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Frequency and temperature dependent dielectric studies of propylene glycol-sulfolane binary mixtures in the microwave frequency region

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ABSTRACT

The dielectric permittivity of propylene glycol/sulfolane binary mixtures have been determined at various temperatures in the frequency range of 0.02 ˂ v/GHz˂ 20 using open-ended coaxial probe method. The permitivity spectra of propylene glycol/sulfolane mixtures with an asymmetric shape is observed. The experimental dielectric permittivity, relaxation time values are used to obtain remaining excessive parameters such as excess permittivity (ε^E), deviation in refractive index (Δn_D) excess inverse relaxation time ($1/\tau$)$^\varepsilon$, Kirkwood effective correlation factor (g^{eff}) and active thermodynamic parameters. Redlich-Kister polynomial equation is used to fit the excessive dielectric parameters. The molecular interaction between propylene glycol and sulfolane binary mixtures is interpreted in terms of short and long-range interactions among the dipoles. The experimental dipole moment values are compared with the theoretical dipole moment values from DFT/B3LYP, MP2 methods. Natural bond orbital (NBO) analysis is performed on the optimized geometrical structure of the above system to understand molecular interaction between the binary mixtures in terms of hydrogen bonding. The chemical stability of the system is studied from the HOMO-LUMO calculations. The energy of H- bond interaction between propylene glycol and sulfolane binary mixture is calculated from the single point energy calculations, and the results are correlated.

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1. Introduction

The temperature and frequency dependent dielectric relaxation studies of liquid mixtures play a significant role in the investigation of various processes such as intra and intermolecular interactions, rotational dynamics of the molecules, interfacial polarization, relaxation process, solute-solvent interactions and strength of the interaction among the dipoles. The study of interest in carrying the dielectric spectra of binary and ternary liquid mixtures resides in analyzing the molecular dynamics of the systems and describing the possible variation from the pure components of the liquids and their ideal mixtures. The non-covalent interactions present in the liquid systems such as hydrogen bond, Van der walls, and electrostatic forces play an essential role in the field of biological activity, enzyme catalysis, and drug design [1]. The dielectric studies of different polar binary mixtures at different concentrations and temperature lead to analyze the strength of the hydrogen bond interaction in terms of thermodynamic parameters, ordering nature of the dipoles and their mutual interactions [2–6]. The dielectric relaxation spectroscopy is one of the sensitive methods to detect small changes occur in the structural parameters of a molecule in a liquid system. Several researchers performed dielectric studies on different liquid compounds in water as well as in alcoholic medium in recent past [7–17], at the same time molecular simulations are also performed to interpret experimental results [18–22]. The different spectroscopic studies such as FT-IR, proton NMR, and Neutron diffraction studies are also carried by the researchers to confirm the existence of hydrogen bond between the different liquid mixtures [23–25].

The present work is in continuation of our systematic studies in order to understand the molecular interaction between binary mixtures of propylene glycol and sulfolane. In our previous paper [43] (Vishwam et al.), we reported the molecular interaction behaviour of propylene glycol in ethanol medium and the data is interpreted in terms of thermodynamic parameters, strength of the hydrogen bond interaction from the single point energy method.

In the present manuscript, we are interested to analyze the effect of sulphonyl group on the dielectric relaxation process of propylene glycol medium. The molecular interaction of sulfolane in propylene glycol is studied in terms of short and long-range ordering of the dipoles, excess molar volume (V_m^E), molar polarization (P_m), Natural Bond Orbital analysis to identify the position of hydrogen bond. The chemical stability of the molecule is studied by Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital (HOMO, LUMO) calculations and Redlich-Kister polynomial fitting procedure for excess dielectric

parameters. In our previous paper we have reported the dielectric relaxation behaviour of propylene glycol in ethanol medium and their molecular polarizability by using Lippincott δ function potential model. Whereas in the present paper for all concentration regions relaxation mechanism follows distributive behaviour and the type of molecular interactions are different. It is quite interesting to analyze and understand the molecular interaction behaviour in terms of volumetric, dielecric and thermodynamic parameters.

Propylene glycol is an odorless, colorless liquid used in making of products like deodorant sticks, sunscreen lotions, shampoos and face creams. Propylene glycol is also used in industries such as a heat-transfer medium that protects against pressure burst and corrosion, viscosity control, active agents solvation, surface coatings for weather protection and as a solvent for printing ink. Sulfolane is an organosulfur compound with the chemical formula $(CH_2)_4SO_2$, and it is a colorless liquid having higher macroscopic dielectric constant as well as higher dipole moment value [26]. Sulfolane is a polar liquid and aprotic solvent readily soluble in water. In general, sulfolane is used in the chemical industry as a solvent for extractive distillation and chemical reaction due to higher chemical, thermal stability and low autoprotolysis constant. Only few research articles are available for individual sulfolane and propylene glycol liquids in the literature [27–35] describing dielectric relaxation but not in terms of thermodynamic, volumetric, chemical stability, molecular interactions studies through hydrogen bonding (-S=O——HO-). This factor motivated us to study the molecular interactions between propylene glycol and sulfolane binary mixtures.

2. Experiment details

2.1. Chemicals

Extra pure compounds of propylene glycol (PG) (purity 99%) are purchased from Merck, whereas sulfolane (99%) and benzene are from Sigma Aldrich India. These chemicals further purified by double distillation process under reduced pressure and collected only middle fractions of the compound [36]. The densities of the pure liquids and their mixtures were determined by using specific gravity bottle method [37]. The different volume concentrations of propylene glycol and sulfolane binary mixtures are prepared, and from that number of moles, mole fractions of solute and solvent are determined. The comparison data in terms of density (ρ), refractive index (n_D), dielectric permittivity (ε_0), dipole moment (μ) and relaxation time (τ) for the pure liquids with literature and the uncertainty in the measurements are listed in Table 1.

2.2. Measurements

The experiment dipole moment of the compounds and their equimolar binary liquid mixtures at different temperatures 298.15 K–323.15 K are determined from Higsi's method [38]. By using the digital capacitance meter (820 Hz) and Carl-Zeiss Abbe refractometer, the static dielectric constant and refractive index (n_D) are obtained. The experimental dipole moments (μ) of the pure and equimolar binary mixtures and excessive dipole moment (Δμ) [39,40] at different temperatures are listed in Table 2. The dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) measurements of different concentrations of propylene glycol,

sulfolane and their binary mixtures are determined in the frequency range 20 MHz-20 GHz by using PNA-L Network analyzer (N5230C) with Agilent 85070E high-temperature probe kit in the temperature range 298.15 K–323.15 K. The thermostat controlled water circulation bath set up (Scientific Instruments, Model number SE-131, New Delhi, India) is used to vary the sample temperature within a variation of ± 0.01 K. The sample cell holder covered with a container through which water is supplied continuously with a constant temperature. The temperature inside the sample holder is measured with the lab thermometer. The same water bath setup used for the measurements of optical refractive index (n_D) measurements at different temperatures. The calibration procedure for the complex dielectric permittivity measurements of the liquid samples by coaxial probe method [41,42] and their error analysis is explained in our previously published manuscript [43,44]. The uncertainties in the measurements of real (ε′) and imaginary part of dielectric permittivity (ε″) are ±2% and ±2–3% respectively.

2.3. Computation details

Geometry optimization procedure performed on propylene glycol, sulfolane monomer, and dimer by using Density Functional Method (DFT/B3LYP) [45–50] and Møller–Plesset perturbation theory (MP2) [51,52] calculations by using Gaussian 09 software. The basis set used for the entire calculation is 6-311G* and 6-311G**. The Natural Bond Orbital (NBO) analysis is performed on geometry optimized conformer structure inorder to study the molecular association between the monomers. The single point energy calculation is performed on optimized structures of individual monomers and dimers are tabulated in Table 4. The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies calculated for the individual monomers of PG and Sulfolane to know the capability of electron donor and electron acceptor based on the energy gap values [19].

2.4. Determination of the parameters

The determination of some of the dielectric parameters such as dipole moment (μ), excess dielectric permittivity (ε^E), Brueggemann factor (f_B), excess inverse relaxation time $(1/\tau)^E$, excess dielectric field strength (Δε), Kirkwood correlation factor (g^{eff}), thermodynamic parameters, long range and short range ordering of the dipoles from the excess Helmholtz energy (ΔF^E) equation are explained in our previous published papers [43,44]. The excess molar volume (V_m^E) and excess molar polarization (P_m), deviation in refractive index (Δn_D) are determined by using the following mathematical expressions [53].

$$V_m^E\left(cm^3 mol^{-1}\right) = \sum_i^k x_i M_i\left(\rho^{-1}-\rho_i^{-1}\right) \tag{1}$$

where V_m^E is the excess molar volume, ρ and ρ_i are the densities of the mixtures and the pure components of the liquid *i*, M_i is the molecular weight of component *i*, and

$$P_m = \left(\varepsilon-n_D^2\right)\left(2\varepsilon-n_D^2\right) V_m/9\varepsilon \tag{2}$$

where ε, n_D are the relative permittivity and refractive index, V_m is the

Table 1
Experimental and literature values for density (ρ), refractive index (n_D), dipole moment (μ), dielectric permittivity (ε_0) and relaxation time (τ) of the pure liquids at 298.15 K.

Liquid sample	Density ρ (g/cm³)		ε_0 (20 MHz)		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	1.0356	1.0361	28.95	27.50[a]	1.4300	1.4324	3.32	3.60[67]	307.26	268.8[68]
Sulfolane	1.2645	1.2651[69]	43.81	44.00[4]	1.4840	1.4836[69]	4.76	4.70[26]	44.01	39.89[4]

Standard uncertainties u are u(ρ) = 0.0002, u(ε_0) = 2–3%, u(n_D) = 0.0001, u(μ) = 0.02D and u(τ) = 5–7%.
[a] crc handbook of chemistry and physics (2003–2004), 84th edition, Pg No:6–157,6–162, CRC press.

Table 2
Dipole moment (μ) and excess dipole moment (Δμ) of propylene glycol, sulfolane and their equimolar binary systems of propylene glycol and sulfolane.

T (K)	Propylene glycol, μ (D)	Sulfolane, μ (D)	Equimolar binary mixture of propylene glycol and sulfolane, μ (D)	Δμ (D)
298.15	3.32	4.76	5.16	−2.92
303.15	3.33	4.74	5.15	−2.92
308.15	3.35	4.71	5.13	−2.93
313.15	3.36	4.69	5.10	−2.95
318.15	3.37	4.65	5.08	−2.94
323.15	3.39	4.63	5.07	−2.95

Standard uncertainties u are $u(\mu) = 0.02D$ and $u(T) = \pm 0.01$ K.

molar volume of the mixture, P_m is the molar polarization, and the deviation in refractive index (Δn_D) [53] is given by

$$\Delta n_D = n_D - (n_1 x_1 + n_2 x_2) \tag{3}$$

where n_D is the refractive index of the liquid mixture, x_1, x_2 are the molar fraction of the solute and solvent respectively and

The excess parameters, i.e., V_m^E, ε^E, (Δn_D), $(1/\tau)^E$ are fitted with Redlich–Kister type polynomial equation [54] given as

$$y^E = x_1 x_2 \sum_{i=0}^{k} A_i (x_i - x_2)^i \tag{4}$$

where y^E indicates the excess values and A_i are the coefficients, x_1 and x_2 are the molar fractions of the solute and solvent respectively

The standard deviation is evaluated by using the below mathematical expression

$$\sigma = \left[\frac{\sum \left(y_{exp}^E - y_{cal}^E \right)^2}{N - P} \right]^{0.5} \tag{5}$$

where N is the number of experimental points and P is number of coefficients.

The coefficients of Redlich-Kister polynomial equations A_0, A_1, A_2, A_3, A_4, and its standard deviation values are tabulated in Table 3 respectively.

3. Results and discussion

The graph of dielectric permittivity (ε_0, measured at 20 MHz) of liquid mixture against the mole fraction of sulfolane (X_1) is as shown in Fig. 1. From Fig. 1 it is noticed that the dielelectric permittivity (ε_0) increases with rise in sulfolane concentration in propylene glycol medium. Initially when the concentration of sulfolane is lower in propylene glycol medium, the interaction between the propylene glycol is higher leads to increase in the dielectric permittivity value. Since the propylene glycol molecules forms the intermolecular hydrogen bonding [33,34] between PG molecules results an increase in the dielectric permittivity value. As increase in the sulfolane concentration the dielectric permittivity value increased further due to the formation of strong H-bonding between propylene glycol to sulfolane molecules [55]. Sulfolane has two oxygen atoms; these oxygen atoms are ready to form hydrogen bonds (S=O−H-O) with the self-associated propylene glycol molecules due to more polarity. Further, increase in sulfolane concentration the dielectric permittivity value shows an increasing behaviour and it is due to dipole-dipole interactions [28]. The similar behaviour is noticed for high frequency dielectric permittivity ($\varepsilon_\infty = n_D^2$) values of the binary system, which is as shown in Fig. 2. There is a decrease in the dielectric permittivity (ε_0) (Fig. 1) and high frequency permittivity values with an increase of temperature. This is due to the breakage of H- bond networks in the solution and further decreases the number of dipole-dipole interactions results in a decrease of polarization and susceptibility of the binary liquid system.

The plot of excess molar volume (V_m^E) with respective molar fraction of sulfolane at different temperatures are shown in Fig. 3. The excess molar volume (V_m^E) reveals three types of interactions that take place in the liquid mixture [56,57]. The first type of interaction is due to dipole-dipole interaction (weak) making a positive contribution, and the second one is due to chemical species interaction between the components present in the liquid mixture. This interaction is due to by charge transfer mechanism or either forming hydrogen bonds in the mixture, and it contributes negative values. The third one is due to structural contribution in terms of differences in
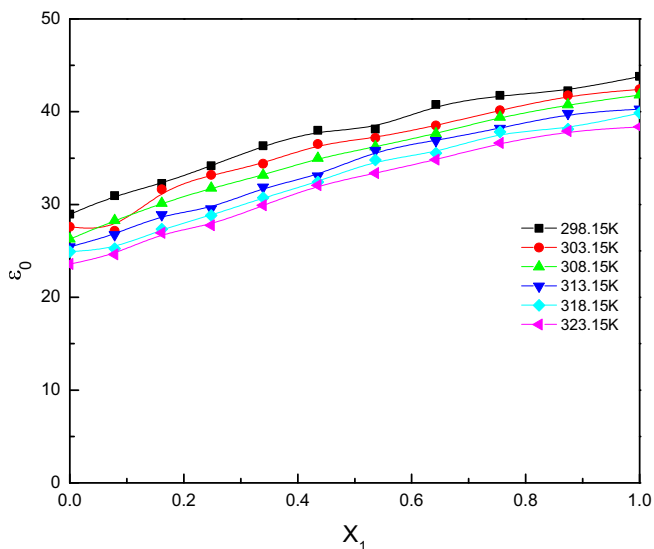
Table 3
Redlich–Kister coefficient and standard deviation values for propylene glycol-sulfolane binary mixtures at different temperatures.

Function	Temp.(K)	A0	A1	A2	A3	A4	σ
V_m^E	298.15	−0.1035	−0.0236	−0.0053	−0.0013	−0.0003	0.000931
	303.15	−0.1300	−0.0297	−0.0068	−0.0016	−0.0004	0.000935
	308.15	−0.1316	−0.0300	−0.0068	−0.0016	−0.0004	0.000859
	313.15	−0.1294	−0.0295	−0.0067	−0.0016	−0.0004	0.001448
	318.15	−0.1011	−0.0230	−0.0052	−0.0012	−0.0003	0.001516
	323.15	−0.0306	−0.0069	−0.0016	−0.0004	−0.0001	0.000976
Δn_D	298.15	0.0085	0.0048	0.0036	−0.0289	0.0059	0.004195
	303.15	0.0068	−0.0046	0.0358	−0.0075	−0.0438	0.010115
	308.15	0.0030	−0.0109	0.0674	0.0056	−0.0857	0.017056
	313.15	−0.0021	−0.0004	0.0539	−0.0151	−0.0768	0.015745
	318.15	−0.0016	−0.0043	0.0480	0.0250	−0.1105	0.01134
	323.15	−0.0049	0.0270	0.0113	−0.0441	−0.0227	0.007034
ε^E	298.15	10.9146	−1.6852	−16.9370	10.8478	15.0440	0.181961
	303.15	8.0052	14.4435	17.3360	−48.2749	−51.1962	0.111485
	308.15	7.2949	4.7835	−3.2594	−6.6474	10.9023	0.278935
	313.15	5.8835	−8.6159	0.0317	2.4622	4.1508	0.236147
	318.15	4.3083	−0.9425	−3.3145	−7.6076	−16.1825	0.248237
	323.15	8.7720	−0.3477	−22.9193	−16.2860	31.1310	0.186155
$(1/\tau)^E$	298.15	−0.0196	0.0048	0.0091	−0.0183	0.0143	0.070020
	303.15	−0.0256	−0.0030	0.0209	0.0274	−0.0444	0.001571
	308.15	−0.0284	0.0002	0.0342	−0.0129	−0.0234	0.001328
	313.15	−0.0287	−0.0081	0.0402	0.0026	−0.0395	0.005714
	318.15	−0.0349	−0.0220	0.0481	0.0430	−0.0658	0.005968
	323.15	−0.0390	−0.0276	0.0725	0.0268	−0.0702	0.006632

Standard uncertainties in $u(T) = \pm 0.01$ K.

Fig. 1. Experimental data of low frequency dielectric permittivity (ε_0 at 20 MHz) versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.

Fig. 3. Excessive molar volume (V_m^E) versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.

size and shape of the components present in the mixture. This type of interactions reduces the volume and compressibility of the mixture leads to negative contribution towards excess molar volume (V_m^E). From Fig. 3 it is observed that excess molar volume (V_m^E) is negative for all concentrations and temperature, and it indicates the presence of hydrogen bonds between propylene glycol and sulfolane binary system. The excess molar volume (V_m^E) decreases with rise in temperature due to breakage of the number of hydrogen bond networks in the binary liquid system.

From Fig. 4 it is marked that the dielectric field strength value ($\Delta\epsilon$) increases with increase in mole fraction of sulfolane in propylene glycol medium and it may be due to increase in the chain length of the molecule [58]. That means there is a possibility of interstitial accommodation of sulfolane in the glycol structure taking place and causes an increase in the chain length and net dipole moment of the molecular entity in the solution. It creates an increment in dielectric field strength ($\Delta\epsilon$) values, which is as shown in Fig. 4. The molar polarization (P_m) reveals the presence of specific (hetero) interactions taking place in the liquid mixtures and also indicates the information about the molecular chain
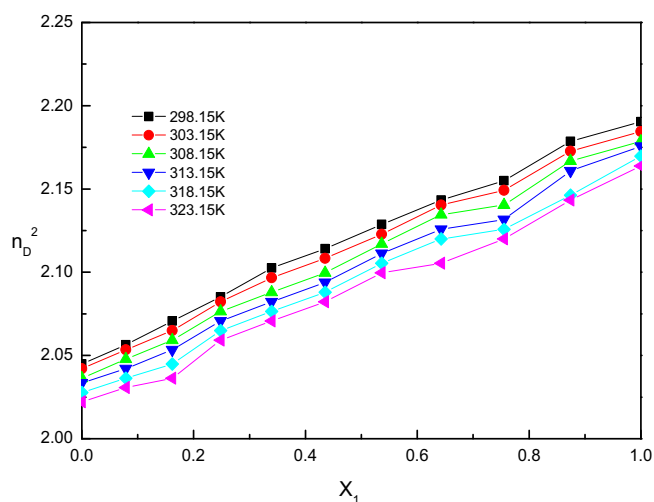
length, molecular size differences in the mixture. From Fig. 5, it is observed that molar polarization (P_m) [53] increases with increase in sulfolane concentration, and it is due to the allignment of the molecular dipoles with respective field direction. The molar polarization decreases with rise in temperature, and is expected to thermal energy dominates the interaction among the dipoles and allign the dipoles in a random direction. Also, another dielectric parameter explains the heterogeneous interaction taking place in the liquid mixture, i.e., deviation in refractive index (Δn_D) and its variation with concentration and temperature as shown in Fig. 6. From Fig. 6, it is noticed that there is a change in deviation in refractive index (Δn_D) values with increase in sulfolane concentration and it may be due to molecular interaction changes from hydrogen bond to dipole-dipole interactions. The deviation in refractive index (Δn_D) [53] values are positive up to certain temperatures (35 °C) indicating that molecular interactions dominating the thermal energy and above 35^{0}C deviation in refractive index (Δn_D) values are negative. The negative values of n_D^E shows that thermal energy separates the molecular dipoles or randomizes so that net interaction energy between the dipoles is decreased.

Fig. 2. Experimental data of high frequency dielectric constant ($\varepsilon_\infty = n_D^2$) versus mole fraction ($X_1$) of sulfolane in propylene glycol at different temperatures.
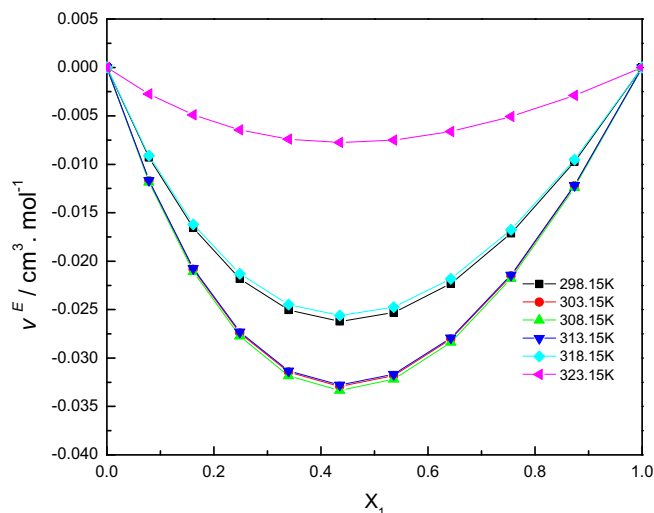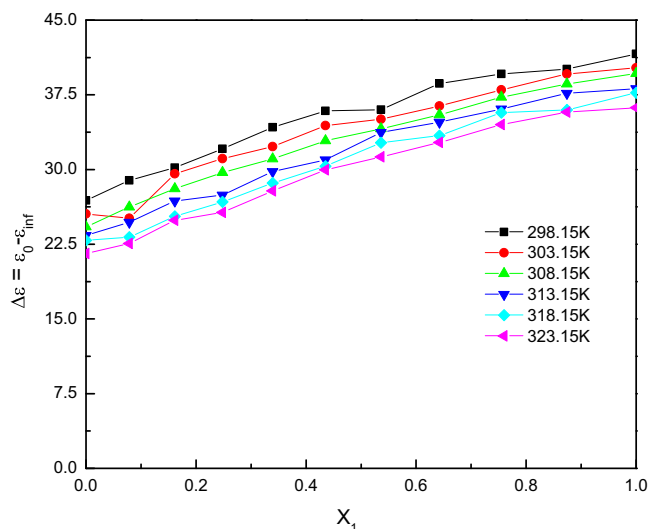

Fig. 4. Experimental values of dielectric relaxation strength ($\Delta\epsilon$) versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.
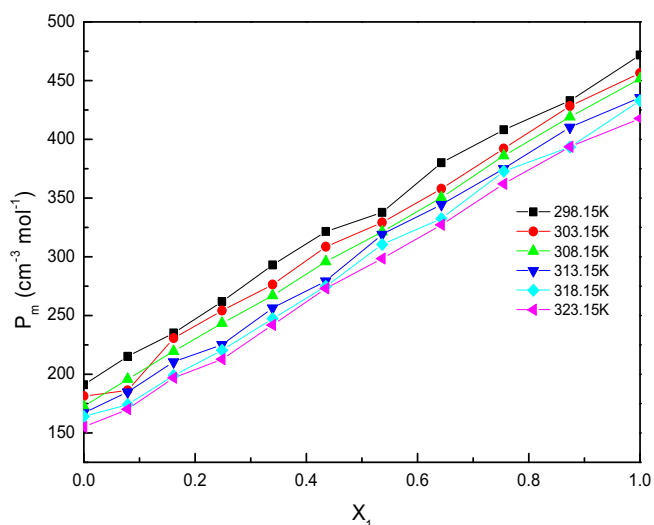
Fig. 5. Molar polarization (P_m) versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.

Fig. 7. Frequency-dependent of real (ε') and imaginary part of dielectric permittivity (ε'') of sulfolane with respective frequency at different temperatures (Inserted Fig- relaxation plot).

The dielectric permittivity and relaxation spectra of sulfolane and its equimolar binary mixtures of propylene glycol and sulfolane at various temperatures are shown in Figs.7 and 8 respectively. The complex permittivity spectra of propylene glycol are reported in our previously published manuscript [43]. In the case of propylene glycol, dielectric loss is observed at lower frequencies (<1 GHz) and it corresponds to self-associative nature of propylene glycol molecules. The self-associative molecules absorb more electromagnetic energy to oscillate the dipoles from one equilibrium position to another equilibrium position and produce higher relaxation time values. In the case of sulfolane, dielectric loss peak (ε'') is observed between 7.0 and 7.5 GHz frequency region. The width of the loss spectrum is wider and it is due to dipole-dipole interactions between sulfolane-sulfolane molecules which is as shown in Fig. 7. Moreover, due to more polarity nature of sulfolane, the dielectric loss peak is slightly higher when compared to the propylene glycol. From Fig. 8, it is noticed that due to the presence of H- bond between propylene glycol and sulfolane molecules, the dielectric loss peak is somewhat moderate and shifting towards higher frequencies (>7 GHz).

Further, the width of the loss spectrum (dielectric loss ε'') is broader when compared to the sulfolane and propylene glycol [43], and it
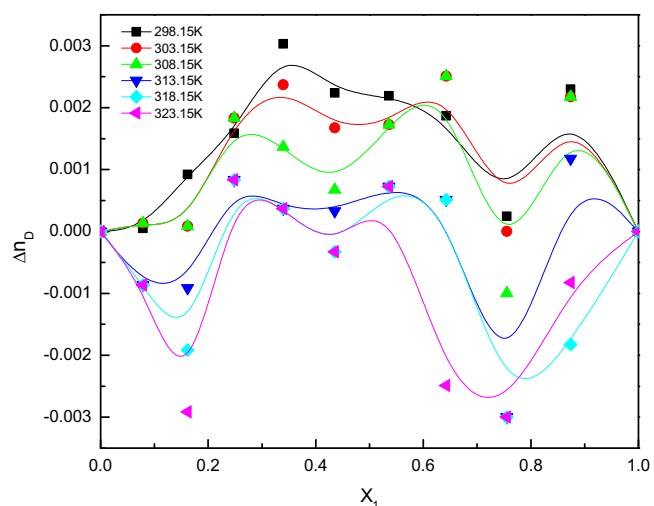
indicates asymmetric relaxation times are probable [59]. The increase in the sulfolane concentration leads to more number of dipole-dipole interactions and causes distributive relaxation times at higher frequencies. The real part of the dielectric permittivity decreases with increase in frequency and temperature for all concentrations (represented only one equimolar concentration) as shown in Figs.7 and 8. The rise in temperature reduces the number of H-bonds between the components in the liquid system causes decrease in the dielectric loss and which is noticed for all the concentrations.

Based on the dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) values of entire concentrations of propylene glycol and sulfolane binary mixtures, the dielectric relaxation time (τ) is calculated from the Cole-Davidson plot [60]. The relaxation spectra of sulfolane and their equimolar binary mixtures are shown in Figs. 7 and 8 (Inserted Fig). Further, the relaxation time of pure propylene glycol is about 307 ps at 298 K [43], and it is due to self-associative nature of propylene glycol. The relaxation time

Fig. 6. Deviation in refractive index (Δn_D) versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.

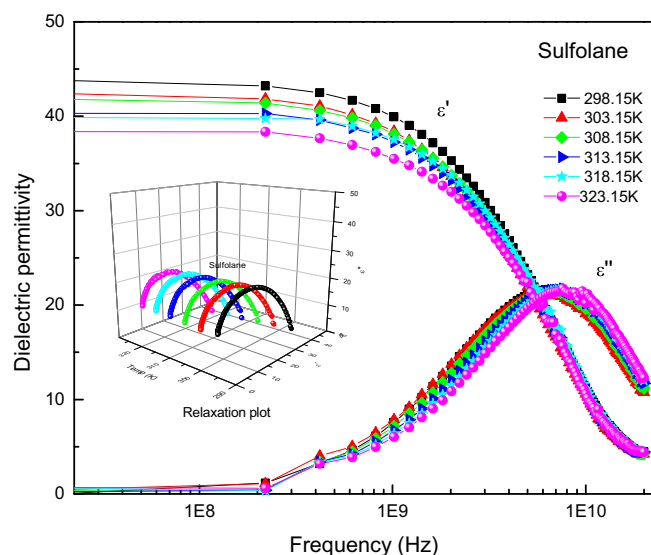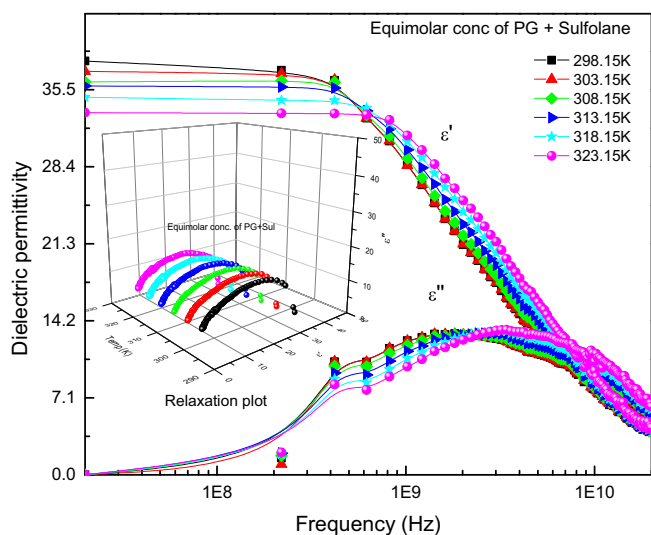**Fig. 8.** Frequency-dependent of real (ε') and imaginary part of dielectric permittivity (ε'') of equimolar binary mixtures of sulfolane + propylene glycol with respective frequency at different temperatures (Inserted Fig- relaxation plot).
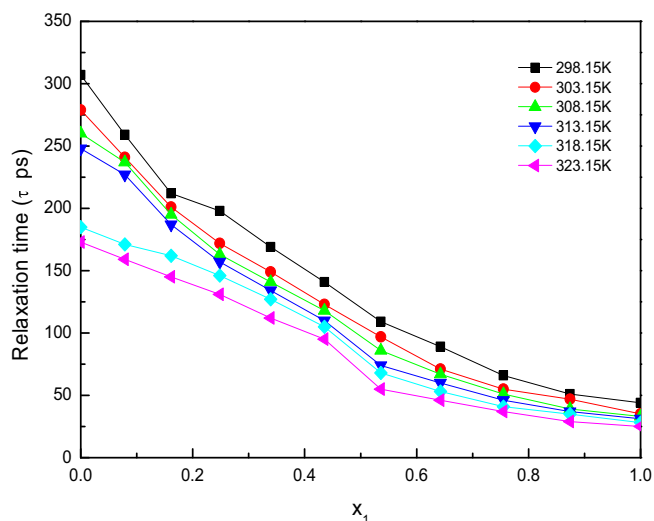
Fig. 9. Experimental values of average relaxation time (τ/ps) versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.
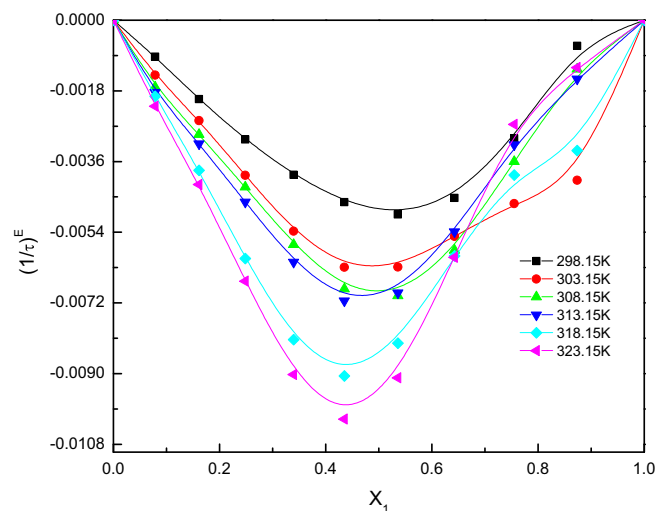

Fig. 11. Experimental values of excessive relaxation time (($1/\tau)^E$) versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.

of pure sulfolane is 44 ps at 298 K [4], and its value is lesser in magnitude when compared to propylene glycol and its binary mixtures. Because the interactions present between sulfolane molecules are dipole-dipole interactions. The interaction energy associated with sulfolane molecules is lesser when compared to the hydrogen bonding. The increase in the accumulation of charge density in a liquid medium due to dipole-dipole interactions is responsible for asymmetric relaxation times at higher frequencies. The skewed relaxation times are due to the rotation of individual groups present in the molecular structure. From Fig. 9, it is seen that relaxation time is decreased with increase in sulfolane concentration in the liquid mixture and also with the temperature. The increase in concentration of sulfolane in the propylene glycol medium, sulfolane molecules percolated into the propylene glycol structure reduces the number of hydrogen bonds [61], and results decrease in the relaxation time values. Further increase in sulfolane concentration, majority number of molecules becomes sulfolane, and the interaction present between them is dipole-dipole interactions which leads to a further decrease in the relaxation times values.

The positive and negative values of excess dielectric permittivity (ε^E) depend upon the type of interaction that exists between the components

present in the mixture. From Fig. 10 it is observed that excess dielectric permittivity (ε^E) values are positive for entire concentrations which indicates the presence of solute-solvent interaction taking place in the mixture in such a manner that the total dipole moment of the solution gets enhanced and also it represents the presence of polymeric structures in the solution [61]. The information about the rotation of the dipoles is provided by the excessive inverse relaxation time plot, which is as shown in Fig. 11 for entire mole fractions at different temperatures. It is observed that excessive inverse relaxation time $(1/\tau)^\varepsilon < 0$, and it represents slower rotation movement of the dipoles. The presence of hydrogen bond and dipole-dipole interactions in the liquid solution producing the net field such that net rotational dipole moment is hindered. There is a non-linear variation of Bruggeman parameter (f_B) with the entire concentration of sulfolane in propylene glycol at all temperatures as shown in Fig. 12 and it imparts the presence of strong molecular interactions exists in the liquid mixtures [62].

The ordering nature and their interaction among the dipoles is explained by the effective Kirkwood correlation factor (g^{eff}), which is as shown in Fig. 13. From Fig. 13, it is noticed that the correlation factor (g^{eff}) of all the concentrations is greater than one and it decreases with increase in temperature. It indicates that electric dipoles in the
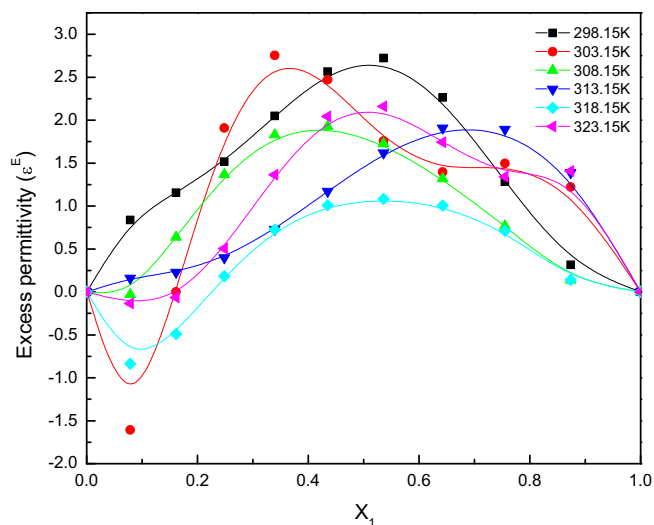

Fig. 10. Experimental values of excessive dielectric permittivity (ε^E) versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.
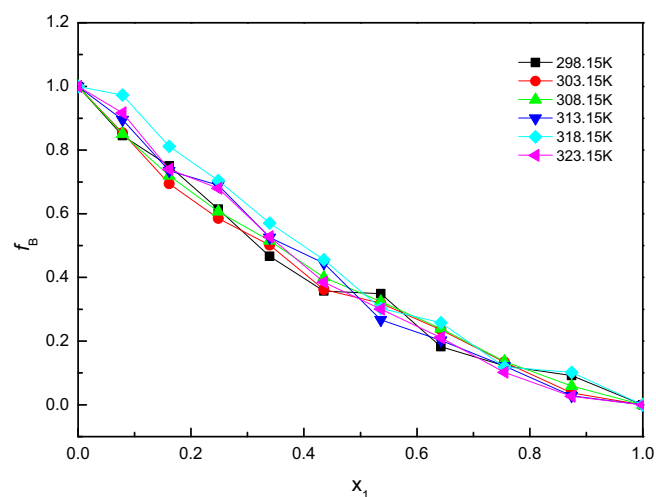

Fig. 12. Experimental values of Bruggeman parameter (f_B) versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.
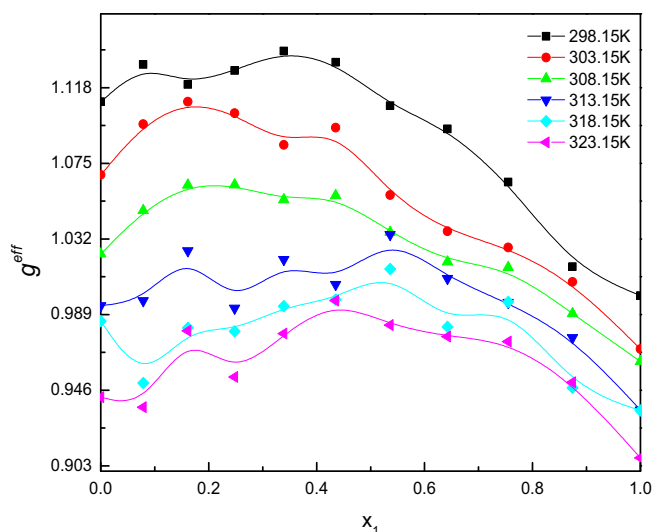
Fig. 13. Kirkwood effective (g^{eff}) correlation factor versus mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.
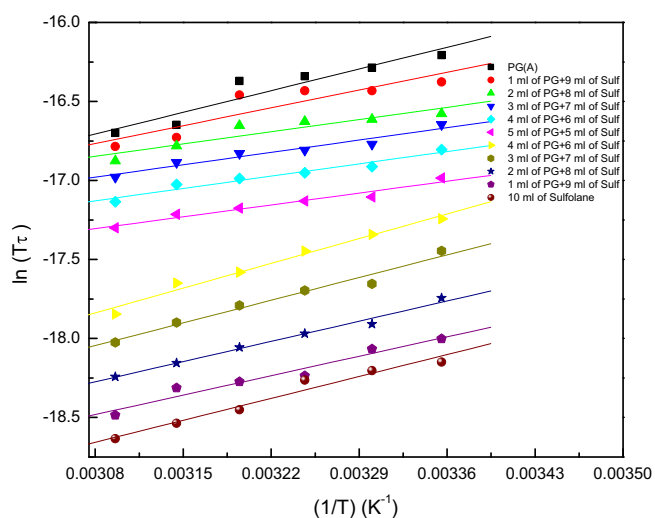

Fig. 14. Temperature dependence of $\ln(T\tau)$ vs. $1/T$ of different mole fraction (X_1) of sulfolane in propylene glycol at different temperatures.

system will be alligned in such a way that the effective dipole moment is greater than the individual dipole moment of the pure liquids. Due to the parallel orientation of all the electric dipoles and stronger interaction between the propylene glycol and sulfolane molecules, the excess dielectric permittivity (Fig. 10) values are positive and excess inverse

relaxation time values are negative (Fig. 11) in sulfolane rich region. The decrease in g^{eff} factor with increase in temperature and it corresponds to thermal energy that dominates the interaction energy and makes the dipoles in a random direction.

The Arrhenius graph of entire mole fraction of sulfolane in propylene glycol as shown in Fig. 14. The slope of the graph between $\ln(T\tau)$ vs. $1/T$ is used to calculate the enthalpy of activation ΔH^*. From that activation entropy ΔS^* is evaluated from Eyring's rate equation [63]. The values of enthalpy of activation ΔH^*, the entropy of activation ΔS^* and Gibbs free energy of activation ΔG^* are summarized for entire molar concentrations and listed in Table 5 respectively. From Fig. 14, it is noticed that the variation of $\ln(T\tau)$ vs. $1/T$ for complete molar concentrations is linear, and it indicates that there is a possibility of multimeric structures exists in the solution. The self-associative nature of propylene glycol molecules is responsible for the formation of multimeric structures in the binary solution through hydrogen bonding. From Table 5, it is clear that enthalpy of activation ΔH^* is a positive value for entire molar concentrations and it indicates that the liquid system absorbs the heat energy during the reorientation process of the molecular dipoles. The positive value of ΔH^* also shows the information that the surrounding environment is highly supportive in favor of forming the hydrogen-bonded network in the liquid system [61]. Gibbs free energy of activation ΔG^* is a positive value, and its magnitude value decreases with an increase in molar concentration of sulfolane in the binary mixture. It indicates that the molecular interaction changes from hydrogen bond (PG-PG, PG-Sulfolane) to dipole-dipole interaction (Sulfolane-Sulfolane). The sign of entropy of activation ΔS^* provides the information about the rate of molecularity reaction whether the reactants in the liquid solutions are bonded with each other, or not. The positive value of ΔS^* [64] reveals that the environment of the system is not supported for the orientation process and non-cooperation among the dipoles. Due to more disorder in the allignment of the dipoles and they are loosely bonded with each other responsible for the increase in the entropy and activated system is becoming to dissociate. Whereas negative values for ΔS^* suggests that the supportive environment of the system results decrease in the entropy values. The decrease in entropy suggests the allignment of the dipoles in an ordered state, and there is a transition towards the associative nature of forming a single activated complex system. From Table 5, it is marked that ΔS^* values are positive for all concentrations, which indicates that the self-associated system becomes dissociated system.

The excess Helmholtz energy (ΔF^E) and its parameters $\Delta F^{E_{or}}$, $\Delta F^{E_{rr}}$ and $\Delta F^{E_{12}}$ indicate the type of interaction that exists among the dipoles either long-range interaction or short-range interaction [65]. The excess Helmholtz energy (ΔF^E) values of propylene glycol-sulfolane binary mixtures are listed in Table 6. The first term in the equation $\Delta F^{E_{or}}$ represents the repulsive or attractive forces between the dipoles. If $\Delta F^{E_{or}}$ is positive means repulsive forces, if it is negative indicates the attractive forces among the dipoles. From Table 6, it is observed that up to 0.8 ml volume fraction of sulfolane in propylene glycol, $\Delta F^{E_{or}}$ values are negative and it indicates the presence of hydrogen bond interaction between propylene glycol and sulfolane binary system.

Table 4
Experimental and theoretical dipole moments (μ) of pure system of propylene glycol, sulfolane and their equimolar binary systems at 298.15 K.

Dipole moment in Debye	Gaseous state				Experimental	Literature
System/basis sets	DFT/B3LYP		MP2			
	6-311G*	6-311G**	6-311G*	6-311G**		
Propylene glycol (PG)	2.478D	2.401D	2.511D	2.511D	3.32D	3.60D
Energy (a.u), E_{PG}	−269.570	−269.570	−269.801	−269.800		
Sulfolane	5.607D	6.726D	6.286D	5.425D	4.76D	4.70D[26]
Energy (a.u), E_{Sul}	−705.975	−705.909	−705.841	−705.841		
Equimolar binary mixtures of PG and Sulfolane	5.225D	7.447D	7.714D	7.292D	5.16D	......
Energy (a.u) E_{PG+Sul}	−975.613	−975.592	−975.358	−975.355	–	–
Difference in energy (kcal/mol) $E_T = E_{PG+Sul} - (E_{PG} + E_{Sul})$	42.670	70.90	178.21	179.46	–	–

Uncertainties u in u (μ exp) = 0.02D and u(E) = 0.002.

Further increase in sulfolane concentration, majority number of molecules in the solution becomes sulfolane, and the dipole-dipole interactions leads to the negative value of $\Delta F^{E_{or}}$ for all temperatures. The second parameter in the equation $\Delta F^{E_{rr}}$ represents the short-range interaction between similar molecules. From Table 6, it is noticed that $\Delta F^{E_{rr}}$ values are negative for lower concentrations of sulfolane in the solution, and it is due to self-associative nature of propylene glycol molecules forms intermolecular hydrogen bonding. The strength of the hydrogen bonding depends upon the thermal energy and the concentration. The third parameter $\Delta F^{E_{12}}$ represents the force of interaction between different molecules present in the system. In the current system $\Delta F^{E_{12}}$ are negative values up to certain concentrations ($0 < x < 0.6$) due to the presence of hydrogen bond whereas for other concentrations it is positive and which indicates dipole-dipole interactions. The positive values of ΔF^{E} suggests the existence of β clusters with an anti-parallel arrangement of dipoles in the system that reduces the internal energy of the system [66]. If ΔF^{E} values are negative that indicates the presence of α clusters in the solution which increases the internal energy as well as net dipole moment of the system. From Table 6, it noted that ΔF^{E} values are negative up to specific concentrations and indicates an increase in internal energy, as well as net dipole moment and the same is observed for dipole moment of equimolar concentrations of propylene glycol and sulfolane.

The dipole moments of propylene glycol, sulfolane and their equimolar binary mixtures at different temperatures are listed in Table 2 respectively. These dipole moments are determined by using Higasi's method. There is a variation in experimental dipole moments values with the literature values because Higasi's method takes into the consideration of the distribution of relaxation times [60] and also the contribution of partial polarity due to π electron cloud of the benzene ring. There is a change in the dipole moment values with increase in temperature, and it may be due to an increase in the bond lengths or cancellation of net dipole moment due to the random orientation of dipoles. From Table 2, it is noticed that excess dipole moment ($\Delta\mu$) values are negative that shows the presence of polarization effect or it may be due to induced solvent medium effect in the binary mixtures [39,40].

The dipole moment and single point energy of the monomers of propylene glycol, sulfolane and the dimer are computed by DFT/B3LYP and MP2 methods with 6-311G*, 6-311G** basis sets are listed in Table 4 respectively. It is observed that there is a deviation in the experimental dipole moment values with theoretical values. It may be due to the solvent effect in the case of experimental method and different theories, perturbations involved in electronic wave functions in quantum mechanical calculations. From Table 4 it is noticed that the values of DFT calculation method with 6-311G* basis set are

close with the experimentally determined values. The difference in interaction energy between propylene glycol and sulfolane is the range of 40–170 kcal/mol with different theoretical methods. This

Fig. 15. Optimized converged geometrical structure of the hydrogen-bonded system of PG + Sulfolane in the gaseous state from DFT 6-311G* basis set using Gaussian-03 (with full natural bond analysis (NBO)).

Table 5
Variation of thermodynamical parameters ΔG^*, ΔH^* and ΔS^* with respective molar concentration of sulfolane in propylene glycol at different temperatures.

Variation of Concentration of Sulfolane in PG solution	T/K	ΔH^*/(kcal/mol)	ΔG^*/(kcal/mol)	ΔS^*/(Cal/mol/K)
0	298.15	37.547	18.716	63.19
	303.15		18.830	61.77
	308.15		19.003	60.21
	313.15		19.230	58.52
	318.15		18.804	58.94
	323.15		18.962	57.54
0.1	298.15	30.788	18.294	41.93
	303.15		18.462	40.68
	308.15		18.765	39.03
	313.15		19.000	37.66
	318.15		18.596	38.34
	323.15		18.735	37.32
0.2	298.15	21.138	17.798	11.21
	303.15		18.004	10.34
	308.15		18.266	9.32
	313.15		18.495	8.44
	318.15		18.453	8.44
	323.15		18.487	8.21
0.3	298.15	21.387	17.629	12.61
	303.15		17.612	12.46
	308.15		17.807	11.62
	313.15		18.040	10.69
	318.15		18.178	10.09
	323.15		18.215	9.82
0.4	298.15	21.291	17.236	13.61
	303.15		17.250	13.34
	308.15		17.435	12.52
	313.15		17.628	11.70
	318.15		17.810	10.95
	323.15		17.794	10.83
0.5	298.15	20.506	16.788	12.48
	303.15		16.767	12.34
	308.15		16.979	11.45
	313.15		17.138	10.76
	318.15		17.306	10.06
	323.15		17.352	9.77
0.6	298.15	42.793	16.150	89.41
	303.15		16.169	87.87
	308.15		16.169	86.44
	313.15		16.082	85.34
	318.15		16.158	83.76
	323.15		15.884	83.31
0.7	298.15	39.232	15.647	79.14
	303.15		15.383	78.71
	308.15		15.530	76.96
	313.15		15.537	75.70
	318.15		15.499	74.63
	323.15		15.404	73.77
0.8	298.15	34.943	14.906	67.24
	303.15		14.739	66.68
	308.15		14.831	65.30
	313.15		14.845	64.21
	318.15		14.820	63.28
	323.15		14.819	62.30
0.9	298.15	33.641	14.268	65.01
	303.15		14.343	63.69
	308.15		14.144	63.30
	313.15		14.278	61.86
	318.15		14.401	60.50
	323.15		14.165	60.30
1	298.15	37.930	13.902	80.63
	303.15		13.999	78.98
	308.15		14.077	77.44
	313.15		13.818	77.04
	318.15		13.811	75.84
	323.15		13.766	74.81

Table 6
Variation of ΔF^E_{Or}, ΔF^E_{rr}, ΔF^E_{12} and ΔF^E with volume fraction of sulfolane in propylene glycol medium.

Volume fraction of Sulfolane per ml in propylene glycol	ΔF^E_{Or} (J·mol^{-1})	ΔF^E_{rr} (J·mol^{-1})	ΔF^E_{12} (J·mol^{-1})	ΔF^E (J·mol^{-1})
T = 298.15 K				
0	0.0000	0.0000	0.0000	0.0000
0.1	−52.3533	−6.8685	2.2455	−56.9763
0.2	−61.6473	−7.3876	2.2251	−66.8098
0.3	−66.9057	−8.5473	0.1074	−75.3456
0.4	−62.4431	−8.6690	−4.0547	−75.1668
0.5	−43.4347	−5.7511	−7.2339	−56.4197
0.6	−3.3103	−0.2575	−4.4438	−8.0116
0.7	−2.1621	−0.2045	−7.8382	−10.2048
0.8	13.6412	0.8778	−4.8247	9.6942
0.9	27.0722	0.4408	−0.7671	26.7459
1	0.0000	0.0000	0.0000	0.0000
T = 303.15 K				
0	0.0000	0.0000	0.0000	0.0000
0.1	18.5994	−0.0513	−0.0975	18.4506
0.2	−84.5533	−9.3050	1.2806	−92.5777
0.3	−80.3488	−8.3140	−0.5246	−89.1873
0.4	−59.5595	−5.0883	−2.1025	−66.7503
0.5	−46.1581	−4.3949	−5.6161	−56.1691
0.6	−10.6216	−0.6057	−3.9464	−15.1737
0.7	11.4808	0.4175	−2.9277	8.9706
0.8	18.3478	0.4973	−2.1717	16.6734
0.9	8.3161	0.0634	−0.4269	7.9527
1	0.0000	0.0000	0.0000	0.0000
T = 308.15 K				
0	0.0000	0.0000	0.0000	0.0000
0.1	−62.8743	−3.0324	1.0168	−64.8900
0.2	−87.6723	−5.4956	1.0389	−92.1291
0.3	−85.3877	−5.3614	−0.1330	−90.8820
0.4	−64.6478	−3.5065	−1.3861	−69.5403
0.5	−43.5376	−2.4705	−3.2881	−49.2962
0.6	−11.6189	−0.4155	−2.7724	−14.8067
0.7	13.1126	0.2489	−1.7155	11.6460
0.8	20.5114	0.3238	−1.4227	19.4125
0.9	18.0487	−0.1887	0.6379	18.4979
1	0.0000	0.0000	0.0000	0.0000
T = 313.15 K				
0	0.0000	0.0000	0.0000	0.0000
0.1	−44.9303	0.1351	−0.0790	−44.8742
0.2	−84.8512	−2.1513	0.5062	−86.4963
0.3	−62.5597	0.4625	−0.1239	−62.2212
0.4	−64.1337	−1.3030	−0.4811	−65.9178
0.5	−33.3481	−0.2063	−0.2965	−33.8508
0.6	−27.5414	−0.9525	−3.2609	−31.7547
0.7	2.1914	0.0211	−0.9758	1.2366
0.8	15.9813	−0.0655	0.3915	16.3073
0.9	5.0695	−0.1220	1.5894	6.5369
1	0.0000	0.0000	0.0000	0.0000
T = 318.15 K				
0	0.0000	0.0000	0.0000	0.0000
0.1	−8.9131	0.4452	−1.7865	−10.2544
0.2	−58.8426	1.0902	−0.6449	−58.3973
0.3	−60.5367	1.2413	−0.4257	−59.7211
0.4	−54.1111	0.3373	0.0810	−53.6928
0.5	−32.1160	0.0809	0.1196	−31.9155
0.6	−18.8704	−0.2830	−1.3392	−20.4925
0.7	19.7366	−0.3546	1.6747	21.0567
0.8	15.3832	−0.0579	0.3770	15.7023
0.9	38.9924	−2.0508	3.2307	40.1723
1	0.0000	0.0000	0.0000	0.0000
T = 323.15 K				
0	0.0000	0.0000	0.0000	0.0000
0.1	−39.7862	2.5338	−2.0482	−39.3006
0.2	−95.2378	1.9343	−0.4642	−93.7678
0.3	−75.3019	3.5011	−0.7193	−72.5201
0.4	−72.7051	1.5895	0.5955	−70.5202
0.5	−56.2045	0.1724	0.2244	−55.8077
0.6	−21.7615	0.3697	1.6706	−19.7212
0.7	4.8026	−0.1126	2.6581	7.3481
0.8	9.8513	−0.2589	2.9472	12.5396

Table 6 (continued)

Volume fraction of Sulfolane per ml in propylene glycol	ΔF^E_{Or} (J·mol^{-1})	ΔF^E_{rr} (J·mol^{-1})	ΔF^E_{12} (J·mol^{-1})	ΔF^E (J·mol^{-1})
0.9	4.9615	−0.2452	3.7033	8.4196
1	0.0000	0.0000	0.0000	0.0000

indicates the presence of hydrogen bond interaction between propylene glycol and sulfolane molecules. Based on Natural Bond Orbital analysis, one of the possible conformational structure of hydrogen bond formation between propylene glycol and sulfolane is shown in Fig. 15. From Fig. 15, it is noticed that the closest distance between the high electron density of oxygen of S = 0 group and the hydrogen of propylene glycol is 1.4113 Å compared to the other oxygen and hydrogen. It indicates the probable location of formation of hydrogen bond between the propylene glycol and sulfolane molecule. This optimized structure is obtained with DFT/B3LYP method at 6-311G* basis set.

The computed HOMO and LUMO energies of propylene glycol, sulfolane with DFT method are tabulated in Table 7 respectively. The HOMO explains the electron donating ability, whereas electron acceptor ability is explained by LUMO. The difference in energy between HOMO and LUMO gives the energy gap, which reveals the information about the chemical stability of the molecule. If the energy gap value is higher than it indicates stable and unreactive, if it is less, then it is an active structure [19]. From Table 7, it observed that sulfolane has the least energy gap, and propylene glycol has more energy gap. Then it indicates sulfolane is actively involved in the formation of a hydrogen bond with propylene glycol molecules due to more polarity.

4. Conclusions

In this paper, the temperature and concentration-dependent dielectric permittivity of propylene glycol/sulfolane binary mixtures are studied in the microwave frequency region. The low frequency dielectric permittivity and the refractive index values increase with the increase in sulfolane concentration in propylene glycol medium due to the presence of hydrogen bonding between the system. The relaxation time values decrease with increase in sulfolane concentration and it is due to the change of molecular interaction from hydrogen bond to dipole-dipole interaction. The excess dielectric permittivity (ε^E) values are positive for entire concentrations, which indicates the existence of solute and solvent interactions in the liquid mixtures. The presence of hydrogen bond between propylene glycol and sulfolane is responsible for the increase in the dipole moment (μ), molar polarization (P_m), effective Kirkwood correlation factor (g^{eff}) values. From the HOMO and LUMO calculations it is confirmed that sulfolane molecules are actively involved in the formation of a strong hydrogen bond with propylene glycol molecules.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 7
DFT calculations of HOMO, LUMO and energy gap.

Molecule	HOMO	LUMO	ΔE (eV)
Propylene glycol	−11.7086	0.9464	12.6550
Sulfolane	−7.8867	−0.6128	7.2739

Uncertainties u are u(eV) = ±0.0001.

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