

Dielectric relaxation and thermodynamic study of Dimethylformamide/1,4-Butanediol binary mixtures in the temperature range 298K–323K

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ABSTRACT

In the present paper, the permittivity of Dimethylformamide (DMF) with 1,4-Butanediol (BD) binary mixtures are determined at the temperature range of 298 K–323 K in the microwave frequency. Dipole moment (μ), excess molar volume (V_m^E), partial molar volume ($V_{m,i}$), excess permittivity (ϵ^E), excess refractive index (n_D^E), excess inverse relaxation time ($1/\tau$)^e, thermal expansion coefficient (α_p), excess Helmholtz energy (ΔF^E) are determined at different temperatures. Redlich-Kister polynomial equation is used to fit the excess parameters. Havriliak-Negami equation is used to analyse the relaxation time of the binary mixtures throughout the measured temperature range. The heteromolecular interaction between DMF and 1,4-Butanediol binary mixtures are interpreted in terms of Kirkwood correlation (g^{eff}) factor. The stability of the system is analysed from the activation energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) parameters. The various mixing rules were applied in order to estimate the permittivity and refractive indices of the binary system at different temperatures.

1. Introduction

The complex permittivity of binary liquid mixtures provides information regarding the solute-solvent interactions and also the existence of monomers and multimers in the solution. The permittivity is a macroscopic parameter plays a significant role in understanding the nature of molecular interaction between polar-polar, polar in a non-polar liquid medium and also the alignment of dipoles in the solution [1–10]. The profound knowledge in thermodynamics and transport properties of pure liquids and their binary mixtures is essential to solving many chemical engineering problems, heat and mass transfer, and drug design calculations. The temperature dependent dielectric relaxation studies of different polar liquids at different microwave frequency region can yield the information regarding the structure of the molecule, inter and intra molecular hydrogen bonding and orientational polarization of the dipoles [11–23]. Investigation of permittivity of polar liquids having the hydrogen bond donor and acceptor group compounds are very much useful for various number of applications in the field of biological, medical, material science and technology [24,25].

Dimethylformamide (DMF) is a polar (hydrophilic) aprotic solvent with a high boiling point. DMF is used as a solvent in peptide coupling for pharmaceuticals, pesticides production, manufacture of adhesives,

synthetic leathers, fibre films and surface coatings. Whereas 1,4-Butanediol (BD) is used in the manufacturing of plastics, fibres, and as solvent for many chemical reactions. Several researchers and scientists reported the dielectric relaxation of DMF in the different solvent medium such as toluene, benzene, benzoates, 3-Nitrotoulene in the recent past [26–37]. Stockhausen et al. [38] studied the dielectric relaxation of BD + DMF binary mixtures in the range of 5 MHz–72 GHz at 20 °C. The relaxation times of the binary mixtures are interpreted in terms of empirical equation by considering viscosity terms and the rotation of carbon chain group. Navarkhele et al. [39] also studied the dielectric relaxation behaviour of BD + DMF binary mixtures in the frequency range 10 MHz–20 GHz between the temperatures 20 °C–40 °C. The relaxation time of these mixtures is calculated from the Cole-Cole plot and the molecular interaction are discussed in terms of excess permittivity and Kirkwood g factor [40]. The physico-chemico properties of the binary mixtures of DMF with alkanols and their interactions are interpreted by considering the molar volume and refraction values [41]. Whereas in the present study we have considered volumetric and thermal expansion (α_p) parameters [42,43], electrical dipole moment, molar polarization [23], long-range and short-range interactions between the dipoles by excess Helmholtz energy (ΔF^E) equation [44], thermodynamic quantities [45] to interpret the molecular interaction between 1,4- Butanediol

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Table 1Experimental and literature values for density (ρ), dielectric constant (ϵ_0), refractive index (n_D), dipole moment (μ), and relaxation time (τ) of the pure liquids at 298 K.

Liquid sample	Density ρ (g/cm ³)		ϵ_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 (BD)	1.0134	1.01345 [83]	31.423	31.53 [83]	1.4430	1.4445 [1,83]	2.72	2.58 [†]	2150	2350 [21]
Dimethylformamide (DMF)	0.9446	0.9487 [22]	39.23	40.21 [86]	1.4300	1.4282 [84]	3.84	3.86 [32]	12.86	10.30 [23]

Standard uncertainties u are $u(\rho) = 0.0002$, $u(\epsilon_0) = 2\text{--}3\%$, $u(n_D) = 0.0001$, $u(\mu) = 0.04D$ and $u(\tau) = 5\text{--}7\%$, $u(T) = 0.01$ K^a CRC handbook of chemistry and physics (2003–2004), 84th edition, Pg No:6–157,6–162, CRC press.

(BD) and Dimethylformamide (DMF) binary mixtures at different concentrations effectively apart from the reported parameters at different temperatures. The relaxation time of the binary mixtures are determined from the Cole-Davidson, Cole-Cole relaxation plots [46–48] by using Havriliak-Negami relation [49]. Our primary interest is to study the effect of hydroxyl group (-OH) of 1,4-Butanediol (BD) on C=O group of dimethylformamide (DMF) on volumetric, dielectric relaxation and thermodynamic parameters to understand the nature of molecular interactions. The improved mixing rules of effective permittivity and refractive index are also applied at different temperatures as a function of volume fractions of solute and solvent in the mixture and compared with experimental values and the results are analysed.

2. Experimental

2.1. Materials

1,4-Butanediol (BD), Dimethylformamide (DMF) of AR grade were procured from Sigma Aldrich India and are used directly without any purification. The binary mixtures are prepared for eleven volume concentrations throughout the complete mixing range at 298 K. At the same time weight measurements, mole fractions of the solute (X_1) and solvent (X_2) were evaluated. The equimolar binary mixture of the sample is prepared by considering equal number of moles of 1,4-Butanediol (BD) and Dimethylformamide (DMF) i.e., (5 ml of BD and 4.5 ml of DMF) of liquids. The purity information about the liquid samples such as density (ρ), permittivity (ϵ_0), refractive index (n_D), dipole moment (μ) and relaxation time (τ) were presented in Table 1 and compared with the literature values.

2.2. Measurements

The dipole moments of 1,4-Butanediol (BD), Dimethylformamide (DMF) and their equimolar binary mixtures are determined by using Higasi's method [50] at the temperatures i.e., 298 K, 303 K, 308 K, 313 K, 318 K and 323 K. To determine the experiment dipole moments (μ) of pure compounds of 1–4 Butanediol (BD) and Dimethylformamide (DMF), dilute solutions of the pure compounds are prepared in a non-polar solvent benzene within the concentration range of 0–1 ml (solute) in a 10 ml solution (benzene). 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 similar procedure is followed for the 1,4-Butanediol (BD) and Dimethylformamide (DMF) equimolar binary mixtures. The experimental dipole moment of the pure and their equimolar binary system is determined by using Higasi's method [50] using the below equation

$$\mu^2 = \frac{27k_B T M_2}{4\pi N d_1} \frac{(a_0 - a_\infty)}{(\epsilon_1 + 2)^2} \quad (1)$$

Where

- a_0 and a_∞ are the slopes of ϵ_0 and ϵ_∞ with respect to the weight fraction of solute in a solvent medium
- d_1 = density of solvent medium
- ϵ_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 determined dipole moment of pure (BD, DMF) and their equimolar binary system (BD + DMF) at different temperatures are listed in Table 2 and compared with the literature values.

The complex permittivity ($\epsilon^* = \epsilon' - j\epsilon''$) of the liquid samples were measured in the frequency range from 20 MHz to 20 GHz using a Microwave Vector Network Analyzer (Agilent Technologies, E 8361C, PNA Network Analyzer) using dielectric probe kit (Agilent Technologies, 85070 E). The calibration procedure is followed while doing the measurement of the above liquid samples with Agilent standard kit [51–55]. The complete experimental measuring unit system is maintained in air-conditioned room at the temperature of 298 ± 0.5 K. The error involved in the real and imaginary part of the permittivity is determined using 85070-Measurement Software (Agilent) with an accuracy of $\epsilon_r' = \epsilon_r' \pm 0.05|\epsilon_r^*|$, $\epsilon_r'' = \epsilon_r'' \pm 0.05|\epsilon_r^*|$. The temperature of the samples is varied by using a thermostat-controlled water circulation bath set up with an accuracy of ± 0.01 K. The dielectric permittivity (ϵ_0) of pure and equimolar binary mixtures of 1,4-Butanediol (BD) and Dimethylformamide (DMF) at different temperatures are listed in Table 2 and compared with the available literature data. Similarly, high frequency permittivity ($\epsilon_\infty = n_D^2$) values of pure system as well as binary mixtures are calculated by measuring the refractive index (n_D) at different temperatures using Abbe's refractometer, with the uncertainty in measurement of 0.001 units.

2.3. Determination of the parameters

The experimental parameters such as density (ρ), excess molar volume (V_m^E), partial molar volume ($V_{m,i}$) apparent molar volume ($V_{\phi,i}$), coefficient of thermal expansion (α_p) were calculated [1,23] and summarized in Table 3, and molar polarization (P_m) [23], excess refractive index (n_D^E) [56] are presented in Figs. 3 and 4 respectively. The excess dielectric parameters such as excess permittivity (ϵ^E), excess inverse relaxation time ($(1/\tau)^E$), Kirkwood correlation factor (g^{eff}), activation enthalpy (ΔH^*) and activation entropy (ΔS^*), reaction field parameters from excess Helmholtz energy (ΔF^E) equation are determined for the binary mixtures and their necessary theory is described in our earlier published papers [57–59]. The excess parameters such as V_m^E , ϵ^E , η^E , $(1/\tau)^E$ were fitted with Redlich-Kister type polynomial equation [60] and their coefficients and standard deviation are listed in Table 4. The dielectric relaxation time of BD and DMF binary mixture for entire concentrations are determined by using Havriliak-Negami relation [49] using WINFIT software provided by Novo Control Technologies (See Table 2).

The permittivity values of DMF + BD binary mixtures were compared to those estimated by five mixing rules, which were proposed by, Looyenga [61]

$$\epsilon = \left[\epsilon_1^{\frac{1}{2}} + \varphi_2 \left(\epsilon_2^{\frac{1}{2}} - \epsilon_1^{\frac{1}{2}} \right) \right]^2 \quad (2)$$

Table 2
Experimental permittivity ϵ_0 at 20 MHz and the dipole moment (μ in Debye), relaxation time (τ) of 1,4 Butanediol, DMF and their binary mixtures at different temperatures.

T/K	1,4 Butanediol (A)				DMF (B)				Equimolar concentration of 1,4 Butanediol + DMF (A + B) mixture				$\Delta\mu = \mu_{AB} - \mu_A - \mu_B$				
	ϵ_0	Lit.	μ_A	τ ps	Lit.	ϵ_0	Lit.	μ_B	τ ps	Lit.	ϵ_0	Lit.		μ_{AB}	τ ps	Lit.	
298 K	31.42	31.53 [83]	2.72	2.58 ^a	2150	2350 [83]	39.23	40.21	3.84	3.86 [32]	12.86	10.30 [22]	36.05	4.78	153.70	-	-1.78
		31.633 [16]		2.73 [16]				39.48 [22]		3.62 [26, 31]							
		25.00 [39]						42.68 [85]		3.68 [27]							
303 K	30.31	30.20 [21]	2.70	2.42 [21]	1810	575-590 [39]	38.62	36.63 [34]	3.83	3.85 [32]	12.20	9.30 [28]	35.94	4.76	99.90	60-70 [39]	-1.77
								36.69 [28]		3.65 [31]		11.90 [34]					
308 K	29.21	29.240 [16]	2.68	2.69 [16]	1216	-	37.94	37.03 [22]	3.82	3.84 [32]	11.95	9.20 [22]	34.71	4.77	80.54	-	-1.73
										3.66 [26]							
313 K	28.16	28.72 [21]	2.65	2.40 [21]	812	450-475 [39]	37.52	32.00 [34]	3.80	3.78 [32]	11.02	8.50 [28]	33.90	4.75	67.55	40-50 [39]	-1.70
						876 [21]		35.35 [28]		3.77 [31]		9.70 [34]					
318 K	26.91	27.041 [16]	2.64	2.65 [16]	551	-	37.09	35.23 [22]	3.79	3.67 [26]	10.72	8.12 [22]	32.37	4.74	50.50	-	-1.69
323 K	25.52	27.23 [21]	2.62	2.37 [21]	364	458 [21]	36.84	33.36 [28]	3.78	-	10.03	7.60 [28]	32.25	4.74	39.45	-	-1.66

Standard uncertainties u are $u(\epsilon_0) = 2-3\%$, $u(\mu) = 0.04D$, $u(\tau) = 5-7\%$, $u(T) = 0.01 K$
^a crc handbook of chemistry and physics (2003-2004), 84th edition, Pg No.6-157,6-162, CRC press.

Table 3

Experimental density (ρ), excess molar volume (V_m^E), partial molar volume ($V_{m,i}$) apparent molar volume ($V_{\phi,i}$) and coefficient of thermal expansion (α_p) of mole fraction of DMF in BD mixtures at different temperature 298 K–323 K.

X_1	$\rho/\text{g cm}^{-3}$	$V_m^E/\text{cm}^3 \text{ mol}^{-1}$	$V_{m,1}/\text{cm}^3 \text{ mol}^{-1}$	$V_{m,2}/\text{cm}^3 \text{ mol}^{-1}$	$V_{\phi,1}/\text{cm}^3 \text{ mol}^{-1}$	$V_{\phi,2}/\text{cm}^3 \text{ mol}^{-1}$	$\alpha_p \times 10^4/\text{K}^{-1}$
298K							
0.0000	1.0134	0.0000	–	88.927	77.381	88.927	6.08
0.1131	1.0065	0.0003	77.380	88.927	77.380	88.927	6.46
0.2230	0.9996	0.0006	77.379	88.927	77.379	88.927	6.85
0.3298	0.9927	0.0007	77.379	88.928	77.378	88.927	7.24
0.4336	0.9858	0.0008	77.379	88.928	77.378	88.927	7.63
0.5345	0.9790	0.0009	77.378	88.929	77.377	88.928	8.03
0.6327	0.9721	0.0008	77.378	88.929	77.377	88.928	8.44
0.7282	0.9652	0.0007	77.378	88.929	77.377	88.929	8.85
0.8212	0.9583	0.0005	77.377	88.930	77.377	88.929	9.27
0.9117	0.9514	0.0003	77.377	88.930	77.377	88.930	9.70
1.0000	0.9446	0.0000	77.377	–	77.377	88.930	10.10
303K							
0.0000	1.0099	0.0000	–	89.237	77.759	89.237	6.10
0.1131	1.0028	–0.0004	77.761	89.236	77.761	89.237	6.49
0.2230	0.9958	–0.0008	77.761	89.235	77.762	89.236	6.87
0.3298	0.9888	–0.0011	77.762	89.235	77.763	89.236	7.27
0.4336	0.9818	–0.0012	77.762	89.234	77.764	89.235	7.66
0.5345	0.9748	–0.0013	77.763	89.234	77.764	89.235	8.07
0.6327	0.9678	–0.0012	77.763	89.233	77.765	89.234	8.48
0.7282	0.9608	–0.0011	77.764	89.232	77.765	89.234	8.89
0.8212	0.9538	–0.0008	77.764	89.232	77.765	89.233	9.31
0.9117	0.9468	–0.0004	77.765	89.231	77.765	89.232	9.74
1.0000	0.9398	0.0000	77.765	–	77.765	89.232	10.21
308K							
0.0000	1.0064	0.0000	–	89.545	78.149	89.545	6.12
0.1131	0.9992	–0.0014	78.154	89.543	78.154	89.545	6.51
0.2230	0.9921	–0.0026	78.155	89.542	78.158	89.544	6.90
0.3298	0.9850	–0.0033	78.157	89.540	78.160	89.543	7.29
0.4336	0.9778	–0.0038	78.158	89.538	78.162	89.542	7.69
0.5345	0.9707	–0.0039	78.159	89.537	78.164	89.540	8.10
0.6327	0.9635	–0.0037	78.161	89.535	78.165	89.538	8.51
0.7282	0.9564	–0.0033	78.162	89.533	78.166	89.536	8.93
0.8212	0.9493	–0.0025	78.164	89.531	78.166	89.534	9.36
0.9117	0.9421	–0.0013	78.165	89.529	78.167	89.533	9.79
1.0000	0.9350	0.0000	78.167	–	78.167	89.531	10.23
313K							
0.0000	1.0035	0.0000	–	89.799	78.534	89.799	6.14
0.1131	0.9962	–0.0028	78.543	89.795	78.543	89.799	6.53
0.2230	0.9889	–0.0050	78.546	89.792	78.550	89.797	6.92
0.3298	0.9815	–0.0066	78.549	89.789	78.556	89.795	7.32
0.4336	0.9742	–0.0075	78.551	89.785	78.560	89.792	7.72
0.5345	0.9669	–0.0077	78.554	89.782	78.563	89.789	8.13
0.6327	0.9595	–0.0074	78.557	89.778	78.565	89.785	8.55
0.7282	0.9522	–0.0064	78.560	89.775	78.566	89.781	8.97
0.8212	0.9449	–0.0048	78.563	89.771	78.567	89.778	9.40
0.9117	0.9376	–0.0027	78.566	89.768	78.568	89.774	9.84
1.0000	0.9302	1.4210	78.569	–	78.569	89.771	10.31
318K							
0.0000	1.0007	0.0000	–	90.053	78.922	90.053	6.16
0.1131	0.9932	–0.0043	78.936	90.048	78.936	90.053	6.55
0.2230	0.9856	–0.0077	78.940	90.043	78.946	90.051	6.94
0.3298	0.9781	–0.0100	78.944	90.038	78.955	90.048	7.34
0.4336	0.9706	–0.0114	78.948	90.033	78.961	90.044	7.75
0.5345	0.9631	–0.0118	78.952	90.028	78.965	90.038	8.17
0.6327	0.9555	–0.0113	78.957	90.023	78.968	90.033	8.59
0.7282	0.9480	–0.0098	78.961	90.017	78.971	90.027	9.01
0.8212	0.9405	–0.0074	78.965	90.012	78.972	90.021	9.45
0.9117	0.9330	–0.0041	78.970	90.006	78.973	90.016	9.89
1.0000	0.9254	0.0000	78.974	–	78.974	90.011	10.30
323K							
0.0000	0.9979	1.4210	–	90.309	79.312	90.309	6.18
0.1131	0.9901	–0.0059	79.331	90.302	79.331	90.309	6.57
0.2230	0.9824	–0.0105	79.337	90.295	79.346	90.306	6.97
0.3298	0.9747	–0.0138	79.343	90.288	79.357	90.301	7.37
0.4336	0.9670	–0.0156	79.348	90.281	79.366	90.295	7.78
0.5345	0.9593	–0.0162	79.354	90.274	79.372	90.288	8.20
0.6327	0.9515	–0.0155	79.360	90.267	79.376	90.281	8.62
0.7282	0.9438	–0.0134	79.366	90.259	79.379	90.273	9.05
0.8212	0.9361	–0.0102	79.372	90.252	79.381	90.265	9.49
0.9117	0.9284	–0.0057	79.378	90.244	79.383	90.258	9.94
1.0000	0.9207	0.0000	79.384	–	79.384	90.251	10.40

Table 4

Redlich–Kister coefficient and standard deviation values for DMF and 1,4-Butanediol binary mixtures at different temperatures.

Function	Temp(K)	A_0	A_1	A_2	A_3	A_4	σ
V_m^E	298	0.0037	-0.0004	0.0000	0.0000	0.0000	0.000105
	303	-0.0053	0.0006	-0.0001	0.0000	0.0000	0.000121
	308	-0.0159	0.0017	-0.0002	0.0000	0.0000	0.001002
	313	-0.0310	0.0033	-0.0004	0.0000	0.0000	0.037761
	318	-0.0473	0.0051	-0.0006	0.0001	0.0000	0.046644
n_D^E	323	-0.0648	0.0071	-0.0008	0.0001	0.0000	0.054595
	298	1.6728	-0.2851	-0.3071	0.0824	0.0958	0.002071
	303	1.6717	-0.2852	-0.3028	0.0906	0.0869	0.004287
	308	1.6711	-0.2838	-0.3061	0.0860	0.1024	0.002619
	313	1.6701	-0.2818	-0.3061	0.0808	0.0967	0.000962
ϵ^E	318	1.6625	-0.2778	-0.3188	0.0917	0.0997	0.005477
	323	1.6674	-0.2855	-0.2917	0.0935	0.0771	0.004356
	298	-0.7506	4.3123	12.1014	-5.5442	-22.5752	0.008689
	303	-0.3070	4.7853	13.3490	3.8175	-30.0446	0.016711
	308	0.9881	5.5403	18.1288	-2.3365	-40.2399	0.015060
$(1/\tau)^E$	313	3.0266	15.6997	0.9417	-16.1223	-24.4458	0.017270
	318	2.6303	18.6750	31.5027	-21.5888	-74.0695	0.111525
	323	-0.9500	6.1987	30.2663	-13.6718	-63.0449	0.022000
	298	-0.1354	0.1776	-0.3338	-0.2096	0.5803	0.016139
	303	-0.1433	0.1073	-0.1114	-0.0821	0.2064	0.001680
	308	-0.1424	0.0679	-0.0072	-0.0505	0.0717	0.000807
	313	-0.1430	0.0301	0.0916	0.0017	-0.0840	0.001492
	318	-0.1323	0.0113	0.1312	0.0442	-0.1586	0.000141
	323	-0.1126	-0.0015	0.0029	0.0757	0.0196	0.001542

Bottcher-Bordewijk [62]

$$\frac{3\epsilon_1}{2\epsilon + \epsilon_1}\varphi_1 + \frac{3\epsilon_2}{2\epsilon + \epsilon_2}\varphi_2 = 1 \quad (3)$$

Kraszewski [63]

$$\epsilon^{\frac{1}{3}} = \varphi_1 \epsilon_1^{\frac{1}{3}} + \varphi_2 \epsilon_2^{\frac{1}{3}} \quad (4)$$

Lichtenecker-Rother [64]

$$\epsilon = \epsilon_1^{\varphi_1} \epsilon_2^{\varphi_2} \quad (5)$$

and Iglesias-Peon [65]

$$\epsilon = \varphi_A \epsilon_A + \varphi_B \epsilon_B \left[1 - \frac{2}{3} \ln \left(\frac{1 + \varphi_A \left(\frac{\epsilon_A}{\epsilon_B} - 1 \right)}{\left(\frac{\epsilon_A}{\epsilon_B} \right)^{\varphi_A}} \right) \right] \quad (6)$$

Where in Equations (1)–(5), ϵ is static permittivity of the mixture and ϕ is volume fraction. Suffix 1 and 2 or A and B represents DMF and BD, and these values are tabulated in Table 7.

For the binary mixtures of DMF + BD various mixing rules for predicting the refractive index (n) given below were used

Gladstone-Dale (G-D) [66]

$$n_m - 1 = (n_1 - 1)\varphi_1 + (n_2 - 1)\varphi_2 \quad (7)$$

Newton (Nw) [67]

$$n_m^2 - 1 = (n_1^2 - 1)\varphi_1 + (n_2^2 - 1)\varphi_2 \quad (8)$$

Arago-Biot (A-B) [68]

$$n_m = n_1 \varphi_1 + n_2 \varphi_2, \quad (9)$$

Heller (H) [69]

$$\frac{(n_m - n_1)}{n_1} = \frac{3}{2} \left(\frac{\left(\frac{n_2}{n_1} \right)^2 - 1}{\left(\frac{n_2}{n_1} \right)^2 + 2} \right) \varphi_2 \quad (10)$$

and Lorentz-Lorentz (L-L) [70]

$$\frac{n^2 - 1}{n^2 + 2} = \varphi_A \left(\frac{n_A^2 - 1}{n_A^2 + 2} \right) + \varphi_B \left(\frac{n_B^2 - 1}{n_B^2 + 2} \right) \quad (11)$$

where n_m , n_A , n_B , ϕ_A , ϕ_B represent refractive index of the mixture and volume fraction of solute (DMF) and solvent (BD) respectively and listed in Table 8 respectively.

The root mean square deviation (RMSD) values for the above mixing rules are determined with ‘equation (12)’ and the values are tabulated in Table 9

$$RMSD = \left[\frac{1}{p} \sum (A_{exp} - A_{cal})^2 \right]^{\frac{1}{2}} \quad (12)$$

Where A_{exp} represents experimental permittivity and refractive index, A_{cal} represents calculated permittivity and refractive index and p represents the total number of concentrations.

3. Results and discussion

The dipole moment (μ) and permittivity (measured at 20 MHz) of 1,4-Butanediol (BD), Dimethylformamide (DMF) and their equimolar binary mixture at different temperature from 298 K–323 K are tabulated in Table 2. From Table 2, it is observed that the dipole moment and permittivity of pure liquids is in good agreement with the reported literature values. There is a small variation in the measured values of the dipole moment with literature values and it may be due to the π electron density cloud of benzene influencing the dipole moment of the liquid system [46]. As expected, there is an increase in the value of the dipole moment of the equimolar binary system when compared to the pure liquids and it is due to the presence of hydrogen bonding between DMF and BD molecules. The increase in the dipole moment of the binary system that depends upon the environment associated in the liquid system [33,34,58,59]. The net dipole moment of the pure liquids as well as binary system is decreased with increase in temperature. It is due to the increase in thermal energy disturbs the alignment of the dipoles in the field direction causes decrease in the dipole moment value. The excess dipole moment ($\Delta\mu$) values are negative (Table 2) for all temperatures and indicates the presence of dipolar association or induced polarization effect in the liquid solution [71,72]. The negative values of $\Delta\mu$ confirms that there is a proton transfer in the bond and absence of

Table 5Variation of ΔF_{Or}^E , ΔF_{rr}^E , ΔF_{12}^E and ΔF^E with volume fraction of DMF in 1,4-Butanediol.

Volume fraction of DMF per ml in 1,4-Butanediol	ΔF_{Or}^E (J. mol ⁻¹)	ΔF_{rr}^E (J. mol ⁻¹)	ΔF_{12}^E (J. mol ⁻¹)	ΔF^E (J. mol ⁻¹)
T = 298K				
0	0.0000	0.0000	0.0000	0.0000
0.1	-7.5734	0.0203	-0.0345	-7.5876
0.2	-10.1698	-0.0549	0.0703	-10.1544
0.3	-5.3731	-0.0503	0.0675	-5.3559
0.4	7.2690	-0.0290	-0.0169	7.2232
0.5	17.2439	-0.1519	0.0182	17.1102
0.6	22.7257	-0.1466	0.0615	22.6406
0.7	24.9490	-0.1218	0.0681	24.8953
0.8	34.9328	-0.7559	0.2342	34.4111
0.9	19.1807	-0.1548	0.0753	19.1012
1	0.0000	0.0000	0.0000	0.0000
T = 303K				
0	0.0000	0.0000	0.0000	0.0000
0.1	-12.8971	-0.0979	0.0955	-12.8995
0.2	-13.0529	-0.1419	0.1411	-13.0537
0.3	-8.0071	-0.1331	0.0949	-8.0453
0.4	5.9989	0.0091	0.0033	6.0113
0.5	17.7734	-0.1045	0.0231	17.6919
0.6	23.2434	-0.0627	0.0331	23.2137
0.7	29.8254	-0.2679	0.1322	29.6898
0.8	37.1469	-0.7940	0.2702	36.6230
0.9	34.8961	-0.8576	0.2131	34.2516
1	0.0000	0.0000	0.0000	0.0000
T = 308K				
0	0.0000	0.0000	0.0000	0.0000
0.1	-11.7081	-0.0163	0.0206	-11.7038
0.2	-14.6502	-0.1801	0.1725	-14.6578
0.3	-12.6507	-0.3722	0.0702	-12.9526
0.4	-2.0105	-0.0520	-0.1658	-2.2283
0.5	15.4938	0.0550	-0.0291	15.5197
0.6	22.8318	0.0728	-0.0500	22.8546
0.7	25.5198	0.0710	-0.0552	25.5356
0.8	34.8113	-0.5126	0.2326	34.5314
0.9	31.9899	-0.6342	0.2071	31.5628
1	0.0000	0.0000	0.0000	0.0000
T = 313K				
0	0.0000	0.0000	0.0000	0.0000
0.1	-11.6158	0.0245	-0.0354	-11.6266
0.2	-22.9342	-0.7111	0.3275	-23.3179
0.3	-21.4394	-1.1434	-0.2280	-22.8108
0.4	-1.5269	-0.0365	-0.1420	-1.7055
0.5	12.1310	0.1618	-0.1706	12.1221
0.6	27.5655	-0.1200	0.0660	27.5116
0.7	41.1233	-0.8856	0.3328	40.5705
0.8	41.0351	-0.8893	0.3552	40.5010
0.9	38.6144	-1.0359	0.2939	37.8723
1	0.0000	0.0000	0.0000	0.0000
T = 318K				
0	0.0000	0.0000	0.0000	0.0000
0.1	-13.1540	0.0248	-0.0362	-13.1654
0.2	-29.8549	-1.4266	0.4126	-30.8689
0.3	-29.9542	-2.4594	-0.9544	-33.3680
0.4	-0.7730	-0.0221	-0.2173	-1.0124
0.5	16.8689	0.2108	-0.1733	16.9064
0.6	30.4976	0.0591	-0.0380	30.5186
0.7	36.2672	-0.0359	0.0236	36.2549
0.8	46.6595	-0.8929	0.3753	46.1418
0.9	46.7130	-1.3585	0.3657	45.7202
1	0.0000	0.0000	0.0000	0.0000
T = 323K				
0	0.0000	0.0000	0.0000	0.0000
0.1	-4.8525	0.1359	-0.7411	-5.4577
0.2	-17.3901	-0.0362	0.0475	-17.3789
0.3	-13.7033	-0.3312	0.1544	-13.8802
0.4	3.5869	0.0551	-0.0794	3.5626
0.5	28.8515	-0.3399	0.1066	28.6182
0.6	39.6509	-0.4325	0.2265	39.4448
0.7	35.0045	0.1610	-0.1445	35.0210

Table 5 (continued)

Volume fraction of DMF per ml in 1,4-Butanediol	ΔF_{Or}^E (J. mol ⁻¹)	ΔF_{rr}^E (J. mol ⁻¹)	ΔF_{12}^E (J. mol ⁻¹)	ΔF^E (J. mol ⁻¹)
0.8	38.9969	-0.2371	0.1658	38.9256
0.9	36.4015	-0.6006	0.2799	36.0809
1	0.0000	0.0000	0.0000	0.0000

ionic contribution in the liquid mixture.

Table 3 lists the values of density (ρ) along with volumetric parameters such as excess molar volume (V_m^E), partial molar volume ($V_{m,i}$), apparent molar volume ($V_{\phi,i}$) and coefficient of thermal expansion (α_p) of the DMF and BD binary mixtures at different temperatures. It is observed that excess molar volume (V_m^E) values are negative [42,43,73,74] for all concentration ranges and temperatures except at 298 K and it is due to the nonspecific interactions exist between the components present in the mixture. The negative values of excess molar volume (V_m^E) indicate that there is an intermolecular interaction that exists in the liquid mixtures and which leads to decrease in the excess molar volume as shown in Fig. 1. The decrease in excess molar volume is due to structural contribution i.e., interstitial accommodation of one component into another component reduces the effective free and molar volume. There is a variation of partial molar volume for all concentrations and temperature which suggest that the presence of intermolecular forces prevail in the liquid mixture (See Table 3).

The positive values of thermal expansion (α_p) indicate that the presence of molecular interaction between the components from self-association nature to the dissimilar type of interactions in the binary system [75]. Since BD molecules exhibit more self-associative when compared to the DMF molecules due to hydrogen bonding. The rise in the thermal expansion (α_p) with an increase in DMF concentration corresponds to strong molecular interaction between DMF and BD molecules in terms of hydrogen bonding (See Table 3). Further, α_p value increases with increase in temperature and it might be due to the increased dipolar association in the binary liquid mixtures.

From Figs. 2 and 3, it is observed that the permittivity (ϵ_0) (measured at 20 MHz), molar polarization (P_m) increased with increase in the concentration of DMF in BD liquid medium and decreases with increase in temperature. The increase in the permittivity (ϵ_0), molar polarization (P_m) [75,76] is due to the increase in the dipolar association in the liquid mixture that enhances the polarizability and in turn increases the dielectric susceptibility. The non-linear response of this graph indicates heteromolecular interaction exists in the liquid mixtures. The decrease in the permittivity, molar polarization values with an increase in temperature due to the breakage of hydrogen bond networks in the solution cause a decrease in the net polarization of the system. The excess refractive index (n_D^E) values are positive for entire concentration range at all temperatures and it is due to increase in charge transfer complexes and intermolecular forces between the species present in the mixture which is as shown in Fig. 4. The excess permittivity (ϵ^E) [40,77,78] values are positive up to $0 < x_1 < 0.5$ M fractions of DMF in BD medium and negative for remaining concentrations at all temperatures as shown in Fig. 5. The positive values of ϵ^E indicate that the effective number of dipoles in the liquid solution might be greater than the dipole of the individual liquids leading to new multimolecular structures that enhance the macroscopic permittivity. The negative values of ϵ^E for higher concentrations of DMF region represents a lesser polar structure which lowers the macroscopic permittivity values in the liquid solution.

The complex permittivity ($\epsilon^* = \epsilon' - j\epsilon''$) of 1,4-Butanediol (BD), Dimethylformamide (DMF) and its equimolar binary mixtures, and their relaxation plots (Inserted Figs) are shown in Figs. 6–8 respectively. From graph 6, it is observed that the dielectric loss peak is maximum at lower frequency and it is due to self-associative nature of BD molecules. The self-associative nature of the BD molecules is originated due to the presence of intermolecular hydrogen bonding between the BD

Table 6

Variation of thermodynamically parameters ΔG^* , ΔH^* and ΔS^* with respective molar concentration of DMF in 1,4-Butanediol at different temperatures.

Variation of molar concentration of DMF in 1,4-Butanediol solution	T/ K	$\Delta H^*/$ (kcal/ mole)	$\Delta G^*/$ (kcal/ mole)	$\Delta S^*/(Cal/$ mole/K)	
1,4-Butanediol	298	116.22	23.539	311.02	
	303		23.542	305.88	
	308		22.954	302.82	
	313		22.317	300.02	
	318		21.968	296.40	
	323		21.457	293.39	
	0.1	298	179.28	23.445	522.94
		303		23.259	514.92
		308		22.655	508.53
		313		22.186	501.90
318			20.100	500.57	
323			19.023	496.15	
0.2		298	183.23	23.036	537.58
		303		23.112	528.46
		308		22.419	522.13
		313		21.648	516.25
	318		19.684	514.31	
	323		18.596	509.72	
	0.3	298	176.14	22.402	515.92
		303		22.607	506.73
		308		21.951	500.63
		313		21.419	494.33
318			19.089	493.89	
323			18.255	488.82	
0.4		298	143.02	20.653	410.66
		303		20.480	404.45
		308		20.693	397.19
		313		19.751	393.86
	318		18.370	392.01	
	323		17.209	389.53	
	0.5	298	103.03	17.824	285.96
		303		17.382	282.70
		308		17.044	279.21
		313		16.814	275.48
318			16.196	273.09	
323			15.404	271.32	
0.6		298	95.628	16.976	263.93
		303		16.486	261.20
		308		15.893	258.88
		313		15.824	254.97
	318		15.291	252.63	
	323		14.819	250.18	
	0.7	298	100.95	16.172	284.50
		303		14.448	285.49
		308		13.939	282.51
		313		13.644	278.94
318			13.512	274.97	
323			13.542	270.62	
0.8		298	85.093	14.720	236.15
		303		14.015	234.58
		308		13.202	233.41
		313		13.041	230.20
	318		12.922	226.95	
	323		12.808	223.79	
	0.9	298	7.893	11.456	-19.23
		303		11.678	-19.65
		308		11.781	-19.66
		313		11.946	-19.87
318			12.125	-20.13	
323			12.209	-20.07	
DMF		298	4.970	10.854	-21.59
		303		10.949	-21.55
		308		11.129	-21.79
		313		11.286	-21.94
	318		11.451	-22.12	
	323		11.568	-22.14	

Table 7

Comparison of experimental relative permittivities from those estimated by the mixing rules proposed by Looyenga (Lg), Bottcher-Bordewijk (B), Kraszewski (Kz), Lichtenecker-Rother (L-R), Peon Iglesias (Ig) for binary mixture of DMF and BD at temperatures from 298 K–323 K.

Φ_1	Exp.	Lg	B	Kz	L-R	Ig
Temp = 298 K						
0.0000	31.420	31.420	31.420	31.420	31.420	31.420
0.0999	32.220	32.149	32.147	32.162	32.125	32.150
0.1998	33.370	32.890	32.887	32.912	32.846	32.891
0.2998	34.350	33.641	33.639	33.671	33.583	33.642
0.3998	34.720	34.405	34.403	34.439	34.337	34.405
0.4998	35.350	35.179	35.179	35.216	35.107	35.179
0.5998	36.190	35.966	35.967	36.001	35.895	35.965
0.6998	36.980	36.764	36.767	36.795	36.701	36.763
0.7998	37.070	37.574	37.577	37.598	37.525	37.573
0.8999	38.270	38.396	38.398	38.410	38.368	38.395
1.0000	39.230	39.230	39.230	39.230	39.230	39.230
Temp = 303K						
0.0000	30.310	30.310	30.310	30.310	30.310	30.310
0.1000	31.490	31.081	31.079	31.096	31.053	31.009
0.2001	32.540	31.866	31.863	31.892	31.816	31.736
0.3001	33.630	32.664	32.661	32.698	32.596	32.491
0.4002	34.020	33.475	33.473	33.515	33.396	33.275
0.5002	34.610	34.299	34.299	34.341	34.215	34.088
0.6002	35.530	35.136	35.138	35.177	35.054	34.931
0.7001	36.090	35.987	35.990	36.023	35.914	35.805
0.8001	36.400	36.851	36.854	36.878	36.794	36.711
0.9000	36.990	37.728	37.731	37.744	37.696	37.649
1.0000	38.620	38.620	38.620	38.620	38.620	38.620
Temp = 308K						
0.0000	29.210	29.210	29.210	29.210	29.210	29.210
0.1002	30.260	30.017	30.014	30.033	29.985	29.935
0.2004	31.560	30.838	30.834	30.868	30.781	30.691
0.3005	33.050	31.674	31.671	31.713	31.598	31.479
0.4006	33.890	32.525	32.523	32.570	32.436	32.298
0.5006	34.050	33.390	33.390	33.438	33.295	33.151
0.6006	34.880	34.270	34.272	34.316	34.177	34.038
0.7005	35.710	35.165	35.169	35.206	35.082	34.959
0.8004	35.900	36.075	36.079	36.106	36.010	35.916
0.9002	36.490	36.999	37.003	37.017	36.963	36.909
1.0000	37.940	37.940	37.940	37.940	37.940	37.940
Temp = 313K						
0.0000	28.160	28.160	28.160	28.160	28.160	28.160
0.0999	29.170	29.016	29.012	29.035	28.979	28.920
0.1998	31.190	29.889	29.884	29.923	29.822	29.717
0.2998	32.910	30.780	30.775	30.826	30.690	30.550
0.3998	33.020	31.688	31.686	31.741	31.583	31.422
0.4998	33.650	32.615	32.615	32.670	32.503	32.333
0.5998	33.980	33.559	33.562	33.613	33.449	33.284
0.6998	34.290	34.521	34.526	34.569	34.423	34.278
0.7998	35.130	35.502	35.508	35.539	35.426	35.314
0.8999	35.770	36.501	36.506	36.523	36.457	36.394
1.0000	37.520	37.520	37.520	37.520	37.520	37.520
Temp = 318K						
0.0000	26.910	26.910	26.910	26.910	26.910	26.910
0.1006	28.000	27.837	27.832	27.860	27.793	27.721
0.2011	30.530	28.785	28.777	28.826	28.704	28.575
0.3015	32.650	29.752	29.746	29.807	29.643	29.472
0.4017	32.180	30.739	30.735	30.803	30.612	30.414
0.5018	32.720	31.746	31.747	31.814	31.610	31.403
0.6017	33.370	32.774	32.778	32.840	32.640	32.439
0.7015	34.220	33.822	33.829	33.880	33.702	33.525
0.8011	34.540	34.890	34.898	34.935	34.797	34.661
0.9006	35.110	35.979	35.985	36.005	35.926	35.849
1.0000	37.090	37.090	37.090	37.090	37.090	37.090
Temp = 323K						
0.0000	25.520	25.520	25.520	25.520	25.520	25.520
0.1008	26.100	26.536	26.528	26.565	26.480	26.390
0.2015	28.150	27.576	27.566	27.629	27.475	27.312
0.3020	29.970	28.642	28.633	28.712	28.505	28.288
0.4022	30.940	29.732	29.727	29.814	29.571	29.320
0.5023	31.250	30.848	30.848	30.934	30.676	30.412
0.6022	32.370	31.989	31.995	32.072	31.819	31.563

(continued on next page)

Table 7 (continued)

Φ_1	Exp.	Lg	B	Kz	L-R	Ig
0.7020	33.960	33.155	33.165	33.229	33.003	32.777
0.8015	34.620	34.347	34.359	34.405	34.228	34.056
0.9008	35.260	35.565	35.574	35.598	35.497	35.399
1.0000	36.810	36.810	36.810	36.810	36.810	36.810

Standard uncertainties u are $u(\text{exp}) = 2\text{--}3\%$, $u(\text{lg}, \text{B}, \text{Kz}, \text{L-R}, \text{Ig}) = 0.002$.

molecules. Whereas for DMF the dielectric loss is located at a higher frequency due to non-associated nature which is shown in Fig. 7. The increase in molar concentration of DMF in BD medium, the dielectric loss is increasing and shifting towards higher frequencies and it is due to heteromolecular interaction between the components present in the liquid mixture (as shown in graphical abstract). The dielectric loss of the equimolar binary system lies between BD and DMF systems and it is due to the presence of hydrogen bond ($-\text{OH}-\text{O}=\text{C}$) between hydroxyl group of alcohol and $\text{C}=\text{O}$ group of dimethyl formamide. The real and imaginary part of the permittivity decreases with increase in the concentration and as well as temperature. The rise in temperature dissociates the number of bonds formed between the components present in the liquid mixture and hence decreases the effective dipole moment, degree of polarization results in decrease in dielectric loss values which are as shown in inserted Figs. 6–8 respectively. In addition, the increase in temperature causes increases in the molar volume (See Table 3) and decreases the liquid viscosity is also responsible for the decrease in the polarization and degree of electrical susceptibility.

The dielectric relaxation time of BD and DMF binary mixtures for entire mole fractions at different temperatures are calculated using Havriliak-Negami relation [49]. The Havriliak-Negami relation is used to fit the Cole-Davidson and Cole-Cole [47,48] relaxation plots by using WINFIT software provided by Novocontrol Technologies. The shape factor (β) of BD varying from 0.5320 to 0.6100 in a Cole-Davidson plot and $\beta = 1$ for DMF for Cole-Cole plot in the temperature range 298 K–323 K. The change in the shape factor (β) of BD with respective temperature is due to changes in the size of the clusters in the solution [21]. The relaxation time value decreases with an increase in the molar concentration of DMF in BD medium which is as shown in Fig. 9. The relaxation time of BD is higher when compared to the DMF and is due to the presence of intermolecular hydrogen bonding. The intermolecular hydrogen bonding between the BD molecules causes an increase in size, the shape of the structure and friction between the molecules. The increase in DMF concentration decreases the number of hydrogen bonds in the liquid mixture and also reduces the friction between the molecules. The decrease in relaxation values increases with temperature and it might be due to breakage of a number of hydrogen bonds and reduces the sample viscosity.

The variation of excessive inverse relaxation $(1/\tau)^E$ with the mole fraction of DMF in BD medium at different temperatures is shown in Fig. 10. From Fig. 10 it is noticed that $(1/\tau)^E$ values are negative [79,80] at all temperatures and it suggests that the presence of clusters in the solution leads to decrease in rotational movement of the dipoles with respective electric field. The resistance field increased with increase in the concentration of DMF in BD medium which obstructs the free rotation moment of the dipole in the solution.

The correlation among the dipoles (g^{eff}) in a BD and DMF binary mixtures at different temperatures is shown in Fig. 11. From Fig. 11 it is observed that effective Kirkwood correlation factor (g^{eff}) for BD is higher for all the temperatures [21] which indicates that there is mutual cooperation among the self-associated dipoles is higher and it enables higher polarization in the pure liquid state. The g^{eff} value of DMF is lesser in magnitude when compared to the BD and it is due to lack of mutual exchange interaction among the non-self-associated dipoles and results in an antiparallel alignment of the dipoles. The non-linear variation of effective Kirkwood correlation factor (g^{eff}) with an increase in

Table 8

Comparison of experimental Refractive Indices from those estimated by the mixing rules proposed by Gladstone-Dale (G-D), Newton (N-W), Arago-Biot (A-B), Heller, Lorentz-Lorentz (L-L) for binary mixture of DMF and BD at temperatures from 298 K–323 K.

ϕ	$n_{D,\text{mixture}}$	G-D	N-W	A-B	Heller	L-L
Temp = 298K						
0.0000	1.4430	1.4430	1.4430	1.4430	1.4364	1.4430
0.0999	1.4412	1.4428	1.4417	1.4416	1.4358	1.4416
0.1998	1.4403	1.4424	1.4404	1.4403	1.4351	1.4403
0.2998	1.4390	1.4417	1.4391	1.4390	1.4345	1.4390
0.3998	1.4376	1.4408	1.4378	1.4377	1.4338	1.4377
0.4998	1.4365	1.4397	1.4365	1.4364	1.4332	1.4364
0.5998	1.4352	1.4383	1.4352	1.4351	1.4325	1.4351
0.6998	1.4339	1.4366	1.4339	1.4338	1.4319	1.4338
0.7998	1.4325	1.4345	1.4326	1.4325	1.4312	1.4325
0.8999	1.4315	1.4326	1.4313	1.4312	1.4306	1.4312
1.0000	1.4300	1.4300	1.4300	1.4300	1.4300	1.4300
Temp = 303K						
0.0000	1.4420	1.4420	1.4420	1.4420	1.4357	1.4420
0.1000	1.441848	1.4418	1.4407	1.4407	1.4351	1.4407
0.2001	1.441497	1.4414	1.4395	1.4394	1.4344	1.4394
0.3001	1.440857	1.4408	1.4382	1.4382	1.4338	1.4382
0.4002	1.439996	1.4399	1.4370	1.4369	1.4332	1.4369
0.5002	1.438846	1.4388	1.4357	1.4357	1.4326	1.4357
0.6002	1.437497	1.4374	1.4345	1.4344	1.4319	1.4344
0.7001	1.435837	1.4358	1.4332	1.4332	1.4313	1.4332
0.8001	1.433998	1.4339	1.4320	1.4319	1.4307	1.4319
0.9000	1.431649	1.4316	1.4307	1.4307	1.4301	1.4307
1.0000	1.4295	1.4295	1.4295	1.4295	1.4295	1.4295
Temp = 308K						
0.0000	1.4410	1.4410	1.4410	1.4410	1.4350	1.4410
0.1002	1.4409	1.4409	1.4398	1.4398	1.4344	1.4398
0.2004	1.4405	1.4405	1.4386	1.4386	1.4338	1.4386
0.3005	1.4399	1.4399	1.4374	1.4374	1.4332	1.4374
0.4006	1.4392	1.4392	1.4362	1.4362	1.4326	1.4362
0.5006	1.4380	1.4380	1.4350	1.4350	1.4320	1.4350
0.6006	1.4365	1.4365	1.4338	1.4338	1.4314	1.4338
0.7005	1.4351	1.4351	1.4326	1.4326	1.4308	1.4326
0.8004	1.4334	1.4334	1.4314	1.4314	1.4302	1.4314
0.9002	1.4315	1.4315	1.4302	1.4302	1.4296	1.4302
1.0000	1.4290	1.4290	1.4290	1.4290	1.4290	1.4290
Temp = 313K						
0.0000	1.4400	1.4400	1.4400	1.4400	1.4340	1.4400
0.0999	1.4398	1.4398	1.4388	1.4388	1.4334	1.4388
0.1998	1.4395	1.4395	1.4376	1.4376	1.4328	1.4376
0.2998	1.4389	1.4389	1.4364	1.4364	1.4322	1.4364
0.3998	1.4381	1.4381	1.4352	1.4352	1.4316	1.4352
0.4998	1.4370	1.4370	1.4340	1.4340	1.4310	1.4340
0.5998	1.4355	1.4355	1.4328	1.4328	1.4304	1.4328
0.6998	1.4340	1.4340	1.4316	1.4316	1.4298	1.4316
0.7998	1.4323	1.4323	1.4304	1.4304	1.4292	1.4304
0.8999	1.4305	1.4305	1.4292	1.4292	1.4286	1.4292
1.0000	1.4280	1.4280	1.4280	1.4280	1.4280	1.4280
Temp = 318K						
0.0000	1.4390	1.4390	1.4390	1.4390	1.4332	1.4390
0.1006	1.4388	1.4388	1.4379	1.4378	1.4327	1.4378
0.2011	1.4384	1.4384	1.4367	1.4367	1.4321	1.4367
0.3015	1.4376	1.4376	1.4356	1.4355	1.4315	1.4355
0.4017	1.4366	1.4366	1.4344	1.4344	1.4309	1.4344
0.5018	1.4352	1.4352	1.4333	1.4332	1.4304	1.4332
0.6017	1.4336	1.4336	1.4321	1.4321	1.4298	1.4321
0.7015	1.4316	1.4316	1.4310	1.4309	1.4292	1.4309
0.8011	1.4298	1.4298	1.4298	1.4298	1.4286	1.4298
0.9006	1.4282	1.4282	1.4287	1.4286	1.4281	1.4286
1.0000	1.4275	1.4275	1.4275	1.4275	1.4275	1.4275
Temp = 323K						
0.0000	1.4370	1.4370	1.4370	1.4370	1.4320	1.4370
0.1008	1.4369	1.4369	1.4360	1.4360	1.4315	1.4360
0.2015	1.4367	1.4367	1.4350	1.4350	1.4310	1.4350
0.3020	1.4361	1.4361	1.4340	1.4340	1.4305	1.4340
0.4022	1.4356	1.4356	1.4330	1.4330	1.4300	1.4330
0.5023	1.4345	1.4345	1.4320	1.4320	1.4295	1.4320
0.6022	1.4334	1.4334	1.4310	1.4310	1.4290	1.4310

(continued on next page)

Table 8 (continued)

ϕ	$n_{D,mixture}$	G-D	N-W	A-B	Heller	L-L
0.7020	1.4324	1.4324	1.4300	1.4300	1.4285	1.4300
0.8015	1.4306	1.4306	1.4290	1.4290	1.4280	1.4290
0.9008	1.4289	1.4289	1.4280	1.4280	1.4275	1.4280
1.0000	1.4270	1.4270	1.4270	1.4270	1.4270	1.4270

Standard uncertainties u are $u(n_{D,mixture}, G-D, N-W, A-B, Heller, L-L) = 0.0001$.

Table 9

Values of RMSD against various mixing rules.

Mixing rules	RMSD					
	298 K	303 K	308 K	313 K	318 K	323 K
Static permittivity						
Lg	0.3348	0.5098	0.7214	0.9534	0.2106	0.6647
B	0.3360	0.5115	0.7227	0.9558	1.2045	0.6660
Kz	0.3218	0.4950	0.6955	0.9295	1.1703	0.6192
L-R	0.3643	0.5425	0.7742	1.0031	1.2662	0.7611
Ig	0.3343	0.6006	0.8588	1.0868	1.3735	0.9205
Refractive Index						
G-D	0.7322	0.6940	0.6588	0.6674	0.8355	0.5235
Nw	0.5831	0.3575	0.5119	0.4743	0.4926	0.8170
A-B	0.5620	0.3373	0.5167	0.4596	0.4879	0.8442
H	0.0037	0.0036	0.0035	0.0035	0.8692	0.0031
L-L	0.5583	0.3347	0.5177	0.4581	0.4875	0.8428

DMF concentration at all temperatures confirms the presence of hydrogen-bonded structures with a decrease in the parallel alignment of the dipoles. Further, the increase in temperature reduces the coordination among the electrical dipoles and destabilizes the active structure and hence the correlation among the dipoles decreases which is inferred from Fig. 11.

The determined values of excess Helmholtz energy (ΔF^E) [44] corresponds to long-range and short-range interactions at different temperatures and are listed in Table 5. For studied temperature range, $\Delta F^{E_{or}}$ values are negative in the region $0 < x_1 < 0.3$ and positive for remaining concentrations. The negative values of $\Delta F^{E_{or}}$ represents the strength of hydrogen bond interaction among the BD molecules is higher, and its value changes to positive with increase in DMF concentration. The positive value of $\Delta F^{E_{or}}$ suggests the presence of long-range coulombic attractive forces between the DMF and BD molecules. From Table 5, it is

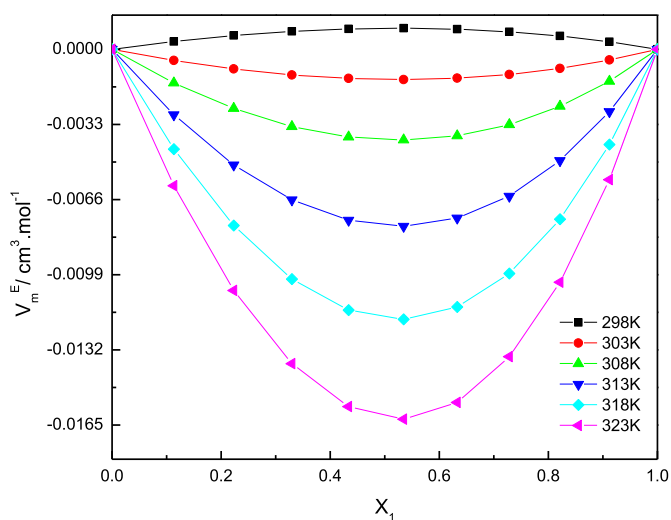


Fig. 1. Excessive molar volume (V_m^E) versus mole fraction (X_1) of DMF in 1,4-Butanediol at different temperatures.

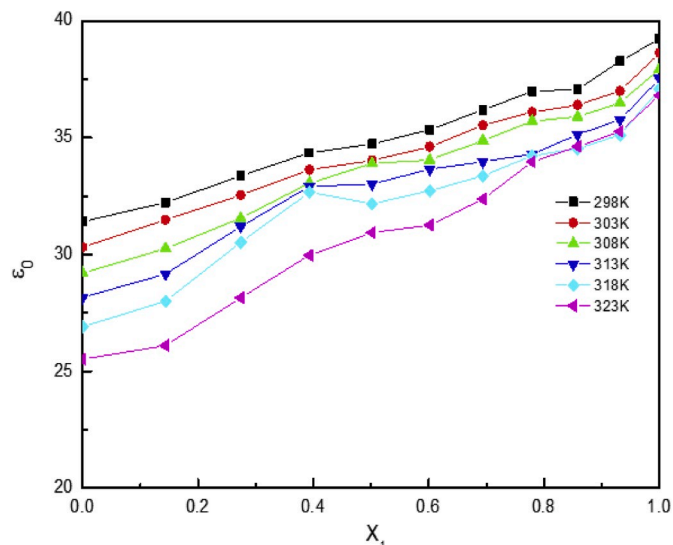


Fig. 2. Plot of low frequency permittivity (ϵ_0) versus mole fraction (X_1) of DMF in 1,4-Butanediol at different temperatures.

observed that $\Delta F^{E_{rr}}$ values are negative which suggests the existence of heteromolecular interactions in the liquid mixture. The term $\Delta F^{E_{12}}$ represents the force of interaction between dissimilar molecules. The negative values $\Delta F^{E_{12}}$ indicate the parallel alignment of the dipoles (BD rich region) and positive values represents the anti-parallel ordering of the dipoles in the (DMF rich region) liquid system. In the total investigated temperature range, the excess Helmholtz energy (ΔF^E) values are positive for all concentrations. It indicates the presence of α clusters to β clusters in the solutions with the parallel and anti-parallel alignment of the dipoles which reduces the total internal energy of the system [80, 81].

The thermodynamic parameters i.e., enthalpy of activation ΔH^* , the entropy of activation ΔS^* and Gibbs free energy of activation ΔG^* of the binary mixtures are calculated from Eyring's rate equation [45] and are listed in Table 6. From Table 6, it is observed that enthalpy of activation ΔH^* is positive which indicates that heat energy is observed during the formation of hydrogen-bonded between BD and DMF molecules [36].

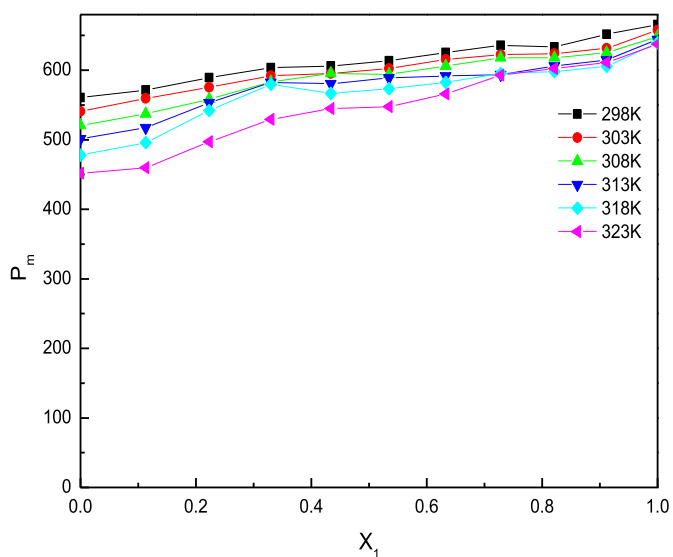


Fig. 3. Molar polarization (P_m) versus mole fraction (X_1) of DMF in 1,4-Butanediol at different temperatures.

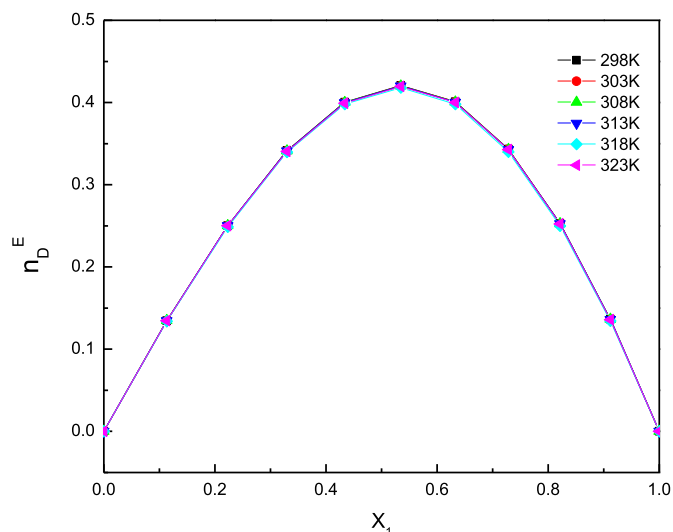


Fig. 4. Excessive refractive index (n_D^E) versus mole fraction (X_1) of DMF in 1,4-Butanediol at different temperatures.

The Gibbs free energy of activation ΔG^* values are positive and its magnitude decreases with increase in the concentration of DMF and temperature. The decrease in ΔG^* values with increase in DMF concentrations may be due to the type of interaction in the liquid system that changes from hydrogen bond to dipole-dipole interactions. Entropy is a measure of orderly nature and describes the environment of the surrounding system. From Table 6, it is noticed that change in entropy of the system is positive [82] and it suggests that the environment of the system is obstructive to the orientational process of the dipoles. The interaction energy between the dipoles is lesser and due to this, the activated system become a dissociated system.

Based on the molar average values of the pure systems the static permittivity and refractive index are measured by using different mixing rules and these values are compared with the experimentally determined values at different temperatures which are tabulated in Tables 7 and 8 respectively. The standard deviation from the experimental values with the proposed mixing rules are also calculated and listed in Table 9. In the present study, we have tested five mixing rules for static permittivity proposed by Looyenga (Lg), Bottcher-Bordewijk (B), Kraszewski (Kz), Lichtenecker-Rother (LR), Iglesias-Peon (Ig) and five refractive index mixing rules proposed by Gladstone-Dale (GD),

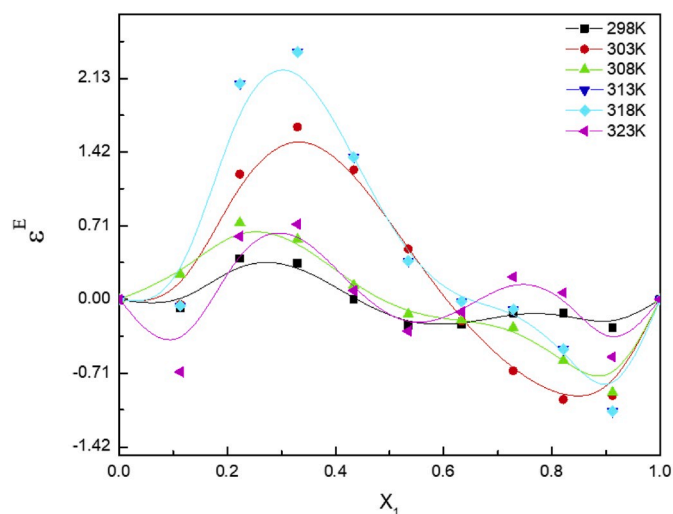


Fig. 5. Experimental values of excessive permittivity (ϵ^E) versus mole fraction (X_1) of DMF in 1,4- Butanediol at different temperatures.

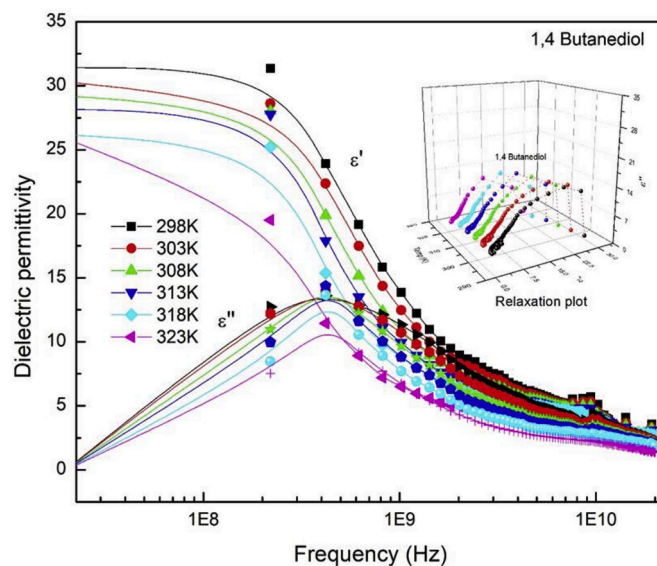


Fig. 6. Frequency-dependent of real (ϵ') and imaginary part of permittivity (ϵ'') of 1,4-Butanediol with respective frequency at different temperatures (Inserted Fig- relaxation plot).

Newton (Nw), Arago-Biot (AB), Heller (H), Lorentz-Lorentz (LL). From the standard deviation Table 9, it is noticed that almost all the mixing rules are substantially equivalent except Iglesias-Peon (Ig) and Gladstone-Dale (GD) for permittivity and refractive index rules. The deviation of this mixing rule is more than the other mixing rules. Kraszewski (Kz) and Heller (H) model are best suited for static permittivity and refractive index values at all temperatures.

4. Conclusions

The complex permittivity of Dimethylformamide/1,4- Butanediol binary mixtures for entire concentrations have been studied in the temperature range of 298 K–323 K at microwave frequency region. The dielectric relaxation time value decreases with increase in mole fraction of DMF in BD medium due to the interaction between the molecule's

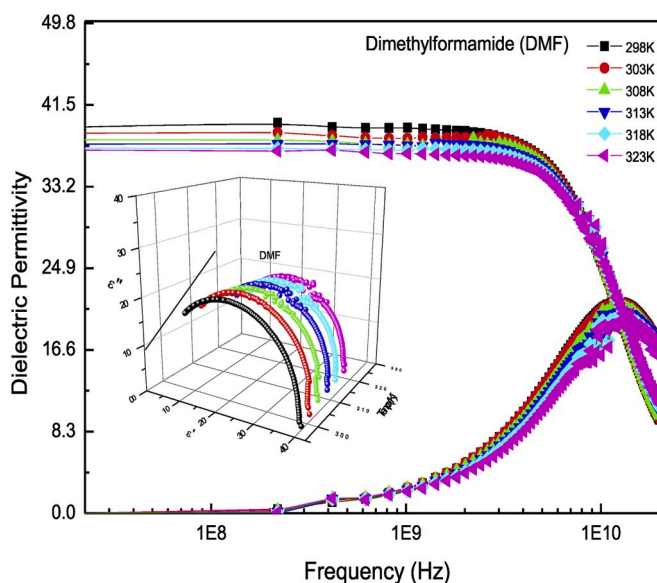


Fig. 7. Frequency-dependent of real (ϵ') and imaginary part of permittivity (ϵ'') of DMF with respective frequency at different temperatures (Inserted Fig- relaxation plot).

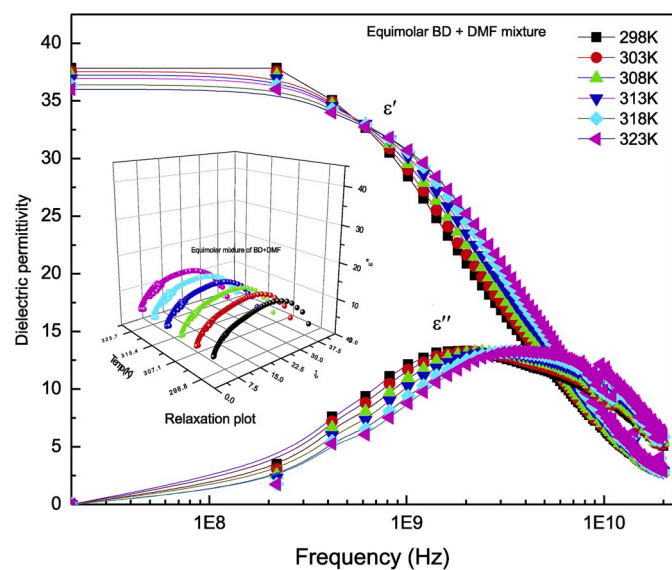


Fig. 8. Frequency-dependent of real (ϵ') and imaginary part of permittivity (ϵ'') of equimolar binary mixtures of DMF + 1,4- Butanediol with respective frequency at different temperatures (Inserted Fig- relaxation plot).

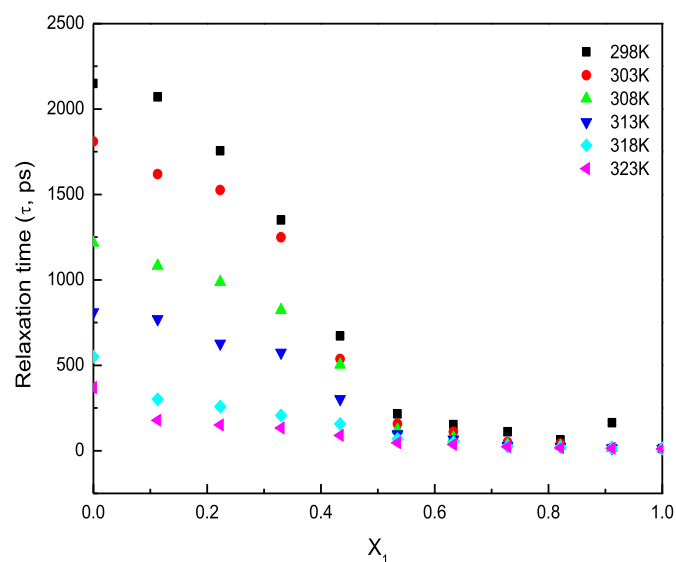


Fig. 9. Plot of average relaxation time (τ /ps) versus mole fraction (X_1) of DMF in 1,4- Butanediol at different temperatures.

changes from self-associative to nonself associative nature. The excess dipole moment values are negative for all temperatures which shows the presence of induced polarization effect in the liquid system. The non-linear behaviour of the parameters such as dielectric permittivity (ϵ_0), effective Kirkwood correlation factor (g^{eff}) with an increase in mole fraction of DMF in BD medium indicates the presence of heteromolecular interaction taking place in the liquid mixtures. The excess Helmholtz energy (ΔF^E) values are positive for most of the concentrations and suggest the existence of clusters in the solution. The mixing rules of permittivity and refractive index shows that Kraszewski (Kz) and Heller (H) have lower fluctuations and these values are closer in agreement with the experimental values.

Declaration of competing interest

The authors declare that they have no known competing financial

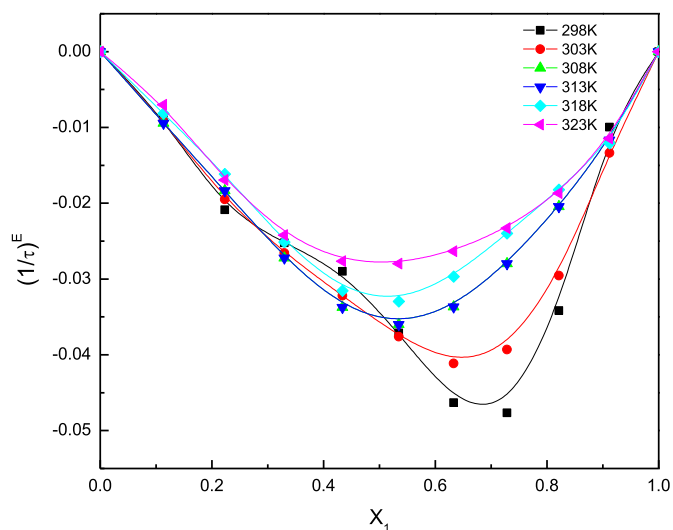


Fig. 10. Plot of excessive relaxation time ($(1/\tau)^E$) versus mole fraction (X_1) of DMF in 1,4- Butanediol at different temperatures.

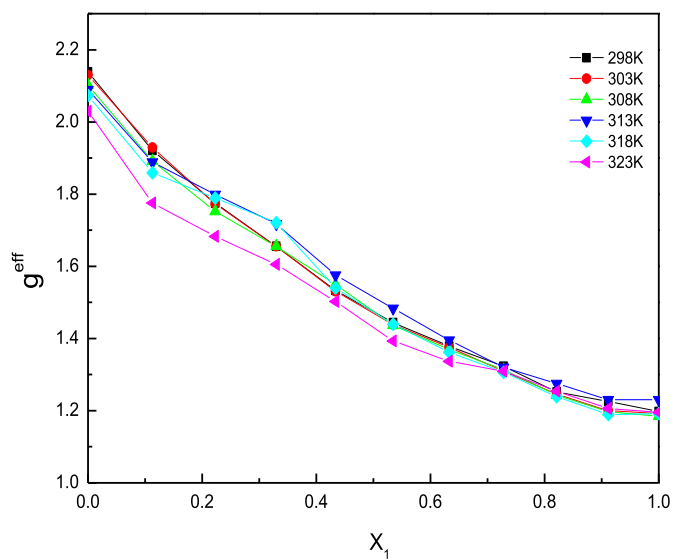


Fig. 11. Kirkwood effective (g^{eff}) correlation factor versus mole fraction (X_1) of DMF in 1,4- Butanediol at different temperatures.

interests or personal relationships that could have appeared to influence the work reported in this paper.

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