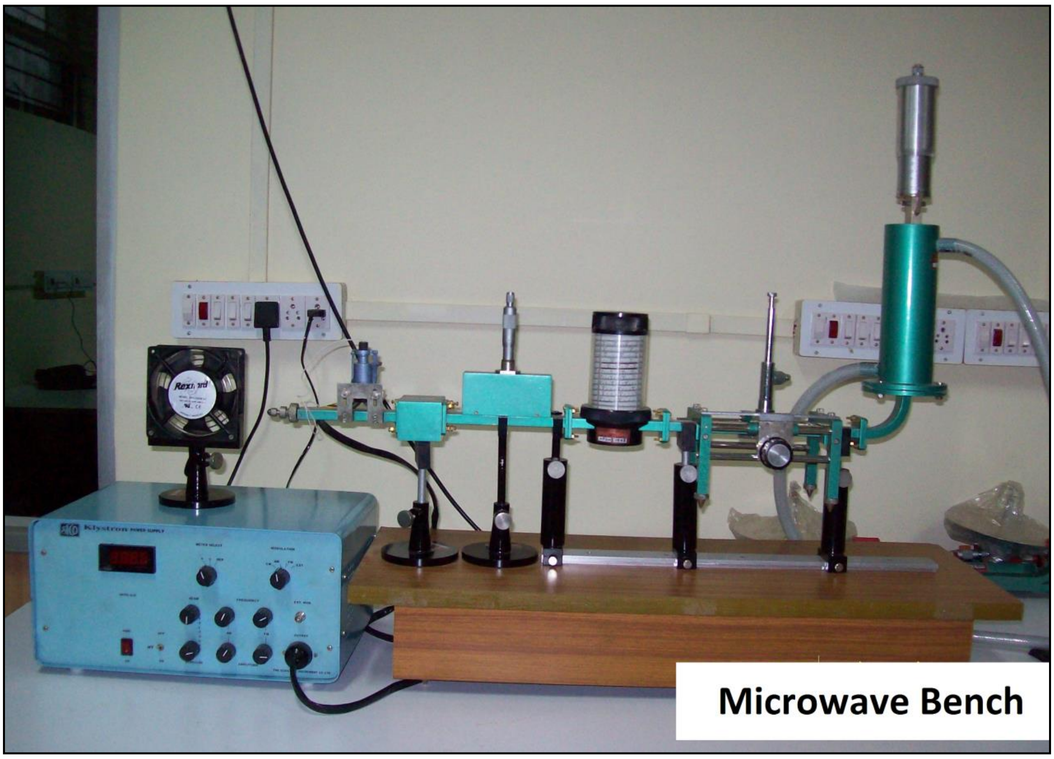

Fig.1 X-Band Microwave Bench

B. Determination of Static Dielectric Constant (ε_{12}) at Radio frequency:

The static dielectric constant of a medium is usually measured as the ratio of the capacitance of a condenser cell with the dielectric medium and without the dielectric medium in it. For the measurement of very small changes in capacitance, several methods have been suggested in the literature and the method suggested by Le Fevre et al. is widely used. In the present investigation, for the determination of static dielectric constant (ε_{12}) of various dilute solutions of different weight fractions, we have used a digital LCR meter of model MT-4080D supplied by Aplab Ltd, Thane, India working at 10 kHz frequency having a resolution of 0.001 pF and accuracy of ±0.01pF.

Experimental Cell:

The dielectric cell used for the determination of static dielectric constant was fabricated by the author in this laboratory and the set up used for the determination of static dielectric constant is as shown in Fig.2. The dielectric cell consists of two concentric metallic cylinders kept in position with small glass strips inside the surface of the cylinders. In order to determine the static dielectric constant, the dielectric cell is connected to the LCR Data Bridge and the capacitance of the empty dielectric cell (C_1) was noted down. Next the dielectric cell was completely immersed in the required solution of particular weight fraction and the capacitance (C_2) of the dielectric cell was noted down. Then by knowing (C_1) and (C_2) the static dielectric constant (ε_{12}) of the solution can be calculated by the ratio of capacitance of the cell with and without the sample i.e.

$$\varepsilon_{12} = C_2 / C_1 \qquad (29)$$

Since the leads connecting to the dielectric cell and LCR meter would have some capacitance, therefore for the accurate determination of the dielectric constant of the solution, this leads capacitance (C_x) must also be included. Hence the modified expression for dielectric constant is given by

$$\varepsilon_{12} = (C_2 - C_x) / (C_1 - C_x) \quad (30)$$

Where C_x corresponds to the leads capacitance

The value of leads capacitance (C_x) was determined by using LCR Data Bridge by carrying out measurements on several standard non-polar liquids like benzene, n-hexane, carbon tetrachloride, etc., and the mean value of (C_x) was determined. Using this value of (C_x), the dielectric constant of some more standard liquids were determined and it was observed that, the values of dielectric constants of these liquids were found to be in good agreement with the literature values.

Fig.2 Static dielectric constant measurement setup

C. Measurement of Refractive Index (n) & Density (D):

1. Refractive Index Measurement (n):

The refractive indices of each weight fraction of the probe samples were measured using Abbe’s refractometer. The refractive index values measured by the refractometer were verified for the known standard non-polar solvents and the obtained values were found to be accurate up to fourth decimal place.

2. Density Measurement (D):

The densities of the various samples were determined by using a 10 ml specific gravity bottle. The uncertainty in the measurement of density was found to be ± 0.005 g/ml. The density was determined by using the Eq. (31)

$$D_u = \frac{W_u}{W_d} x \, D_d \qquad (31)$$

Where

D_u - Density of unknown liquid

W_u - Weight of unknown liquid

W_d - Weight of Distilled water

D_d - Density of Distilled water

The value of density of distilled water was taken from literature. The setup used for the density measurement is as shown in Fig.3.

Fig.3 Density measurement set up.

D. Computational Method:

The ground state geometries of all probe molecules were optimised using Gaussian 09W software by using DFT with basis sets B3LYP/6-31G(d).

IV. Materials and Methods:

The samples 2-Nitroaniline, 4-Bromoaniline, 4-Chloroaniline and 4-Chlorophenol are of AR grade with purity 99% and were procured from Sd-Fine Chem. Co Ltd. India and the molecular structures are as shown in Fig-4.1a-d respectively.

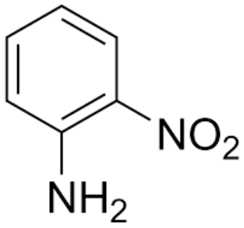

Fig-4.1a

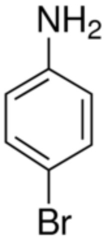

Fig-4.1b

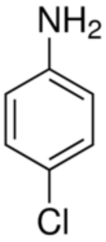

Fig-4.1c

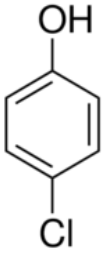

Fig-4.1d

The X-band microwave bench supplied by Scientific Instrument Co. Ltd (SICO), Ghaziabad, India, is used to determine dielectric constant (ε') and dielectric loss (ε'') by employing standing wave techniques. For the generation of microwaves, Klystron (2K25) source was used and the frequency 9.59 GHz was fixed, so that the intensity was maximum at the output. The static dielectric constants of the various solutions of different concentrations were determined with the help of Aplab MT-4080D model LCR Data Bridge at 10 kHz frequency using a suitably calibrated brass cell of small capacitance by measuring the capacitance of the solution, air. The refractive indices of various solutions of different concentrations for Sodium D line were determined by using the Abbe's Refractometer. The square of the refractive index (n) is taken as optical permittivity ($\varepsilon_\infty = n_D^2$). A 10 ml specific gravity bottle was used to determine the density. The uncertainty in measurement of capacitance, refractive index, density and mass are ±0.1 pF, ± 0.0005, ± 0.005 g/ml and 0.001g respectively. All the measurements were carried out at room temperature. All theoretical computations were performed using Gaussian 09W software by using DFT level of theory with basis sets B3LYP/6-31G(d) for calculating dipole moment.

V. Results and Discussions:

1. Estimation of dipole moments and relaxation times:

Dielectric constant (ε') and dielectric loss (ε") are determined from microwave bench and static dielectric constant (ε_0) and optical permittivity (ε_∞) are determined using LCR-Data Bridge and Abbe's Refractometer respectively for different weight fractions (W) of all the four samples in benzene and are given in Tables-1.1a to 1.1d. Further, the parameters like X, Y, K' and K" are also calculated following Gopalkrishna and microwave conductivity methods for all the samples and are also given in Tables-1.1a to 1.1d.

Table-1.1a: Dielectric constant, dielectric loss, static dielectric constant, optical permittivity and various calculated parameters for 2-Nitroaniline.

W	ε'	ε"	ε_0	ε_∞	X	Y	K' (Hz)	K'' (Hz)
0.0175	2.5050	0.0621	2.5808	2.2575	0.3342	0.0092	4.40E+07	1.60E+09
0.0138	2.4687	0.0536	2.5373	2.2605	0.3288	0.0081	3.86E+07	1.58E+09
0.0099	2.4251	0.0354	2.5144	2.2560	0.3221	0.0054	2.60E+07	1.54E+09
0.0060	2.3725	0.0233	2.4090	2.2545	0.3139	0.0037	1.75E+07	1.51E+09
0.0020	2.3256	0.0081	2.3899	2.2515	0.3065	0.0013	6.23E+06	1.47E+09

Table 1.1b: Dielectric constant, dielectric loss, static dielectric constant, optical permittivity and various calculated parameters for 4-Bromoaniline.

W	**ε'**	**ε''**	**ε_0**	**ε_∞**	**X**	**Y**	**K' (Hz)**	**K'' (Hz)**
0.0171	2.3622	0.0177	2.4541	2.2545	0.4003	0.0658	3.15E+08	1.92E+09
0.0139	2.3548	0.0108	2.3928	2.2515	0.3825	0.0630	3.02E+08	1.83E+09
0.0108	2.3413	0.0107	2.3444	2.2530	0.3676	0.0605	2.90E+08	1.76E+09
0.0068	2.3252	0.0038	2.2949	2.2515	0.3523	0.0581	2.78E+08	1.69E+09
0.0029	2.3014	0.0012	2.3533	2.2500	0.3709	0.0611	2.93E+08	1.78E+09

Table-1.1c: Dielectric constant, dielectric loss, static dielectric constant, optical permittivity and various calculated parameters for 4-Chloroaniline.

W	**ε'**	**ε''**	**ε_0**	**ε_∞**	**X**	**Y**	**K' (Hz)**	**K'' (Hz)**
0.0189	2.4165	0.0367	2.5139	2.2545	0.4163	0.0683	3.28E+08	2.00E+09
0.0159	2.4007	0.0308	2.4808	2.2530	0.4073	0.0669	3.21E+08	1.95E+09
0.0128	2.3846	0.0198	2.4613	2.2530	0.4023	0.0661	3.17E+08	1.93E+09
0.0098	2.3580	0.01460	2.4328	2.2545	0.3942	0.0648	3.11E+08	1.89E+09
0.0068	2.3425	0.00820	2.4072	2.2515	0.3870	0.0637	3.05E+08	1.86E+09

Table-1.1d: Dielectric constant, dielectric loss, static dielectric constant, optical permittivity and various calculated parameters for 4-Chlorophenol.

W	**ε'**	**ε''**	**ε_0**	**ε_∞**	**X**	**Y**	**K' (Hz)**	**K'' (Hz)**
0.0191	2.36421	0.0222	2.4689	2.2545	0.4043	0.0664	3.18E+08	1.94E+09
0.0159	2.35803	0.0209	2.4271	2.2530	0.3922	0.0645	3.09E+08	1.88E+09
0.0119	2.34862	0.0145	2.3342	2.2515	0.3643	0.0600	2.88E+08	1.75E+09
0.0089	2.33241	0.0094	2.3694	2.2515	0.3754	0.0618	2.96E+08	1.80E+09
0.0059	2.3208	0.0050	2.3294	2.2515	0.3632	0.0599	2.87E+08	1.74E+09

It is observed from Tables 1.1a-d that, the dielectric constant (ε'), dielectric loss (ε''), static dielectric constant (ε_0) and optical permittivity (ε_∞) values increases with increase in weight fraction for all the samples in benzene, which indicates that the observed experimental values are of the right order. Further, in order to determine relaxation time (τ) and dipole moment (μ), different linear plots of X vs. Y , X vs. W , ε' vs. W , ε'' vs. W, ε_0 vs. W, n^2_D vs. W, K'' vs. K' and K' vs. W were made and are shown in Figs. 5.1a-h for all the samples.

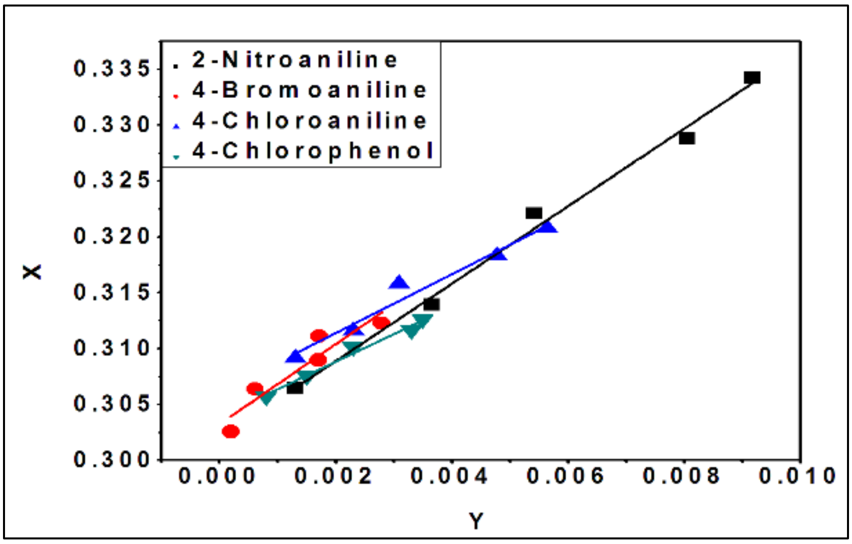

Fig.5.1a: X vs. Y plot

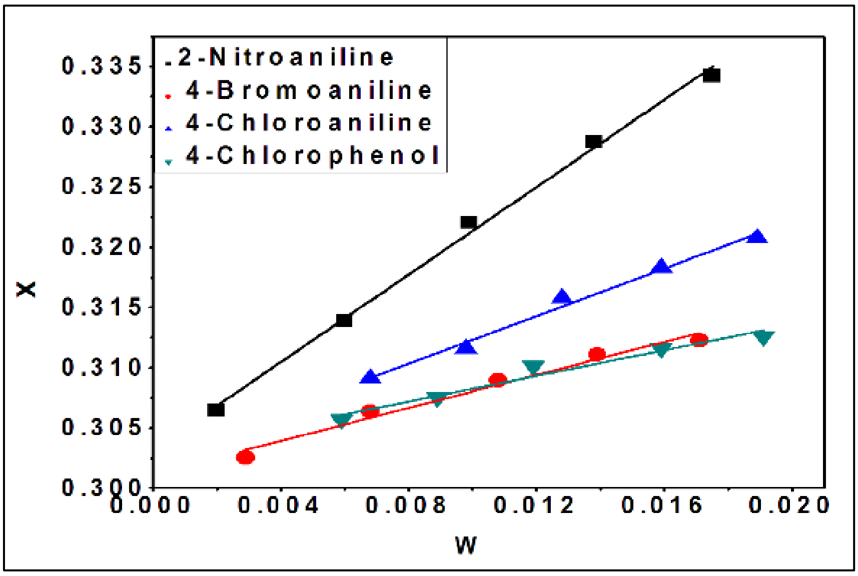

Fig.5.1b: X vs. W plot

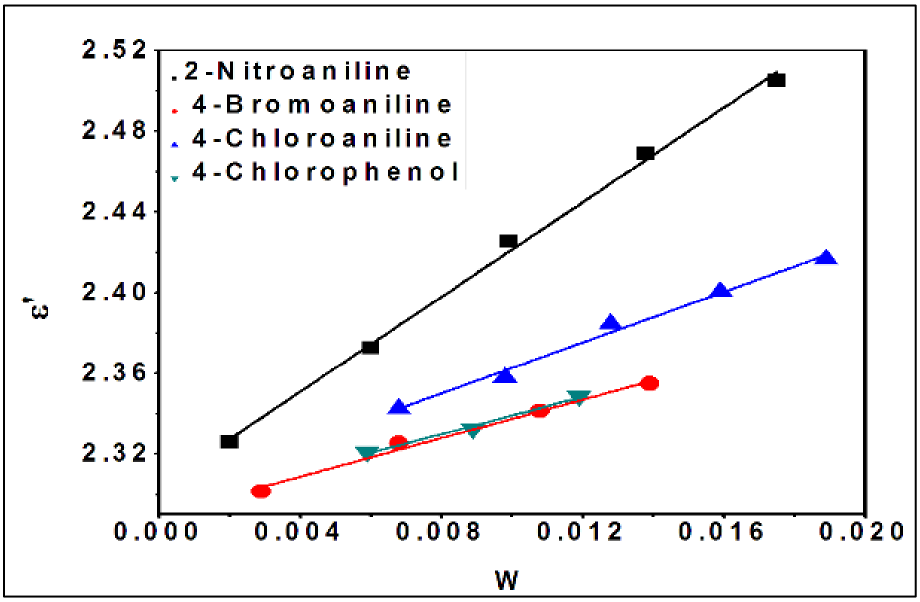

Fig.5.1c: ε' vs. W plot

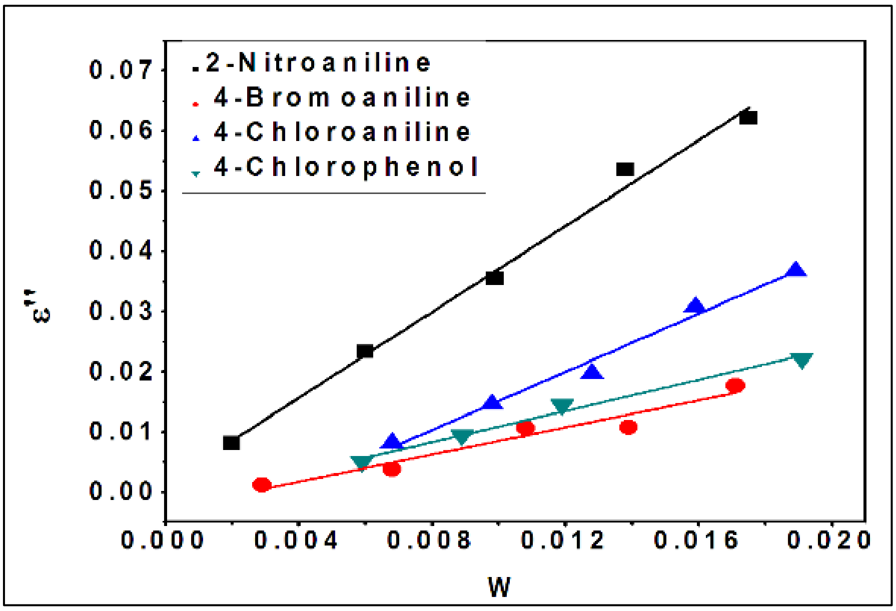

Fig.5.1d: ε'' vs. W plot

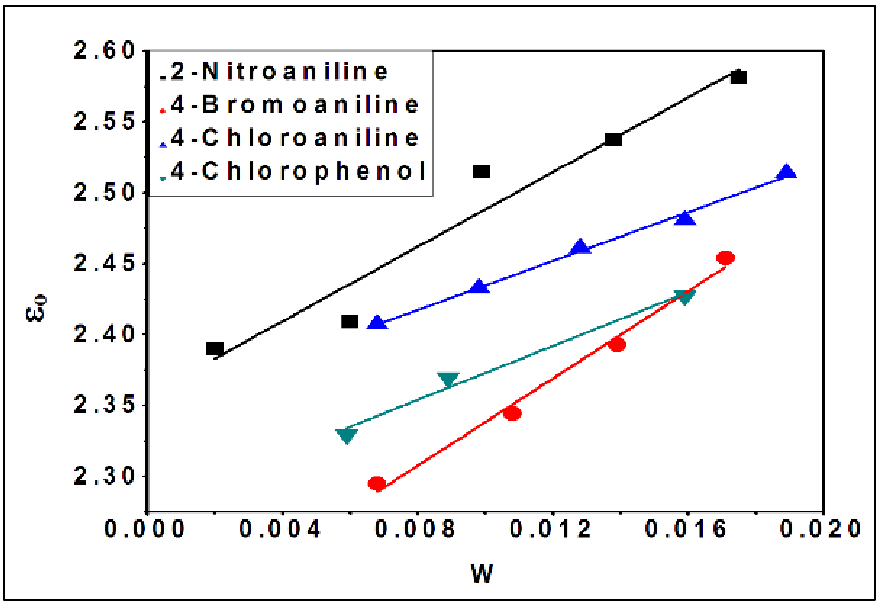

Fig.5.1e: ε_o vs. W plot

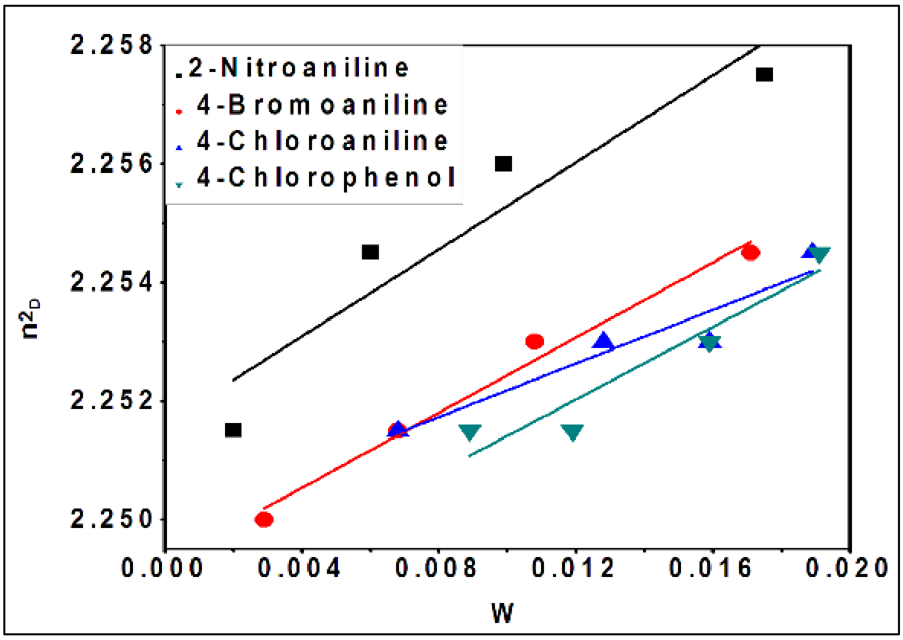

Fig.5.1f: n^2_D vs. W plot

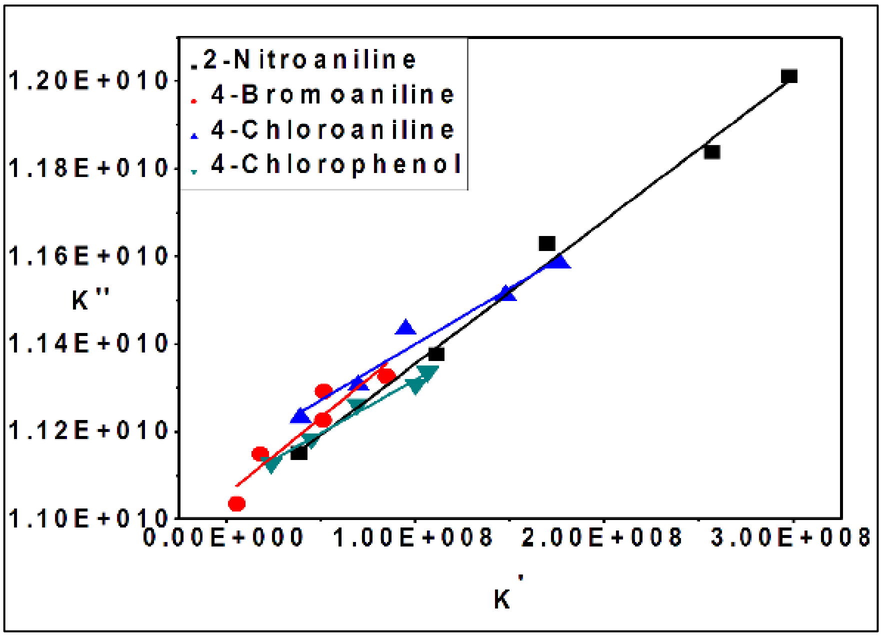

Fig.5.1g: K" vs. K' plot

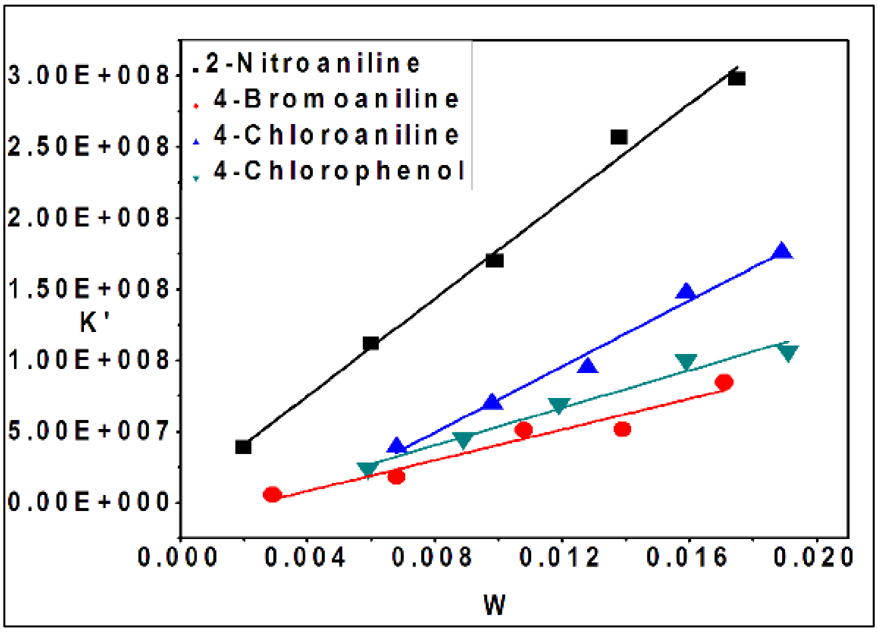

Fig.5.1h: K' vs. W plot

Then, from the slopes of the above plots and following Gopalkrishna, microwave conductivity and Higasi methods, parameters like dipole moment (μ), relaxation time (τ), distribution parameter (α) and most probable relaxation time (τ_0) were calculated for all the four samples and are presented in Table-2.

Table-2: Dipole moment and relaxation times from different methods.

Molecule	**G.K.Method**		**Microwave Conductivity Method**		**Higasi Method**			**Theoretical Dipole moment μ (D)**
	μ (D)	**τ (ps)**	**μ (D)**	**τ (ps)**	**μ (D)**	**τ_0 (ps)**	**α**	
2-Nitroaniline	3.91	4.78	4.31	5.07	3.98	5.10	0.04	5.45
4-Bromoaniline	2.68	4.63	2.48	4.71	3.50	5.23	0.76	4.16
4-Chloroaniline	2.85	6.30	2.66	6.50	3.12	6.75	0.25	4.55
4-Chlorophenol	2.12	6.71	2.19	6.83	3.29	20.01	0.61	2.75

From Table-2, it is observed that the dipole moments determined from Gopalkrishna and microwave conductivity methods are found to be in very good agreement with each other for all the samples except 2-Nitro aniline. Further, the dipole moments determined from Higasi method for all the samples are found to be slightly higher compared to the Gopalkrishna and microwave conductivity methods. It may be due to the reason that, the Higasi method takes into consideration the distribution of relaxation times, whereas the other two methods do not consider the distribution of relaxation times. This is supported by the finite non-zero values of the distribution parameter (α) for all the molecules as given in the Table-2. The higher values of dipole moments in case of Higasi method may also be partly due to the inherent inaccuracies involved in the measurement of various slopes like a', a'', a_o and a_∞ which are supposed to be measured very accurately.

It is observed from the literature that, the value of τ in case of benzene substituted molecules having one benzene ring in its chemical structure would be around 8-15 ps. In the present study also, the relaxation times obtained for the benzene substituted molecules were found to be in agreement with this order. Further, experimentally determined relaxation times were analysed in terms of SED theory. For this purpose, the SED radii of all the four molecules were calculated by using the experimentally determined relaxation times and viscosity of neat solvent from literature (0.5946 mPa.s for benzene) and also radii of all the four molecules were computed form DFT and Edward’s atomic increment method. The molecular radii of all the molecules calculated from different methods are given in Table-3.

Table-3: Molecular radii from different methods.

Molecule	**Molecular Radius(Å)**		
	SED Theory	**Edward’s Method**	**DFT Computations**
2-Nitroaniline	1.995	3.048	3.058
4-Bromoaniline	1.974	3.001	3.276
4-Chloroaniline	2.187	2.962	3.182
4-Chlorophenol	2.234	2.932	3.101

From Table-3 it is observed that, the calculated SED radii are nearly in order with the molecular radii calculated from the other two methods. These observations suggest that, the experimentally determined relaxation times of all the four molecules are in right order and the molecular dynamics follows SED theory.

It is noticed from Table-2 that, the relaxation times determined from Gopalkrishna, microwave conductivity and Higasi methods were found to be in very good agreement with each other except in the case of 4-Chlorophenol. Further, the low non zero value of the distribution parameter (α=0.04) in case of 2-Nitroaniline suggests a simple Debye type relaxation behaviour for this molecule.

It is also observed that, the distribution parameter (α) calculated according to Higasi method for the samples 4-Bromoaniline, 4-Chloroaniline and 4-Chlorophenol are found to be large non-zero values. The finite non-zero value of distribution parameter (α) suggests that, the observed absorption may be due to both intra-molecular rotations due to internal rotation of a polar group in the molecule and the overall rotations of the molecules.

It is evident from Table-2 that, 4-Chlorophenol is having higher relaxation time than the three anilines. It may be due to the fact that, alcohols are strongly associated in solution because of dipole-dipole interaction and hydrogen bonding, whereas aromatic amines are non-associative in nature. Because of the ability of the alcohols to undergo self-association, 4-Chlorophenol experience large steric hindrance for dipole rotation which in turn may lead to the higher relaxation time.

2. Theoretical dipole moments from *ab initio* computations:

The optimized molecular geometries of 2-Nitroaniline, 4-Bromoaniline, 4-Chloroaniline and 4-Chlorophenol along with the direction of dipole moments are shown in Figs.6.1a-d respectively.

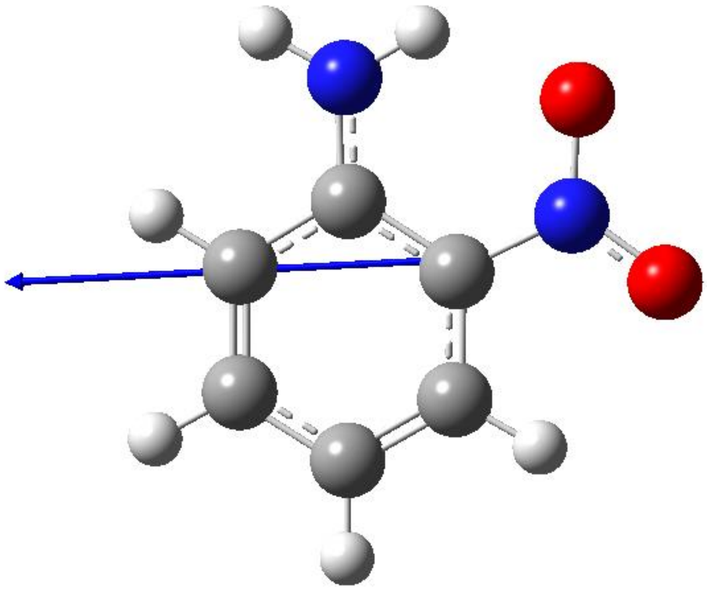

Fig.6.1a Optimized molecular geometry of 2-Nitroaniline

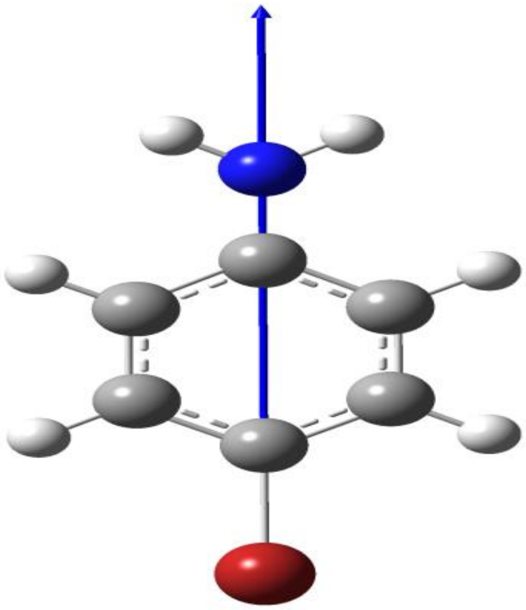

Fig.6.1b Optimized molecular geometry of 4-Bromoaniline

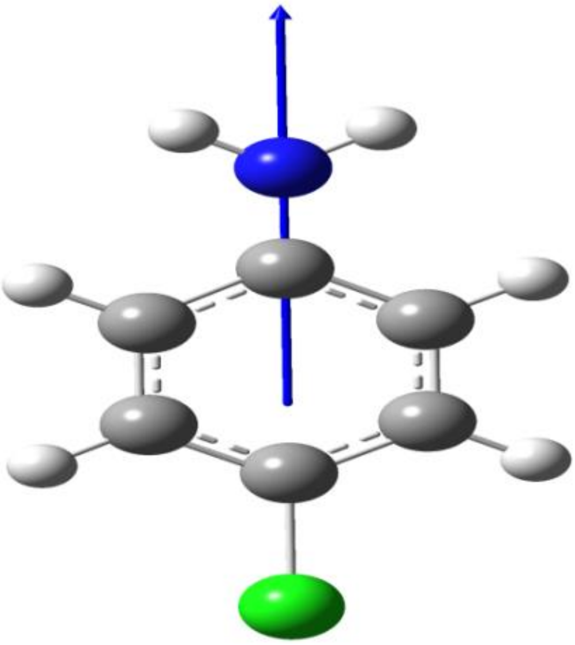

Fig.6.1c Optimized molecular geometry of 4-Chloroaniline

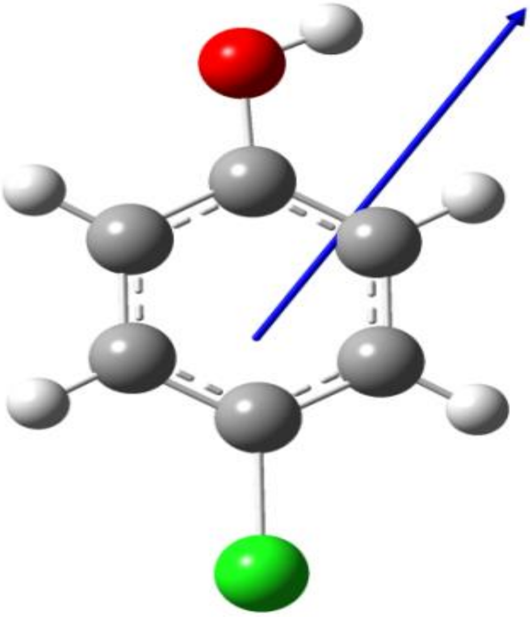

Fig.6.1d Optimized molecular geometry of 4-Chlorophenol

The dipole moments for all these molecules determined theoretically from *ab initio* computations by using DFT level of theory with basis sets B3LYP/6-31G(d) with the help of Gaussian 09W software are given in Table-2.

The dipole moments calculated theoretically for all the samples are found to be higher than the experimentally determined dipole moments. This could be due to the reason that, the dipole moments calculated from theoretical methods do not take into account the solvent and environmental effects like solute-solvent interactions and the dipole moments were obtained from these models by considering the molecules in gas phase. The deviation between the experimental and theoretical dipole moment values may also be due to the π electron cloud of non-polar solvent benzene affecting the dipole moment values of the solute systems. Further, it is to be noted that the theoretically computed dipole moments which are based on charge densities obtained from Eigen functions of the molecular orbital approximations are found to be considerably higher than the actual experimental dipole moments.

In order to check the validity of the theoretically calculated dipole moments, the dipole moments of all the four molecules were also estimated by taking the dipole moments of Aniline, Nitrobenzene, Bromobenzene, Chlorobenzene and Phenol from literature. The approximate dipole moment of every molecule is estimated by taking vector sum of group moments by neglecting the interaction between pendant groups. The estimated values of dipole moments of 2-Nitroaniline, 4-Bromoaniline, 4-Chloroaniline and 4-Chlorophenol are found to be 3.78 D, 2.83 D, 2.82 D and 2.91 D respectively. It is observed that, these estimated dipole moments are in order with the theoretically calculated dipole moments and are also in good agreement with the experimentally determined dipole moments from different methods.

VI. Conclusions:

The dielectric relaxation behaviour of four polar molecules namely 2-Nitroaniline, 4-Bromoaniline, 4-Chloroaniline and 4-Chlorophenol in dilute solutions of benzene were studied at microwave frequency 9.59 GHz. The two important molecular parameters dipole moment (μ) and relaxation time (τ) were determined by Gopalkrishna, microwave conductivity and Higasi method. The dipole moments determined from Gopalkrishna and conductivity method were found to be in good agreement with each other. However the dipole moments determined from Higasi method were found to be slightly higher than the other two methods. The dipole moments for all these molecules were also determined theoretically from *ab initio* computations by using DFT. The validity of dipole moments obtained from DFT computations were verified and it is observed that the dipole moments obtained from DFT computations were found to be in order with the dipole moments estimated by taking vector sum of group moments. The agreement in the values of estimated molecular radii from SED, Edward’s and DFT methods suggests that the experimentally determined relaxation times are of the right order and the molecular dynamics follows SED theory. The dielectric relaxation behaviour studies revealed that, 2-Nitroaniline exhibits simple Debye type relaxation behaviour while the other three samples exhibit the Higasi’s distribution of relaxation times which may be due to both, intra-molecular rotations due to internal rotation of a polar group in the molecule and the overall rotations of the molecules.

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