Dielectric Spectroscopic Studies of Propylene Glycol/Aniline Mixtures at Temperatures Between 303K to 323K

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Abstract—Dielectric spectra of propylene glycol, aniline and their binary mixtures with different concentrations were studied at 303K-323K by using Coaxial cable method in the microwave frequency range 20 MHz-20 GHz. The relaxational response of the propylene glycol, aniline and their binary liquid mixtures over the entire composition range is analysed by using Cole-Cole relaxation model. Dipole moments obtained from the Higasi’s method are compared with the quantum mechanical HF and DFT calculations. From the experimental data- dipole moment, Bruggeman parameter, Kirkwood g factor, excess dielectric and thermodynamic parameters have been calculated. The obtained data have been analysed in terms of the parallel and anti parallel orientation of the dipoles, chain length and hydrogen bond interaction in the mixture composition.

Keywords--- Relaxation Time, Dipole Moment, Excess Dielectric And Thermodynamic Parameters

1.INTRODUCTION
Dielectric relaxation spectroscopy (DRS) is an effective method to explain the structure and molecular dynamics of the liquids and nature of the intermolecular interactions [1-12]. Depending upon the nature of the liquid samples under investigation, DRS may provide sufficient information about the thermodynamics, kinetic and structural features of the solutions. The high susceptibility of DRS to molecular interactions makes this method a valuable tool to get a depth understanding into the liquid state properties which governs with the forces. The dielectric studies of liquid mixtures containing the varying amounts of interacting components helps to investigate the structure of the complexes formed. Hydrogen bonding considerably alerts the dielectric properties of liquids, understanding Hydrogen bonding remains a complex task due to the uncertainty to recognise the particular bonds and the elements are involved [13]. Further the thermodynamic properties of liquids and their liquid mixtures have been used to know the molecular interaction between the constituents involved in the liquid mixture and also for engineering applications related to heat energy transfer, mass transfer, activation energy, enthalpy and entropy of the polar molecules [14]. Relaxational response of liquids depends not only upon intra- and intermolecular interaction but also on the profound features like molecular size and shape, these geometric factors are important to elucidate the structural behaviour of liquid mixtures in which weaker intermolecular interactions, mainly of dipolar nature, are present.

The first systematic dielectric dispersion studies of pure poly (propylene glycol)s of different molecular weight in the glass transition region measured by Baur and Stockmayer [15] and dielectric relaxation spectra of propylene glycols studied as a function of temperature and pressure by Suzuki et al [16]. The complex dielectric permittivity of viscous propylene glycol is studied by impedance methods and observed that there exist two distinct nonlinear features in the super cooled liquid near its glass transition temperature [17]. Park et al [18, 19] explained the liquid glass transition and α relaxation in terms of the thermal and dielectric properties of propylene glycol and polypropylene glycol with different molecular weights. Navarkhele et al [20] studied the dielectric relaxation behaviour of formamide-propylene glycol binary mixture in the frequency range 10 MHz- 20 GHz by using TDR technique and explained the Kirkwood angular correlation factor (g^eff) is more than one in formamide rich region and less than one in propylene glycol region. Mali et al [21] have reported the dielectric relaxation of poly ethylene glycol in aqueous medium and their results shows that intermolecular homogeneous and heterogeneous hydrogen bonding vary significantly with increase in concentration of poly ethylene glycols in aqueous solution medium.

In this article, an attempt has made to investigate the molecular interaction between the self associative propylene glycol and non self associative aniline molecules and also in their mixtures of different molar concentration levels by determining the complex dielectric permittivity and relaxation times. Complex dielectric permittivity of
these liquid mixtures were measured in the frequency range 20MHz – 20 GHz by considering open-ended coaxial probe method [22,23] at different temperatures i.e. 303K, 308K, 313K, 318K and 323K. The experimental dipole moments of propylene glycol, aniline and their equimolar binary mixtures were calculated by using Higasi’s method [24]. The theoretical dipole moments were also calculated by using Quantum mechanical Hartree-Fock and Density Functional Theory (B3LYP) calculations with 6-311G+, 6-311G++ basis sets by using Gaussian software [25-29]. The relaxation response of the propylene glycol, aniline and their binary liquid mixtures over the entire composition range is analysed by using Cole-Cole relaxation model [30, 31]. By using Eyrings rate equation [32, 33], the thermodynamical parameters such as enthalpy of activation ΔH*, entropy of activation ΔS* are determined and also effective Kirkwood ‘g’ factor is obtained from the Kirkwood-Frohlich equation [34]. The long range and short range interactions between dipoles is obtained from the excess Helmholtz energy (ΔF^E) calculations [35]. The obtained experimental data of the binary mixtures of propylene glycol and aniline were interpreted in terms of the parallel and anti parallel orientation of the dipoles, chain length and Hydrogen bond interaction in the liquid mixture composition.

II. MATERIALS AND EXPERIMENTS

a. Materials
The chemicals used in this work such as propylene glycol, aniline and benzene were supplied by Merck, Germany (purity 99 %, AR Grade). These liquids were further purified by double distillation under reduced pressure and only middle fractions were collected [36]. Before use, the chemicals were stored over 4Å molecular sieves for 48 hrs to avoid water content and were then degassed. Initially dilute solutions of polar liquids (Solute) are prepared over a concentration range of 0 to 1 ml in 10 ml of non-polar solvent benzene in order to evaluate the dipole moments of the pure and equimolar binary liquids of propylene glycol and aniline by considering the Higasi’s method in the temperature range 303K-325K.

b. Computational Details
The minimum energy based geometry optimization of the monomers of propylene glycol, aniline and their binary system were carried out by using Quantum mechanical Hartree-Fock and Density Functional Theory (B3LYP) calculations with 6-311G+, 6-311G++ basis sets by using Gaussian software [25-29]. The theoretical dipole moments were also calculated by using Quantum mechanical Hartree-Fock and Density Functional Theory (B3LYP) calculations with 6-311G+, 6-311G++ basis sets by using Gaussian software [25-29].

III. RESULTS AND DISCUSSION

The low frequency dielectric permittivity (ε), dipole moment (μ), relaxation time (τ) values of the pure and equimolar binary systems of propylene glycol and aniline at room temperature (298K) are tabulated in Table 1 and also the variation of dipole moments of the pure and their binary mixtures at different temperatures are reported in Table 2 respectively. The experimentally determined dipole moment values are compared with the theoretical HF, DFT (B3LYP) calculations which are tabulated in Table 3. The maximum errors in the evaluated values of static dielectric constant (εs) and refractive indices (n) are ± 1% and real (ε') and imaginary part of dielectric permittivity (ε'') are ± 2% and ± 2-3% respectively.

The excess Helmholtz energy (ΔF^E) is a dielectric parameter to determine the interaction between the constituents in the liquid mixture through breaking mechanism of hydrogen bond [35] and expressed as

\[
ΔF^E = ΔF^E_{av} + ΔF^E_{av} + ΔF^E_{av}
\]

Where ΔF^E_{av} represents the excess dipolar energy due to long range electrostatic interaction, ΔF^E_{fr} represents the excess dipolar energy due to the short range interaction between identical molecules, ΔF^E_{fr} represents the excess free energy due to the short range interaction between the dissimilar molecules.

The above terms are given in detail in below equation

\[
ΔF^E = \sum_{r=1}^{N_r} \frac{1}{2} \sum_{i=1}^{N_r} \sum_{j=1}^{N_r} \left[ \frac{ε_i - 1}{ε_i + 2} \right] \left[ \frac{R_{ij}}{2} \right] + \sum_{r=1}^{N_r} \frac{8πN_ε}{9V_r} \left( ε_i - 1 \right) \left( ε_i + 2 \right) \left( 2ε_j + ε_{av} \right)
\]

where

\[
R_{ij} = \left( \frac{8πN_ε}{9V_r} \right) \left( ε_i - 1 \right) \left( ε_i + 2 \right) \left( 2ε_j + ε_{av} \right)
\]

and V_r is the molar volume of the components and N_ε is the avagadros number. The parameters ε_i, ε_i and ε_{av} represents the dielectric permittivity values at static (820 Hz) and optical frequencies of the pure liquids, binary mixtures and g_1 and g_2 are the effective g factors of the pure liquid samples respectively.
Table 1 Comparison of low frequency dielectric permittivity ($\varepsilon_0$) and relaxation time ($\tau$) values of the pure compounds

| Liquid                  | $\varepsilon_0$ at 298 K | $\tau$ (ps) |
|------------------------|--------------------------|-------------|
|                        | This work                | Literature† | This work                | Literature† |
| Aniline (A)            | 7.42                     | 7.06        | 84.28$^{11}$            |              |
| Propylene glycol (B)   | 28.95                    | 27.5        | 307.26                  | 268.8$^{11}$ |
| Equimolar binary mixtures of A+B | 16.56                  | ----        | 185.98                  | ----        |

† crc handbook of chemistry and physics (1969-1970), weast nc (ed) (1983-84), hand book of chemistry and physics, 64th edn, crc press, fl 62 Aparicio et al

Table 2 Experimental dipole moment ($\mu$) and excess dipole moment ($\Delta\mu$) values for the pure system aniline, propylene glycol and equimolar binary systems- aniline and propylene glycol

| $T$ (K) | Aniline $\mu$ (D) | Propylene glycol $\mu$ (D) | Equimolar binary mixture of aniline-propylene glycol $\mu$ (D) | $\Delta\mu$ (D) |
|---------|-------------------|-----------------------------|---------------------------------------------------------------|-----------------|
| 303     | 1.48              | 3.52                        | 3.21                                                          | -1.59           |
| 308     | 1.47              | 3.33                        | 3.22                                                          | -1.58           |
| 313     | 1.49              | 3.35                        | 3.24                                                          | -1.60           |
| 318     | 1.50              | 3.37                        | 3.25                                                          | -1.62           |
| 323     | 1.52              | 3.38                        | 3.26                                                          | -1.64           |

Table 3 Experimental and theoretical dipole moment ($\mu$) and excess dipole moment ($\Delta\mu$) values for pure system aniline, propylene glycol and equimolar binary systems- aniline and propylene glycol at 298 K

| System     | Experimental (298K) | Theoretical Calculations | Hatree-Fock (HF) |
|------------|---------------------|--------------------------|-----------------|
|            | $\mu$ (D)           | $\Delta\mu$ (D)          | $\Delta\mu$ (D) |
|            | Literature†         | 6-31G+                    | 6-31G++         |
| aniline (A)| 1.48                | 1.53                     | 1.45            |
| Propylene glycol (A) | 3.32                | 3.60                     | 2.64            |
| A+B        | 3.21                | ----                     | -0.50           |
|            |                     | Density Functional theory (DFT-B3LYP) | 2.42 | -1.67 |
|            | 6-31G+              | $\Delta\mu$ (D)          | 6-31G++         | $\Delta\mu$ (D) |
| 1.45       | 1.91                | 1.80                     |                 |
| 2.48       | 2.47                | 2.40                     |                 |
| 2.83       | -1.10               | 3.14                     | -1.24           |
|            |                     |                          | 3.17             |
|            |                     |                          | -1.03           |

*CRC handbook of chemistry and physics(1969-1970)

of $\Delta\mu$ for the above binary system is negative and it represents the absence of charge-transfer effects. If a charge-transfer effect exists, the value of $\Delta\mu$ would be greater and positive value [45]. In the present investigation $\Delta\mu$ values are negative that presence of a polarization effect. Sabesan et al. [46] and Thenappan and co-workers [47,48] have reported similar conclusions on alcohol mixtures. A small deviation in the experimental dipole moment value when compared to the theoretical values and it may be due to the $\pi$ electron cloud of non polar solvent benzene affecting the dipole moment values of the solute system of propylene glycol and aniline and their binary mixtures. From Table 2, it is noticed that the change in temperature notably influences the experimental dipole moment values of the pure compounds and equimolar binary systems. At low temperatures, the bond lengths between the atoms are very much restricted in their movement, and hence maintain their minimum energy stable conformational structure. This conformational structure permits the cancellation of dipole moments to some extent, resulting in lower dipole moments at low temperatures. As the increase in temperature provides more thermal energy and hence degree of rotation of the individual groups and bond lengths between the atoms also increases, resulting in some changes in the stable structure. The change in the stable structure leads to decrease in the cancellation of the side-group dipole moments and hence consequential increase in the mean dipole moment value.

From Fig.1 it is observed that experimental values of the low frequency dielectric permittivity ($\varepsilon_0$) which is measured at 20 MHz decreases with increase in temperature as well as increase in mole fraction of aniline in propylene glycol binary system is due to increase in temperature that may cause decrease in the degree of polarization of the dipoles. The increased in thermal energy reduces the alignment of the dipoles in the mixture. The decrease in low frequency dielectric permittivity value with increase in the mole fraction of aniline in propylene glycol (X2) at different temperatures of aniline in propylene glycol that may be due to increase in the size and shape of the complex molecules after formation of Hydrogen bond. This hydrogen bond interaction may cause decrease in the volume of the rotation of dipoles. There is non-linear variation of low frequency dielectric permittivity ($\varepsilon_0$) and high frequency dielectric constant ($\varepsilon_{\infty} = N^{-1}$) with mole fraction at all temperatures (Fig.1 and Fig.2) confirms that the
formation of hetero-molecular interaction in the binary system. Similar types of results were observed by Kroeger [13] for the mixture of alcohols and polar liquids.

The real ($\varepsilon'$) and imaginary part of dielectric permittivity ($\varepsilon''$) of pure liquids such as aniline, propylene glycols and their binary mixtures in the frequency range (20 MHz-20GHz) at different temperatures are shown in Figs. 3, 4 and 5 respectively. It is observed that real part of dielectric permittivity ($\varepsilon'$) of pure and binary liquid mixtures decreases with increase in frequency as well as temperature which are as shown in Fig 3, 4 and 5 respectively. Due to the existence of intermolecular hydrogen bonding between one propylene glycol molecule to another propylene glycol molecule (-OH--OH--) leads to the formation of self associated groups causes to absorb more electromagnetic energy which is observed on high dielectric loss ($\varepsilon''$) behavior of propylene glycol system (Fig.4) when compared to the non associated liquid system i.e., aniline (Fig.3) and equi-molar binary mixtures (Fig.5) respectively. The increase in the number of self associated groups formed through hydrogen bonded network in the liquid system takes longer time to attain one equilibrium position to another equilibrium position causing increase in the relaxation time values. The average relaxations times of the pure liquids as well as binary liquid mixtures are determined by using the Cole-Cole relaxation model [31] and which is as shown in Fig.6. From the Fig.6 it is observed that relaxation time value.

Fig.2. Plot of high frequency dielectric constant ($\varepsilon_{\infty} = \Pi^2$) with respective mole fraction of aniline in propylene glycol (X2) at different temperatures

Fig.3. Plot of real ($\varepsilon'$) and imaginary part of dielectric permittivity ($\varepsilon''$) of aniline with respective frequency at different temperatures

Fig.4. Plot of real ($\varepsilon'$) and imaginary part of dielectric permittivity ($\varepsilon''$) of propylene glycol with respective frequency at different temperatures

Fig.5. Plot of real ($\varepsilon'$) and imaginary part of dielectric permittivity ($\varepsilon''$) of equimolar binary system of aniline and propylene glycol with respective frequency at different temperatures

Fig.6. Plot of real ($\varepsilon'$) and imaginary part of dielectric permittivity ($\varepsilon''$) of pure and binary liquid mixtures with respective frequency at different temperatures.
of aniline is smaller compared to the propylene glycol due to the existence of less number of self associated groups when compared to the propylene glycol. The relaxation time value decreases with increase in the molar concentration of aniline in propylene glycol and temperature that may due to greater size of the aniline when compared to the solvent propylene glycol. The increase in temperature results breakage of more number of hydrogen bonds in the liquid mixtures due to the thermal vibrations. As a result, the weakened intermolecular forces lead to a decrease in internal pressure, cohesive energy and relaxation time. At higher temperature the hydrogen bonds become weak due to the thermal vibrations and structure breaking effect prevails the formation of stable conformal structure through hydrogen bonding. The non linear variation of relaxation time and dielectric permittivity of the experimental data confirms the intermolecular interaction taking place in the mixture and similar results were reported by Bhanarkar et al [20].

The excess dielectric parameters like excess permittivity ($\varepsilon^E$); excessive inverse relaxation time (($1/\tau)^E$) provides the information regarding the molecular interaction between the polar-polar liquid mixtures. From the Fig.7 it is observed that negative values of excess permittivity ($\varepsilon^E$) for all concentrations and temperatures. The negative values of $\varepsilon^E$ indicates the formation of multimer structures which leads to decrease in the total number of dipoles in the systems and also interaction among unlike molecules which may cause structural changes in the liquid mixtures [49]. The possitive trend of $((1/\tau)^E)$ provides the information about the fast rotations of dipoles in the system. This may be due to the formation of monomeric structure in liquid system. From the Fig.8 it is observed that negative trend of $((1/\tau)^E)$ with
the compounds i.e., hydrogen bond between the –OH group of propylene glycol and –NH group of aniline leads to the formation of multimers with anti-parallel orientation of the electric dipoles [51]. The $g_f$ values of the above systems are approaching towards one and it indicates that system will be oriented in such a way that the effective dipole moment values will be greater than individual systems. The other dielectric parameter is the Bruggeman parameter ($f_B$), from the Fig. 10 it is recognized that the non linear variation of Bruggeman parameter with volume fraction indicating H-bond interaction through –OH and –NH groups. The thermodynamic parameters such as Gibbs free energy of activation ($\Delta G^*$) and enthalpy of activation ($\Delta H^*$) are obtained with the help of Eyring’s rate equation by considering the slopes of the graph between $\ln(T\tau)$ vs $1/T$ of different molar concentrations of aniline in propylene glycol which is as shown in Fig.11 and

| Variation of volume fraction of aniline per ml in propylene glycol | $T$ / K | $\Delta H^*/(kcal/mole)$ | $\Delta G^*/(kcal/mole)$ | $\Delta S^*/(Cal/mole/K)$ |
|---------------------------------------------------------------|--------|--------------------------|--------------------------|--------------------------|
| 0                                                             | 303    | 42.423                   | 18.830                   | 77.87                    |
|                                                              | 308    | 19.004                   | 36.04                    | 74.09                    |
|                                                              | 313    | 19.231                   | 130.93                   | 72.44                    |
|                                                              | 318    | 18.804                   | 128.44                   | 74.27                    |
|                                                              | 323    | 18.962                   | 128.21                   | 72.64                    |
| 0.1                                                           | 303    | 59.100                   | 18.727                   | 133.24                   |
|                                                              | 308    | 18.774                   | 130.93                   | 72.44                    |
|                                                              | 313    | 18.897                   | 128.44                   | 74.27                    |
|                                                              | 318    | 18.407                   | 127.97                   | 72.64                    |
|                                                              | 323    | 18.335                   | 126.21                   | 72.64                    |
| 0.2                                                           | 303    | 47.903                   | 18.235                   | 97.91                    |
|                                                              | 308    | 18.471                   | 95.56                    | 74.27                    |
|                                                              | 313    | 18.371                   | 94.35                    | 74.27                    |
|                                                              | 318    | 18.203                   | 93.39                    | 74.27                    |
|                                                              | 323    | 18.158                   | 92.09                    | 72.64                    |
| 0.3                                                           | 303    | 37.585                   | 18.042                   | 64.50                    |
|                                                              | 308    | 17.974                   | 63.67                    | 75.80                    |
|                                                              | 313    | 18.007                   | 62.55                    | 75.80                    |
|                                                              | 318    | 18.160                   | 61.09                    | 75.80                    |
|                                                              | 323    | 18.089                   | 60.36                    | 75.80                    |
| 0.4                                                           | 303    | 41.185                   | 17.954                   | 76.67                    |
|                                                              | 308    | 17.838                   | 75.80                    | 74.44                    |
|                                                              | 313    | 17.887                   | 74.44                    | 75.80                    |
|                                                              | 318    | 17.932                   | 73.12                    | 75.80                    |
|                                                              | 323    | 17.914                   | 72.06                    | 75.80                    |
| 0.5                                                           | 303    | 39.998                   | 17.726                   | 73.50                    |
|                                                              | 308    | 17.678                   | 72.47                    | 74.44                    |
|                                                              | 313    | 17.685                   | 71.29                    | 75.80                    |
|                                                              | 318    | 17.746                   | 69.97                    | 75.80                    |
|                                                              | 323    | 17.721                   | 68.97                    | 75.80                    |
| 0.6                                                           | 303    | 41.530                   | 17.522                   | 79.23                    |

Fig.9. Plot of a) Kirkwood effective (geff) correlation factor b) gf with respective mole fraction of aniline in propylene glycol ($X_2$) at different temperatures

Fig.10. Plot of Bruggeman parameter ($f_B$) with volume fraction ($\phi_2$) of aniline in propylene glycol ($X_2$) at different temperatures

Table 4: Variation of thermodynamical parameters $\Delta G^*$, $\Delta H^*$ and $\Delta S^*$ with respective volume fraction of aniline in propylene glycol at different temperatures

Fig.11. Plot of temperature dependence of $\ln(T\tau)$ vs $1/T$ of different mole fraction of aniline in propylene glycol ($X_2$) at different temperatures

The values are listed in Table 4 respectively. From the Table 4 it is observed that Gibbs free energy of activation $\Delta G^*$ shows...
of the system although compared to the sum of individual dipole moments of the systems and thereby reducing internal energy [53]. The reduction of internal energy of a molecule leads to an increase in the excess Helmholtz value. From the high positive values of $\Delta F^E$ (from the Table 5) indicates the formation of $\beta$

| Volume fraction of aniline (ml) in propylene glycol | $\Delta F^E_{0r}$ (J.mol⁻¹) | $\Delta F^E_{rr}$ (J.mol⁻¹) | $\Delta F^E_{12}$ (J.mol⁻¹) | $\Delta F^E$ (J.mol⁻¹) |
|---|---|---|---|---|
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | 110.6423 | 15.3042 | -9.7185 | 116.2280 |
| 0.2 | 190.7504 | 13.3860 | -7.8687 | 216.2678 |
| 0.3 | 218.3136 | 6.1912 | -3.6853 | 220.8196 |
| 0.4 | 215.7568 | 0.2796 | -0.1587 | 215.8777 |
| 0.5 | 185.5650 | -3.0276 | 1.4850 | 184.0223 |
| 0.6 | 133.6017 | -6.3733 | 1.8152 | 129.0436 |
| 0.7 | 63.9609 | -3.0260 | -1.1685 | 59.7665 |
| 0.8 | 2.1411 | -0.1134 | -6.4280 | -2.6004 |
| 0.9 | -39.6629 | -1.1417 | 2.7387 | -38.0660 |
| 1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

The long range and short range interactions among dipoles can be reviewed from the thermodynamic parameter excess Helmholtz energy ($\Delta F^E$) and its constituent parameters $\Delta F_{0r}^E$, $\Delta F_{rr}^E$ and $\Delta F_{12}^E$ [52] which are tabulated in Table 5. The value of $\Delta F_{0r}^E$ represents the long range interaction between the dipoles in the mixture. In the present chosen system the positive values of $\Delta F_{0r}^E$ represents the repulsive force between the dipoles. From Table 5 it is observed that $\Delta F_{0r}^E$ values are positive up to equimolar concentration and negative for remaining concentrations and this value decreases with increase in temperature and mole fractions. The strength of the interaction between the dipoles depends upon the concentration and temperature. The value of $\Delta F_{rr}^E$ provides the information regarding the short range interaction between the similar molecules i.e., through hydrogen bonding. This interaction is strongest at high level of concentration of aniline in propylene glycol and decreases with increase in temperature which is observed from the listed values of Table 5 and it may due to breakage of hydrogen bond network between the molecules. The magnitude of $\Delta F_{12}^E$ reveals the information of interaction forces among different molecules. The values of $\Delta F_{12}^E$ in the aniline+ propylene glycol binary mixture system indicates that there is exist hetero interaction between the compounds which varying with concentration and temperature. The high positive values of $\Delta F^E$ indicates the formation of $\beta$ clusters with anti parallel alignment in system. The formation of $\beta$ clusters in the solution reduces the resultant dipole moment

| Table 5: Variation of $\Delta F^E_{0r}$, $\Delta F^E_{rr}$, $\Delta F^E_{12}$ with volume fraction of aniline in propylene glycol |

| Volume fraction of aniline per ml | $\Delta F^E_{0r}$ (J.mol⁻¹) | $\Delta F^E_{rr}$ (J.mol⁻¹) | $\Delta F^E_{12}$ (J.mol⁻¹) | $\Delta F^E$ (J.mol⁻¹) |
|---|---|---|---|---|
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | 110.6423 | 15.3042 | -9.7185 | 116.2280 |
| 0.2 | 190.7504 | 13.3860 | -7.8687 | 216.2678 |
| 0.3 | 218.3136 | 6.1912 | -3.6853 | 220.8196 |
| 0.4 | 215.7568 | 0.2796 | -0.1587 | 215.8777 |
| 0.5 | 185.5650 | -3.0276 | 1.4850 | 184.0223 |
| 0.6 | 133.6017 | -6.3733 | 1.8152 | 129.0436 |
| 0.7 | 63.9609 | -3.0260 | -1.1685 | 59.7665 |
| 0.8 | 2.1411 | -0.1134 | -6.4280 | -2.6004 |
| 0.9 | -39.6629 | -1.1417 | 2.7387 | -38.0660 |
| 1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
IV. CONCLUSIONS

The complex dielectric permittivity spectra of propylene glycol-aniline binary mixtures have been studied using open-ended coaxial probe method in the frequency range 20 MHz-20 GHz at different temperatures. The nonlinear variation of static dielectric constant, dielectric relaxation time and Bruggeman parameter ($\rho_B$) for all concentrations in the temperature range 303K-323K suggests the heterogeneous interaction between the unlike molecules. The negative trend of excessive inverse relaxation time ($1/\tau$) with respective molar concentration of aniline in propylene glycol at all temperatures shows the solute-solvent interaction produces a field such that the effective dipoles rotates slowly in the binary liquid system. The negative sign of excess dipole moment values ($\Delta \mu$) suggests the absence of charge-transfer effect that may be due to a solvent-induced medium effect in the binary system. The values of $\Delta G^*$ (Gibbs free energy of activation) are positive which represents the presence of molecular interaction between the molecules in the system.

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clusters in the binary system and negative values of $\Delta F^E$ indicates the formation of $\alpha$ clusters. The formation of $\alpha$ clusters increases the effective dipole moment which in turn increases the internal energy.
The formation of hydrogen bond between propylene glycol and aniline which is obtained from the minimum energy based geometry optimization procedure by using the DFT (B3LYP) method with 6-311G+ basis set which is represented in Fig.12 respectively.

Fig.12. Optimized converged geometrical structure of hydrogen bonded system of aniline and propylene glycol from DFT 6-311G+ basis set using Gaussian-09 programming software
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