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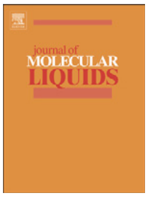

# Investigation of temperature dependent dielectric relaxation studies of 1,4-Butanediol/DMSO binary mixtures at the microwave frequency

V. Manjula [a,b], T. Vamshi Prasad [c], K. Balakrishna [a], K.C. James Raju [d], T. Vishwam [a,*]

[a] Department of Physics and Chemistry, GITAM (Deemed to be University)-Hyderabad, Rudraram, Patancheru (M), TS 502329, India
[b] Department of Physics, Geethanjali College of Engineering and Technology, Hyderabad, Telangana 501301, India
[c] Department of Physics, Jawaharlal Nehru Technological University-Hyderabad, Hyderabad 500 085, India
[d] School of Physics, University of Hyderabad, Hyderabad, Telangana 500046, India

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ABSTRACT

In the present manuscript, we are reporting the complex dielectric permittivity of 1,4-Butanediol/Dimethylsulfoxide binary mixtures for entire concentrations in the temperature range of 298.15 K–323.15 K. The complex dielectric permittivity is measured in the frequency range of 20 MHz–20 GHz. The dielectric relaxation time ($\tau$) of the binary mixtures are analyzed by using the Havriliak-Negami equation. Redlich-Kister polynomial equation is used to fit the excess molar volume ($V_m^E$), excess permittivity ($\varepsilon^E$), excess refractive index ($n_D^E$), excess inverse relaxation time $(1/\tau)^E$. The molecular association and structural packing in the liquid mixture are analyzed by using thermal expansion coefficient ($\alpha_P$) parameter. The ordering nature of the molecular dipoles is discussed by evaluating the Kirkwood correlation factor($g^{eff}$) and stability of the system by thermodynamic quantities. The experimental dipole moments of the pure and equimolar binary system are determined by using Higasi's method and compared with the theoretical dipole moment values obtained from DFT/B3LYP methods. Confirmation of hydrogen bond between 1,4-butanediol and DMSO is supported with the FT-IR and UV-Vis spectroscopy methods. The experimental dielectric and spectroscopic studies confirm the existence of hydrogen bond between the liquid mixtures.

## 1. Introduction

The interaction of electric energy with the material mainly depends upon the characteristic property of the material, which plays a significant role in the determination of structural properties of the compounds. The usage of microwave heating has become important in the field of food processing, synthesis of chemical compounds, local heating of the biological tissues and medicinal industry [1–5]. The capability of the material to absorb microwave energy depends upon the macroscopic permittivity, which is connected with the dielectric loss of the material [6,7]. By choosing the proper polar solvent in the chemical industry can stimulate or prevent the chemical reaction, and modify the structural dynamics of the system. Hence, the study of dielectric properties of the polar liquids in the microwave frequency region is very much important in understanding the applications of microwave energy. The dielectric study of the liquid mixtures having the hydrogen bond donor and acceptor group compounds is useful for a various number of applications in the field of biological, medical, material science and technology [8,9].

Dielectric relaxation studies of 3-Nitrotoulene with diethylacetamide, dimethylsulfoxide binary mixture are studied by Ajay Chaudhari et al. [10] and their studies reveal that effective dipoles rotate slowly in the mixture due to the hindering field produced by the multimers in the solution. The equilibrium properties of butanediols and temperature dependence of shape factor is studied by Zhuravlev et al. [11] and explained that relaxation time depends upon the structural rearrangement of the molecules in the solution. The homogeneous and heterogeneous interaction between a series of three butanediols with 1,4 dioxane is studied by Gilani et al. [12–15] and dipropylsulfoxide in aqueous medium by Gabrielyan et al. [16]. Their studies confirm the presence of hydrogen bonding in the solutions affecting the excess dielectric parameters. The acoustic and thermodynamic properties of butanediols with respective pressure and temperature studied by Edward Zorebski et al. [17] and they reported that thermal expansion, compressibilities are increased with increase in the chain length of the molecules. The average number of hydrogen bonds, bonding energy associated with alcohol-DMSO mixtures are evaluated by Jia Guo-Zhu et al. [18,19] and chemical stability, the reactivity of the anilines, phenols in a nonpolar solvent medium by computational HOMO and LUMO calculations [20]. Molecular dynamics of the hydrogen bond network in the ethanol-water mixtures are reported by

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[*] Corresponding author.
*E-mail address:* vishwam.talloju@gitam.edu (T. Vishwam).

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**Table 1**
Experimental and literature values for density (ρ), refractive index ($n_D$), dipole moment (μ), low frequency dielectric permittivity ($\varepsilon_0$) and relaxation time (τ) of the pure liquids at 298.15 K.

| Liquid sample | Source/purity | Density ρ (g/cm$^3$) | | $\varepsilon_0$ (20 MHz) | | $n_D$ | | Dipole moment (μ, D) | | Relaxation time (τ, ps) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | This work | Literature[a] | This work | Literature | This work | Literature | This work | Literature | This work | Literature |
| 1–4 Butanediol | Sigma-Aldrich/99% | 1.0134 | 1.01345 [15] | 31.42 | 31.53 [15] | 1.4430 | 1.4447 [15] | 2.72 | 2.58[a] | 2157 | 2350 [11] |
| DMSO | Sigma-Aldrich/99.5% | 1.0955 | 1.09537 [66] | 48.22 | 48.40 [67] | 1.4775 | 1.4765 [68] | 3.95 | 3.96[a] | 19.78 | 23.30 [19] |

Standard uncertainties u are u(ρ) = 0.0002, u($\varepsilon_0$) = 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.

Javier Cardona et al. [21] and explained the fast breakage, subsequent reorganization of the hydrogen bonds in the solution. Their studies are in well agreed with the “wait-and-switch” mechanism model [22].

The present work deals with the dielectric relaxation and thermodynamic properties of the hydrogen-bonded polar binary liquid systems at different temperatures. The liquid samples under study are chosen based on scientific and practical importance in the chemical industry as well as in medical research. Dimethylsulfoxide is widely used in the production of microelectronics devices, TFT-LCD flat panel displays and biopreservation of stem cell banking whereas 1,4-Butanediol (BD) is used in the manufacturing of plastics, fibers, and solvent for many chemical reactions. The present work is in continuation of our research studies towards the interpretation of the type of molecular interaction in the binary liquid systems. In the current manuscript, we are reporting the dielectric permittivity of 1,4-butanediol (BD) with polar aprotic solvent-dimethylsulfoxide (DMSO) binary mixture at different temperatures. The aim behind the paper is to identify the type of intra and intermolecular interactions in terms of hydrogen bond donor and acceptor groups present in the compounds. In our earlier studies, molecular interaction between the mixture of alcohols, amines and ketones were studied because these compounds contain hydroxyl (-OH), amine (-$NH_2$) and ketone (-C=0) groups [23–25]. The presence of these groups readily accepts or transfers the electron between the constituents present in the system. Since DMSO is a suitable hydrogen bond acceptor by itself, so it forms strong hydrogen bond interactions between chains of the polymeric structures. In this way, it is interesting to study the molecular interaction between the hydroxyl group (-OH) and sulphonyl group (-S=O). There are only a few research articles available on the thermodynamic and dielectric study of BD with DMSO mixtures in the microwave frequency region [10,18,26–28]. This reason motivated us to study the volumetric, thermodynamic, spectroscopic and computational studies of 1,4-Butanediol with DMSO binary mixtures.

**Table 2**
Dipole moment (μ) and excess dipole moment (Δμ) of 1,4-Butanediol, DMSO and its equimolar binary mixture in the temperature range 298.15 K–323.15 K.

| T (K) | 1,4-Butanediol, $\mu_A$ (D) | DMSO, $\mu_B$ (D) | Equimolar binary mixture (BD + DMSO), $\mu_{AB}$ (D) | $\Delta\mu = \mu_{AB}$-($\mu_A + \mu_B$) in D |
|---|---|---|---|---|
| 298.15 | 2.72 | 3.95 | 4.86 | −1.81 |
| 303.15 | 2.70 | 3.93 | 4.83 | −1.80 |
| 308.15 | 2.68 | 3.91 | 4.82 | −1.77 |
| 313.15 | 2.65 | 3.90 | 4.80 | −1.75 |
| 318.15 | 2.64 | 3.88 | 4.78 | −1.74 |
| 323.15 | 2.62 | 3.87 | 4.76 | −1.73 |

Standard uncertainties u are u(μ) = 0.02D and u(T) = ±0.01 K.

## 2. Experimental

### 2.1. Chemicals

All chemical samples used in the present work are purchased from (AR Grade) from Sigma Aldrich India and further purified by double distillation process under reduced pressure and collected only middle fractions of the compound [29]. The densities of the pure liquids and their mixtures are determined by using specific gravity bottle method [30]. Table 1 represents the information about purity, density (ρ), low frequency dielectric permittivity ($\varepsilon_0$) measured at 20 MHz, refractive index ($n_D$), dipole moment (μ) and relaxation time (τ) of pure liquids, and which are in good agreement with the reported values.

### 2.2. Measurement methods

The dipole moments of the pure and equimolar binary mixtures in the temperature range 298.15 K–323.15 K are determined by using Higasi's method [31]. In order to evaluate the experiment dipole moments (μ) of pure liquids of 1–4 Butanediol, Dimethylsulfoxide (DMSO) and their equimolar binary mixtures, dilute solutions of the pure liquids are prepared in a non-polar solvent benzene in the concentration range of 0 to 1 ml in a 10 ml solution. The static dielectric constant of these diluted samples is determined at 820 Hz using capacitance meter and its optical refractive index ($n_D$) by using Carl-Zeiss Abbe refractometer. The experimental dipole moment of the

**Table 3**
Dielectric permittivity ($\varepsilon_0$ at 20 MHz), refractive index ($n_D$) and relaxation times (τ ps) of 1,4-Butanediol, DMSO and their binary mixtures in the temperature range 298.15 K to 323.15 K.

| Vol. fraction of DMSO per ml in BD/temp. | 298.15 K | | | 303.15 K | | | 308.15 K | | | 313.15 K | | | 318.15 K | | | 323.15 K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\varepsilon_0$ | $n_D$ | τ (ps) | $\varepsilon_0$ | $n_D$ | τ (ps) | $\varepsilon_0$ | $n_D$ | τ (ps) | $\varepsilon_0$ | $n_D$ | τ (ps) | $\varepsilon_0$ | $n_D$ | τ (ps) | $\varepsilon_0$ | $n_D$ | τ (ps) |
| 0 (BD) | 31.42 | 1.4430 | 2157.00 | 30.31 | 1.4420 | 1818.00 | 29.21 | 1.4410 | 1219.00 | 28.16 | 1.4401 | 818.40 | 26.91 | 1.4390 | 556.40 | 25.52 | 1.4372 | 369.69 |
| 0.1 | 32.58 | 1.4462 | 1888.10 | 31.93 | 1.4451 | 1631.00 | 30.52 | 1.4431 | 1069.00 | 29.65 | 1.4412 | 712.20 | 27.77 | 1.4401 | 551.10 | 26.34 | 1.4383 | 369.20 |
| 0.2 | 34.27 | 1.4491 | 1762.20 | 32.78 | 1.4480 | 1451.00 | 31.89 | 1.4463 | 966.10 | 30.68 | 1.4434 | 652.30 | 29.68 | 1.4413 | 451.20 | 28.62 | 1.4402 | 334.10 |
| 0.3 | 35.50 | 1.4523 | 1537.00 | 34.02 | 1.4510 | 1180.00 | 33.82 | 1.4482 | 847.20 | 31.89 | 1.4462 | 512.10 | 31.56 | 1.4432 | 347.10 | 30.86 | 1.4413 | 291.20 |
| 0.4 | 36.45 | 1.4552 | 1317.00 | 35.12 | 1.4532 | 981.10 | 33.94 | 1.4502 | 716.60 | 32.92 | 1.4481 | 429.30 | 32.81 | 1.4454 | 303.40 | 31.47 | 1.4421 | 263.70 |
| 0.5 | 37.58 | 1.4591 | 1056.00 | 35.39 | 1.4580 | 891.10 | 34.92 | 1.4563 | 607.10 | 34.11 | 1.4523 | 362.20 | 34.02 | 1.4503 | 275.30 | 33.92 | 1.4464 | 217.20 |
| 0.6 | 40.87 | 1.4630 | 878.01 | 38.28 | 1.4621 | 731.20 | 37.79 | 1.4591 | 491.30 | 37.23 | 1.4564 | 312.10 | 36.72 | 1.4525 | 210.70 | 35.89 | 1.4502 | 168.40 |
| 0.7 | 42.84 | 1.4681 | 687.21 | 42.59 | 1.4662 | 512.30 | 42.47 | 1.4642 | 367.50 | 42.35 | 1.4614 | 242.50 | 41.47 | 1.4583 | 162.20 | 41.28 | 1.4553 | 117.20 |
| 0.8 | 44.98 | 1.4701 | 418.07 | 44.92 | 1.4683 | 317.10 | 43.88 | 1.4663 | 216.20 | 42.91 | 1.4643 | 161.30 | 41.71 | 1.4614 | 102.20 | 40.32 | 1.4582 | 61.45 |
| 0.9 | 47.75 | 1.4752 | 212.11 | 47.22 | 1.4732 | 119.20 | 46.92 | 1.4702 | 102.30 | 46.53 | 1.4682 | 83.32 | 46.09 | 1.4663 | 56.23 | 45.76 | 1.4644 | 33.57 |
| 1 (DMSO) | 48.22 | 1.4775 | 19.78 | 48.18 | 1.4753 | 19.43 | 47.93 | 1.4750 | 17.12 | 46.91 | 1.4742 | 15.98 | 46.22 | 1.4721 | 15.58 | 45.89 | 1.4702 | 15.30 |

Standard uncertainties u are u($\varepsilon_0$) = 2–3%, u($n_D$) = 0.0001 and u(τ) = 5–7%.

**Table 4**
Density (ρ), excess molar volume $V_m^E$, partial molar volume $V_{m,1}$, $V_{m,2}$, apparent molar volume $V_{\phi,1}$, $V_{\phi,2}$ and coefficient of thermal expansion ($\alpha_p$) for the binary mixtures of DMSO and 1,4-Butanediol at temperatures 298.15 K–323.15 K.

| $X_1$ | $\rho$/g cm$^{-3}$ | $V_m^E$/cm$^3$ mol$^{-1}$ | $V_{m,1}$/cm$^3$ mol$^{-1}$ | $V_{m,2}$/cm$^3$ mol$^{-1}$ | $V_{\phi,1}$/cm$^3$ mol$^{-1}$ | $V_{\phi,2}$/cm$^3$ mol$^{-1}$ | $\alpha_p$ X $10^4$/K$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 298.15 K | | | | | | | |
| 0.0000 | 1.0134 | 0.000000 | 71.346 | 88.927 | – | 88.927 | 6.08 |
| 0.1221 | 1.0216 | 0.002576 | 71.339 | 88.927 | 71.340 | 88.930 | 6.42 |
| 0.2384 | 1.0298 | 0.004435 | 71.333 | 88.928 | 71.338 | 88.932 | 6.75 |
| 0.3492 | 1.0380 | 0.005639 | 71.329 | 88.930 | 71.335 | 88.935 | 7.08 |
| 0.4549 | 1.0463 | 0.006248 | 71.326 | 88.932 | 71.333 | 88.938 | 7.40 |
| 0.5560 | 1.0545 | 0.006313 | 71.324 | 88.935 | 71.330 | 88.941 | 7.72 |
| 0.6525 | 1.0627 | 0.005882 | 71.322 | 88.938 | 71.328 | 88.944 | 8.03 |
| 0.7450 | 1.0709 | 0.004998 | 71.321 | 88.941 | 71.326 | 88.946 | 8.34 |
| 0.8336 | 1.0791 | 0.003700 | 71.320 | 88.944 | 71.323 | 88.949 | 8.64 |
| 0.9185 | 1.0873 | 0.002023 | 71.319 | 88.947 | 71.321 | 88.951 | 8.94 |
| 1.0000 | 1.0955 | 0.000000 | 71.319 | 88.950 | 71.319 | – | 9.22 |
| 303.15 K | | | | | | | |
| 0.0000 | 1.0099 | 0.000000 | 71.687 | 89.237 | – | 89.237 | 6.10 |
| 0.1221 | 1.0180 | 0.003283 | 71.678 | 89.237 | 71.679 | 89.240 | 6.44 |
| 0.2384 | 1.0260 | 0.005653 | 71.671 | 89.238 | 71.676 | 89.244 | 6.78 |
| 0.3492 | 1.0341 | 0.007189 | 71.666 | 89.241 | 71.673 | 89.248 | 7.11 |
| 0.4549 | 1.0421 | 0.007966 | 71.662 | 89.244 | 71.670 | 89.251 | 7.43 |
| 0.5560 | 1.0502 | 0.008050 | 71.659 | 89.247 | 71.667 | 89.255 | 7.75 |
| 0.6525 | 1.0582 | 0.007501 | 71.656 | 89.251 | 71.664 | 89.258 | 8.06 |
| 0.7450 | 1.0663 | 0.006374 | 71.655 | 89.255 | 71.661 | 89.262 | 8.37 |
| 0.8336 | 1.0743 | 0.004719 | 71.654 | 89.259 | 71.658 | 89.265 | 8.68 |
| 0.9185 | 1.0824 | 0.002581 | 71.653 | 89.263 | 71.655 | 89.268 | 8.98 |
| 1.0000 | 1.0904 | 0.000000 | 71.653 | 89.266 | 71.653 | – | 9.26 |
| 308.15 K | | | | | | | |
| 0.0000 | 1.0064 | 0.000000 | 72.030 | 89.545 | – | 89.545 | 6.12 |
| 0.1221 | 1.0143 | 0.003990 | 72.019 | 89.545 | 72.021 | 89.550 | 6.47 |
| 0.2384 | 1.0222 | 0.006870 | 72.010 | 89.547 | 72.017 | 89.554 | 6.80 |
| 0.3492 | 1.0301 | 0.008738 | 72.004 | 89.550 | 72.013 | 89.559 | 7.13 |
| 0.4549 | 1.0380 | 0.009683 | 71.999 | 89.554 | 72.009 | 89.563 | 7.46 |
| 0.5560 | 1.0459 | 0.009787 | 71.995 | 89.558 | 72.006 | 89.567 | 7.78 |
| 0.6525 | 1.0538 | 0.009121 | 71.993 | 89.563 | 72.002 | 89.571 | 8.10 |
| 0.7450 | 1.0617 | 0.007752 | 71.991 | 89.568 | 71.998 | 89.576 | 8.41 |
| 0.8336 | 1.0695 | 0.005740 | 71.989 | 89.572 | 71.995 | 89.580 | 8.72 |
| 0.9185 | 1.0774 | 0.003139 | 71.989 | 89.577 | 71.991 | 89.584 | 9.02 |
| 1.0000 | 1.0853 | 0.000000 | 71.988 | 89.582 | 71.988 | – | 9.31 |
| 313.15 K | | | | | | | |
| 0.0000 | 1.0036 | 0.000000 | 72.375 | 89.799 | – | 89.799 | 6.14 |
| 0.1221 | 1.0113 | 0.004993 | 72.361 | 89.799 | 72.363 | 89.804 | 6.49 |
| 0.2384 | 1.0189 | 0.008599 | 72.350 | 89.801 | 72.359 | 89.810 | 6.82 |
| 0.3492 | 1.0266 | 0.010939 | 72.342 | 89.805 | 72.354 | 89.815 | 7.16 |
| 0.4549 | 1.0343 | 0.012125 | 72.336 | 89.809 | 72.349 | 89.821 | 7.49 |
| 0.5560 | 1.0419 | 0.012256 | 72.332 | 89.815 | 72.345 | 89.826 | 7.81 |
| 0.6525 | 1.0496 | 0.011425 | 72.328 | 89.821 | 72.340 | 89.831 | 8.13 |
| 0.7450 | 1.0573 | 0.009711 | 72.326 | 89.827 | 72.336 | 89.837 | 8.45 |
| 0.8336 | 1.0650 | 0.007192 | 72.324 | 89.833 | 72.331 | 89.842 | 8.76 |
| 0.9185 | 1.0726 | 0.003934 | 72.323 | 89.838 | 72.327 | 89.847 | 9.06 |
| 1.0000 | 1.0803 | 0.000000 | 72.323 | 89.844 | 72.323 | – | 9.35 |
| 318.15 K | | | | | | | |
| 0.0000 | 1.0007 | 0.000000 | 72.726 | 90.053 | – | 90.053 | 6.16 |
| 0.1221 | 1.0082 | 0.005975 | 72.709 | 90.054 | 72.712 | 90.060 | 6.51 |
| 0.2384 | 1.0156 | 0.010291 | 72.696 | 90.056 | 72.706 | 90.067 | 6.85 |
| 0.3492 | 1.0231 | 0.013094 | 72.686 | 90.061 | 72.700 | 90.073 | 7.18 |
| 0.4549 | 1.0305 | 0.014516 | 72.679 | 90.066 | 72.695 | 90.080 | 7.51 |
| 0.5560 | 1.0380 | 0.014676 | 72.674 | 90.073 | 72.689 | 90.086 | 7.84 |
| 0.6525 | 1.0454 | 0.013683 | 72.670 | 90.080 | 72.684 | 90.093 | 8.16 |
| 0.7450 | 1.0529 | 0.011633 | 72.667 | 90.087 | 72.678 | 90.099 | 8.48 |
| 0.8336 | 1.0603 | 0.008616 | 72.665 | 90.094 | 72.673 | 90.105 | 8.79 |
| 0.9185 | 1.0678 | 0.004714 | 72.664 | 90.101 | 72.668 | 90.111 | 9.10 |
| 1.0000 | 1.0752 | 0.000000 | 72.663 | 90.108 | 72.663 | – | 9.39 |
| 323.15 K | | | | | | | |
| 0.0000 | 0.9979 | 0.000000 | 73.079 | 90.309 | – | 90.309 | 6.18 |
| 0.1221 | 1.0051 | 0.006907 | 73.059 | 90.309 | 73.062 | 90.317 | 6.53 |
| 0.2384 | 1.0124 | 0.011900 | 73.044 | 90.312 | 73.055 | 90.324 | 6.87 |
| 0.3492 | 1.0196 | 0.015144 | 73.032 | 90.317 | 73.048 | 90.332 | 7.21 |
| 0.4549 | 1.0268 | 0.016793 | 73.024 | 90.324 | 73.042 | 90.340 | 7.54 |
| 0.5560 | 1.0341 | 0.016981 | 73.018 | 90.331 | 73.036 | 90.347 | 7.87 |
| 0.6525 | 1.0413 | 0.015834 | 73.013 | 90.339 | 73.029 | 90.354 | 8.20 |
| 0.7450 | 1.0485 | 0.013465 | 73.010 | 90.348 | 73.023 | 90.362 | 8.52 |
| 0.8336 | 1.0557 | 0.009975 | 73.008 | 90.356 | 73.017 | 90.369 | 8.83 |

(continued on next page)

**Table 4** (*continued*)

| $X_1$ | $\rho$/g $cm^{-3}$ | $V^E_m$/$cm^3$ $mol^{-1}$ | $V_{m,1}$/$cm^3$ $mol^{-1}$ | $V_{m,2}$/$cm^3$ $mol^{-1}$ | $V_{\phi,1}$/$cm^3$ $mol^{-1}$ | $V_{\phi,2}$/$cm^3$ $mol^{-1}$ | $\alpha_p$ X $10^4$/$K^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0.9185 | 1.0630 | 0.005458 | 73.006 | 90.364 | 73.011 | 90.376 | 9.14 |
| 1.0000 | 1.0702 | 0.000000 | 73.005 | 90.372 | 73.005 | – | 9.44 |

pure as well as equi molar binary systems is determined by using following equation

$$\mu^2 = \frac{27k_BTM_2}{4\pi Nd_1}\frac{(a_0-a_\infty)}{(\epsilon_1+2)^2} \tag{1}$$

where $a_0$ and $a_\infty$ are the slopes of $\varepsilon_o$ and $\varepsilon_\infty$ with respect to the weight fraction of solute in a solvent medium, $d_1$ = density of solvent medium, $\varepsilon_1$ = Static dielectric constant of solvent, $M_2$ = Molecular weight of solute, N = Avogadro's number, $k_B$ = Boltzmann constant, T = Temperature in K. The dipole moments of pure liquids and their equimolar binary mixtures values at different temperatures are listed in Table 2. The complex dielectric permittivity of pure and binary mixtures is measured in the frequency range ($0.02 < \nu/\text{GHz} < 20$) with an open-ended coaxial probe kit (Keysight 85,070 E) and a Vector Network Analyzer (Keysight E 8361C) and the data is analyzed in terms of the lumped coaxial probe model [32–34]. Thermostat controlled water circulation bath set up is used to control the sample temperature. The uncertainty involved in the temperature measurement is ±0.01 K. The refractive index ($n_D$) of the sample is measured by using Abbe's refractometer. The uncertainty involved in the measurement of the refractive index is ±0.0001 units. The experimental data of dielectric permittivity ($\varepsilon_0$ at 20 MHz), refractive index ($n_D$) and the relaxation times ($\tau$ ps) of 1,4-Butanediol, DMSO and their binary mixtures in the temperature 298.15 K to 323.15 K are listed in Table 3 respectively.

### *2.3. Determination of the dielectric parameters*

From the experimentally measured data, excess molar volume ($V^E_m$), partial molar volume ($V_{m,i}$), apparent molar volume ($V_{\phi,i}$), coefficient of thermal expansion ($\alpha_P$) are calculated [35–41] and listed in Table 4 and molar polarization shown in Fig. 6. The excess refractive index [42] of the given liquid mixture is determined by the following equation

$$n_D{}^E = n_D - \left(n_{D1}{}^2\,\varphi_1 + n_{D2}{}^2\,\varphi_2\right)^{1/2} \tag{2}$$

where $n_D$ is the refractive index of the liquid mixture; $n_{D1,}$ $n_{D2,}$ $\varphi_{1,}$ $\varphi_2$ are the refractive index and molar fraction of the solute and solvent respectively. The excess dielectric parameters such as excess dielectric permittivity ($\varepsilon^E$), excess inverse relaxation time $(1/\tau)^E$, Kirkwood correlation factor ($g^{eff}$), activation enthalpy ($\Delta H^*$) and activation entropy ($\Delta S^*$), reaction field parameters from excess Helmholtz energy ($\Delta F^E$) are evaluated for the binary mixtures and their details are explained in our previous published papers [43,44].

The excess parameters, i.e., $V^E_m$, $\varepsilon^E$, $n^E_D$, $(1/\tau)^E$, were fitted with Redlich–Kister type polynomial equation [45] given as

$$y^E = x_1x_2\sum_{i=0}^{4}A_i(x_1-x_2)^i \tag{3}$$

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

$$\sigma = \left[\frac{\sum\left(y^E_{exp}-y^E_{cal}\right)^2}{N-P}\right]^{0.5} \tag{4}$$

where N is the number of experimental points and P is the 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 5.

**Table 5**
Redlich–Kister coefficient and standard deviation values at different temperatures.

| Function | Temp.(K) | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| $\varepsilon^E$ | 298.15 | −12.3800 | 8.3358 | 34.5004 | −32.5026 | −24.1455 | 0.0785 |
| | 303.15 | −20.1813 | 8.6241 | 83.7802 | −26.3377 | −86.6190 | 0.0376 |
| | 308.15 | −18.8232 | 12.4713 | 95.6590 | −41.1836 | −111.909 | 0.1555 |
| | 313.15 | −19.3208 | −0.6106 | 95.1707 | −24.8526 | −95.7045 | 0.1519 |
| | 318.15 | −15.1298 | 3.8472 | 73.1075 | −41.9850 | −77.5624 | 0.1363 |
| | 323.15 | −12.4200 | 1.6366 | 65.5584 | −41.4492 | −73.0822 | 0.0187 |
| $(1/\tau)^E$ | 298.15 | −0.1025 | 0.0632 | 0.0392 | 0.3137 | −0.4871 | 0.0070 |
| | 303.15 | −0.1036 | 0.0716 | 0.0137 | 0.2753 | −0.4119 | 0.0074 |
| | 308.15 | −0.1104 | 0.0753 | 0.0139 | 0.2915 | −0.4328 | 0.0064 |
| | 313.15 | −0.1222 | 0.0827 | 0.0149 | 0.3242 | −0.4812 | 0.0053 |
| | 318.15 | −0.1304 | 0.0962 | 0.0040 | 0.2936 | −0.4455 | 0.0065 |
| | 323.15 | −0.1560 | 0.1288 | −0.0623 | 0.2542 | −0.3162 | 0.0076 |
| $n^E_D$ | 298.15 | −0.0079 | −0.0069 | 0.0346 | −0.0013 | −0.0345 | 0.0004 |
| | 303.15 | −0.0074 | −0.0045 | 0.0172 | 0.0077 | −0.0230 | 0.0002 |
| | 308.15 | −0.0109 | −0.0182 | 0.0113 | 0.0334 | −0.0302 | 0.0003 |
| | 313.15 | −0.0218 | −0.0031 | 0.0455 | 0.0088 | −0.0876 | 0.0000 |
| | 318.15 | −0.0242 | −0.0112 | 0.0030 | 0.0304 | −0.0128 | 0.0000 |
| | 323.15 | −0.0311 | 0.0044 | 0.0382 | 0.0038 | −0.0545 | 0.0005 |
| $V^E_m$ | 298.15 | 0.0254 | −0.0019 | 0.0001 | −0.0000 | 0.0000 | 0.0001 |
| | 303.15 | 0.0323 | −0.0024 | 0.0002 | −0.0000 | 0.0000 | 0.0012 |
| | 308.15 | 0.0393 | −0.0029 | 0.0002 | −0.0000 | 0.0000 | 0.0009 |
| | 313.15 | 0.0492 | −0.0037 | 0.0003 | −0.0000 | 0.0000 | 0.0010 |
| | 318.15 | 0.0589 | −0.0045 | 0.0003 | −0.0000 | 0.0000 | 0.0015 |
| | 323.15 | 0.0682 | −0.0053 | 0.0004 | −0.0000 | 0.0000 | 0.0001 |

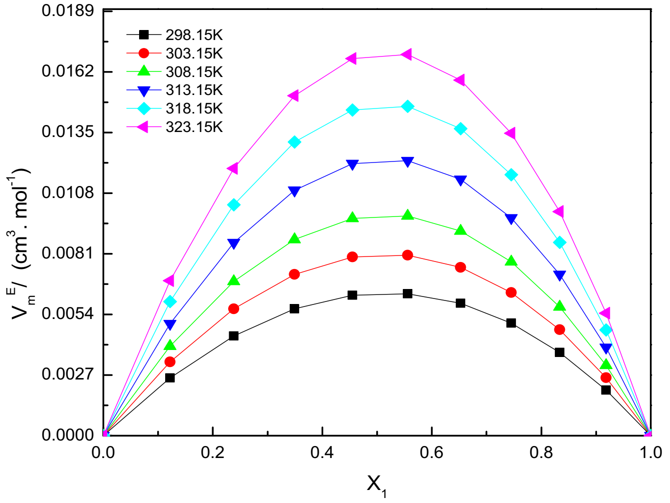


**Fig. 1.** Excess molar volume ($V_m^E$) versus mole fraction ($X_1$) of DMSO in 1,4-Butanediol at different temperatures.

### 2.4. Computational details

The minimum energy-based geometry optimization and single point energy calculation have been performed on 1,4 -Butanediol and DMSO monomer and dimer by using DFT/B3LYP method with 6-311G** basis set [46–48]. The Natural Bond Orbital (NBO) analysis is performed on the geometrical optimized conformer structure of monomers to understand molecular interactions between them and HOMO, LUMO calculations to interpret the chemical stability of the molecule [20].

## 3. Results and discussion

The experimentally determined values of density along with volumetric parameters such as excess molar volume ($V_m^E$), partial molar volume ($V_{m,i}$), apparent molar volume ($V_{\varphi,i}$) and coefficient of thermal expansion ($\alpha_P$) [35,36] of the binary mixtures are summarized in Table 4. In general, the sign of excess molar volume indicates the contraction and expansion of volume of the liquids through mixing. The magnitude of excess molar volume depends upon the type of physical, chemical interactions and changes in structural contributions in the liquid systems. From Fig. 1 it is observed that excess molar volume ($V_m^E$) values are possitivie for 1,4-Butanediol, DMSO and their binary mixtures for all concentrations and temparatures. The positive values of $V_m^E$ arise due to the difference in size and shape of the components, breakage of liquid order due to mixing, variation in the molecular orientation and intermolecular enrgies between like and unlike molecules [40,41,49]. The increase in concentration of DMSO in BD medium reduces the number of hydrogen bonds linkage and increases the dipole-dipole interactions in the liquid mixture results in positive values of $V_m^E$. The rise in temperature weakens the molecular association in the liquid mixtures and causes increase in the magnitude of $V_m^E$ values as shown in Fig. 1.

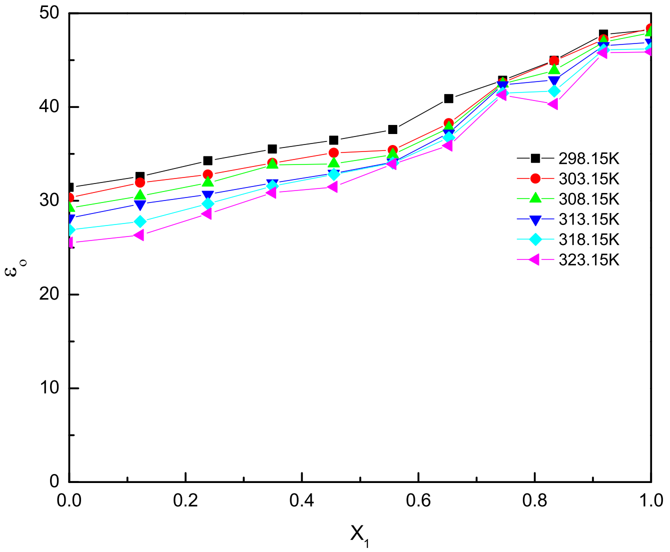


**Fig. 2.** Plot of low frequency dielectric permittivity ($\varepsilon_0$) measured at 20 MHz versus mole fraction ($X_1$) of DMSO in 1,4-Butanediol at different temperatures.

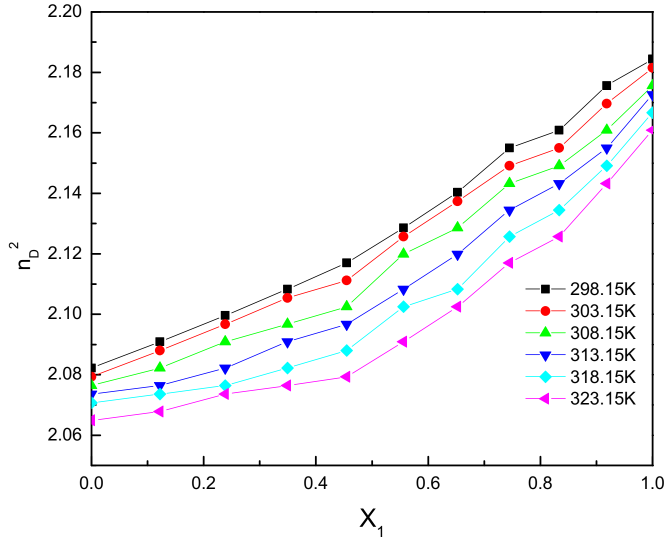


**Fig. 3.** Experimental data of high frequency dielectric constant ($\varepsilon_\infty = n_D^2$) versus mole fraction ($X_1$) of DMSO in 1,4-Butanediol at different temperatures.

The partial molar volume provides information about the level of molecular interactions taking place in the binary liquid systems. It represents the intuitions regarding the structural aspects and environment of the DMSO molecules in the butanediol solutions [35,50]. The vary in the partial molar volume of the solute and solvent at all temperature indicates (from Table 4) the changes in the intermolecular forces between the components present in the system. Based on the density-temperature dependence, the coefficient of thermal expansion $\alpha_p$ [35]

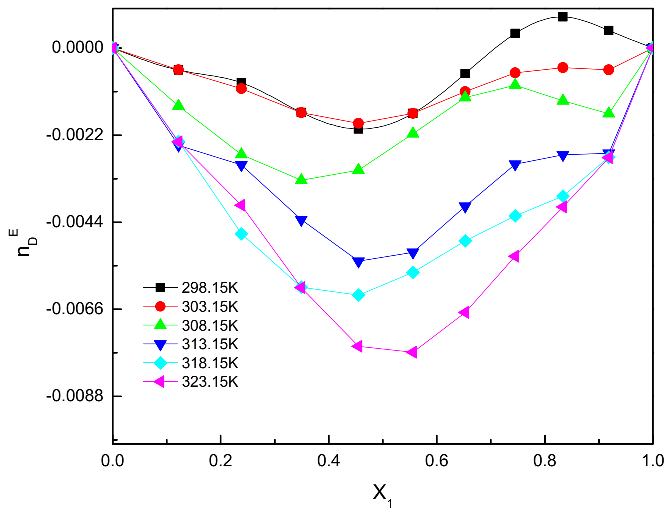


**Fig. 4.** Excess refractive index ($n_D^E$) versus mole fraction ($X_1$) of DMSO in 1,4-Butanediol at different temperatures.

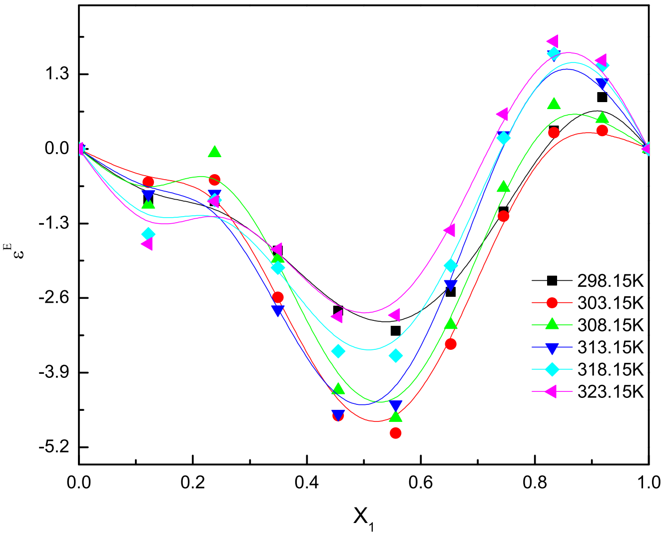


**Fig. 5.** Experimental values of excess dielectric permittivity ($\varepsilon^E$) versus mole fraction ($X_1$) of DMSO in 1,4-Butanediol at different temperatures.

is calculated and tabulated in Table 4. The coefficient of thermal expansion provides information about the orientation of the molecules, type of interaction in the solution and structural packing, which are related to entropic restructuring in terms of structural cavities [35,36]. The positive values of $\alpha_p$ indicates the existence of molecular interaction between the components from self-associative nature to the dissimilar type of interactions in the binary system. The rise in temperature causes increase in thermal vibration of atoms in the solution and results in increase of $\alpha_p$ values (see Table 4) with temperature [35,36,51]. The increase in $\alpha_p$ value may be due to increased dipolar association induced among the molecules by increment in temperature [35].

The variation of low frequency dielectric permittivity ($\varepsilon_0$) measured at 20 MHz with respective molar concentration of DMSO in 1,4-Butanediol (BD) at all temperatures (Table 3), is shown in Fig. 2. From Fig. 2, it is observed that the permittivity value increases with increase in the concentration of DMSO in a BD medium. The dielectric permittivity primarily depends upon the structure of the molecule and type of interaction exists between the component present in the liquid system. Further, there is a non-linear variation of dielectric permittivity with an increase in molar concentration of DMSO at all temperatures and it shows that there is an interaction present between the dissimilar type of molecules which leads to heteromolecular interaction. The DMSO has higher polarity compared to the BD and it is ready to form hydrogen bonds with nearby molecules. In the present system, the heteromolecular interaction is majorly due to the formation of electron donor-acceptor hydrogen bonding between BD and DMSO molecule.

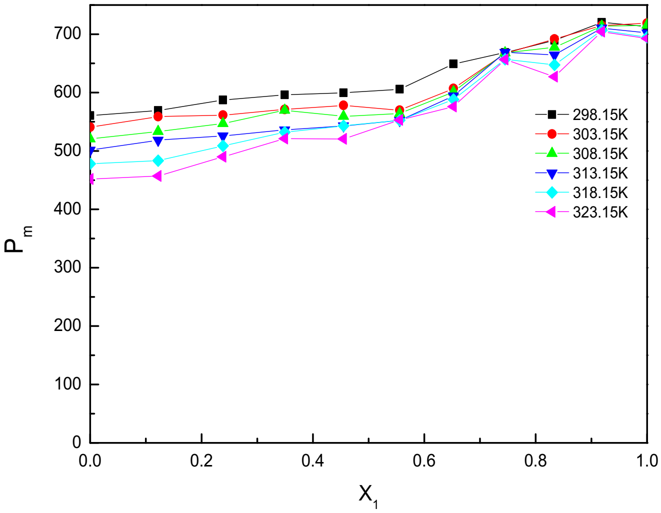
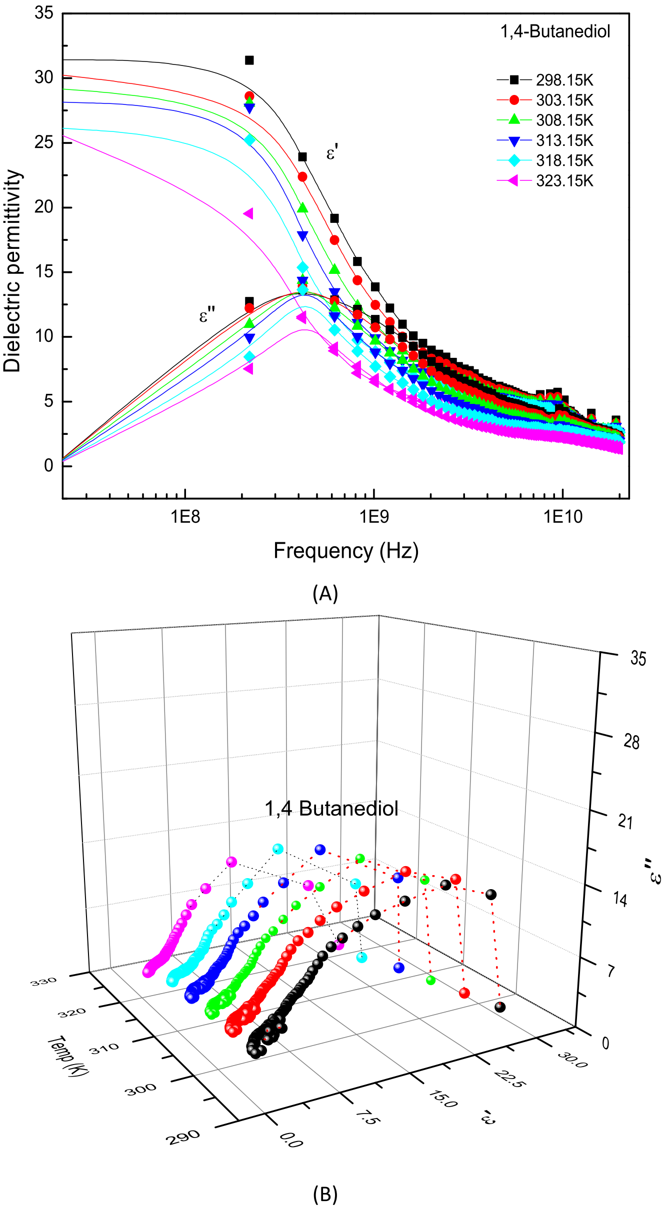


**Fig. 6.** Molar polarization ($P_m$) versus mole fraction ($X_1$) of DMSO in 1,4-Butanediol at different temperatures.

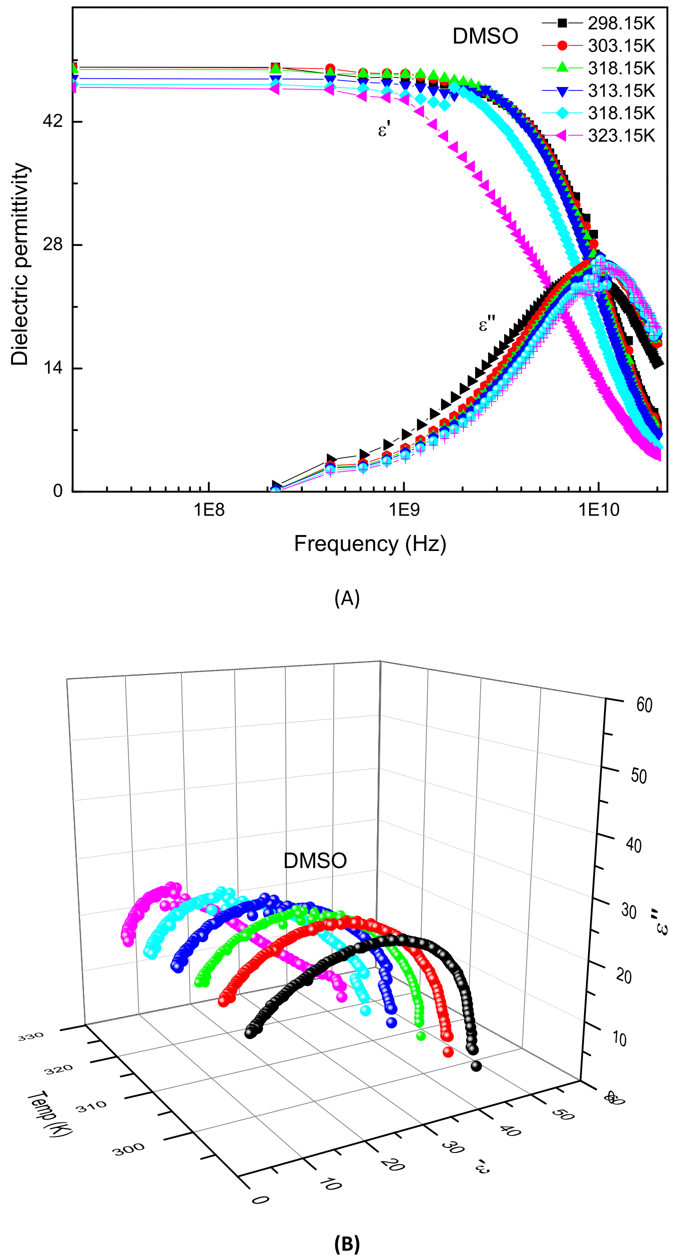
The square of the refractive index, i.e. high frequency dielectric permittivity ($\varepsilon_\infty = n_D^2$) provides valuable information regarding the molecular interaction between the compounds like hetero or homogeneous, and also some of the essential properties like electronic polarizability. The plot of the square of the refractive index ($\varepsilon_\infty = n_D^2$) of DMSO in BD medium for all concentrations and temperature is as shown in Fig. 3. From this graph, it is noticed that the variation of $\varepsilon_\infty$ with mole fractions is non-linear and which indicates the presence of heteromolecular interaction taking place in the liquid mixture. The variation of excess refractive index ($n_D^E$) of a binary mixture is represented in Fig. 4, and it is observed that values of $n_D^E$ are negative for all the concentration ranges and temparatures. The change in excess refractive index with temparature is associated with change in fluid density



(A)

(B)

**Fig. 7.** A) Frequency-dependent of real ($\varepsilon'$) and imaginary part of dielectric permittivity ($\varepsilon''$) of 1,4-Butanediol with respective frequency at different temperatures, B) Complex plane plot $\varepsilon''$ vs $\varepsilon'$ at different temperatures.



(A)

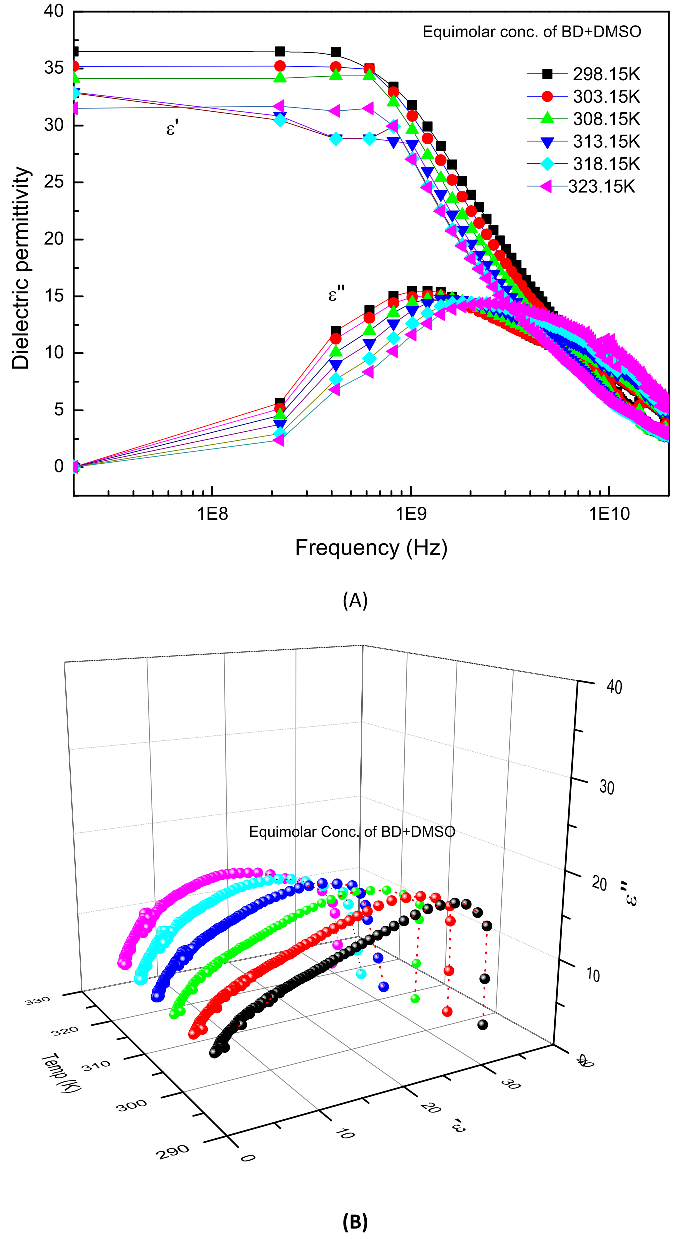
(B)

**Fig. 8.** A) Frequency-dependent of real ($\varepsilon'$) and imaginary part of dielectric permittivity ($\varepsilon''$) of DMSO with respective frequency at different temperatures, B) Complex plane plot $\varepsilon''$ vs $\varepsilon'$ at different temparatures.

with temperature and also dissimilar type of interaction in the liquid mixtures [52].

The excess dielectric permittivity ($\varepsilon^E$) indicates the qualitative information about the existence of multimers in the solution [23]. If $\varepsilon^E$ values are negative, it suggests the weakening of effective dipolar polarization due to the presence of multimers in the solution which causes decrease in the effective dipole moment. The positive values of $\varepsilon^E$ correspond to the strengthening of dipolar polarization due to the net effective addition of individual polarizability of the dipoles as well as an increase in the net dipole moment of the system. From Fig. 5, it is observed that excess dielectric permittivity values are negative up to $0 < x_2 < 0.9$ mol fraction of DMSO and positive after this concentration. This may be due to the molecular interaction changes from hydrogen bond to dipole-dipole interaction due to more polarity of the DMSO. The negative values of excess dielectric permittivity clearly shows the existence of multimers in the solution that causes a decrease in the degree of polarization and reduction in the effective dipole moment. The reduction in the net dipole moment in the binary mixtures might be due to anti-parallel hetero interaction of the mixture components. The minimum value of excess dielectric permittivity of equimolar concentration explains the presence of strong hydrogen bonding between DMSO and BD molecules due to strong polarized S=O bond of DMSO. The increase in temperature causes the breakage of molecular bonds to result in changes in the excess dielectric permittivity ($\varepsilon^E$) values which are shown in Fig. 5.

The molar polarization of the binary mixture ($P_m$) which is calculated from the Kirkwood-Frohlich equation [53,54] is shown in Fig. 6. The molar polarization ($P_m$) strongly depends upon the dielectric permittivity and dipole moment of the solute or solvent medium and it also reveals the information about chain length and molecular size differences in the binary mixtures. From Fig. 6 it is observed that molar



(A)

(B)

**Fig. 9.** A) Frequency-dependent of real ($\varepsilon'$) and imaginary part of dielectric permittivity ($\varepsilon''$) of equimolar binary mixtures of 1,4-Butanediol + DMSO with respective frequency at different temperatures, B) complex plane plot $\varepsilon''$ vs $\varepsilon'$ at different temparatures.

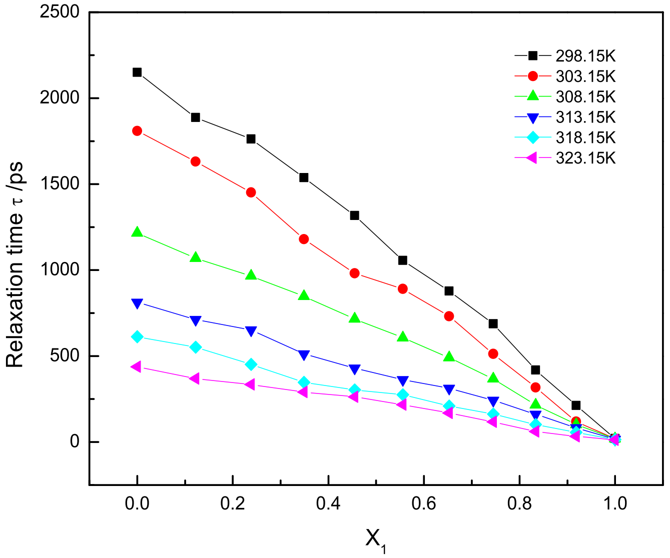


**Fig. 10.** Plot of average relaxation time (τ/ps) versus mole fraction ($X_1$) of DMSO in 1,4-Butanediol at different temperatures.

polarization value increases with increase in the concentration of DMSO in BD medium at all temperatures and it might be due to the progressive alignment of the net dipoles in the liquid mixture towards the electric field direction. The molar polarization value decreases with an increase in temperature, and it corresponds to a decrease in the effective dipole moment and degree of susceptibility of the binary liquid mixtures.

The dielectric spectra and corresponding relaxation plots of 1,4-Butanediol, DMSO and its equimolar binary mixture at different temperatures are shown in Figs. 7, 8 and 9 respectively. Havriliak-Negami relation [55] is used to fit the Cole-Davidson and Cole-Cole plot [56–58] by using WINFIT software (NOVO Control Instruments). The shape factor (β) of the 1,4-Butanediol is in the range of $0.5320 < \beta < 0.6100$ and $\beta = 1$, $0.879 < \alpha < 1$ for DMSO, i.e., Cole-Cole plot in the temperature range 298.15 K–323.15 K. From Fig. 7A, it is observed that the dielectric loss peak is maximum at lower frequencies (MHz) and it is due to self-associative nature of alcohol molecules. Due to the presence of two hydroxyl groups within the molecule, it tries to form inter and intramolecular hydrogen bonds which may cause different self-associative structures in the liquid solution. Whereas in the case of DMSO, the dielectric loss peak shifting towards higher frequencies (see Fig. 8A) due to non-associative nature of DMSO molecules. The possible interaction between the DMSO molecules is dipole-dipole interaction due to higher polarity nature of $\mathrm{S{=}O}$ group.

Further, with the increase in the concentration of DMSO in BD medium, we notice that the dielectric loss peak is slowly shifting towards higher frequencies, which causes a decrease in the relaxation time values. From the permittivity spectra of equimolar binary mixtures (Fig. 9A), it is noticed that there is a possible formation of the hydrogen bond between BD and DMSO molecules which affects the dielectric loss peak and it appears broader when compared to BD and DMSO graphs. The larger surface area of the hydroxyl group of BD and higher polarity nature of $\mathrm{S{=}O}$ group in DMSO readily form a hetero molecular interaction in terms of strong hydrogen bonding. Moreover, the real part of the dielectric permittivity increases with increase in the concentration of DMSO and decreases with increase in frequency at all temperatures as shown in Figs. 7A, 8A and 9A respectively.

The relaxation time of BD, DMSO and its binary mixture are determined by using the Cole-Davidson, Cole-Cole relaxation models [56–58] and their corresponding complex plane plots are shown in the Figs. 7B, 8B and 9B. From Fig. 10, it is observed that the dielectric relaxation time values decrease with increase in the concentration of DMSO in a BD medium and it is due to molecular interaction changes from self-associative nature to dipole-dipole interaction. Initially, as the relaxation time values are higher due to the presence of self-associative nature of BD molecules, these molecular dipoles takes a longer time to attain the mean equilibrium positions. Further with increase in DMSO concentration, there is a decrease in the number of hydrogen bonds that leads to a decrease in the relaxation time values. The increase in temperature decreases the number of hydrogen bond networks in the solution and disturbs the orientation of the dipoles and causes to decrease in the relaxation time values which is as shown in Fig. 10.

The plot of excess inverse relaxation time $(1/\tau)^E$ for an entire molar fraction of DMSO in BD at all temperatures is shown in Fig. 11. From Fig. 11, it is noticed that $(1/\tau)^E$ values are negative [59,60] which suggests the presence of linear polymeric structure which causes the slower rotation movement of the dipoles in the presence of the electric field. The increase of DMSO concentration in BD generates the resistance field in such a way that effective dipoles rotates slowly in the liquid mixture.

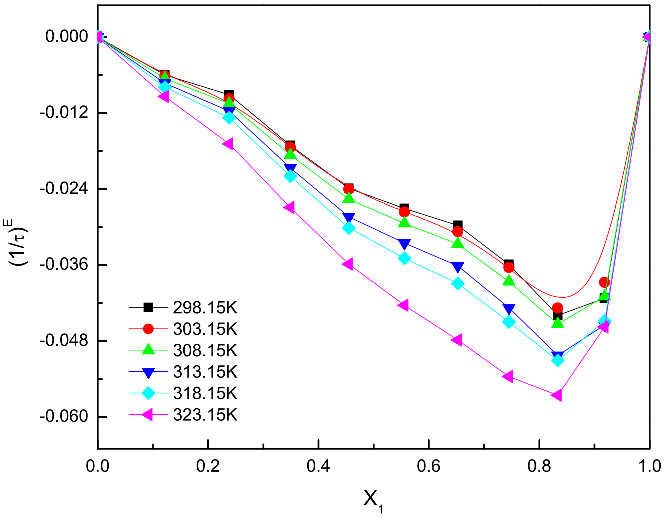


**Fig. 11.** Plot of excess relaxation time ($(1/\tau)^E$) versus mole fraction ($X_1$) of DMSO in 1,4-Butanediol at different temperatures.

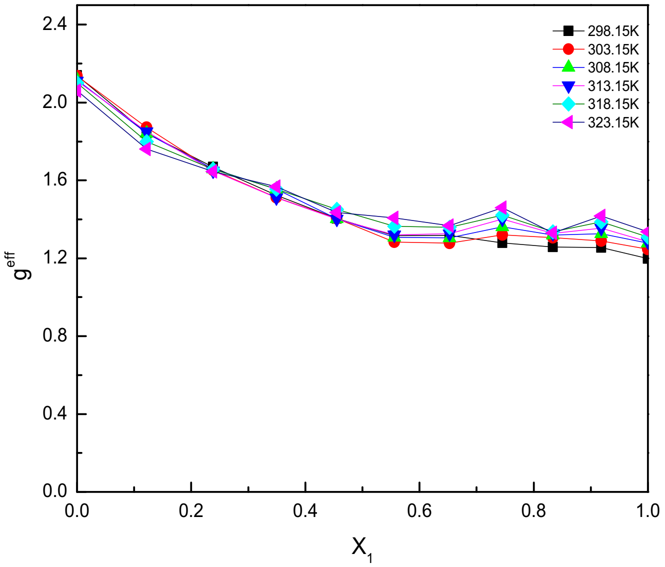


**Fig. 12.** Kirkwood effective ($g^{eff}$) correlation factor versus mole fraction ($X_1$) of DMSO in 1,4-Butanediol at different temperatures.

**Table 6**
Variation of thermodynamically parameters ΔG*, ΔH* and ΔS* with respective volume concentration of DMSO in 1,4-Butanediol at different temperatures.

| Vol. concentration of DMSO per ml in 1,4-Butanediol solution | T/K | ΔH*/(kcal/mol) | ΔG*/(kcal/mol) | ΔS*/(Cal/mol/K) |
|---|---|---|---|---|
| 1,4-Butanediol | 298.15 | 116.223 | 23.539 | 311.02 |
| | 303.15 | | 23.542 | 305.88 |
| | 308.15 | | 22.954 | 302.82 |
| | 313.15 | | 22.317 | 300.02 |
| | 318.15 | | 21.968 | 296.40 |
| | 323.15 | | 21.457 | 293.39 |
| 0.1 | 298.15 | 121.182 | 23.217 | 328.74 |
| | 303.15 | | 23.280 | 323.11 |
| | 308.15 | | 22.624 | 319.99 |
| | 313.15 | | 21.975 | 316.95 |
| | 318.15 | | 21.690 | 312.87 |
| | 323.15 | | 20.996 | 310.17 |
| 0.2 | 298.15 | 122.560 | 23.046 | 333.94 |
| | 303.15 | | 22.985 | 328.63 |
| | 308.15 | | 22.364 | 325.31 |
| | 313.15 | | 21.746 | 322.09 |
| | 318.15 | | 21.161 | 318.87 |
| | 323.15 | | 20.729 | 315.27 |
| 0.3 | 298.15 | 122.618 | 22.707 | 335.27 |
| | 303.15 | | 22.464 | 330.54 |
| | 308.15 | | 22.027 | 326.59 |
| | 313.15 | | 21.117 | 324.28 |
| | 318.15 | | 20.467 | 321.23 |
| | 323.15 | | 20.358 | 316.59 |
| 0.4 | 298.15 | 123.499 | 22.324 | 339.51 |
| | 303.15 | | 21.999 | 334.98 |
| | 308.15 | | 21.597 | 330.85 |
| | 313.15 | | 20.656 | 328.57 |
| | 318.15 | | 20.109 | 325.12 |
| | 323.15 | | 20.087 | 320.16 |
| 0.5 | 298.15 | 119.324 | 21.777 | 327.34 |
| | 303.15 | | 21.756 | 322.01 |
| | 308.15 | | 21.174 | 318.67 |
| | 313.15 | | 20.214 | 316.65 |
| | 318.15 | | 19.852 | 312.81 |
| | 323.15 | | 19.570 | 308.84 |
| 0.6 | 298.15 | 125.222 | 21.320 | 348.67 |
| | 303.15 | | 21.258 | 343.12 |
| | 308.15 | | 20.631 | 339.58 |
| | 313.15 | | 19.828 | 336.72 |
| | 318.15 | | 19.139 | 333.59 |
| | 323.15 | | 18.883 | 329.22 |
| 0.7 | 298.15 | 127.864 | 20.712 | 359.57 |
| | 303.15 | | 20.360 | 354.80 |
| | 308.15 | | 19.885 | 350.58 |
| | 313.15 | | 19.166 | 347.28 |
| | 318.15 | | 18.453 | 344.06 |
| | 323.15 | | 17.911 | 340.41 |
| 0.8 | 298.15 | 133.953 | 19.480 | 384.14 |
| | 303.15 | | 19.152 | 378.88 |
| | 308.15 | | 18.528 | 374.76 |
| | 313.15 | | 18.106 | 370.12 |
| | 318.15 | | 17.230 | 367.05 |
| | 323.15 | | 16.162 | 364.68 |
| 0.9 | 298.15 | 117.793 | 17.798 | 335.55 |
| | 303.15 | | 16.684 | 333.69 |
| | 308.15 | | 16.606 | 328.53 |
| | 313.15 | | 16.381 | 324.00 |
| | 318.15 | | 15.644 | 321.22 |
| | 323.15 | | 14.512 | 319.76 |
| DMSO | 298.15 | 33.411 | 11.948 | 72.02 |
| | 303.15 | | 12.127 | 70.25 |
| | 308.15 | | 12.181 | 68.93 |
| | 313.15 | | 12.096 | 68.10 |
| | 318.15 | | 12.104 | 67.00 |
| | 323.15 | | 11.817 | 66.86 |

The effective Kirkwood correlation factor ($g^{eff}$) of BD-DMSO binary mixtures at all temperatures is shown in Fig. 12. From Fig. 12 it is noticed that, $g^{eff}$ factor for BD is higher than unity for all the temperatures which represents there is a higher degree of cooperation among the self-associated dipoles and polarization in the pure liquid state. Whereas the $g^{eff}$ value of DMSO is lesser than the BD at all temperatures which corresponds to lack of mutual coordination among the non-self-associated electric dipoles. This phenomenon causes all the electrical dipoles aligned in anti-parallel direction. Also, the $g^{eff}$ decreases non-uniformly with increase in DMSO concentration in BD medium and it shows the presence of hydrogen-bonded networks in the binary system between the hydroxyl group of BD and -S=O group of DMSO at all temperatures. Moreover, the decrease of $g^{eff}$ values with increase of DMSO concentration causes weakening of the interaction energy among the self-associated alcohol groups by breaking the number of hydrogen bonds and results in forming anti-parallel dipoles in the liquid mixture. At higher concentration of DMSO, the interactions present in the liquid mixtures dominated by dipole-dipole interactions leads to complete anti-parallel alignment of the dipoles which is observed from Fig. 12. The increase in temperature decreases the coordination among the dipoles and destabilizes the active structure and hence, the correlation among the dipoles decreases.

The thermodynamic parameters such as enthalpy of activation ΔH*, entropy of activation ΔS* and Gibbs free energy of activation ΔG* are evaluated by using Eyring's rate equations [61] and they are summarized in Table 6 respectively. The enthalpy of activation ΔH* provides the information regarding either the system has taken the heat energy or given off to the surroundings during the chemical reaction. If the ΔH* values are positive, that indicates heat energy is absorbed (endothermic reaction) and the system is in favor of forming the hydrogen bonds in the system. If the values of ΔH* are negative and it corresponds to heat energy released to the surroundings (exothermic reaction) and the system is progressing towards attaining a stable position. From Table 6, it is noticed that ΔH* values are positive which suggests that the surrounding medium is supportive to form hydrogen bonds between the BD and DMSO molecules. The values of Gibbs free energy of activation ΔG* are positive and its magnitude is decreasing with increase in the concentration of DMSO and temperature. The decrease in ΔG* values with increase in DMSO concentrations may be due to the type of interaction in the liquid system that changes from hydrogen bond to dipole-dipole interactions. Further, the entropy of activations plays a significant role in concluding the ordering of the dipoles and the surrounding environment during the orientation of the molecules. The positive value of $\Delta S^*$ attributes that the surrounding environment is not supportive for the orientation process of the molecules and the dipoles are spread in a random direction in the activated state. The negative values of $\Delta S^*$prevails that environment of the system is supportive and dipoles being aligned in an orderly in an activated state. As seen from the Table 6, it is clear that the $\Delta S^*$ values are positive for all the concentrations of DMSO in BD medium and which corresponds to surrounding environment of the system is noncooperative in the orientation process of the dipoles in the field direction.

The values of excess Helmholtz energy ($\Delta F^E$) [62] and its components $\Delta F^{E_{or}}$, $\Delta F^{E_{rr}}$ and $\Delta F^{E_{12}}$are tabulated in Table 7. From Table 7 it is noted that the values of $\Delta F^{E_{or}}$are positive and suggests that the existence of long-range coulombic attractive forces between the alcohol and DMSO molecules. The short-range interaction between the similar molecules are given by the term $\Delta F^{E_{rr}}$. The values of $\Delta F^{E_{rr}}$are positive up to certain concentrations ($0 < x < 0.2$) of DMSO and negative for remaining concentrations. It indicates that for lower concentrations the interactions are homogeneous and rest of the concentrations are heterogeneous. The force of interaction between different molecules is given by the term $\Delta F^{E_{12}}$. The negative values of $\Delta F^{E_{12}}$represents the parallel alignment of the dipoles in field direction (alcohol rich region) whereas positive value shows the antiparallel alignment of the dipoles due to dipole-dipole interactions (sulphonyl rich region). Further, the total excess Helmholtz energy ($\Delta F^E$) values are positive for most of the concentrations and which indicates the presence of β clusters in the solutions

**Table 7**
Variation of$\Delta F_{Or,}^{E}$ $\Delta F_{rr,}^{E}$ $\Delta F_{12}^{E}$ and $\Delta F^{E}$ with volume fraction of DMSO in 1,4-Butanediol.

| Volume fraction of DMSO per ml in 1,4-Butanediol | $\Delta F_{Or}^{E}$ (J.mol$^{-1}$) | $\Delta F_{rr}^{E}$ (J.mol$^{-1}$) | $\Delta F_{12}^{E}$ (J.mol$^{-1}$) | $\Delta F^{E}$ (J.mol$^{-1}$) |
|---|---|---|---|---|
| T = 298.15 K | | | | |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | −7.5013 | 0.1744 | −0.7211 | −8.0480 |
| 0.2 | −3.0764 | 0.0811 | −0.9820 | −3.9773 |
| 0.3 | 16.4632 | −0.6625 | −1.3626 | 14.4381 |
| 0.4 | 42.7813 | −2.5145 | −1.5750 | 38.6918 |
| 0.5 | 67.2978 | −4.7865 | −1.0887 | 61.4226 |
| 0.6 | 59.2186 | −1.6876 | 0.3746 | 57.9056 |
| 0.7 | 58.2243 | −1.2028 | 0.4757 | 57.4972 |
| 0.8 | 44.0225 | −0.1947 | 0.1128 | 43.9405 |
| 0.9 | 6.8451 | 0.1454 | −0.4082 | 6.5823 |
| 1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| T = 303.15 K | | | | |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | −13.6200 | 0.1910 | −0.4414 | −13.8704 |
| 0.2 | 2.1373 | −0.1011 | −2.1410 | −0.1048 |
| 0.3 | 23.8393 | −1.5227 | −2.7367 | 19.5800 |
| 0.4 | 51.9687 | −4.1339 | −2.7246 | 45.1102 |
| 0.5 | 91.9193 | −10.8100 | −3.6645 | 77.4448 |
| 0.6 | 92.7835 | −7.9138 | −0.1743 | 84.6954 |
| 0.7 | 61.4845 | −1.2953 | 0.5482 | 60.7373 |
| 0.8 | 45.9771 | −0.1369 | 0.0845 | 45.9246 |
| 0.9 | 18.4223 | 0.1832 | −0.1971 | 18.4084 |
| 1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| T = 308.15 K | | | | |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | −10.1323 | 0.2652 | −0.9346 | −10.8017 |
| 0.2 | 0.0839 | −0.0039 | −2.1471 | −2.0670 |
| 0.3 | 16.0840 | −0.7006 | −1.5914 | 13.7920 |
| 0.4 | 57.3823 | −5.1502 | −3.4519 | 48.7803 |
| 0.5 | 90.5061 | −10.1606 | −3.0579 | 77.2876 |
| 0.6 | 92.5282 | −7.4278 | 0.1415 | 85.2419 |
| 0.7 | 56.2051 | −0.5121 | 0.2890 | 55.9820 |
| 0.8 | 55.5221 | −0.7731 | 0.4027 | 55.1517 |
| 0.9 | 15.8107 | 0.2553 | −0.3500 | 15.7160 |
| 1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| T = 313.15 K | | | | |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | −13.3356 | 0.2627 | −0.7120 | −13.7849 |
| 0.2 | 1.9805 | −0.0994 | −2.5243 | −0.6432 |
| 0.3 | 26.9517 | −1.9043 | −3.3915 | 21.6559 |
| 0.4 | 59.7109 | −5.4241 | −3.5789 | 50.7079 |
| 0.5 | 91.2744 | −9.6351 | −2.6648 | 78.9746 |
| 0.6 | 89.2699 | −6.0425 | 0.4530 | 83.6804 |
| 0.7 | 45.0254 | 0.7145 | −0.6172 | 45.1227 |
| 0.8 | 56.7487 | −0.6598 | 0.3572 | 56.4461 |
| 0.9 | 5.1402 | 0.1661 | −0.7739 | 4.5324 |
| 1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| T = 318.15 K | | | | |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | −4.1382 | 0.1901 | −1.9829 | −5.9310 |
| 0.2 | −0.6732 | 0.0319 | −2.4255 | −3.0668 |
| 0.3 | 18.3954 | −0.8878 | −1.9478 | 15.5599 |
| 0.4 | 50.1792 | −3.2888 | −1.8597 | 45.0306 |
| 0.5 | 82.2523 | −6.9316 | −1.1977 | 74.1230 |
| 0.6 | 86.9137 | −4.8926 | 0.7169 | 82.7379 |
| 0.7 | 47.9006 | 0.8029 | −0.7044 | 47.9990 |
| 0.8 | 66.4595 | −1.3519 | 0.6451 | 65.7528 |
| 0.9 | 0.6991 | 0.0278 | −1.0416 | −0.3147 |
| 1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| T = 323.15 K | | | | |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1 | −3.5708 | 0.1945 | −2.6161 | −5.9924 |
| 0.2 | −4.3488 | 0.2083 | −2.5519 | −6.6924 |
| 0.3 | 13.3474 | −0.5267 | −1.4624 | 11.3583 |
| 0.4 | 57.1430 | −4.5182 | −2.5624 | 50.0624 |
| 0.5 | 75.1821 | −4.7623 | −0.1880 | 70.2319 |
| 0.6 | 92.6893 | −5.6376 | 0.9927 | 88.0444 |
| 0.7 | 44.6942 | 1.3036 | −1.4511 | 44.5467 |
| 0.8 | 85.9301 | −3.5003 | 1.3094 | 83.7391 |
| 0.9 | 0.5566 | 0.0235 | −1.2216 | −0.6415 |

**Table 7** (*continued*)

| Volume fraction of DMSO per ml in 1,4-Butanediol | $\Delta F^E_{Or}$ (J.mol$^{-1}$) | $\Delta F^E_{rr}$ (J.mol$^{-1}$) | $\Delta F^E_{12}$ (J.mol$^{-1}$) | $\Delta F^E$ (J.mol$^{-1}$) |
|---|---|---|---|---|
| 1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

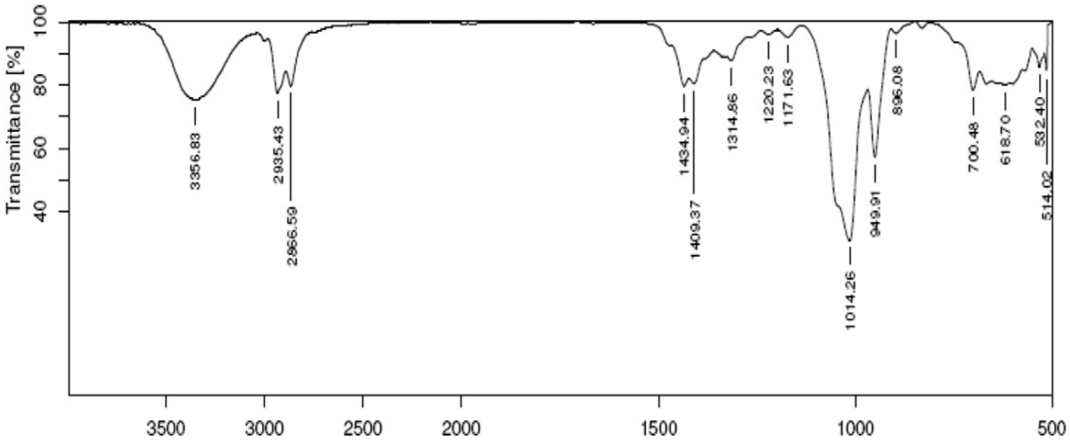


**Fig. 13.** FT-IR Spectra of equimolar binary mixtures of 1,4-Butanediol and DMSO.

with the anti-parallel orientation of the dipoles so that total internal energy of the system is decreased [63].

Moreover, Fig. 13 indicates the influence of hydrogen bonding in the frequency scale compare to individual stretching frequencies of 1,4-Butanediol and DMSO. This FT-IR spectrum clearly suggests that there is a change in the frequency from 3364 to 3356 cm$^{-1}$ by a difference of 8 cm$^{-1}$ units. This is due to the hydrogen bonding interaction of hydroxy hydrogen atom in 1,4-Butanediol with sulphoxide in DMSO. This effect also decreased the C—O stretching frequency from 1044 to 1014 cm$^{-1}$ by 30 cm$^{-1}$. This change in frequency indicates the result of hydrogen bonding in the equimolar mixture of 1,4-Butanediol and DMSO. This influence also observed in their UV–Vis absorption spectra. Fig. 14 shows the UV absorption spectra of 1,4- Butanediol, DMSO and its equimolar mixture. From the UV–Vis graph, it is observed that there is a redshift concerning BD whereas blue shift concerning DMSO which indicates the electronic influence of components in the mixture. Both the FT-IR and UV–Vis spectra studies confirm the existence of hydrogen bond between 1,4 Butanediol and DMSO binary mixtures.

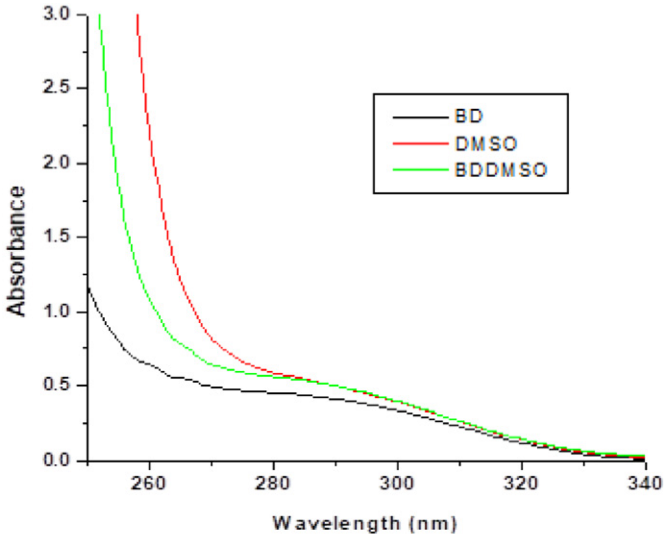


**Fig. 14.** UV–Vis absorption spectra of 1,4-Butanediol, BD and its equimolar concentration.

The experimental dipole moment of BD, DMSO and their binary system is compared with the theoretical dipole moments values which are calculated using DFT/B3LYP with 6-311G** basis set and tabulated in Table 8. The theoretical dipole moment of 1,4-Butanediol is equal to zero due to its symmetry of the structure and its value is verified with the computational chemistry comparison and benchmark database (CCCBDB-NIST). From Table 8, it is observed that the difference in interaction energy between BD and DMSO is found to be 167 kcal/mol and it supports the existence of hydrogen bond between BD and DMSO molecules. Based on the Natural Bond Orbital analysis the possible conformation structure of formation of hydrogen bonding between BD and DMSO is analyzed and shown in Fig. 15. The excess dipole moment (Δμ) values are negative (see Table 2) which indicates the absence of ionic contribution. The negative values of Δμ is due to the presence of the polarization effect or effect of an induced solvent medium in the binary mixture [64,65].

The calculated HOMO and LUMO energies of BD, DMSO with DFT method are listed in Table 9. The HOMO-LUMO energies describe the electron donating, electron acceptor ability and difference in energy indicates the energy gap. If the energy gap is more then it suggests stable and unreactive, if it is a smaller value then it resembles active structure [20]. From Table 9, it is noticed that DMSO has lesser energy gap than

**Table 8**
Experimental and theoretical dipole moments (μ) of pure system of 1,4-Butanediol, DMSO and their equimolar binary systems at 298.15 K.

| Dipole moment in Debye | Gaseous state | Experiment |
|---|---|---|
| System/basis sets | DFT/B3LYP 6-311G** | Higasis's method |
| 1,4-Butanediol (BD) | 0.00[a] | 2.72 |
| Energy (a.u), $E_{BD}$ | −308.953 | |
| DMSO | 3.88 | 3.95 |
| Energy (a.u), $E_{DMSO}$ | −553.2501 | |
| Equimolar binary mixtures (BD + DMSO) | 7.65 | 4.86 |
| Energy (a.u) $E_{BD+DMSO}$ | −861.9356 | |
| Difference in energy (kcal/mol) | 167.8588 | |
| $E_T = E_{BD+DMSO} - (E_{BD} + E_{DMSO})$ | | |

Uncertainties u in u(μ) = 0.02D and u(E) = 0.0002.

[a] CCCBDB, National Institute of Standard and Technology, Standard Reference Database, 2018.

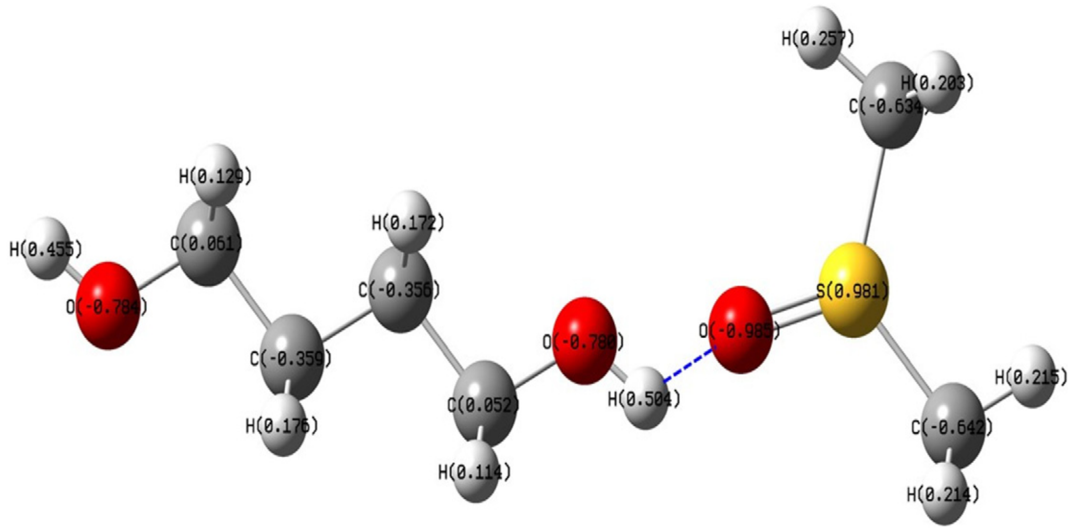


**Fig. 15.** Optimized converged geometrical structure of the hydrogen-bonded system of 1,4-Butanediol + DMSO in the gaseous state from DFT 6-311G* basis set using Gaussian-09 (with full natural bond analysis (NBO)).

**Table 9**
DFT calculations of HOMO, LUMO and energy gap.

| Molecule | HOMO | LUMO | ΔE (eV) |
|---|---|---|---|
| 1,4-Butanediol | −7.185 | 0.969 | 8.154 |
| DMSO | −6.026 | 1.163 | 7.190 |

butanediol and it suggests that DMSO is actively involved in forming the hydrogen bond with the butanediol molecules.

## 4. Conclusions

The complex dielectric permittivity of 1,4- Butanediol/ Dimethylsulfoxide binary mixtures for entire concentrations have been investigated in the microwave frequency region at different temparatures 298.15 K–323.15 K. The dielectric relaxation time value decreases with increase in DMSO concentration in 1,4-Butanediol medium due to interaction between the molecules changes from self-associative to dipole-dipole interaction. The excess dielectric parameters such as excess dielectric permittivity ($\varepsilon^E$), excess relaxation time $(1/\tau)^E$, excess refractive index ($n_D^E$) values are negative which indicates the presence of heteromolecular interactions taking place in the binary mixtures. The excess dipole moment ($\Delta\mu$) of the equimolar binary mixture for all temperatures shows negative value which indicates the presence of polarization contribution due to the solvent -induced medium effect. The excess Helmholtz energy ($\Delta F^E$) values are positive for most of the concentrations and it reveals the existence of clusters in the solution through hydrogen bonding. The presence of hydrogen bond between DMSO and BD molecules is confirmed from the experimental FT-IR and UV spectroscopic studies.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2019.112190.

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