

Dielectric relaxation studies of acetonitrile/propylene glycol and their binary mixtures

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Dielectric relaxation spectra in the frequency range $0.02 < \nu/\text{GHz} < 20$ have been collected for propylene glycol (PG), acetonitrile (AN) and their binary mixtures between 303 K-323 K. The average relaxation times have been calculated by the Cole-Davidson and Cole-Cole relaxation models. The experimentally determined values of static dielectric permittivity (ϵ_0), relaxation time (τ), excess permittivity (ϵ^E) and excess inverse relaxation time $(1/\tau)^E$ show smooth temperature dependence. The larger relaxation time values of propylene glycol when compared to acetonitrile are due to the co-operative process of multimers with O-H-O linkage and also the steric hindrance behavior phenomena. The activation entropy (ΔS^*), activation enthalpy (ΔH^*), Kirkwood correlation factor (g_f), Helmholtz energy (ΔF^E) parameters have also been determined for propylene glycol and acetonitrile and the results have been correlated.

Keywords: Complex permittivity, Dielectric relaxation, Excess permittivity, Kirkwood correlation factor, Helmholtz energy

1 Introduction

The study of interaction between the material and the electromagnetic waves yields the information related to the dynamics of the molecules. Hydrogen bond is one of the most significant non-covalent interactions that exist in many biological systems¹. The profound knowledge in H-bond is required to understand the nature of molecular interaction taking place in biological activities, proteins, and enzyme catalysis, and drug synthesis, chemical and electrical properties of the material. The number of experimental, theoretical and correlation studies have been performed related to the structural aspects, spectroscopic and energetic issues of distinct hydrogen bonds²⁻⁷. Dielectric relaxation spectroscopy (DRS) is an effective tool to explore the structural dynamics in the liquid samples and the nature of intermolecular interactions. Several researchers and scientists carried out the complex dielectric permittivity measurements of different polar liquids in a polar and non-polar liquid medium by various methods in during recent-past to interpret the hydrogen bond interactions in a liquid systems⁸⁻¹³. Since the hydrogen bond interactions in the liquid state is complex in nature to interpret the dielectric results.

Chaube *et al.*¹⁴ studied the dielectric dispersion studies of diethylene glycol mono phenyl ether-methanol solutions at various concentrations at different temperatures. Based on thermodynamical data experimental results were interpreted in terms of the force of hindrance experienced by the molecules and their cooperative orientation phenomena in the liquid system. The effect of diol hydrogen bonding to water in propylene glycol-water mixtures were analyzed by Tombari *et al.*¹⁵ and also Kaatzte *et al.*¹⁶. They have determined the dielectric properties of high molecular weight PEG's in aqueous solution over a wide frequency range to obtain an insight in to the macromolecular size, shape and flexibility upon dynamics of surrounding molecules. Monoalkyl ethers of ethylene glycol, propylene glycol and butylene glycol are commercially known as cello solves. These compounds have different hydrogen bonding sites that form both inter and intra molecular interaction which in turn leads to different conformational structures¹⁷. The first systematic dielectric dispersion studies of pure poly (propylene glycol)s of different molecular weight in the glass transition region were reported by Baur and Stockmayer¹⁸ and with respective temperature and pressure by Suzuki *et al.*¹⁹. Navarkhele *et al.*²⁰ evaluated the excess dielectric and Kirkwood

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correlation factor (g^{eff}) of formamide-propylene glycol system and reported that the $g^{\text{eff}} > 1$ for formamide rich region and $g^{\text{eff}} < 1$ in propylene glycol rich region. Further, the dielectric study of propylene glycol in aqueous medium shows intermolecular homo and heterogeneous H-bonding and varies with increase in concentration of poly ethylene glycols in aqueous solution medium.

Acetonitrile (AN) is a non-hydrogen-bonded system with large value of electric dipole moment. Its static dielectric constant (ϵ_0) value is high (35.96 at 25 °C) and it allows precise conductometry and potentiometry measurement, yet it is more inert than hydroxylic solvents in that it solvates the majority of the cations and particularly anions much more weakly²¹. Shere *et al.*²² reported the dielectric relaxation studies of acetonitrile with chlorobenzene at different temperatures in the microwave frequency region and reported that the excess dielectric permittivity (ϵ^{E}) values are negative. These negative excess permittivity (ϵ^{E}) values are interpreted in terms of interaction between the molecules and slower rotation of dipoles in the mixture. The values of dielectric relaxation time (τ) depend on the size and shape of the molecule, chain length, nature of molecular interactions, temperature and orientation phenomena. Therefore, it is of great interest to study the temperature dependent dielectric behavior of acetonitrile in propylene glycol as a solvent medium at different molar concentration levels.

In the present manuscript, an attempt has been made to investigate the molecular interaction between the acetonitrile and propylene glycol molecules and also their binary mixtures at different molar concentration levels by determining the complex dielectric permittivity and structural relaxation times. The complex dielectric permittivity ($\epsilon^* = \epsilon' - j\epsilon''$) of these liquid mixtures was measured in the frequency range 20 MHz – 20 GHz by using open-ended coaxial probe method^{23,24} at different temperatures, i.e., 303 K–323 K. By using the Higasi's method²⁵, the experimental dipole moments (μ) of acetonitrile, propylene glycol, and their equimolar binary mixtures

were determined. The theoretical dipole moments were also computed by using Quantum mechanical Hartree-Fock²⁶⁻²⁸ and Density Functional Theory²⁹⁻³¹ (B3LYP) calculations with 6-311G*, 6-311G** basis sets by using Gaussian software 09 package. The average relaxation times (τ) are determined from the Cole-Davidson and Cole-Cole plots^{32,33} and thermodynamical parameters such as enthalpy of activation ΔH^* , entropy of activation ΔS^* are determined from the Eyrings rate equation³⁴. The effective Kirkwood correlation g factor is obtained from the Kirkwood-Frohlich equation³⁵. The interaction among the electrical dipoles is interpreted in terms of long range and short range ordering by using the excess Helmholtz energy (ΔF^{E}) equation³⁶.

2 Experimental Details

2.1 Materials

The chemical samples used in this work such as propylene glycol, acetonitrile and benzene were supplied by Merck, Germany (purity 99 %, AR Grade). These liquid samples further purified by double distillation under reduced pressure and only middle fractions were collected³⁷. The collected middle fractions of the liquid samples were stored in a dark bottle over 4 Å molecular sieves for 48 h to avoid water content. The purities of the propylene glycol, acetonitrile were cross checked by comparing with the densities (ρ) and refractive indices (n_D) at 298 K with the literature values and which are given in Table 1, and it shows that reasonable agreement with the reported values.

2.2 Dielectric studies

In order to determine the experimental dipole moments (μ) of the acetonitrile, propylene glycol and their equimolar binary mixtures by using the Higasi's method²⁵, at first step dilute solutions are prepared by varying the polar solute concentration (0 to 1 mL) in a 10 mL of non-polar solvent benzene. Further, the static dielectric permittivity (ϵ_0) is measured by using digital capacitance meter at 820 Hz and high frequency dielectric constant ($\epsilon_\infty = n^2$) is measured by

Table 1 — Experimental data for the liquid samples used with the literature values at 298 K

| Liquid sample | Density ρ (g/cm ³) | | ϵ_0 | | n_D | | Dipole moment μ (D) | | Relaxation time τ (ps) | |
|------------------|-------------------------------------|-------------------------|--------------|-------------------------|-----------|-------------------------|-------------------------|----------------------|-----------------------------|-----------------------|
| | This work | Literature [†] | This work | Literature [†] | This work | Literature [†] | This work | Literature | This work | Literature |
| Propylene glycol | 1.035 | 1.0361 | 28.95 | 27.50 [†] | 1.430 | 1.4324 | 3.32 | 3.60 ^[48] | 368.26 | 268.8 ^[49] |
| Acetonitrile | 0.785 | 0.7857 | 35.53 | 35.96 ^[50] | 1.343 | 1.3442 | 3.41 | 3.47 ^[51] | 11.52 | 12.12 ^[22] |

† CRC handbook of chemistry and physics (2003-2004), 84th edition, Pg No:6-157,6-162, CRC press

using the Abbe’s refracto-meter in the temperature range 298 K–323 K with a variation of ± 0.01 K. The uncertainty in the static dielectric permittivity (ϵ_0) and optical refractive indices (n) are 1%, respectively. The experimental determined dipole moment (μ) and excess dipole moment ($\Delta\mu$) values of acetonitrile and propylene glycol, and their equimolar binary systems are given in Table 2, respectively.

The complex dielectric permittivity ($\epsilon^* = \epsilon' - j\epsilon''$) of pure liquids of acetonitrile, propylene glycol, and the different molar concentration levels of acetonitrile in propylene glycol are measured in the microwave frequency range (20 MHz–20 GHz) by using the open-ended coaxial probe method^{23,24}. The detailed analysis and procedure of the open ended coaxial probe method and importance of evaluating the excess dielectric parameters such as excess permittivity (ϵ^E), Bruggeman factor (f_B), excess inverse relaxation time ($1/\tau^E$), Gibbs free energy of activation, ΔG^* , Kirkwood correlation factor (g^{eff}) were explained in recently published manuscript^{38,39}. The uncertainties involved in the real (ϵ') and imaginary part of dielectric permittivity (ϵ'') are ± 2% and ± 2-3%, respectively.

2.3 Computation details

The individual monomers of acetonitrile, propylene glycol and their binary system which are optimized geometrically at gaseous state based on minimum energy configuration by considering different quantum mechanical methods such as Hartree Fock²⁶⁻

Table 2 — Experimental dipole moment (μ) and excess dipole moment ($\Delta\mu$) values for the pure system of acetonitrile (AN), propylene glycol (PG), and their equimolar binary system of PG and AN

| T (K) | μ (D) | | | $\Delta\mu$ (D) |
|-------|-----------|------|---------------------------------------|-----------------|
| | AN | PG | Equimolar binary mixture of PG and AN | |
| 303 | 3.43 | 3.32 | 3.98 | -2.77 |
| 308 | 3.44 | 3.33 | 3.99 | -2.78 |
| 313 | 3.45 | 3.35 | 4.02 | -2.78 |
| 318 | 3.47 | 3.37 | 4.03 | -2.81 |
| 323 | 3.48 | 3.38 | 4.04 | -2.82 |

Table 3 — Experimental and theoretical dipole moment (μ) and excess dipole moment ($\Delta\mu$) values of pure system acetonitrile, propylene glycol and equi-molar binary systems- acetonitrile and propylene glycol at 298 K

| System | Experimental (298 K) | | Theoretical calculations | | | |
|----------------------|----------------------|----------------------|--------------------------|----------|-------------------------------------|----------|
| | μ (D) | Literature | Hartree-Fock (HF) | | Density Functional theory DFT-B3LYP | |
| | | | 6-311G* | 6-311G** | 6-311G* | 6-311G** |
| Acetonitrile(A) | 3.41 | 3.47 ^[51] | 4.23 | 4.26 | 3.88 | 4.05 |
| Propylene glycol (B) | 3.32 | 3.60 ^[48] | 2.64 | 2.74 | 2.47 | 2.40 |
| A+B | 3.98 | | 7.37 | 7.34 | 7.51 | 7.60 |

(HF) and DFT²⁹⁻³¹ B3LYP using 6-311G*, 6-311G** basis sets. The computed dipole moments of the acetonitrile, propylene glycol and their binary system are given in Table 3, respectively, based on above methods and compared with the experimental dipole moment values.

3 Results and Discussion

The temperature variation of static dielectric permittivity (ϵ_0), high frequency dielectric constant ($\epsilon_\infty = n^2$) of various molar concentration levels of acetonitrile in propylene glycol are shown in Figs 1 and 2, respectively. From the Fig. 1, it is observed that static dielectric permittivity (ϵ_0) value increases with increase in molar concentration level of acetonitrile in propylene glycol whereas decreasing trend in the case of high frequency dielectric constant values which is as shown in Fig. 2. From the Figs 1 and 2, it is noticed that both the values of ϵ_0 and ϵ_∞ decrease with increase in temperature due to disturbance in the alignment of the dipoles in the field direction. Further it is observed that the non-linear variation of static dielectric permittivity (ϵ_0) and high frequency dielectric constant ($\epsilon_\infty = n^2$) for all concentration levels of acetonitrile in propylene

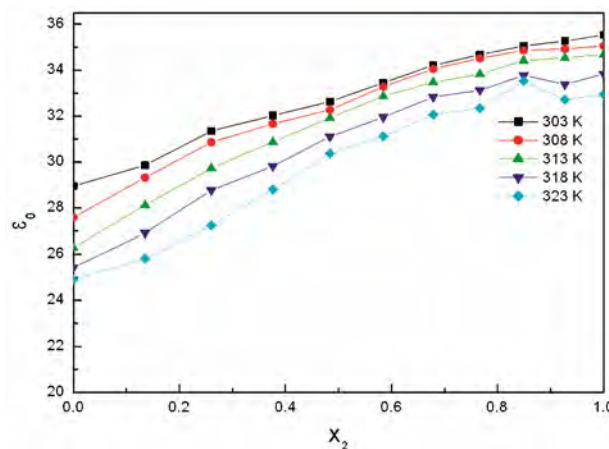


Fig. 1 — Graph of static dielectric permittivity (ϵ_0) with respective mole fraction of acetonitrile in propylene glycol (X_2) at different temperatures

glycol medium indicate that molecular interaction taking place in the liquid binary system. From the Fig. 3, it is observed that an increase in the dielectric field strength, i.e., $\Delta\epsilon = (\epsilon_0 - \epsilon_\infty)$ values for all the concentrations indicates the formation of clusters in the solution⁴⁰. The dielectric field strength values ($\Delta\epsilon$) decrease with increase in temperature and it may due to the restriction involved in the rotational of number of polar groups in the liquid solution.

The complex dielectric permittivity ($\epsilon^* = \epsilon' - j\epsilon''$) of pure liquids of acetonitrile (AN), propylene glycol (PG), and their equimolar binary mixtures with respective frequency at different temperatures which are shown in Figs 4-6, respectively. From the Figs 4-6, it is observed that real part of dielectric permittivity (ϵ') decreases with increase in frequency as well as temperature. The imaginary part of dielectric

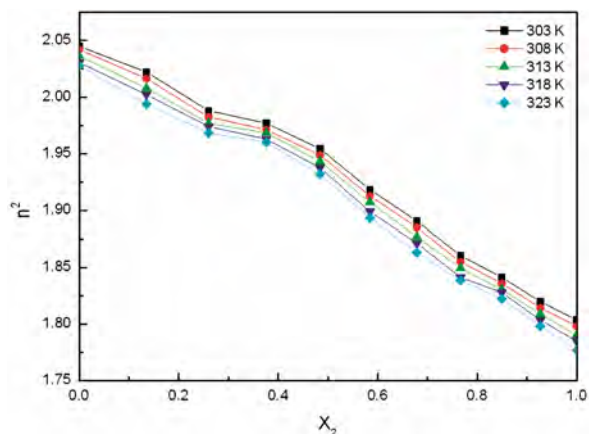


Fig. 2 — Graph of high frequency dielectric constant ($\epsilon_\infty = n^2$) with respective mole fraction of acetonitrile in propylene glycol (X_2) at different temperatures

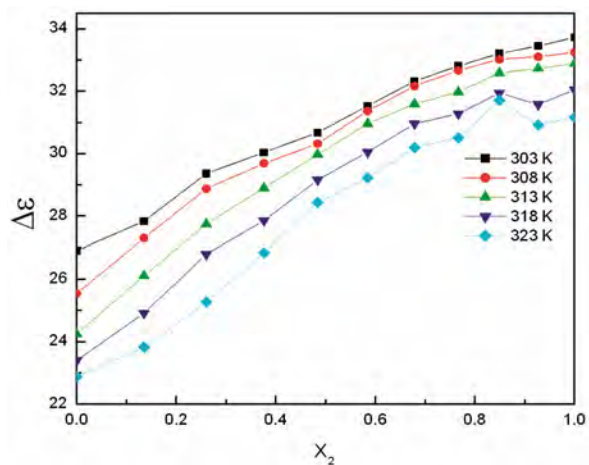


Fig. 3 — Graph of the dielectric field strength $\Delta\epsilon = (\epsilon_0 - \epsilon_\infty)$ with respective mole fraction of acetonitrile in propylene glycol (X_2) at different temperatures

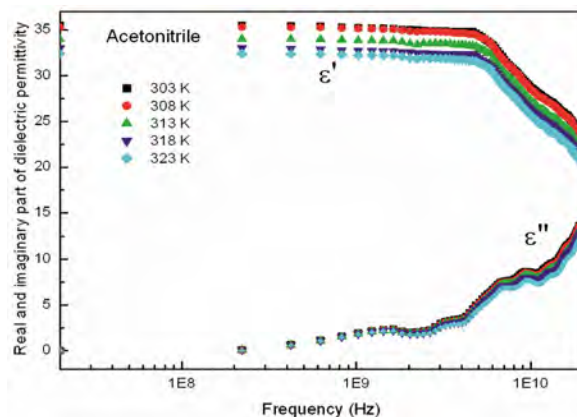


Fig. 4 — Graph of real (ϵ') and imaginary part of dielectric permittivity (ϵ'') of acetonitrile with respective frequency at different temperatures

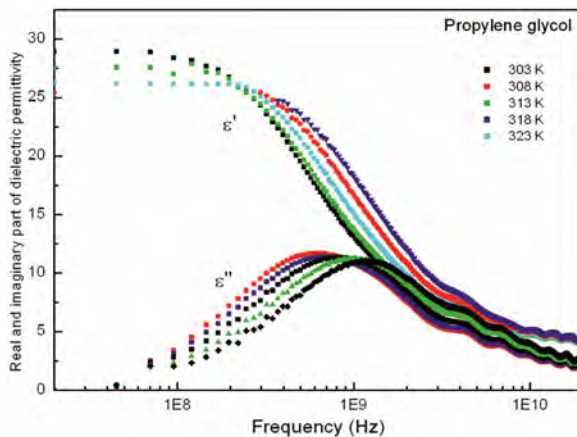


Fig. 5 — Graph of real (ϵ') and imaginary part of dielectric permittivity (ϵ'') of propylene glycol with respective frequency at different temperatures

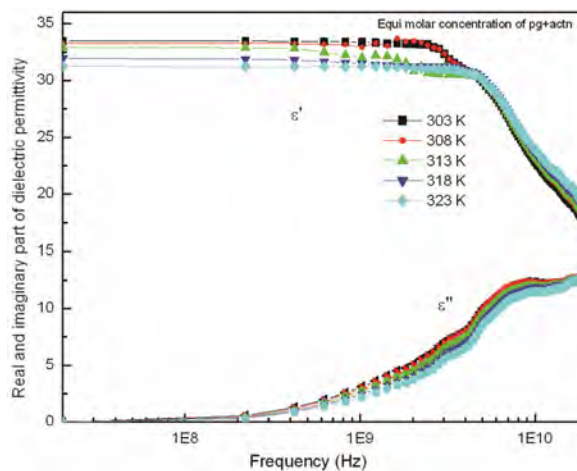


Fig. 6 — Graph of real (ϵ') and imaginary part of dielectric permittivity (ϵ'') of equimolar binary system of acetonitrile and propylene glycol with respective frequency at different temperatures

permittivity of propylene glycol, i.e., dielectric loss (ϵ'') is maximum at lower frequencies whereas for acetonitrile shifts towards higher frequencies which are noticed from the Figs 4 and 5. From the Fig. 6 (i.e., equimolar binary system) it is observed that the dielectric loss (ϵ'') peak is appeared between the frequency region of 5-6 GHz. It may be due to the formation of inter molecular hydrogen bond between acetonitrile and propylene glycol molecules. Since the self-associative nature of propylene glycol molecules forms multimers (clusters of PG) in the solution that leads to absorbs more electromagnetic energy when compared to the non-associated liquid system, i.e., acetonitrile and equi-molar binary system and which is observed from the Figs 4-6. The increase in the number of self-associated groups formed through hydrogen bonded network in the PG 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 and Cole-Davidson relaxation model^{32,33} and which are represented in Fig. 7.

From Fig. 7 it is observed that relaxation time value of acetonitrile is smaller when compared to the propylene glycol due to the existence of less number of self-associated groups. The relaxation time values decrease with increase in the molar concentration of acetonitrile in propylene glycol and temperature. The decrease in relaxation time values with increase in temperature and it may due to the breakage of intermolecular interactions and degree of polarization. Both the plots of relaxation time (τ) and static dielectric permittivity (ϵ_0) with respective mole fraction of acetonitrile in propylene glycol indicates non linear variation response and prevails that intermolecular interaction exists in the liquid mixture⁴¹.

The excess dielectric parameters like excess permittivity (ϵ^E) and excessive inverse relaxation time $(1/\tau)^E$ yield the information about the molecular interaction between the polar-polar liquid mixtures. From the Fig. 8 it is noticed that ϵ^E values are positive which shows that effective number of dipoles in the binary mixture may be larger than the average number of dipoles in the individual pure liquid systems and it may due to the creation of new structures leading to higher macroscopic permittivity⁴². The negative trend of excessive inverse relaxation time $(1/\tau)^E$ with respective molar concentration of acetonitrile in propylene glycol at all temperatures (Fig. 9) shows

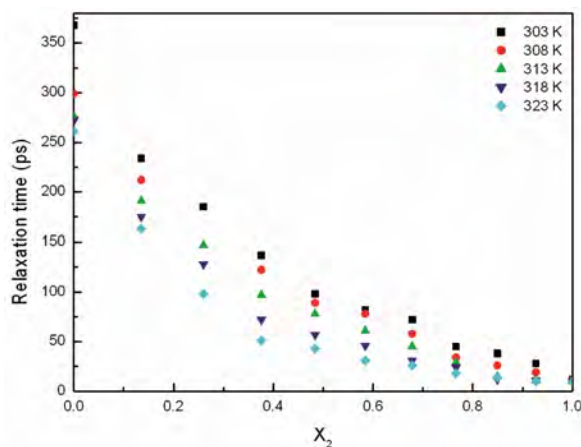


Fig. 7 — Graph of relaxation time (τ /ps) with respective mole fraction of acetonitrile in propylene glycol (X_2) at different temperatures

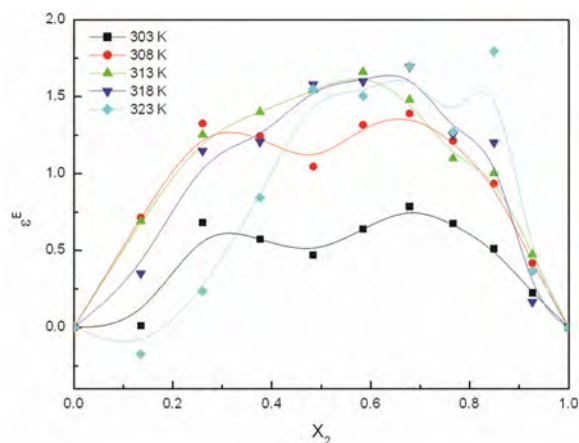


Fig. 8 — Graph of excessive dielectric permittivity (ϵ^E) with respective mole fraction of acetonitrile in propylene glycol (X_2) at different temperatures

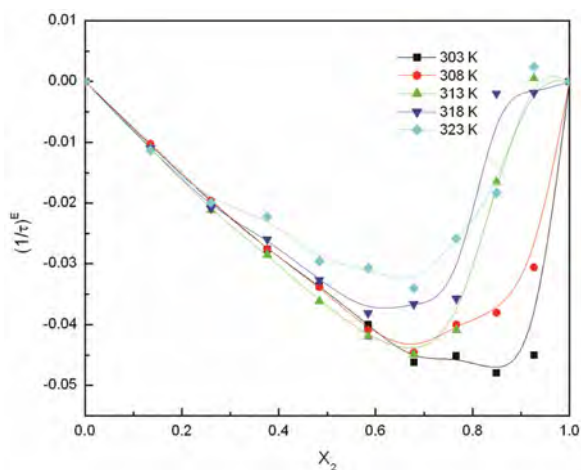


Fig. 9 — Graph of excessive relaxation time $((1/\tau)^E)$ with respective mole fraction of acetonitrile in propylene glycol (X_2) at different temperatures

that the solute-solvent interaction produces a field such that the effective dipoles rotates slowly in the liquid system⁴³.

The magnitude of Kirkwood correlation factor (g^{eff}) is small for the pure propylene glycol and it may be due to the weak intra-molecular interactions between the molecules that lead to the less number of molecular dipoles having parallel orientation among them. The high value of g^{eff} for the pure acetonitrile indicates the anti-parallel orientation of the electric dipoles. Since acetonitrile has simple molecular structure with high symmetry. But for the mixture of acetonitrile and propylene glycol, the parameter g^{eff} exhibits increasing trend with increase in concentration of acetonitrile in propylene glycol which is as shown in Fig. 10. This tendency leads to the conclusion that heterogeneous interaction takes place between the binary system through hydrogen bonding, i.e., formation of hydrogen bond between the -OH group of propylene glycol and -CN group of acetonitrile. This leads to the formation of multimers with anti-parallel orientation of the electric dipoles⁴⁴.

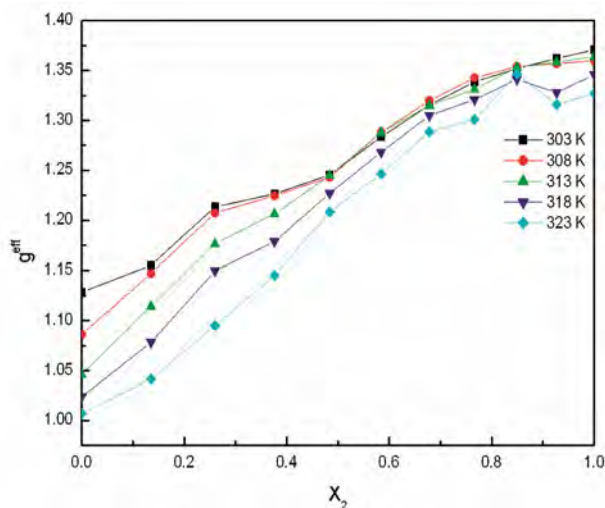


Fig. 10 — Plot of Kirkwood effective (g^{eff}) correlation factor with respective mole fraction of acetonitrile in propylene glycol (X_2) at different temperatures

The single point energy of the individual monomers of propylene glycol, acetonitrile and their dimer is calculated by using HF, DFT (B3LYP) and MP2 methods with one of the basis set 6-311G** at gaseous state which is given in Table 4, respectively. It is observed that the difference in energy between dimer and its individual monomers, i.e., $E = E_{\text{ab}} - (E_{\text{a}} + E_{\text{b}})$ is in the range of 6-15 kcal/mol with different computational methods. These calculations reveals that the strength of the hydrogen bond interaction that exist between the propylene glycol and ethanol molecules is in the range of 6-15 kcal/mol in the liquid system.

The other dielectric parameter is the Bruggeman parameter (f_{B}). From Fig. 11, it is recognized that the nonlinear variation of Bruggeman parameter with volume fraction indicates H-bond interaction through -OH and -CN groups. From Table 2, it is noticed that the change in temperature notably influence 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

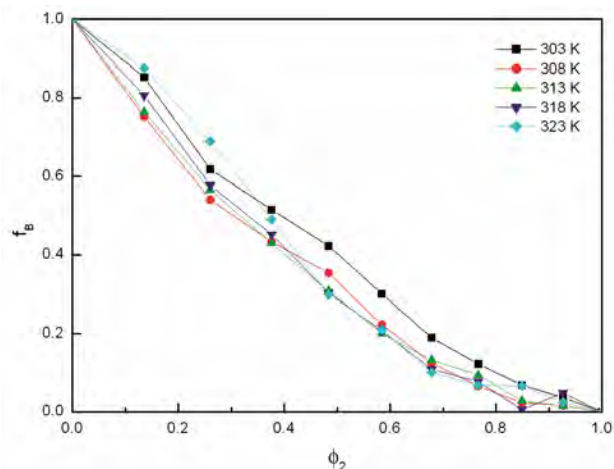


Fig. 11 – Plot of Bruggeman parameter (f_{B}) with volume fraction (ϕ_2) of acetonitrile in propylene glycol at different temperatures

Table 4 — The single point energy values of monomer and dimer and their difference in energy level which are calculated from the HF, DFT and MP2 methods

| System/Energy (a. u.) | Theoretical calculations (gaseous state) with 6-311G** basis set | | |
|---|--|---------------------------------------|----------|
| | Hartree-Fock (HF) | Density Functional theory (DFT-B3LYP) | MP2 |
| Propylene glycol (E_{a}) | -267.920 | -269.570 | -268.452 |
| Acetonitrile (E_{b}) | -131.958 | -132.795 | -132.409 |
| Propylene glycol + Acetonitrile (E_{ab}) | -399.897 | -402.375 | -400.885 |
| Difference in energy ($E = E_{\text{ab}} - E_{\text{a}} - E_{\text{b}}$) | 0.019 | 0.01 | 0.024 |
| Difference in energy ($E = E_{\text{ab}} - E_{\text{a}} - E_{\text{b}}$) (kcal/mol) | 11.92 | 6.275 | 15.06 |

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. The excess dipole moment ($\Delta\mu$) values are negative for all temperatures which indicate the presence of polarization effect. Similar type of results was observed in the case of alcohols^{45,46}.

From Table 5, it is observed that Gibbs free energy of activation ΔG^* shows a positive value which indicates the existence of interaction between the molecules in the system and also ΔH^* value is maximum for self-associated propylene glycol molecules and decreases with increase in volume concentration of acetonitrile in propylene glycol mixtures. Since the enthalpy of activation ΔH^* depends upon the local environment of the molecules. The interactions among dipoles can be analyzed in terms of long range and short range ordering by using thermodynamic parameter excess Helmholtz energy (ΔF^E) and its constituent parameters³⁶ ΔF_{or}^E , ΔF_{tr}^E and ΔF_{12}^E which are mentioned in Table 6. The value of ΔF_{or}^E represents the long range interaction between the dipoles in the mixture. In the present system, the majority values of ΔF_{or}^E are negatives which shows the attractive force between the dipoles. The value of ΔF_{tr}^E provides the information regarding the short range interaction between the similar molecules, i.e., through hydrogen bonding. The strength of the interaction decreases with increase in acetonitrile concentration in propylene glycol due to lack of hydrogen bonding. ΔF_{12}^E value reveals the information on the force of interactions among different molecules. From observing the values of ΔF_{12}^E i.e., 0.3-0.7 mL of binary liquid system of acetonitrile and propylene glycol shows that interaction exists in the system and it forms clusters in the solution. The high positive values of ΔF^E indicates the formation of β clusters and

Table 5 — Variation of thermo dynamical parameters ΔG^* , ΔH^* and ΔS^* with respective volume fraction of acetonitrile in propylene glycol at different temperatures

| Variation of volume fraction of acetonitrile per mL in propylene glycol | T (K) | ΔH^* (kcal/mole) | ΔG^* (kcal/mole) | $\Delta S^*/$ (Cal/mole/K) |
|---|-------|--------------------------|--------------------------|----------------------------|
| 0.0 | 303 | 42.423 | 18.830 | 77.87 |
| | 308 | | 19.004 | 76.04 |
| | 313 | | 19.231 | 74.09 |
| | 318 | | 18.804 | 74.27 |
| | 323 | | 18.962 | 72.64 |
| 0.1 | 303 | 36.092 | 17.876 | 60.12 |
| | 308 | | 17.944 | 58.92 |
| | 313 | | 17.939 | 58.00 |
| | 318 | | 17.971 | 56.98 |
| | 323 | | 18.045 | 55.87 |
| 0.2 | 303 | 17.182 | 17.182 | 34.67 |
| | 308 | | 17.044 | 34.55 |
| | 313 | | 17.275 | 33.26 |
| | 318 | | 17.381 | 32.41 |
| | 323 | | 17.435 | 31.74 |
| 0.3 | 303 | 16.169 | 16.169 | 122.94 |
| | 308 | | 16.109 | 121.14 |
| | 313 | | 16.186 | 118.96 |
| | 318 | | 15.913 | 117.95 |
| | 323 | | 15.681 | 116.84 |
| 0.4 | 303 | 14.873 | 14.873 | 92.59 |
| | 308 | | 14.453 | 92.45 |
| | 313 | | 14.546 | 90.68 |
| | 318 | | 14.548 | 89.24 |
| | 323 | | 14.512 | 87.97 |
| 0.5 | 303 | 14.060 | 14.060 | 151.77 |
| | 308 | | 14.077 | 149.25 |
| | 313 | | 13.818 | 147.69 |
| | 318 | | 13.615 | 146.00 |
| | 323 | | 13.298 | 144.73 |
| 0.6 | 303 | 13.375 | 13.375 | 113.71 |
| | 308 | | 13.295 | 112.12 |
| | 313 | | 13.258 | 110.45 |
| | 318 | | 13.051 | 109.37 |
| | 323 | | 12.884 | 108.19 |
| 0.7 | 303 | 12.753 | 12.753 | 115.20 |
| | 308 | | 12.558 | 113.96 |
| | 313 | | 12.544 | 112.18 |
| | 318 | | 12.332 | 111.09 |
| | 323 | | 12.209 | 109.75 |

(Contd.)

Table 5 — Variation of thermo dynamical parameters ΔG^* , ΔH^* and ΔS^* with respective volume fraction of acetonitrile in propylene glycol at different temperatures —(Contd.)

| Variation of volume fraction of acetonitrile per mL in propylene glycol | T (K) | ΔH^* (kcal/mole) | ΔG^* (kcal/mole) | $\Delta S^*/$ (Cal/mole/K) |
|---|-------|--------------------------|--------------------------|----------------------------|
| 0.8 | 303 | 11.925 | 11.925 | 121.21 |
| | 308 | | 11.862 | 119.45 |
| | 313 | | 11.928 | 117.33 |
| | 318 | | 11.571 | 116.61 |
| | 323 | | 11.305 | 115.63 |
| 0.9 | 303 | 11.465 | 11.465 | 63.83 |
| | 308 | | 11.330 | 63.24 |
| | 313 | | 11.121 | 62.89 |
| | 318 | | 11.341 | 61.22 |
| | 323 | | 11.305 | 60.38 |
| 1.0 | 303 | 10.800 | 10.800 | 5.37 |
| | 308 | | 10.942 | 4.82 |
| | 313 | | 10.945 | 4.73 |
| | 318 | | 11.089 | 4.21 |
| | 323 | | 11.174 | 3.88 |

Table 6 — Variation of ΔF_{or}^E , ΔF_{rr}^E and ΔF_{12}^E with volume fraction of acetonitrile in propylene glycol

| Volume fraction of acetonitrile per mL in propylene glycol | ΔF_{or}^E (J.mol ⁻¹) | ΔF_{rr}^E (J.mol ⁻¹) | ΔF_{12}^E (J.mol ⁻¹) | ΔF^E (J.mol ⁻¹) |
|--|--|--|--|-------------------------------------|
| <i>T</i> = 303K | | | | |
| 0.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | -19.9177 | -3.0882 | 2.7103 | -20.2955 |
| 0.2 | -34.4332 | -7.3479 | 2.2569 | -39.5242 |
| 0.3 | -24.3579 | -5.5115 | 0.8067 | -29.0626 |
| 0.4 | -12.5469 | -3.0793 | -1.2026 | -16.8288 |
| 0.5 | -5.3432 | -1.5154 | -4.4413 | -11.2999 |
| 0.6 | -0.9243 | -0.2915 | -7.1689 | -8.3847 |
| 0.7 | 3.3175 | 1.1233 | -7.7217 | -3.2809 |
| 0.8 | 4.3976 | 1.5480 | -6.5921 | -0.6466 |
| 0.9 | 4.4149 | 1.5988 | -3.8530 | 2.1607 |
| 1.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| <i>T</i> = 308 K | | | | |
| 0.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | -43.4463 | -6.3963 | 2.2275 | -47.6151 |

(Contd.)

Table 6 — Variation of ΔF_{or}^E , ΔF_{rr}^E and ΔF_{12}^E with volume fraction of acetonitrile in propylene glycol —(Contd.)

| Volume fraction of acetonitrile per mL in propylene glycol | ΔF_{or}^E (J.mol ⁻¹) | ΔF_{rr}^E (J.mol ⁻¹) | ΔF_{12}^E (J.mol ⁻¹) | ΔF^E (J.mol ⁻¹) |
|--|--|--|--|-------------------------------------|
| 0.2 | -53.2979 | -11.0414 | 1.1013 | -63.2380 |
| 0.3 | -39.7583 | -8.9277 | -1.1318 | -49.8178 |
| 0.4 | -23.3405 | -5.6711 | -3.4790 | -32.4907 |
| 0.5 | -15.4685 | -4.4571 | -7.9701 | -27.8957 |
| 0.6 | -9.0305 | -2.8874 | -10.7992 | -22.7170 |
| 0.7 | -3.7593 | -1.2883 | -10.9763 | -16.0239 |
| 0.8 | -1.6169 | -0.5723 | -8.8879 | -11.0771 |
| 0.9 | 1.5901 | 0.5677 | -4.8196 | -2.6617 |
| 1.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| <i>T</i> = 313 K | | | | |
| 0.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | -50.1424 | -5.7328 | 2.1259 | -53.7493 |
| 0.2 | -60.3480 | -10.6421 | 1.4872 | -69.5029 |
| 0.3 | -48.7883 | -10.0737 | -1.4896 | -60.3516 |
| 0.4 | -34.4091 | -8.4220 | -5.7980 | -48.6290 |
| 0.5 | -21.9004 | -6.3063 | -10.4499 | -38.6566 |
| 0.6 | -10.0395 | -3.1615 | -12.5272 | -25.7283 |
| 0.7 | -0.3629 | -0.1202 | -11.9195 | -12.4026 |
| 0.8 | -1.1943 | -0.4217 | -10.5067 | -12.1227 |
| 0.9 | 1.6423 | 0.5890 | -5.7988 | -3.5675 |
| 1.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| <i>T</i> = 318 K | | | | |
| 0.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | -43.1775 | -3.3850 | 1.7970 | -44.7655 |
| 0.2 | -62.1928 | -9.3068 | 1.5256 | -69.9739 |
| 0.3 | -48.6751 | -8.6947 | -0.8639 | -58.2336 |
| 0.4 | -37.2906 | -8.4607 | -5.8812 | -51.6326 |
| 0.5 | -22.3966 | -6.0067 | -10.1260 | -38.5294 |
| 0.6 | -14.1725 | -4.3227 | -13.7213 | -32.2165 |
| 0.7 | -3.1965 | -1.0258 | -12.7736 | -16.9959 |
| 0.8 | -5.3288 | -1.8183 | -11.2635 | -18.4107 |
| 0.9 | 9.0167 | 2.9556 | -5.2629 | 6.7094 |
| 1.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| <i>T</i> = 323 K | | | | |
| 0.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | -26.4075 | -1.1001 | 1.1842 | -26.3235 |
| 0.2 | -42.1682 | -4.0045 | 2.2268 | -43.9460 |
| 0.3 | -43.3408 | -6.2917 | 0.0632 | -49.5693 |
| 0.4 | -38.3375 | -7.9888 | -5.5594 | -51.8857 |
| 0.5 | -22.2928 | -5.4943 | -9.2775 | -37.0646 |
| 0.6 | -15.6219 | -4.5088 | -13.3661 | -33.4968 |
| 0.7 | -4.7345 | -1.4250 | -12.3226 | -18.4821 |
| 0.8 | -18.7873 | -6.5095 | -13.1243 | -38.4211 |
| 0.9 | 3.8596 | 1.2194 | -5.3722 | -0.2932 |
| 1.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

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