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Insights into molecular interactions: Dielectric relaxation and DFT based studies on n-hexanol/N, N-dimethylformamide binary mixtures

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ABSTRACT

The complex permittivity spectra of n-Hexanol, N, N-Dimethylformamide (DMF), and their binary mixtures over the entire range (0.0 → 1.0) obtained using Vector Network Analyzer (VNA) in the frequency span 200 MHz to 20 GHz at different temperatures. The obtained spectra were analyzed using the Havriliak-Negami model to determine the static dielectric constant (ϵ_0) and relaxation time (τ_0). Additionally, the optical dielectric constant ($\epsilon_\infty = n^2$) and viscosity (η) of the binary mixtures were determined. The excess static dielectric constant (ϵ_0^E), excess high frequency limiting dielectric constant (ϵ_∞^E), excess inverse relaxation time ($1/\tau_0^E$) and excess viscosity (η^E) were calculated and fitted using the Redlich-Kister polynomial. Various dielectric parameters were determined to analyze interactions and structural information within the binary mixtures, including the Kirkwood factors (g^{eff} , g^F), Bruggeman parameter (f_B), thermodynamic parameters (ΔFe , ΔHe and ΔSe) and microwave heating parameters (P_r , P_h and d_p). Density functional theory (DFT) calculations employing the B3LYP approach with a 6-311G (d, p) basis set were conducted to explore the quantum chemical characteristics of pristine and (DMF + n-Hexanol) mixtures. These calculations aimed to elucidate chemical stability, reactivity, and electrochemical parameters, including the HOMO-LUMO energy gap. Overall, the study provides comprehensive insights into the dielectric properties, microwave heating behavior, and quantum chemical characteristics of these binary mixtures, offering valuable understanding of their interaction mechanisms.

1. Introduction

Dielectric spectroscopy has great potential in studying the H-bond interactions, dipolar alignments, hydrogen bond connectivity, and stoichiometric ratio of stable adduct formation in liquid mixtures [1–25]. Precise measurement of complex permittivity (ϵ^*) of a material under investigation as a function of frequency at a constant or different temperatures, is now recognized as one of the important tool for exploring the molecular structure of molecular systems for a deeper understanding of inter/intra molecular interaction [1–30]. In the study of the molecular association of polar liquid mixtures, the formation/breaking of H-bonds are centre of interest for many researchers in dielectric analysis [7–9,11–14,20–38]. Such study provides an important information on intermolecular interactions and the resulting structural rearrangement of molecular species in mixture solutions. Alcohols are among the most common polar solvents because of their high solubility and their ability to form self-molecular associations through dipole-dipole inter-

actions and hydrogen bonding via –OH group. The alcohols play an important role in chemistry and biology, their associative properties with multiple internal structures depend on the length of the carbon chain and the position of the –OH group have been subjects of several studies [7–15,17–25,27–41]. Alcohols are widely used in medical, agriculture and chemical industry for various applications. Among them n-Hexanol is often used as antibacterial agents (medical), insecticides (agriculture) and flavoring additives (chemical industry). On the other hand amides possess strong solvating power and high polarity making them one of the highly sought after solvents in chemical industries. N, N-dimethylformamide (DMF) is a common amide. It is made up of two hydrophobic –CH₃ groups and one high polar group C = O. It can easily form C–H...O and C = O...H type hydrogen bonds with other molecules (alcohols). The wide range of hydrogen interactions in binary mixtures of DMF with other molecules creates different complexions of varied complex dielectric properties because complexions are related to mole fractions, frequencies and other factors [8,10,15,23,24,30–32].

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Understanding of Microwave heating parameters are important in selection of solvents for microwave assisted organic reactions. When materials absorb microwave radiation at commercial microwave frequency 2.45 GHz the power reflected (P_r), Power transmitted (P_t) and penetration depth (d_p) are mainly depend on dielectric constant (ϵ') and dielectric loss (ϵ'') values at corresponding frequencies [42,43]. Computational approaches have been widely employed by several researchers to get knowledge regarding the molecular interactions occurring inside binary mixtures of liquids [44]. Density functional theory (DFT) is a promising theoretical approach to molecular investigation because it produces conclusions that are in excellent accordance with experiments [45,46]. DFT is used to investigate molecule geometry and electron density, which are required to acquire data defining molecular characteristics in a short amount of time.

The main objective of the current research is of three-fold. First is to understand dipolar relaxation process and molecular interaction between constituent molecules. Second is to report microwave heating parameters at commercial microwave frequencies. Third is to report, using DFT study optimize structure of binary mixtures.

2. Experimental and theoretical details

n-Hexanol (AR Grade) and N, N-Dimethylformamide (DMF) (AR grade) were sourced from Loba Chemie Pvt Ltd, India, and utilized without further purification. Their purity, grade, CAS No., and experimental static dielectric constant (ϵ_0), refractive index (n) and viscosity (η) values were meticulously documented and compared with literature values [23,37,47–49] (Table 1). Binary mixtures were meticulously prepared in hermetically sealed glass vials with varying volume percentages of DMF in n-Hexanol, with conversions to mole fractions facilitated by established formulas [7,8]. Complex permittivity measurements were conducted using a Vector Network Analyzer (VNA) (Model-MS46322A, Anritsu Shockline with SPEAG DAK 3.5 probe) across frequencies ranging from 200 MHz to 20 GHz, at three distinct temperatures. Calibration procedures addressed probe sensitivity to temperature and cable movement, ensuring precise magnitude and phase normalization between the probe and cable [50]. Complex permittivity data (real ϵ' and imaginary ϵ'' parts) had uncertainties within 4.0 %. Optical dielectric constants (ϵ_∞) were determined from refractive index (n) measurements using Abbe's refractometer within uncertainty to 0.06 %. The viscosities of the pure liquids (DMF & n-Hexanol) and their binary mixtures were determined across varying compositions and temperatures using Stabinger viscometers (Model-SVM 2001, Anton Paar). The maximum measurement error for viscosity measurement were ± 0.35 %. Temperature control for the binary mixture samples was carefully maintained using a precise constant temperature water bath from Model Industrial Corporation, India, with an accuracy of ± 0.1 K. Geometry optimization procedure performed by using Density Functional Method (DFT/B3LYP) calculations by using ORCA 4.2.1 software. The basis set used for the entire calculation is 6-311G(d,p). The HOMO-LUMO energy calculations are performed on optimized structures of individual and their binary mixture of molecules which are tabulated in (supplementary information Table S3). The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies calculated for the individual DMF, n-Hexanol

and its 1:1 M ratio of binary mixtures to know the capability of electron donor and electron acceptor based on the energy gap values [40].

3. Results and discussion

3.1. Complex dielectric permittivity spectra

Fig. 1(a)–(c) illustrate the frequency-dependent spectra of the dielectric constant (ϵ') across the frequency range of 200 MHz to 20 GHz for the complete mole fraction (0.0 $\rightarrow$ 1.0) of n-Hexanol at different temperatures (293.15 K, 303.15 K, 313.15 K). The figures clearly demonstrate a monotonic decrease in the dielectric constant (ϵ') values with increasing temperatures as the concentration of n-Hexanol increases in the binary mixtures. Similarly, Fig. 2(a)–(c) showcase the frequency-dependent spectra of the dielectric loss (ϵ'') across the entire concentration range (0.0 $\rightarrow$ 1.0) within the frequency span of 200 MHz to 20 GHz at various temperatures. The figures reveal that the dielectric loss (ϵ'') values decrease with both increasing temperatures and frequency. Moreover, the peak values of dielectric loss (ϵ'') decrease and shift towards the lower frequency side as the concentration of n-Hexanol increases in the binary mixtures. The experimental complex dielectric data were fitted to different asymmetry and broadness dependent dielectric relaxation models by the CNLS method [51]. The general form of dielectric relaxation model, including asymmetric and broadening of dielectric relaxation, is given by Havriliak–Negami (HN) [52]

$$\epsilon(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau_0)^\alpha]^\beta} \quad (1)$$

In this study, the complex permittivity at angular frequency ω , is analyzed. The algebraic difference between a static dielectric constant (ϵ_0) and an optical dielectric constant (ϵ_∞) is defined as dielectric strength ($\Delta\epsilon = \epsilon_0 - \epsilon_\infty$), while τ_0 represents the relaxation time of the mixture concentration. Two shape parameters, α and β , play a crucial role in selecting dielectric relaxation models. Specifically, the Cole-Davidson (CD) model, characterized by $\alpha = 1$, and the Cole-Cole (CC) model, characterized by $\beta = 1$, represent symmetrical and asymmetric relaxation curves, respectively. The real and imaginary parts of the complex permittivity spectra of binary mixtures at different concentrations are fitted into the dielectric models (Cole-Davidson (CD)/Cole-Cole (CC)) using a CNLS fitting program. Evaluated parameters such as high-frequency limiting dielectric constant (ϵ_∞), dielectric relaxation strength ($\Delta\epsilon$), relaxation time (τ), the values of α and β and viscosity (η) are tabulated in Table 2 at various temperatures. Fig. 3 displays typical model-fitted data plots for representative mole fractions ($X_1 = 0, 0.3805, 0.8468$, and 1.0) at a temperature of 293.15 K. While none of the models achieved a perfect fit to the experimental data across the entire frequency range, upon critical evaluation, it was observed that the Cole-Cole (CC) model (for $0 \leq X_1 \leq 0.8468$) and the Cole-Davidson (CD) model ($X_1 = 1$) exhibited superior agreement with the real (ϵ') and imaginary parts (ϵ'') of the experimental complex permittivity data compared to other models. Furthermore, it is observed the viscosity (η) of binary mixtures increases nonlinearly with increasing mole fraction of n-Hexanol with increasing temperature. Such nonlinear variation of viscosity from ideal mixture composition of polar compounds have

Table 1

Chemicals used and their Purity, Grade, CAS No, and comparison of static dielectric constant (ϵ_0), refractive index (n) and viscosity (η) of pure liquid with literature values at 293.15 K temperatures.

Compound	Purity	Grade	Cas No	ϵ_0		n		η (mPa s)	
				Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
DMF	99.8	AR	68-12-2	37.00	37.69 [23]	1.4305	1.4305 [37]	0.920	0.925 [49]
n-Hexanol	99.0	AR	111-27-3	14.64	13.05 [47]	1.4170	1.4178 [48]	4.590	4.731 [48]

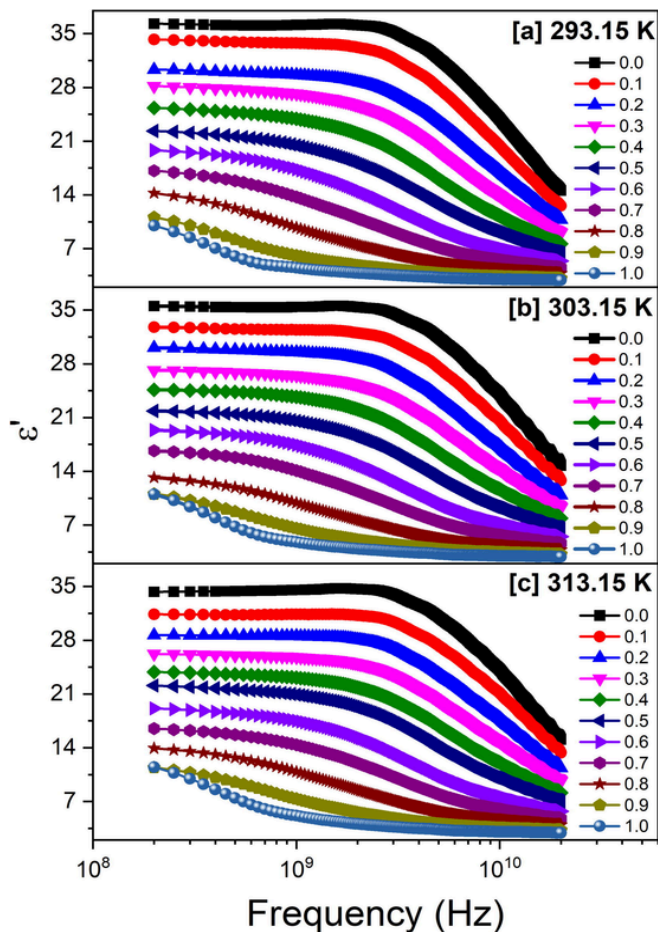


Fig. 1. Frequency dependent dielectric constant (ϵ') spectra of (n-Hexanol + DMF) binary mixtures in frequency span 200 MHz to 20 GHz frequency at different temperatures.

been observed by H. Iloukhani et al. [48] and D. Keshapolla [49]. The observed nonlinear behavior of viscosity indicates the presence of specific interaction among mixture constituents [53]. The specific interactions amid unlike molecules leading to the hydrogen bond formation and charge transfer complexes may cause rise in viscosity in mixtures than in pure molecules [54].

3.2. Static dielectric constant and relaxation time

The change of the static dielectric constant is significantly influenced by temperature, the molecular structure of the material and hydrogen bonding in the liquid [7,8,14,15,23,28–30,32]. It is apparent from Table 2 that the concentration of n-Hexanol increases in the mixture the dielectric relaxation strength ($\Delta\epsilon$) decreases. This trend remains unaltered at 293.15, 303.15 and 313.15 K temperatures. Furthermore, it has been observed that as the mole fraction of n-Hexanol increases in the mixture, the static dielectric constant values decrease systematically in a non-linear manner (Supplementary information (SI) Fig. S1). The most plausible explanation for decrease in static dielectric constant (ϵ_0) values with the increase in temperature is due to (i) rapid fall in orientation polarization because the increased thermal motion reduces the alignment of the permanent dipoles [28–30,32,43]. Table 2 shows the variation of relaxation time (τ) against mole fraction of n-Hexanol in the binary mixture at different temperatures. The relaxation time values increase with increases in mole fraction of n-Hexanol and decreases with increases in temperature (Supplementary information

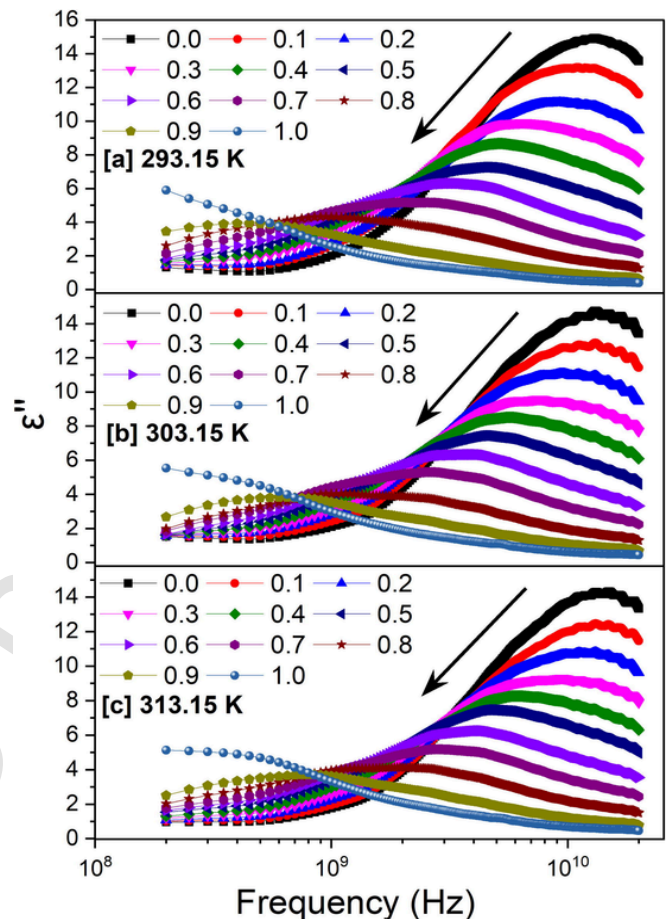


Fig. 2. Frequency dependent dielectric loss (ϵ'') spectra of (n-Hexanol + DMF) binary mixtures in frequency span 200 MHz to 20 GHz frequency at different temperatures.

(SI Fig. S2). It has been observed that in the mole fraction range ($0 \leq X_1 \leq 0.5890$) the values of relaxation time increase moderately as the concentration of n-Hexanol increases in the mixture, this suggests that in the DMF rich region, the self-associated H-bonds of n-Hexanol disrupt and forms new weak H-bonds with DMF molecules due to highly polar nature of DMF. While $X_1 \geq 0.5890$ the relaxation time increases rapidly due to large number n-Hexanol molecules present in the mixture moiety which unaltered the self associated H-bonds of n-Hexanol. Similar inferences were drawn by Sengwa et al., Patil et al., Khumbarkhane et al. and Ramchandran et al. in their study [10,18,31, 33]. The excess parameters related with (ϵ_0) and (τ_0) provide important insights into the mixing behavior of binary liquid mixtures interaction. The excess static dielectric constant (ϵ_0)^E, excess inverse relaxation time ($1/\tau$)^E, excess high frequency limiting dielectric constant (ϵ_∞)^E, excess viscosity (η)^E and excess Gibbs free energy (G^*)^E are computed using the following relations [55,56].

$$(\epsilon_0)^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_1 X_1 + (\epsilon_0 - \epsilon_\infty)_2 X_2] \quad (2)$$

$$\left(\frac{1}{\tau_0}\right)^E = \left(\frac{1}{\tau_0}\right)_m - \left[\left(\frac{1}{\tau_0}\right)_1 X_1 + \left(\frac{1}{\tau_0}\right)_2 X_2\right] \quad (3)$$

$$(\epsilon_\infty)^E = (\epsilon_\infty)_m - [(\epsilon_\infty)_1 X_1 + (\epsilon_\infty)_2 X_2] \quad (4)$$

$$(\eta)^E = (\eta)_m - [(\eta)_1 X_1 + (\eta)_2 X_2] \quad (5)$$

$$(G^*)^E = RT[\ln(\eta_m V_m) - [X_1 \ln(\eta_1 V_1) + X_2 \ln(\eta_2 V_2)]] \quad (6)$$

Table 2

Values of optical dielectric constant ($\epsilon_{\infty 0}$), CNLS fitting parameters high frequency limiting dielectric constant ($\epsilon_{\infty 1}$), dielectric relaxation strength ($\Delta\epsilon$), relaxation time (τ_0), shape parameter (α, β), effective Kirkwood correlation factor (g^{eff}), corrective Kirkwood correlation factor (g^{f}), Bruggeman factor (f_B) and viscosity (η (mPa s)) of binary mixtures of n-Hexanol + DMF at different temperatures (293.15, 303.15, 313.15 K)*.

X_1	$\epsilon_{\infty 0}$	$\epsilon_{\infty 1}$	$\Delta\epsilon$	$\tau(\text{ps})$	α	Model	g^{eff}	g^{f}	f_B	η
Temperature = 293.15 K										
0.0000	2.046	5.11 (2.53)	31.88(0.53)	12.93(0.45)	0.95(0.37)	C-C	1.117	1.000	1.000	0.920
0.0639	2.041	4.40 (2.41)	30.46(0.49)	14.88(0.43)	0.91(0.37)	C-C	1.117	0.982	0.922	0.933
0.1331	2.037	4.06 (1.98)	26.76(0.45)	16.43(0.40)	0.88(0.35)	C-C	1.054	0.906	0.769	0.932
0.2084	2.033	3.89(1.88)	24.99(0.52)	21.12(0.50)	0.85(0.42)	C-C	1.069	0.894	0.692	0.942
0.2905	2.031	3.68(1.54)	23.47(0.53)	26.64(0.59)	0.82(0.44)	C-C	1.046	0.845	0.564	0.962
0.3805	2.026	3.32 (1.22)	20.01(0.52)	35.04(0.69)	0.78(0.42)	C-C	1.057	0.817	0.453	1.040
0.4795	2.023	3.50(0.89)	17.45(0.65)	51.43(1.02)	0.78(0.47)	C-C	1.091	0.794	0.341	1.322
0.5890	2.019	3.33(0.68)	15.27(0.80)	81.97(1.46)	0.76(0.51)	C-C	1.161	0.775	0.223	1.734
0.7107	2.014	3.05(0.42)	13.32(0.92)	157.42(1.87)	0.73(0.47)	C-C	1.317	0.768	0.102	2.360
0.8468	2.011	2.77(0.25)	12.50(1.30)	438.56(2.79)	0.71(0.46)	C-C	1.830	0.839	0.038	3.201
1.0000	2.008	2.73(0.40)	11.91(2.10)	985.18(4.16)	0.69(0.78) β	C-D	3.971	1.000	0.000	4.590
Temperature = 303.15 K										
0.0000	2.041	5.79(8.00)	30.01(1.30)	12.47(2.09)	0.98(0.82)	C-C	1.125	1.000	1.000	0.919
0.0639	2.038	4.64(7.90)	28.41(1.14)	13.60(1.90)	0.93(0.81)	C-C	1.101	0.960	0.897	0.931
0.1331	2.032	4.01(6.45)	26.47(0.92)	15.83(1.56)	0.89(0.75)	C-C	1.086	0.927	0.797	0.932
0.2084	2.028	3.70(4.75)	24.07(0.74)	18.80(1.23)	0.85(0.68)	C-C	1.069	0.888	0.686	0.940
0.2905	2.025	3.67(2.86)	21.79(0.56)	23.99(0.87)	0.83(0.56)	C-C	1.075	0.863	0.586	0.946
0.3805	2.022	3.56(1.63)	19.30(0.42)	32.16(0.64)	0.81(0.44)	C-C	1.078	0.828	0.469	1.000
0.4795	2.019	3.49(0.90)	16.97(0.35)	45.41(0.56)	0.79(0.35)	C-C	1.108	0.802	0.353	1.068
0.5890	2.015	3.32(0.63)	14.79(0.40)	69.12(0.72)	0.77(0.35)	C-C	1.176	0.782	0.232	1.440
0.7107	2.012	2.99(0.48)	11.89(0.57)	118.93(1.17)	0.75(0.41)	C-C	1.235	0.718	0.048	2.072
0.8468	2.010	2.79(0.33)	11.46(1.37)	304.02(2.81)	0.73(0.55)	C-C	1.765	0.808	0.009	2.899
1.0000	2.007	2.71(0.40)	11.39(1.45)	708.87(2.96)	0.72(0.73) β	C-D	3.966	1.000	0.000	4.321
Temperature = 313.15 K										
0.0000	2.029	6.78(0.57)	27.97(1.14)	12.25(1.78)	1.00(0.68)	C-C	1.139	1.000	1.000	0.916
0.0639	2.027	5.43(6.14)	26.29(1.08)	12.66(1.78)	0.96(0.69)	C-C	1.100	0.949	0.885	0.923
0.1331	2.022	4.55(5.37)	24.59(0.88)	14.30(1.51)	0.92(0.65)	C-C	1.081	0.913	0.783	0.942
0.2084	2.017	4.02(4.38)	22.68(0.74)	16.85(1.27)	0.88(0.63)	C-C	1.071	0.882	0.682	0.961
0.2905	2.014	3.78(2.99)	20.65(0.58)	21.01(0.94)	0.85(0.56)	C-C	1.074	0.856	0.584	0.979
0.3805	2.011	3.71(2.22)	19.00(0.54)	27.55(0.83)	0.82(0.56)	C-C	1.118	0.854	0.506	1.005
0.4795	2.007	3.45(1.40)	16.48(0.48)	38.64(0.73)	0.79(0.49)	C-C	1.127	0.812	0.373	1.065
0.5890	2.005	3.28(0.92)	14.23(0.49)	56.68(0.83)	0.77(0.47)	C-C	1.185	0.787	0.248	1.189
0.7107	2.001	3.05(0.57)	12.26(0.57)	100.76(1.14)	0.75(0.44)	C-C	1.333	0.778	0.125	1.677
0.8468	1.998	2.81(0.37)	10.84(0.85)	252.29(1.84)	0.74(0.43)	C-C	1.766	0.815	0.025	2.399
1.0000	1.995	2.74(0.36)	10.53(0.91)	621.33(1.99)	0.72(0.59) β	C-D	3.915	1.000	0.000	4.121

* Number in brackets denote relative standard deviation in percentage as obtained by CNLS fitting, e.g., 31.88 (0.53) means $31.88 \pm 0.53 \%$.

where 'X' is mole fraction and suffixes 'm', '1', '2' represent mixture, liquid 1 (n-Hexanol) liquid 2 (DMF) respectively. ϵ_{∞} is high frequency limiting dielectric constant, η is viscosity, V is molar volume, R is gas constant and T is temperature of kelvin. Excess static dielectric constant (ϵ_0^E), excess inverse relaxation time ($1/\tau_0^E$) excess high frequency limiting dielectric constant (ϵ_{∞}^E), excess viscosity (η^E) and excess Gibb's free energy (G^E) data fitted in R. K. Polynomial, their coefficients, correlation coefficient (R) and standard deviation (σ) are tabulated in (supplementary information (Table S1)).

$$(A)^E = X_1 X_2 \sum_{i=0}^n a_i \cdot (X_2 - X_1)^i \quad (7)$$

$$\sigma = \left[\frac{\sum (X_{\text{exp}} - X_{\text{cal}})^2}{(p - m)} \right]^{\frac{1}{2}} \quad (8)$$

where 'a_i' (Where i = 0,1,2,3) stands for fitting parameters, X_1 and X_2 have usual meanings, n is the degree of polynomial expansion, p is the total number of data points and m is the number of coefficients considered [57]. Fig. 4 shows the excess dielectric constant (ϵ_0^E) against mole fraction of n-Hexanol in DMF binary mixtures at different temperatures. The observed that the (ϵ_0^E) values show negative deviation over the entire mixture range, which suggests that one of the mixture constituents molecules act as 'structure-breaker' and hence there is decrease in the

total number of aligned effective dipoles that contributed to the mixture dielectric polarization [7–14,29–31,33,35]. The pronounced maxima for (ϵ_0^E) values were observed at $X_1 = 0.7107$ mol fraction of n-Hexanol for all temperatures (except 303.15 K) with different magnitudes. Further it has been observed that the pronounced maxima values (ϵ_0^E) systematically decreases as the temperatures increases. The spectral line broadening analogy for inverse relaxation time is obtained from resonant spectroscopy, which is the inverse of relaxation time [7, 15,31,38]. Fig. 5 shows the variation of ($1/\tau_0^E$) against mole fraction of n-Hexanol for all three temperatures. The observed excess inverse relaxation time ($1/\tau_0^E$) values are found negative over the entire concentration range, which denotes the formation of a linear structure that rotate slowly under the influence of an external applied field [7,15,31, 38].

Fig. 6 illustrates the excess high-frequency limiting dielectric constant (ϵ_{∞}^E) as a function of the mole fraction of n-Hexanol at different temperatures. The negative values of (ϵ_{∞}^E) across the entire concentration range for DMF and n-Hexanol mixtures indicate weak molecular interactions. The hydrogen-bond formation between the –OH group of n-Hexanol (proton donor) and –CONH₂ group of DMF (proton acceptor) alters electronic distribution within the molecules in such a way that polarization is hindered [58,59].

Fig. 7 illustrates the variation of excess viscosity (η^E) for binary mixtures of DMF and n-Hexanol across a temperature range of 293.15–313.15 K. The observed trend shows that (η^E) becomes pro-

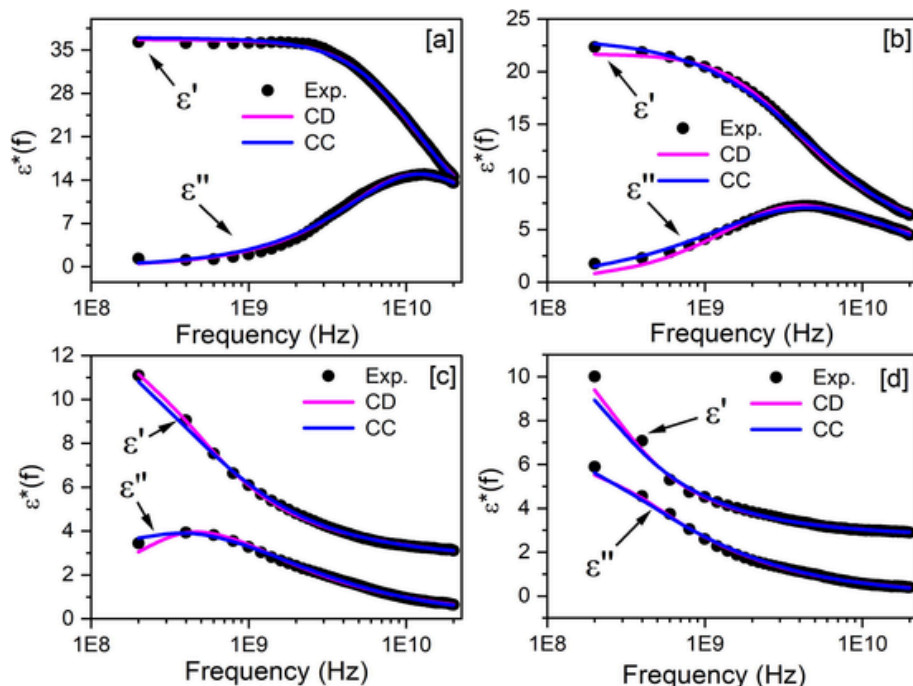


Fig. 3. Plots of complex permittivity vs frequency for different concentration of (a) $X_1 = 0.0$, (b) $X_1 = 0.3805$, (c) $X_1 = 0.8468$, and (d) $X_1 = 1.0$ for the binary liquid system at 293.15 K temperature. The solid line (—) shows the CNLS fitted dielectric relaxation models for CD-Cole Davidson, and CC-Cole Cole.

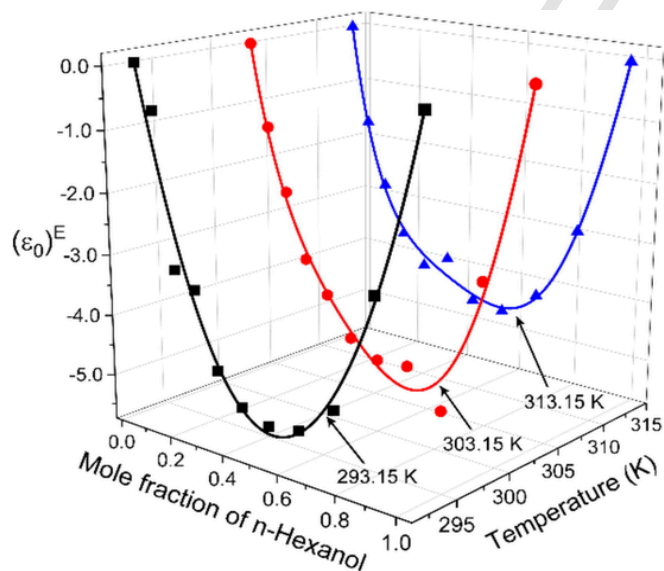


Fig. 4. Plot of excess dielectric constant $(\epsilon_0)^E$ against mole fraction of n-Hexanol in binary mixtures at different temperature.

gressively less negative as the temperature increases. This behavior is consistent with the expectation that elevated thermal energy disrupts inter and intramolecular associations between dissimilar molecules, leading to reduced interaction strength [58]. In systems where dipolar interactions and dispersion forces are predominant, negative values of $(\eta)^E$ are indicative of charge transfer interactions. The deviation in viscosity reflects the extent of molecular interaction and structural hindrance to flow. For the DMF + n-Hexanol system, the overall negative excess viscosity suggests that the mixture exhibits lower resistance to flow compared to the individual pure components, primarily due to

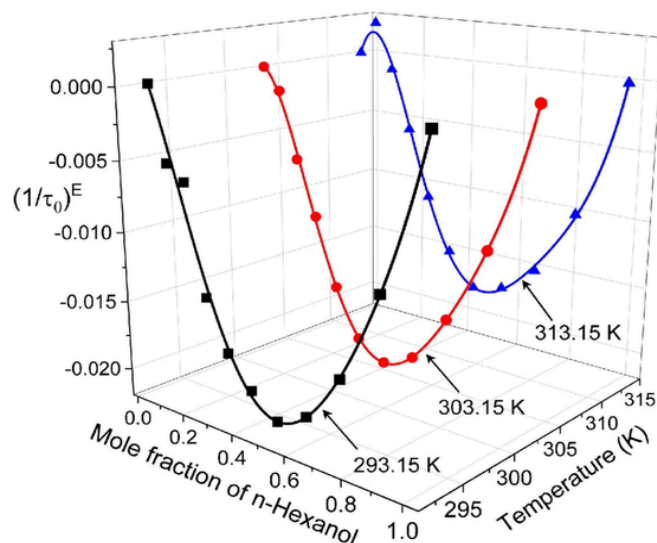


Fig. 5. Plot of excess inverse relaxation time $(1/\tau_0)^E$ against mole fraction of n-Hexanol in binary mixtures at different temperature.

the dominance of dispersive interactions over hydrogen bonding [60, 61, 62]. Fig. 8 depicts the variation of excess Gibbs free energy of activation for viscous flow $(G^*)^E$ as a function of the mole fraction of n-Hexanol at different temperatures. This parameter provides insight into molecular orientation hindrance, which reflects the extent of short-range intermolecular interactions within the liquid mixture. Across the entire composition range (0.0–1.0), the observed negative values of $(G^*)^E$ suggest weak interactions between the dissimilar molecules in the solvent mixture.

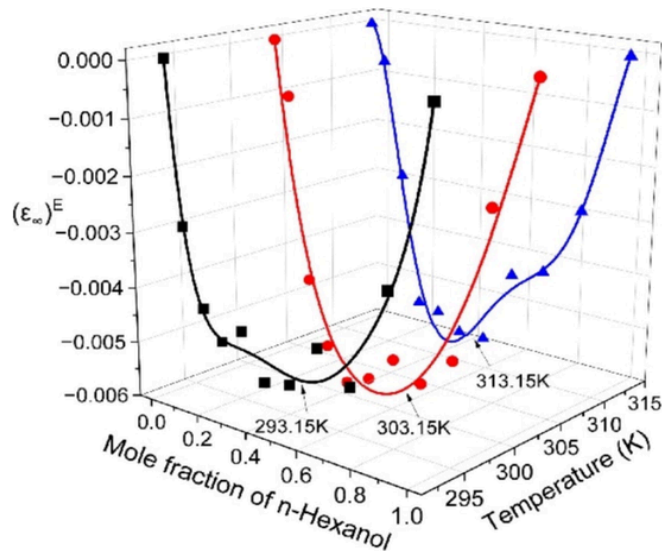


Fig. 6. Plot of excess high-frequency limiting dielectric constant $(\epsilon_{\infty})^E$ against mole fraction of n-Hexanol in binary mixtures at different temperature.

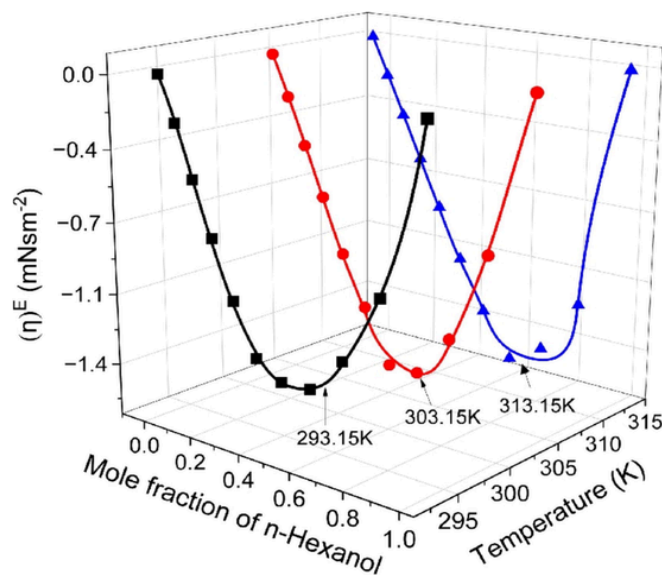


Fig. 7. Plot of excess viscosity $(\eta)^E$ against mole fraction of n-Hexanol in binary mixtures at different temperature.

3.3. Kirkwood correlation factor

Some valuable insights into dipole–dipole correlation and the orientation of electric dipoles in polar liquids can be gained using the Kirkwood correlation factor (g). The expression for the pure liquids is as follows: [7–13,15,18,20,29–31,33–35,63]

$$\left(\frac{4\pi N \mu^2 \rho}{9KT M}\right) g = \frac{(\epsilon_0 - \epsilon_{\infty})(2\epsilon_0 + \epsilon_{\infty})}{\epsilon_0(\epsilon_{\infty} + 2)^2} \quad (9)$$

Here, N is Avogadro's number, μ is the dipole moment of the molecules forming the liquid, ρ is represent density of the liquid at temperature T in the kelvin scale and K is the Boltzmann constant. M is the molecular weight, ϵ_{∞} and ϵ_0 are the calculated square of the refractive index and the complex permittivity obtained by fitting the data to the

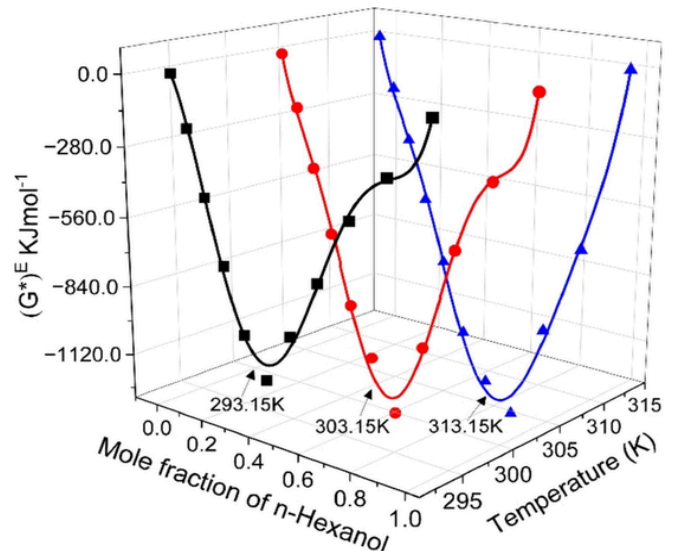


Fig. 8. Plot of excess Gibbs free energy $(G^*)^E$ against mole fraction of n-Hexanol in binary mixtures at different temperature.

Havriliak-Negami (HN) dielectric relaxation model, respectively. The modified Kirkwood equation is used to determine the effective averaged angular Kirkwood correlation factor (g^{eff}) of the two constituent molecules of the mixture of two polar liquids. This modified Kirkwood equation is given below:

$$\frac{4\pi N}{9KT} \left(\frac{\mu_1^2 \rho_1}{M_1} X_1 + \frac{\mu_2^2 \rho_2}{M_2} X_2 \right) g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (10)$$

The corrective correlation factor (g^F) which influences the angular correlation factors of pristine substances 1 and 2 is represented as:

$$\frac{4\pi N}{9KT} \left(\frac{\mu_1^2 \rho_1 g_1}{M_1} X_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} X_2 \right) g^F = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (11)$$

where, X_1 and X_2 represents the mole fractions of the liquids n-Hexanol (1) and DMF (2), respectively. The value of g^{eff} varies from g_1 to g_2 as the concentration of DMF (2) is increased from 0.0 to 1.0. The Table 2 represents the evaluated Kirkwood parameters (g^{eff} and g^F) for the binary mixtures. A high degree of parallel dipole ordering in n-Hexanol and antiparallel dipole ordering in DMF is indicated through g^{eff} of the pure DMF (1.117 at 293.15 K, 1.125 at 303.15 K, and 1.139 at 313.15 K) and n-Hexanol (3.971 at 293.15 K, 3.966 at 303.15 K, and 3.915 at 313.15 K), respectively. Fig. 9 illustrates a non-linear relation between g^{eff} and the concentration of the n-Hexanol at all temperatures, concluding an increment in the parallel alignment of the dipoles and the formation of H-bonded structures. Furthermore, the stabilization of the active structures is achieved upon increasing the temperature due to the coordination among the electrical dipoles. The value of g^{eff} is unchanged upon addition of n-Hexanol into DMF until the mole fraction X reaches to 0.5890 in the mixture; A rapid increment in g^{eff} is observed at $X_1 \geq 0.7107$. This suggests that the number of parallel-aligned dipoles increases in the mixture with the addition of n-Hexanol to DMF. More parallel-aligned dipoles are compensated by the anti-parallel-aligned dipoles beyond the mole fraction $X_1 = 0.7107$. This trend is found to be consistent for the entire temperature range considered in the current study. The corrective Kirkwood correlation factor g^F is '1' for pure liquids. The dipole–dipole interaction between the two hetero molecules causes a deviation in the value of g^F from unity. The evaluated values of g^F for the liquid mixtures are observed to be less than

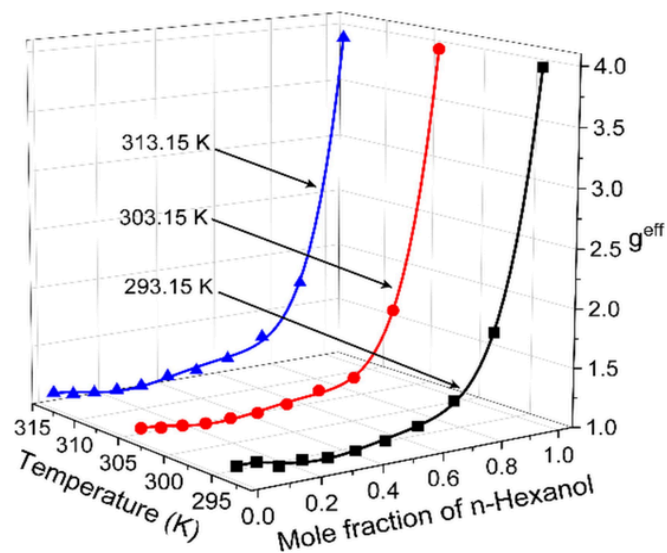


Fig. 9. Variation of effective Kirkwood correlation factor (g^{eff}) versus mole fraction of n-Hexanol in binary mixtures at different temperature.

unity at all concentrations as mentioned in the Table 2. The variation of the g^F as a function of the mole fraction of n-Hexanol at different temperatures is presented in Fig. 10. The maximum deviation of g^F from unity is observed at $X_1 = 0.7107$, showing high molecular interaction among the hetero molecules within the mixture at this concentration. The root of this phenomenon may be explained with the following reasoning: there are a large number of alcohol molecules (n-Hexanol) at high concentrations which surround the DMF molecules. Thus, the voids of the clusters of alcohol molecules are occupied by these DMF molecules. And the hydrogen bonding between the two hetero molecules is enabled due to the role of alcohol molecules as proton donors. As a result, owing to the formation of multimers and the reduction of the parallel-aligned electric dipoles there is a large dipole-dipole interaction in the binary mixtures.

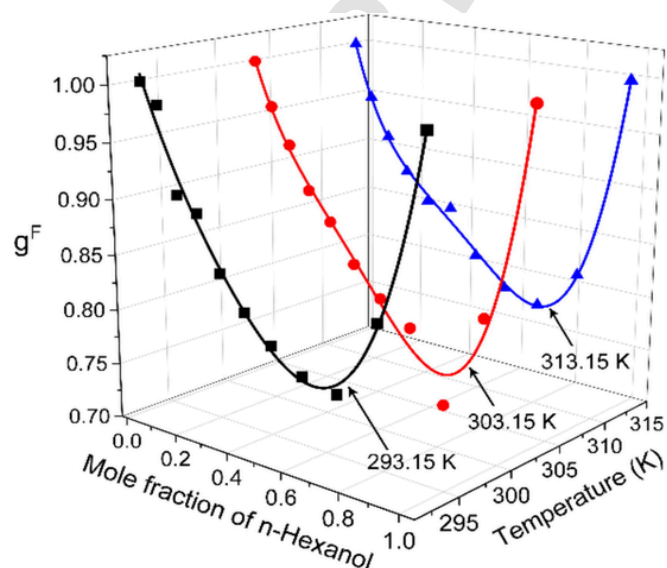


Fig. 10. Variation of corrective Kirkwood correlation factor (g^F) versus mole fraction of n-Hexanol in binary mixtures at different temperature.

3.4. Bruggeman factor

The Bruggeman parameter (f_B), provides information on the interaction that occurs between the participating components of the mixture [5,7,20,23,29,30,64]. According to Bruggeman ϵ_{01} , ϵ_{02} and ϵ_{0m} are related to volume fraction of solute by the following equation.

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{02}}{\epsilon_{01} - \epsilon_{02}} \right) \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{\frac{1}{3}} = (1 - \Phi_2) \quad (12)$$

Equation (12) defines Φ_2 as the volume fraction of liquid 2 (DMF), while ϵ_{01} , ϵ_{02} , and ϵ_{0m} correspond to the static dielectric constants of liquid 1 (n-Hexanol), liquid 2 (DMF), and the binary mixture, respectively. Despite the linear relationship expected by Eq. (8), the experimental f_B values for the binary system display deviations. Hence, to accurately account for these deviations, the experimental data underwent fitting using a modified Bruggeman model.

$$f_B = 1 - [a - (a - 1)\Phi_2] \Phi_2 \quad (13)$$

where a is a numerical fitting parameter that represents a change in molecular orientation and quantifies the degree to which the binary mixture's polar liquid components interact through dipoles in terms of molecular size and volume. The value a numerical fitting parameter of $a = 1$ indicates the ideal Bruggeman mixture formula, while deviations from linearity suggest molecular interactions among the components. Fig. 11 illustrates the plot of the Bruggeman factor (f_B) against the volume fraction of n-Hexanol at varying temperatures, highlighting the influence of temperature on molecular interactions within the system. It has been observed that the values of ' a ' founds to be greater than unity at all temperatures ($a = 1.2295$, $a = 1.2182$ and $a = 1.1376$ at 293.15 K, 303.15 K, 313.15 K respectively) indicate that the effective volumes of DMF increases as concentration of n-Hexanol molecules increases in the mixtures [20,23,29,30,64].

3.5. Thermodynamical parameters

Dielectric relaxation process can be understood of as the dipole rotating between two equilibrium positions separated by a potential bar-

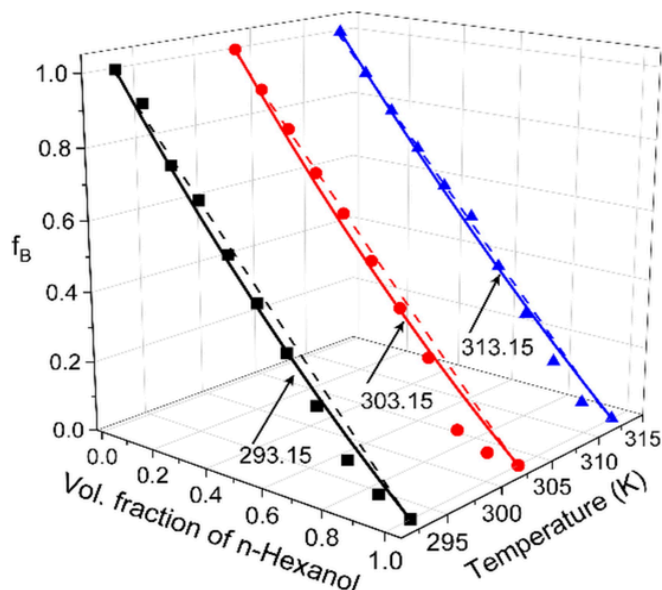


Fig. 11. Plot of Bruggeman factor (f_B) against mole fraction of n-Hexanol in binary mixtures at different temperatures.

rier. The dielectric relaxation time (τ_0), depends on the height of the potential barrier, a constant that changes with temperature, and the average time it takes for an excited molecule to move from one equilibrium position to the other [65]. According to Eyring dielectric relaxation is related to the chemical rate theory [66–69].

$$\tau_0 = \left(\frac{h}{kT}\right) \exp\left(\frac{\Delta F_e}{RT}\right) \quad (14)$$

$$\Delta F_e = RT \ln\left(\frac{\tau_0 K T}{h}\right) \quad (15)$$

The change in activation energy is also expressed as

$$\Delta F_e = \Delta H_e - T \Delta S_e \quad (16)$$

where ΔF_e , ΔH_e , ΔS_e , τ_0 , h , R , K and T denotes the activation energy, enthalpy of activation, entropy of activation, dipolar relaxation time, Planck's constant, universal gas constant, Boltzmann's constant, and absolute temperature in Kelvin. It has been observed (supplementary information Table S2) that the activation energy (ΔF_e) decreases with increasing mole fraction of n-Hexanol, indicating a trend where higher concentrations of n-Hexanol promote the formation of hydrogen-bonded networks between DMF and n-Hexanol. This results in larger effective sizes of rotating dipoles and high dielectric frictional force between them. Negative values of entropy of activation (ΔS_e) are observed, which stem from cooperative molecular orientation likely caused by steric forces or parallel alignment of dipoles involved in dipole-dipole interactions. Positive values of enthalpy of activation (ΔH_e), especially noticeable at higher mole fractions of n-Hexanol ($X_2 \geq 0.0639$), indicate an endoergic reaction involving heat absorption. This absorption of energy is attributed to the formation of hydrogen bonds, leading to the conversion of monomers into multimers and increased orderliness within the system, consequently resulting in cooperative molecular orientation.

3.6. Microwave heating parameters

The microwave frequency 2.45 GHz is chosen for industrial use to prevent interference with frequencies crucial for telecommunications, military, and navigation applications. The microwave heating parameters like penetration depth (d_p), power reflected (P_r) and power transmitted (P_t) are determined from the observed values of dielectric constant (ϵ') and dielectric loss (ϵ'') at 2.45 GHz frequency using following equations [42,43].

$$P_r = \left(\frac{\sqrt{\epsilon'} - 1}{\sqrt{\epsilon'} + 1}\right)^2 \quad (17)$$

$$P_t = \left[100 - \left(\frac{\sqrt{\epsilon'} - 1}{\sqrt{\epsilon'} + 1}\right)^2\right] \quad (18)$$

$$d_p = \frac{\lambda_0 \sqrt{\epsilon'}}{2\pi \epsilon''} \quad (19)$$

where $\lambda_0 = \frac{c}{f}$. c is the speed of light in free space (3×10^8 m/s) and f is the microwave frequency (Hz).

The variation of power reflected, power transmitted and penetration depth at different temperature against mole fraction of n-Hexanol are shown in (Supplementary information (SI) Fig. S3). It has been observed that there is no appreciable change in power reflected and power transmitted values at different temperatures. The penetration depth shows significant change against temperatures and concentration of n-Hexanol in the binary mixtures. The penetration depth (d_p) at the intermediate concentration is lower than its average values.

3.7. DFT study of these liquids

To comprehend the geometrical effect on the intermolecular interaction between component molecules, density functional theory (DFT) calculations were incorporated. The optimized structures of the studied pure (DMF and n-Hexanol) and binary molecules in a 1:1 ratio (DMF + n-Hexanol) were represented in Fig. 12 and Fig. 13 making use of Avogadro software/MMFF94 and ORCA 4.2.1 with functional B3LYP and 6-311G (d,p) basic set [39–41,44–46]. We investigated three different orientations of 1:1 binary mixtures and observed the 2-DH structure to be the most stable among the three based on the total energies of the each. Fig. 10 represents the three binary combinations 1-DH, 2-DH, 3-DH of DMF and n-Hexanol after the optimization. Following the optimization of the structures, a HOMO-LUMO study was conducted. The concept of the highest occupied molecular orbital (HOMO) elucidates the capacity of a molecule to donate electrons, whereas the lowest unoccupied molecular orbital (LUMO) elucidates the ability of a molecule to absorb electrons. The energy difference that exists between the HOMO and the LUMO determines the magnitude of the energy gap. A greater value of the energy gap signifies higher amount of energy required for an electronic transition. Electrophilic and nucleophilic substitution reactions can be better understood with the help of Figs. 14 and 15 molecular electron density. The red area denotes a high concentration of electrons, while the blue area signifies a low concentration of electrons, indicating a positive charge. In this study, a HUMO-LUMO

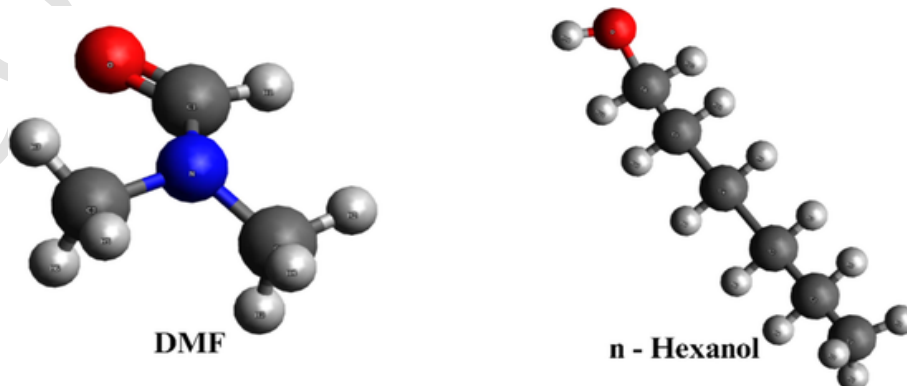


Fig. 12. Optimized structure of DMF and n-Hexanol.

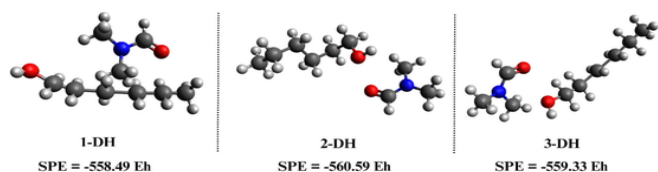


Fig. 13. Optimized structure of three different oriented 1:1 M ratio of binary mixture of DMF and n-Hexanol with single point energy.

analysis was conducted to determine various parameters, including the HOMO and LUMO energies (E_{HOMO} and E_{LUMO}), energy gap (E_g), optical softness (σ_o), electron affinity (EA), global electrophilicity index (ω), softness (S), maximum charge transfer index (ΔN_{max}), electronegativity (χ), ionization potential (IP), hardness (η), chemical potential (μ), and nucleophilicity index (N) for the pure compounds (DMF & n-hexanol) and its 1:1 M ratio of mixture concentration. According to the data provided in (supplementary information (Table S3)), E_{HOMO} ranged from -6.60 to -3.53 eV, while E_{LUMO} ranged from -3.14 to 0.58 eV for all studied substances. 2-DH exhibited the highest E_g value (approximately 7.01 eV). Conversely, 3-DH displayed the lowest E_g value (about 0.73 eV).

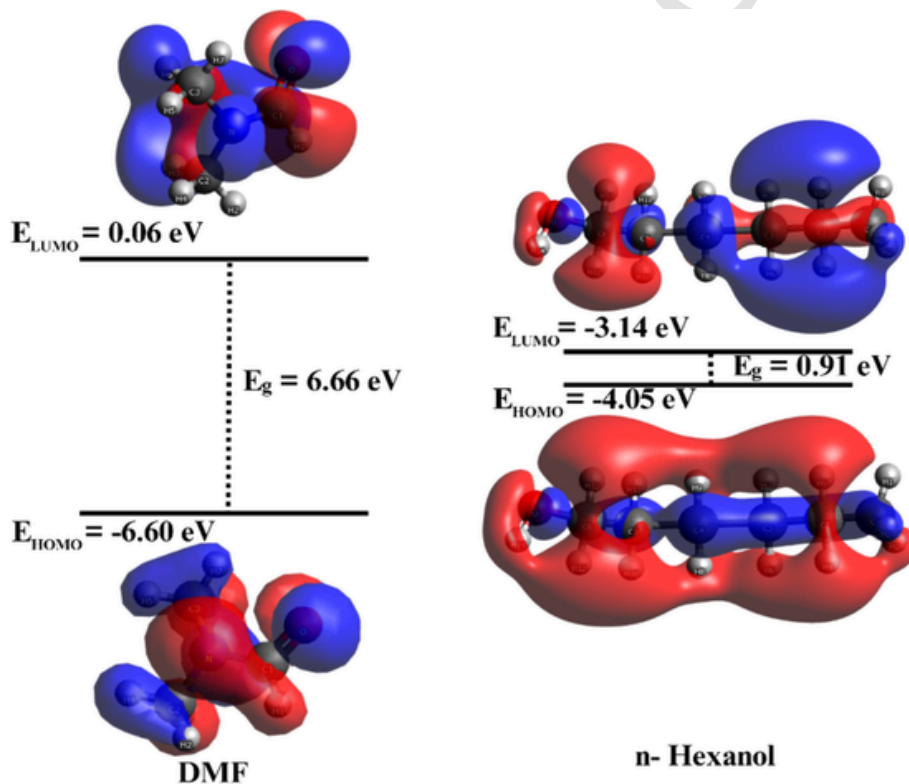


Fig. 14. Optimized structure of three different oriented 1:1 M ratio of binary mixture of DMF and n-Hexanol with single point energy.

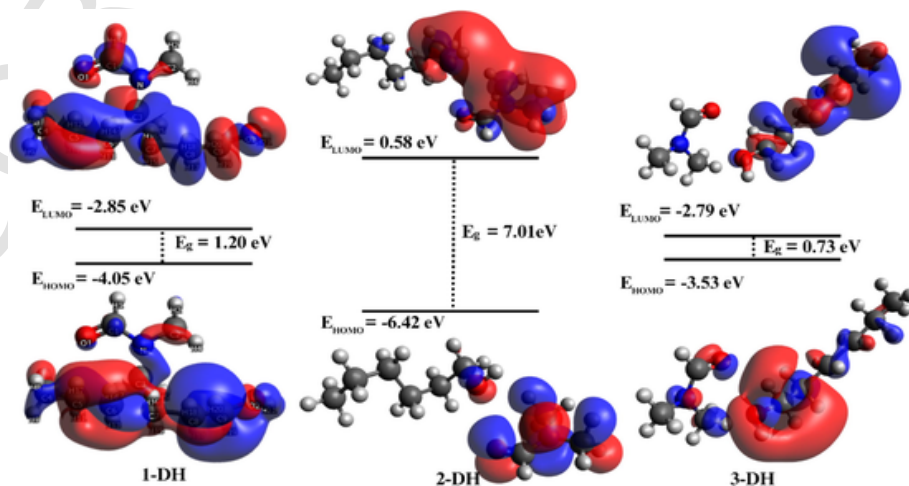


Fig. 15. HOMO-LUMO structure of three different oriented 1:1 M ratio of binary mixture of DMF and n-Hexanol.

4. Conclusions

The paper presents accurately measured complex permittivity spectra (CPS), including the real (ϵ') and imaginary (ϵ'') part, for n-Hexanol, DMF, and their binary mixtures, with a focus on applications driven by their dielectric constants in pharmaceutical, analytical, and technological industries. The CPS of these solvents and mixtures exhibit a consistent Cole-Cole or Cole-Davidson type dispersion, reflecting common trends in their dielectric behavior. Systematic variations in key dielectric parameters are observed as functions of concentration and temperature.

The study evaluates a range of dielectric properties, including static dielectric constant, high-frequency dielectric constant, relaxation time, Kirkwood correlation factor, Bruggeman factor, and excess dielectric properties such as excess static permittivity and excess inverse relaxation time, across various temperatures and mole fractions of n-Hexanol for the binary mixtures. The formation and strength of complexes in the mixtures, attributed to heteromolecular interactions between participating molecules, are revealed through changes in these parameters with varying concentrations of n-Hexanol. Nonlinear trends in static dielectric constant, high-frequency dielectric constant, and relaxation time with increasing mole fraction of n-Hexanol suggest significant intermolecular interactions. In DMF-rich mixtures, the effective dipole moments rotate slowly, while in n-Hexanol-rich regions, dipole rotation occurs rapidly. In the studied binary system (n-Hexanol + DMF) show deviation in Bruggeman parameter from linearity indicating deviation in the static dielectric constant value at different concentrations from normal mixture values resulting molecular interaction between dissimilar molecular species. Activation energy, enthalpy of activation, and entropy of activation have been calculated and reported for n-Hexanol, DMF, and their binary mixtures across the range of studied temperatures, providing insights into the energy requirements and thermodynamic aspects of the systems. Microwave heating parameters, namely reflected power (P_r), transmitted power (P_t), and penetration depth (D_p), have been determined, offering valuable information for understanding the efficiency and behavior of microwave heating in these mixtures. Furthermore, the chemical stability of the compounds has been confirmed through total energy analysis. HOMO-LUMO analysis and evaluation of electronic properties, providing a deeper understanding of their molecular structures and potential interactions. This comprehensive analysis contributes to the understanding of the dielectric behavior, heating characteristics, and chemical properties of n-Hexanol, DMF, and their mixtures, which can be beneficial for various industrial and scientific applications.

CRedit authorship contribution statement

N.A. Chaudhary: Writing – original draft, Validation, Software, Resources, Methodology, Formal analysis, Conceptualization. **C.R. Vaja:** Validation, Methodology, Formal analysis. **K.J. Agheda:** Validation, Software, Formal analysis. **K.N. Shah:** Writing – review & editing, Formal analysis. **V.A. Rana:** Writing – review & editing, Validation, Resources, Methodology. **A.N. Prajapati:** Writing – review & editing, Supervision, Methodology, Conceptualization.

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Declaration of competing interest

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

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Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2024.126675>.

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Study of Dielectric Properties of Binary Mixtures of *n*-Octanol and *N,N*-Dimethylformamide in Lower Microwave Radiation

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Abstract

The complex permittivity spectra of binary mixtures (0.0 → 1.0) of *n*-octanol and *N,N*-dimethylformamide (DMF) were obtained in the lower microwave radiation region using a vector network analyzer (VNA) at 293.15 K. The complex permittivity spectra of *n*-octanol with DMF and binary mixtures were fitted in a dielectric relaxation model (Havriliak–Negami) to obtain the static dielectric constant (ϵ_0) and relaxation time (τ). Complex nonlinear least-squares (CNLS) fitting was used to fit the complex dielectric spectra. The nonlinear variation in ϵ_0 and τ against DMF concentration in binary mixtures of *n*-octanol + DMF indicated hetero-molecular interaction between participating molecular species. The variation in the dielectric constant and dielectric loss against concentration is discussed in light of their dependence on frequency. The microwave radiation heating parameters including power reflected (p_r), power transmitted (p_t), and penetration depth (d_p) were investigated at general purpose and commercial microwave radiation of 2.45 GHz, respectively.

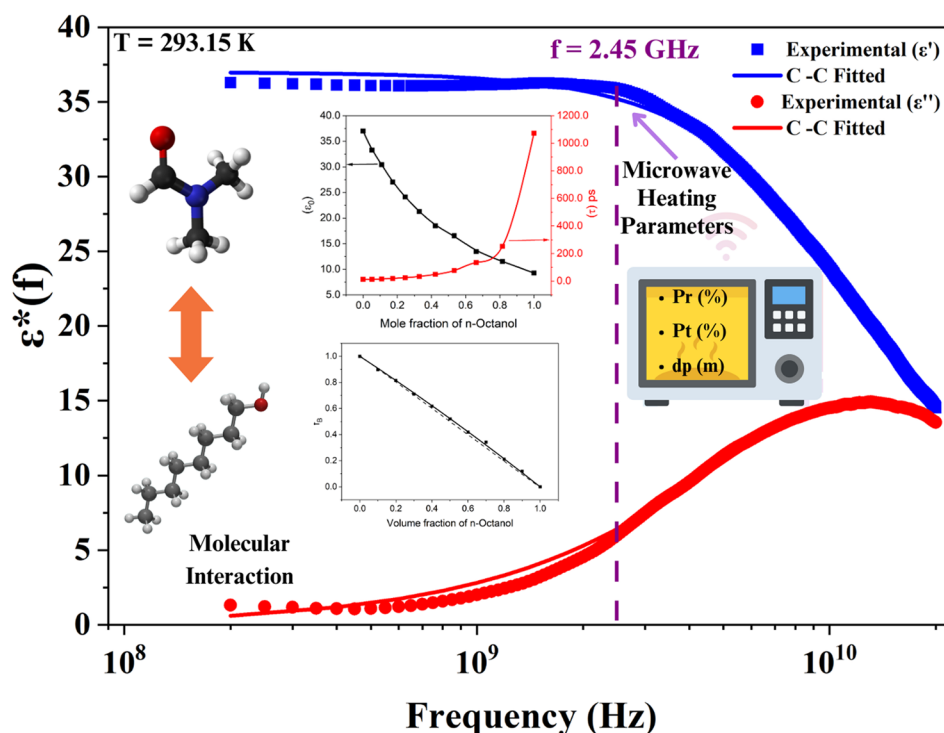
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Graphical Abstract



Keywords Binary mixtures · complex permittivity · vector network analyzer · microwave radiation

Introduction

Frequency-dependent dielectric behavior in solvent mixtures serves as a valuable tool for extracting information about molecular interactions and the mechanisms governing molecular processes. This approach enables the exploration of fundamental liquid structures, their persistence, and dynamic behavior. Additionally, the dielectric property serves as a useful tool for practical applications, offering insights applicable to various scientific and technological domains.^{1,2} The dielectric relaxation response of binary mixtures of polar molecules is crucial as it offers insights into the relaxation process within these mixtures under different compositions and conditions. Through dielectric relaxation spectroscopy (DRS) studies of such liquids and their binary mixtures, we gain knowledge about various relaxation processes, dielectric polarization, intermolecular and intramolecular interactions, and electrical conduction.² Dielectric spectroscopy has long been utilized to explore interactions within systems characterized by hydrogen bonding. In such mixtures, the intermolecular interactions in binary structures mainly arise from either dipole–dipole interactions or hydrogen bonds.^{3–6} In recent years, there has been a growing focus on using dielectric properties as interaction parameters for understanding molecular interactions in binary

liquid mixtures, both theoretically and experimentally. The dielectric permittivity (ϵ) shows a stronger frequency dependence in radio frequency (RF) and microwave ranges, making the dielectric permittivity (ϵ) a critical parameter for evaluating a material's electromagnetic behavior. Extensive research on the electromagnetic properties of materials has demonstrated that a material's performance is often closely linked to its dielectric characteristics, and monitoring variations in the dielectric constant can provide valuable insights. The precise measurement of the dielectric constant has emerged as a key research area due to the widespread use of dielectric materials in fields such as aerospace, chemistry, and communications.^{7–9} In dielectrics, the real part (ϵ') serves as an indicator of a dielectric material's ability to store energy in an electric field, while the imaginary part (ϵ'') represents the electromagnetic energy absorbed by the material, subsequently converted into thermal energy through the Joule heating effect. In mixed solvents (polar + polar, polar + nonpolar), the deviation of ϵ' and ϵ'' from rectilinearity depends on the strength of intermolecular and intramolecular hydrogen bonding in mixtures.¹⁰ Measuring dielectric properties across a wide frequency range provides insights into molecular dynamics and relaxation behavior. Alcohols have diverse applications in medicine and many industries and other fields.¹¹ Recently,

the longer-chain alcohol, *n*-octanol, has been recognized as a biofuel candidate obtained from biomass-derived platform chemicals.¹² Primary alcohols of medium chain length are crucial industrial products, serving as valuable compounds for detergent and surfactant production, as well as in perfumery and flavor applications. Notably, 1-octanol holds significance and is employed in synthesizing 1-octene, a key co-monomer in polyethylene production and petrochemical processes.¹³ Amides are highly polar and have a strong ability to dissolve substances, making them crucial solvents in industries and biological processes.^{14,15} *N,N*-Dimethylformamide (DMF) is a significant member of the amide solvent group, essential in the production of acrylic fibers and plastics.¹⁶ Structurally, it comprises two hydrophobic $-\text{CH}_3$ groups and one highly polar $\text{C}=\text{O}$ group. DMF readily forms hydrogen bonds, such as $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}=\text{O}\cdots\text{H}$, with other molecules like alcohols.¹⁷

The present paper aims to explore the dielectric dispersion and relaxation behavior in binary mixtures of *n*-octanol and DMF at microwave frequencies and also to shed light on how the change in concentration of the components influences the dielectric and microwave heating properties of the mixtures. These data are essential for designing processes in chemical and petrochemical industries.

Experimental and Theoretical Details

n-Octanol (synthesis grade) and DMF (analytical reagent grade) were acquired from Loba Chemie Pvt Ltd, India, and used without further purification. Table 1 presents information on the purity, grade, CAS number, and a comparison of the static permittivity (ϵ_0) and relaxation times (τ) of the pure compounds with literature values. Binary mixtures were meticulously prepared in hermetically sealed glass vials at different volume percentages (0, 10, 20, ..., 100%) of DMF in *n*-octanol. Under the assumption of perfect mixing, volume percentage may be converted into mole fraction using the following formula:²¹

$$x_1 = \frac{\left(\frac{V_1 \rho_1}{M_1}\right)}{\left(\frac{V_1 \rho_1}{M_1}\right) + \left(\frac{V_2 \rho_2}{M_2}\right)} \quad (1)$$

where V_1 and V_2 are the volume percentage, ρ_1 and ρ_2 are the density, and M_1 and M_2 are the molecular weight of *n*-octanol and DMF, respectively.

Complex permittivity measurements were carried out over a frequency range of 200 MHz to 20 GHz using a vector network analyzer (VNA) (model MS46322A, Anritsu Shockline with SPEAG DAK 3.5 probe) at constant temperature. Complex dielectric measurements of the binary liquid samples were carried out after the completion of proper calibration. As part of the calibration process, considerations were given to factors such as temperature fluctuations and cable movements, which could influence probe measurements. Calibration procedures involved normalizing both magnitude and phase differences between the probe and cable. It should be noted that the real (ϵ') and imaginary (ϵ'') components of the complex permittivity data were subject to uncertainties within a range of 4.0%. During the measurements, the temperature was consistently monitored and controlled using a precision constant-temperature water bath (Model Industrial Corporation, India), maintaining precision at ± 0.1 K.

Results and Discussion

Complex Permittivity Spectra

Frequency based on spectra of dielectric constant (ϵ') over the frequency span $200 \text{ MHz} \leq f \leq 20 \text{ GHz}$ for entire mole fraction ($0.0 \rightarrow 1.0$) of *n*-octanol at constant temperature (293.15 K) is shown in Fig. 1. In Fig. 1, the solid line shows the Cole–Cole fitted values of the dielectric constant (ϵ') using LEVMW software and symbol represents the experimental values of the real part of permittivity. It has been observed from Fig. 1 that the dielectric constant (ϵ') values decrease with increase in frequency monotonically as the concentration of *n*-octanol increases in the binary liquid mixtures. Furthermore, the dielectric constant (ϵ') of *n*-octanol exhibited frequency-independent behavior across various concentrations within the range of 200 MHz–3 GHz. However, beyond this range, there was a notable decrease in the dielectric constant with increasing frequency. This decrease in ϵ' beyond 3 GHz, extending up to 20 GHz, can be attributed to the phase lag between dipolar orientation and the alternating electric field, particularly pronounced at frequencies exceeding 20 GHz.^{22,23}

It can be observed from Fig. 2 that the dielectric loss (ϵ'') values decrease with an increase in frequency. Further, the

Table 1 Chemicals used and their purity, grade, CAS no., and comparison of static permittivity (ϵ_0) and relaxation time (τ) of pure liquid with literature values at 293.15 K

Compound	Purity (%)	Grade	CAS no.	Static permittivity		Relaxation time (ps)	
				Exp.	Lit.	Exp.	Lit.
<i>N,N</i> -Dimethylformamide	99.8	AR	68–12–2	37.00	37.65 ¹⁸	12.93	14.22 ¹⁹
<i>n</i> -Octanol	99.0	AR	111–87–5	9.28	10.08 ²⁰	1072.8	1085.6 ²⁰

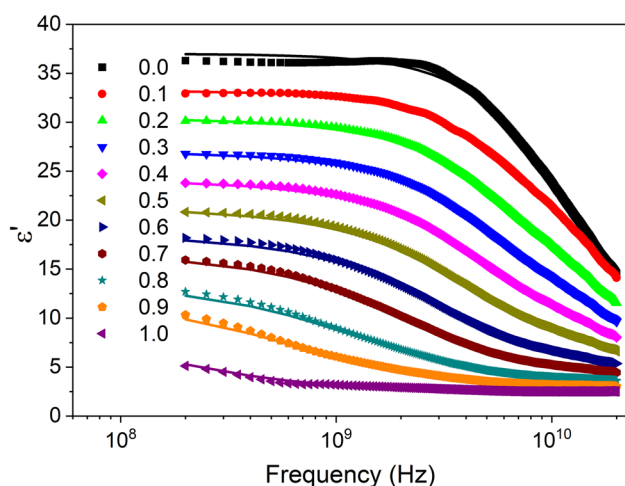


Fig. 1 Variation in dielectric constant (ϵ') against frequency at different concentrations of *n*-octanol in binary mixtures. Solid line represents Cole–Cole (C–C) fitted curve.

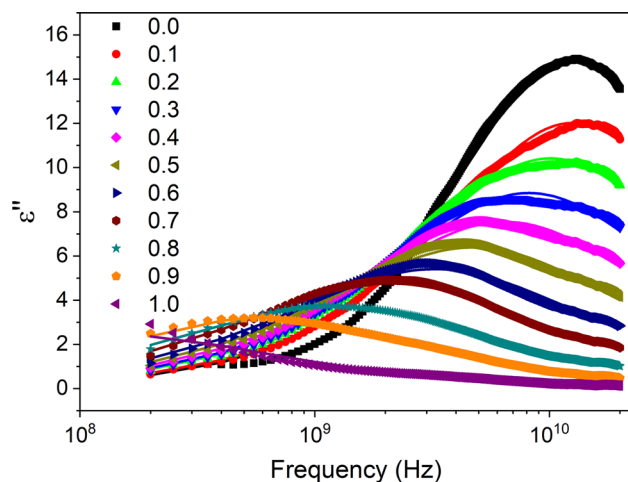


Fig. 2 Variation in dielectric loss (ϵ'') against frequency at different concentrations of *n*-octanol in binary mixtures. Solid line represents Cole–Cole (C–C) fitted curve.

dielectric loss (ϵ'') peak values decrease and shift towards the lower-frequency side as the concentration of *n*-octanol increases in the binary liquid mixtures (Fig. 2). Because of the hydroxyl group present in the molecular structures and intramolecular linked clusters created by the (O–H ...O) type of linkage, *n*-octanol has a longer relaxation time (1072.80 ps).^{21,24} The shorter relaxation time (12.93 ps) of DMF indicates its inflexible and non-associative nature. The complex nonlinear least-squares (CNLS) fitting method was used to fit the experimental complex dielectric data to different dielectric relaxation models that are dependent on asymmetry and broadness.²⁵ The Havriliak–Negami (HN) model, which encompasses both asymmetry and broadening

in dielectric relaxation, is expressed by the following equation:²⁶

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\Delta\epsilon}{[1 + (i\omega\tau)^{\alpha}]^{\beta}} \quad (2)$$

In Eq. 2, $\epsilon(\omega)$ denotes the complex permittivity at an angular frequency ω , $\Delta\epsilon$ is relaxation strength, and τ is relaxation time of the mixture concentration, while α and β serve as shape parameters. Specifically, α characterizes the symmetrical distribution of relaxation time, and β pertains to the shape parameter associated with an asymmetric relaxation curve. In the C–C model, the value of β is fixed at 1. Different values of the high-frequency limiting dielectric constant (ϵ_{∞}), dielectric relaxation strength ($\Delta\epsilon$), relaxation time (τ), shape parameter (α), and mole fraction model are tabulated in Table II at constant temperature (293.15 K).

From Table II, it is observed that the values of the limiting dielectric constant ϵ_{∞} (obtained from CNLS) decrease as the concentration of *n*-octanol increases in (*n*-octanol + DMF) mixtures. It is apparent from Table II that the dielectric strength ($\Delta\epsilon$) of the mixture decreases as the concentration of the mixture increases while the relaxation time increases. Dielectric relaxation parameters, including relaxation times and permittivity, are significantly influenced by factors such as viscosity, density, temperature, and molecular structure.²⁷

Static Dielectric Constant (ϵ_0) and Relaxation Time (τ)

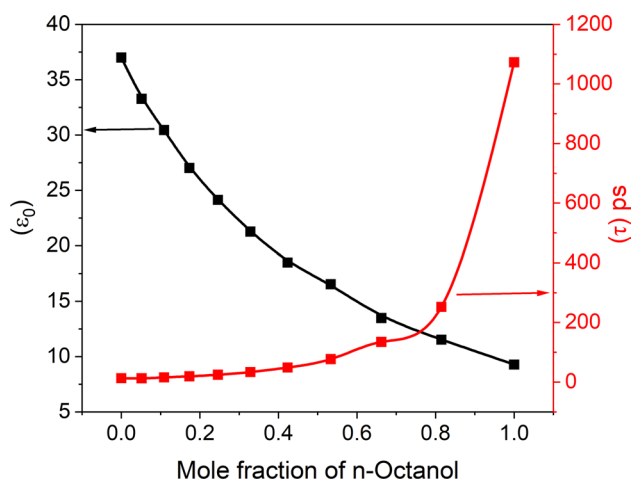
The complex dielectric data were analyzed using the CNLS method in the LEVMW software program. This approach allowed for the determination of key dielectric parameters including static dielectric constant (ϵ_0) and relaxation time (τ). Figure 3 shows the variation in the static dielectric constant (ϵ_0) and average relaxation time (τ) against the mole fraction of *n*-octanol in the binary liquid mixtures at 293.15 K. The variation in the static dielectric constant (ϵ_0) and average relaxation time (τ) shows nonlinear behavior, indicating intermolecular and intramolecular interactions among the molecular species.^{1,6,11,19,21}

The trend observed in Fig. 3, where the static dielectric constant decreases as the mole fraction of *n*-octanol increases, can be explained by the transition of spherical molecular aggregates to elongated structures. This transition causes an antiparallel alignment of dipoles within the mixture. The deviation of the static dielectric constant (ϵ_0) from linearity provides evidence for the formation of hydrogen-bonded intermolecular interactions between DMF and *n*-octanol molecules in the mixtures.²⁸ Moreover, Fig. 3 clearly illustrates a systematic increase in the variation in relaxation time (τ_0) within the mixtures, implying a concentration-dependent formation of small structures. It

Table II CNLS fitting parameters high-frequency limiting dielectric constant ($\epsilon_{\infty 1}$), dielectric relaxation strength ($\Delta\epsilon$), relaxation time (τ), shape parameter (α), and corresponding fitting model of mole fraction (X) of *n*-octanol in binary mixtures of *n*-octanol + DMF at 293.15 K

X	$\epsilon_{\infty 1}$	$\Delta\epsilon$	τ (ps)	α
0.0000	$5.11 \pm (2.53)$	$31.88 \pm (0.53)$	$12.93 \pm (0.45)$	$0.95 \pm (0.37)$
0.0516	$4.71 \pm (3.53)$	$28.55 \pm (0.51)$	$12.66 \pm (0.95)$	$0.89 \pm (0.34)$
0.1090	$4.31 \pm (2.93)$	$26.14 \pm (0.45)$	$15.73 \pm (0.84)$	$0.85 \pm (0.36)$
0.1733	$4.46 \pm (2.56)$	$22.56 \pm (0.50)$	$19.43 \pm (0.91)$	$0.84 \pm (0.46)$
0.2459	$4.26 \pm (2.03)$	$19.86 \pm (0.48)$	$24.66 \pm (0.84)$	$0.82 \pm (0.49)$
0.3285	$4.08 \pm (1.56)$	$17.19 \pm (0.51)$	$33.61 \pm (0.83)$	$0.81 \pm (0.53)$
0.4232	$3.85 \pm (1.16)$	$14.63 \pm (0.58)$	$48.92 \pm (0.96)$	$0.80 \pm (0.57)$
0.5330	$3.57 \pm (0.76)$	$12.96 \pm (0.64)$	$76.99 \pm (1.14)$	$0.80 \pm (0.52)$
0.6618	$3.14 \pm (0.56)$	$10.34 \pm (0.88)$	$134.78 \pm (1.74)$	$0.78 \pm (0.56)$
0.8149	$2.87 \pm (0.35)$	$8.65 \pm (1.12)$	$252.48 \pm (2.13)$	$0.81 \pm (0.45)$
1.0000	$2.44 \pm (0.64)$	$6.84 \pm (8.59)$	$1072.80 \pm (1.46)$	$0.78 \pm (1.16)$

*The relative standard deviation in percentage, as determined by CNLS fitting, is shown by the number in brackets. For example, $31.88 (0.53)$ is $31.88 \pm 0.53\%$.

**Fig. 3** Variation in ϵ_0 and τ against mole fraction of *n*-octanol.

is observed that the relaxation time changes very little with concentration in the mole fraction range of $0.0 \leq X_1 \leq 0.6$. This suggests that the molecular structures formed within this concentration range are such that environmental changes have little impact on the relaxation time.¹¹ On the other hand, relaxation time changes rapidly in the mole fraction range of $0.6 < X_1 \leq 1.0$, which indicates that reducing the concentration of DMF in the mixture alters the relaxation contribution of *n*-octanol, suggesting hetero-interactions with a structure-breaking character.^{19,28,29}

Excess Dielectric Relaxation Parameters

The excess parameters with regard to static dielectric constant (ϵ_0) and relaxation time (τ) give important insights into the interaction between the polar and nonpolar liquid mixtures. These properties play a crucial role in detecting

cooperative domains within the mixture and can serve as indicators of multimer formation due to intermolecular association.¹¹ The excess static dielectric constant (ϵ_0)^E and excess inverse relaxation time $\left(\frac{1}{\tau}\right)^E$ are computed using the following relations.¹

$$(\epsilon_0)^E = (\epsilon_0 - \epsilon_{\infty})_m - [(\epsilon_0 - \epsilon_{\infty})_1 X_1 + (\epsilon_0 - \epsilon_{\infty})_2 X_2] \quad (3)$$

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 X_1 + \left(\frac{1}{\tau}\right)_2 X_2\right] \quad (4)$$

where X represents the mole fraction, the subscripts m , 1, and 2 denote the binary mixture, *n*-octanol, and DMF, respectively, and $(1/\tau)^E$ indicates the average broadening of the dielectric spectra.

The excess static dielectric constant (ϵ_0)^E provides valuable scientific insights into the presence and formation of monomers, dimers, and multimers within the mixture.

- (i) A value of $(\epsilon_0)^E = 0$ suggests that there is no interaction between the constituents of the mixture, or that any interactions present do not result in a change in the net dipole alignments caused by interacting unlike molecules.
- (ii) A value of $(\epsilon_0)^E < 0$ indicates that interactions among the mixture constituents cause some neighboring dipoles to orient in opposite directions. This phenomenon leads to the formation of multimers, resulting in less effective dipoles.
- (iii) When $(\epsilon_0)^E > 0$, it suggests that the constituents of the binary mixture align neighboring dipoles in the same direction. This alignment increases the number of effective dipoles, leading to the formation of monomers and dimers.

Figure 4 shows the variation in excess static dielectric constant $(\epsilon_0)^E$ against mole fraction of *n*-octanol. The negative values observed for $(\epsilon_0)^E$ throughout the concentration range suggest that the interaction between the species of both molecules leads to a reduction in the total effective dipole. This indicates that the binary mixture of *n*-octanol and DMF may give rise to the formation of multimers, resulting in less efficient dipoles. The excess static dielectric constant $(\epsilon_0)^E$ offers qualitative insights into the structural arrangement within the mixture, elucidating the nature of molecular organization.¹¹

The excess inverse relaxation time, $(1/\tau)^E$, gives us information about how the interactions between a solute and solvent affect the movement in the system. It helps estimate how much the dielectric spectra broaden on average, providing insights into the dynamic behavior of the solute–solvent interactions. The inverse relaxation time analogy stems from spectral line broadening, which is the reciprocal of the relaxation time observed in resonant spectroscopy.³⁰

In Fig. 5, the observation of all concentration negative values for the excess inverse relaxation time $(1/\tau)^E$ indicates the presence of linear structures indicated by slow rotation under the influence of an external changing field. This means that addition of *n*-octanol to DMF induces the formation of a hindering field, resulting in a diminished rate of rotation for effective dipoles. The derived information regarding solute–solvent dynamics reveals that the addition of *n*-octanol impedes the rotational motion of molecules, highlighting the nuanced impact of this interaction on the rotational behavior of linear structures within the system.²⁰

- (i) $(1/\tau)^E = 0$: The solute–solvent interaction dynamics remain constant.

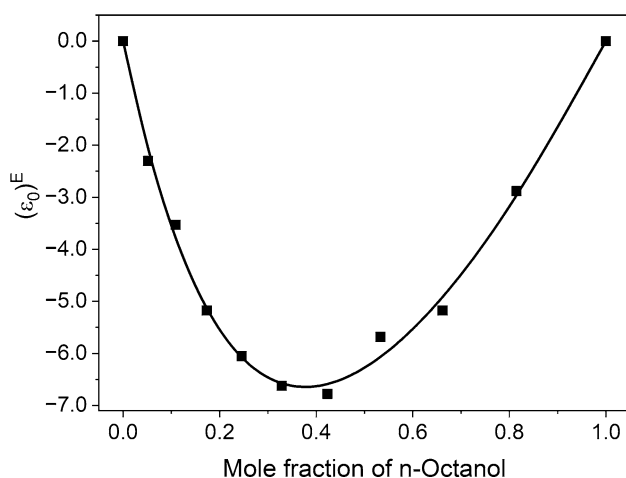


Fig. 4 Variation in $(\epsilon_0)^E$ versus mole fraction of *n*-octanol.

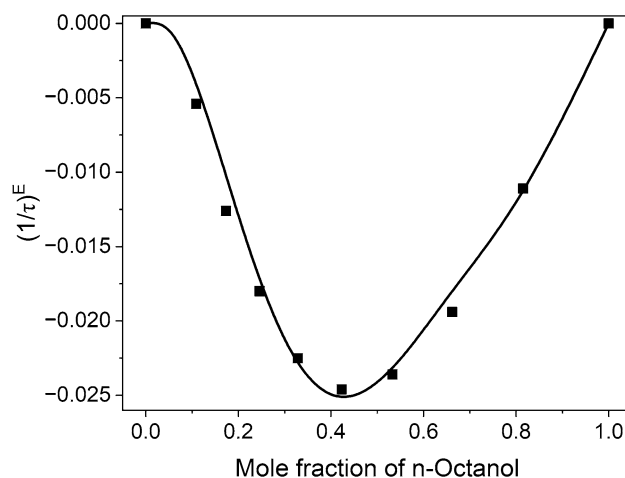


Fig. 5 Variation in $(1/\tau)^E$ versus mole fraction of *n*-octanol.

- (ii) $(1/\tau)^E < 0$: The interaction between solute and solvent induces a field, leading to a gradual rotation of effective dipoles.
- (iii) $(1/\tau)^E > 0$: The solute–solvent interaction generates a field that promotes rapid rotation of effective dipoles, highlighting the cooperative behavior between the field and dipole rotation.

Excess static dielectric constant $(\epsilon_0)^E$ and excess inverse relaxation time $(1/\tau)^E$ data were fitted in the Redlich–Kister (R-K) polynomial. The R-K polynomial and its coefficients with correlation coefficient are tabulated in Table III. The R-K polynomial equation is shown below.³¹

$$(A)^E = x_1 x_2 \sum_i^n a_i \cdot (x_2 - x_1)^i \quad (5)$$

In the above equation, the parameters a_i , X_1 , and X_2 are the mole fraction of DMF and *n*-hexanol, while n is the degree of the polynomial.

Bruggeman Factor

The Bruggeman factor (f_B) is a significant dielectric parameter that offers insights into hetero-interactions between molecular species in a mixture, particularly regarding

Table III Value of coefficients of the R-K polynomial and correlation coefficient (σ) for fitting of excess dielectric constant $(\epsilon_0)^E$ and excess inverse relaxation time $(1/\tau)^E$ at 293.15 K

	a_0	a_1	a_2	a_3	σ
$(\epsilon_0)^E$	−25.0951	11.3416	−5.9447	2.7449	0.9968
$(1/\tau)^E$	−0.0989	0.0579	0.0533	−0.1526	0.9802

volume changes.³² The Bruggeman parameter shows a linear relationship with volume fraction in the absence of intermolecular interactions but becomes nonlinear in the presence of such interactions, indicating the complexity of molecular dynamics within the mixture. The f_B is given by^{21,33}

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{02}}{\epsilon_{01} - \epsilon_{02}} \right) \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{\frac{1}{3}} = (1 - \phi_2) \quad (6)$$

where ϕ_2 represents the volume fraction of DMF, and ϵ_{01} , ϵ_{02} , and ϵ_{0m} indicate the static dielectric constants of *n*-octanol, DMF, and the binary mixture, respectively. Equation 6 suggests a linear relationship, resulting in a straight line when f_B is plotted against ϕ_2 .

In the studied binary system, Fig. 6 shows that deviations of the Bruggeman parameter (f_B) from linearity indicate hetero-molecular interactions between components, emphasizing the need to consider complex intermolecular dynamics in the system. Therefore, to fit the experimental data, Eq. 6 is modified as follows.^{21,31}

$$f_B = 1 - [a - (a - 1)\phi_2]\phi_2 \quad (7)$$

where a represents a numerical parameter obtained by fitting experimental data through least-squares methods. The value of the Bruggeman fitting parameter (a) offers the following insights: (i) If $a = 1$, it suggests no interaction between the components in the mixture. (ii) If $a < 1$, it indicates a reduction in the effective volume occupied by component 1 due to the presence of component 2. (iii) If $a > 1$, it suggests an increase in the effective volume of component 1 due to the presence of component 2 in the mixture.

The modified Bruggeman equation provides insights into the interaction between *n*-octanol and DMF.^{31–33} Figure 6 illustrates the relationship between the Bruggeman factor

(f_B) and the volume fraction of *n*-octanol at a constant temperature (293.15 K). The dashed line shows the linear fit, while the smooth dark line shows nonlinear behavior with numerical fitting value $a = 0.91$, indicating a decrease in the effective volume occupied by *n*-octanol due to the presence of DMF in the mixture.

Microwave Heating Parameters

Dielectric properties play a crucial role in microwave processing applications and in assessing their economic and environmental implications.^{34,35} At the widely used frequency of 2.45 GHz, dielectric measurements of parameters such as ϵ' (dielectric constant), ϵ'' (dielectric loss), and $\tan\delta$ are essential. These measurements are utilized to determine microwave heating parameters including power reflected (P_r), power transmitted (P_t), and penetration depth (d_p) across the entire concentration range (0.0 to 1.0) at a temperature of 293.15 K.

$$P_r = \left(\frac{\sqrt{\epsilon'} - 1}{\sqrt{\epsilon''} + 1} \right)^2 \quad (8)$$

$$P_t = \left[100 - \left(\frac{\sqrt{\epsilon'} - 1}{\sqrt{\epsilon''} + 1} \right)^2 \right] \quad (9)$$

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \quad (10)$$

$$d_p = \frac{\lambda_0}{2\pi} \frac{\sqrt{\epsilon'}}{\epsilon''} \quad (11)$$

In all four equations, ϵ' is the dielectric constant, ϵ'' is the dielectric loss, $\lambda_0 = \frac{c}{f}$, c is the speed of light in free space (3×10^8 m/s), and f is the microwave frequency (Hz).

Reflectance and transmittance, also known as power reflection and transmission coefficients, respectively, quantitatively indicate the proportion of incident power that is reflected and transmitted through a material or interface.

All the parameters are tabulated at the frequency 2.45 GHz in Table IV for the *n*-octanol and DMF binary liquid mixtures. Higher values of dielectric constant and dielectric loss indicate an increased capacity to absorb microwave radiation. Consequently, lower mole fractions of *n*-octanol result in higher reflected power, while higher mole fractions contribute to increased transmitted power in all *n*-octanol-DMF binary mixtures at a temperature of 293.15 K. The reflected power (P_r) decreases with an increase in the mole fraction of *n*-octanol, depending on temperature, attributed to heat losses. This leads to a corresponding increase in the

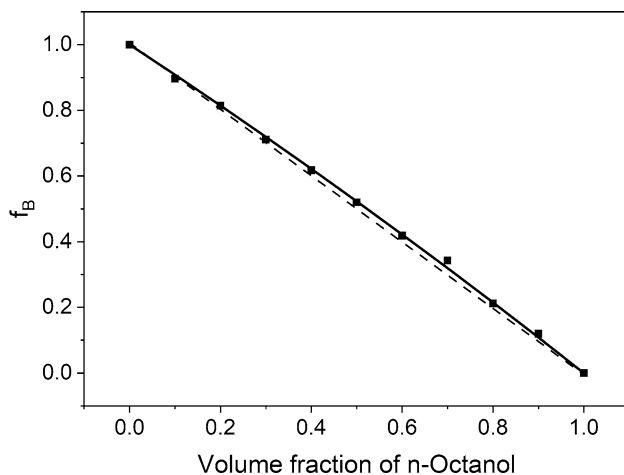


Fig. 6 Bruggeman factor (f_B) versus volume fraction of *n*-octanol.

Table IV Microwave heating parameters of mole fraction of *n*-octanol in binary mixtures of *n*-octanol + DMF at spot frequency (2.45 GHz) at 293.15 K

X_1	ϵ'	ϵ''	$\tan \delta$	P_r (%)	P_t (%)	d_p (m)
0.0000	35.930	5.847	0.163	2.135	97.865	0.020
0.0516	31.057	6.036	0.194	1.750	98.250	0.018
0.1090	27.310	6.523	0.239	1.414	98.586	0.016
0.1733	23.355	6.417	0.275	1.177	98.823	0.015
0.2459	19.767	6.293	0.318	0.965	99.035	0.014
0.3285	16.079	6.043	0.376	0.757	99.243	0.013
0.4232	12.447	5.540	0.445	0.568	99.432	0.012
0.5330	9.374	4.884	0.521	0.413	99.587	0.012
0.6618	6.260	3.346	0.535	0.282	99.718	0.015
0.8149	4.375	2.118	0.485	0.198	99.802	0.019
1.0000	2.852	0.673	0.236	0.143	99.857	0.049

percentage of transmitted power (P_t). The penetration depth plays a crucial role in the scale-up of microwave heating systems and in investigating the distribution of microwave energy within materials.

Conclusions

The complex permittivity spectra (ϵ' and ϵ'') for the *n*-octanol + DMF binary system were assessed at a constant temperature using a vector network analyzer across the frequency spectrum of 200 MHz to 20 GHz. The spectra were fitted to the Cole–Cole type of relaxation. The dielectric parameters (dielectric loss peak) show a systematic change with concentration. A deviation from linearity in both the static dielectric constant and relaxation time indicates the occurrence of intermolecular association within the system. The excess static dielectric constant (ϵ_0)^E, excess inverse relaxation time ($1/\tau$)^E, and Bruggeman parameter (F_B) were assessed and analyzed in the context of molecular interactions between dissimilar molecular species. The findings suggest that the molecules in the studied binary mixtures may engage in a network of interactions, including dipolar and hydrogen bonds, leading to the formation of stable intermolecular complexes between the molecular species. At a spot frequency 2.45 GHz, microwave energy parameters including reflected power (P_r), transmitted power (P_t), and penetration depth (d_p) were evaluated for all mole fractions of *n*-octanol at 293.15 K.

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Validation, Data Curation, Formal analysis. N. K. Acharya: Validation, Formal analysis. V. A. Rana and A. N. Prajapati: Conceptualization, Writing—Review & Editing, Supervision, Project administration.

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Study of the Refractive Index, Density, Excess Properties, and IR Spectra of a Binary Liquid Mixture (*n*-Hexanol + *N,N*-Dimethylformamide)

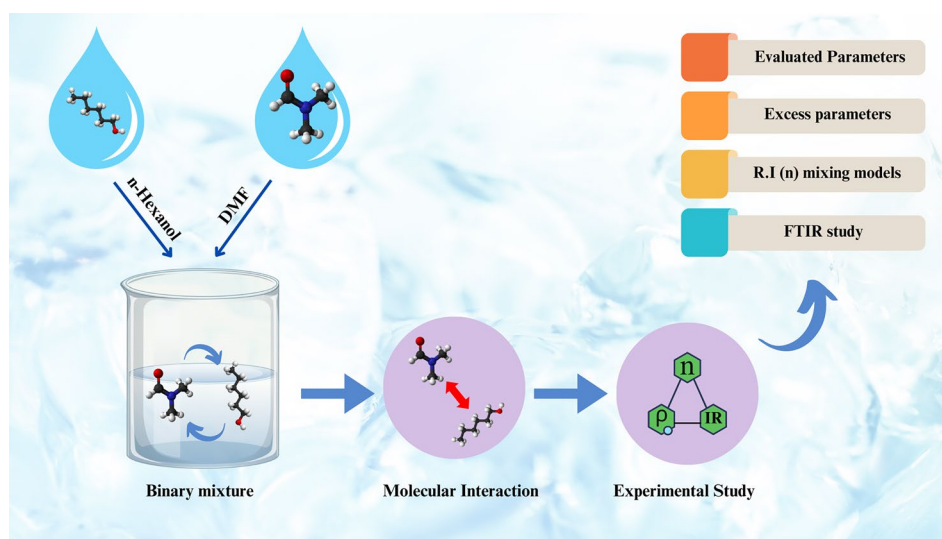
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Abstract

Refractive index (n) and density (ρ) are important physical parameters which are highly susceptible to the solution chemistry of liquids and their binary mixtures. The refractive index (n) and density (ρ) data of pure liquids are readily available in the literature, but the mixture data are often scarce. Therefore, in the present study, measurements of the refractive index (n) and density (ρ) of binary mixtures of *n*-hexanol (*n*-HxOH) with *N,N*-dimethylformamide (DMF) were performed over the composition range of 0–1 at a fixed temperature of 313.15 K. The volumetric and refractive parameters of binary mixtures were calculated using experimentally measured values of the density and refractive index. The excess parameters were evaluated and fitted to the Redlich–Kister (RK) polynomial to estimate the binary coefficients and the standard deviations. The variations in these parameters are discussed in light of molecular interactions in the mixture species. Their conformational study is supported by Fourier transform infrared (FTIR) spectroscopy. The refractive index (n) of the binary mixtures is predicted using the Lorentz–Lorentz (L–L), Weiner (Wi), Eyring–John (E–J), Gladstone–Dale (G–D), Arago–Biot (A–B), Newton (Nw), Oster (Ost), and Eykman (Eyk) mixture models. A comparison of various mixture models with experimental values of refractive indices is conducted, expressed in terms of average percentage deviation.

Graphical Abstract



Keywords Binary mixtures · refractive index · molecular interaction · FTIR

Extended author information available on the last page of the article

Introduction

In the development of industrial-level chemical processes, the refractive index (n) is a key physical property that influences the resolution of various chemical engineering problems.¹ The type of interaction taking place among the various molecules of multicomponent mixtures can be understood substantially through knowledge of the refractive index (n) of such systems.^{2–6} For generality, it should be mentioned that similar relations are widely used for the prediction of physical properties in multicomponent solid-state mediums.^{7–9} Hence, accurate predictions regarding the refractive index of multicomponent liquid mixtures provide us with different physicochemical parameters through calculations. The intermolecular interactions in such liquid systems are better understood by the determination of physicochemical properties and validation of mixing rules.¹⁰ Performing these kinds of investigations provides researchers with explicit information regarding the molecular dynamics of molecules present in liquid mixtures. Many macroscopic properties of fluid mixtures, such as intermolecular interactions and structural features, can be obtained utilizing the experimental thermophysical properties.¹¹ In the exploration of novel design processes in chemical engineering, knowledge of the physicochemical properties of pure alcohols and their multicomponent mixtures formed with an amide reduces the considerable burden on scientists investigating various mixtures of alcohols.^{12–15} Another important characteristic of these liquid systems is hydrogen bonding, whose fundamental nature in defining other physical and chemical properties makes it a hot topic in the current scientific research community. Because of hydrogen bonding, $-OH$ groups produce associative liquids. In order to understand the effect of other groups, understanding the nature of hydrogen bonding is critical.^{16–18} Accordingly, N,N -dimethylformamide (DMF) is chosen as a representative molecule of the amide solvents based on its solubility, polar non-aqueous nature, and purity.^{19,20} In the present study, a detailed exploration of the refractive indices (n) of the binary mixtures of n -hexanol and DMF is reported for a temperature of 313.15 K. To calculate the molar volume (V_m), molar refraction (R_m), atomic polarization (P_A), polarizability (α), molecular radii (r), average molecular radii (r_{ave}), and internal pressure (P_{int}) of the binary liquid

mixtures, the experimental values of the refractive index and density were utilized. To gain a more comprehensive understanding of the physical properties of the investigated mixtures, we computed the excess refractive index (Δn), excess molar volume (ΔV_m), excess reduced molar free volume [$\Delta(V_m/R_m)$], excess atomic polarization (ΔP_A), excess molecular radius (Δr), and excess internal pressure (ΔP_{int}). These values were then fitted to the Redlich–Kister (RK) polynomial equation. The refractive index values obtained in experiments were used to test the validity of eight different refractive index mixture models. Fourier transform infrared (FTIR) spectral analysis was also carried out to identify the functional groups present in the mixtures, revealing intramolecular hydrogen bonding among the molecules.

Experimental

n -Hexanol and DMF (AR grade) were procured from Loba Chemie (India) and were used without further purification. These two liquids were used to prepare binary mixture systems, which were created at a constant temperature (313.15 K) in hermetically sealed glass vials with 11 volume concentrations spanning the entire mixing range (0.0 $\rightarrow$ 1.0). The refractive index (n) of the binary mixtures was measured using an Abbe refractometer with a sodium D-line source (wavelength 589 nm) and accuracy of ± 0.0001 . For measuring the density of liquid binary mixtures, a standard specific gravity bottle was used. A constant temperature of 313.15 K was used for all the measurements.

A constant-temperature bath was used to control the temperature thermostatically. FTIR measurements of binary liquid mixtures of n -hexanol with DMF were carried out with an ALPHA (Bruker, Germany) FTIR spectrometer with precision of 0.05 cm^{-1} . The FTIR spectra were obtained in the region of $4000\text{--}400\text{ cm}^{-1}$. Table I shows a comparison of the experimental and literature values for the refractive index and density of pure n -hexanol and DMF at 313.15 K.

Table I Comparison of experimental and literature values of pure compounds at 313.15 K

Compound	Refractive index (Expt.)	Refractive index (Lit.)	Density (g/cm ³) (Expt.)	Density (g/cm ³) (Lit.)
n -Hexanol	1.4126	1.4100 ²¹	0.7960	0.8034 ²²
N,N -Dimethylformamide	1.4246	1.4220 ²³	0.9382	0.9311 ²⁴

Results and Discussion

Evaluated Parameters of Binary Liquid Mixtures

It can be observed that the experimental values obtained in this study are in good agreement with the literature values.^{21–24} Values of the molar volume (V_m) were determined from the experimentally determined density (ρ) of the pure substances and their mixtures.¹⁵

$$V_m = \frac{(X_i M_i + X_j M_j)}{\rho}, \quad (1)$$

where X_i and X_j are the mole fractions of *n*-hexanol and DMF, M_i and M_j are their molecular masses, and ρ is the density of their solutions.

Information regarding the presence of certain intermolecular interactions in the binary liquid mixture can be obtained by the molar refraction (R_m).²⁵

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2} \right) V_m, \quad (2)$$

where n is the refractive index of the liquid and $V_m = M/\rho$ is the molecular volume, with M and ρ representing the molecular weight and the density of the pure liquid, respectively.

The atomic polarization (P_A) is calculated from the refractive indices (n) of pure substances and mixtures using the following equation.²⁶

$$P_A = 1.05n^2, \quad (3)$$

where n indicates the refractive index of the liquid.

The Lorentz formula is used to calculate the molecular polarizability (α) of the liquid.²⁷

$$\alpha = \frac{3V_m}{4\pi N} \left(\frac{n^2 - 1}{n^2 + 2} \right), \quad (4)$$

where N is the Avogadro constant and V_m is the molar volume.

Molecular radii are key indicators of the structural characteristics of pure liquids and their mixtures. When liquids are combined, their behavior changes due to variations in the strength of interactions between different molecules. A number of efforts have been made to theoretically predict these molecular radii.²⁸ In our study, we calculated both the individual molecular radii (r) and the average molecular radii (r_{ave}) of pure liquids and their binary mixtures using refractive index data. The molecular radii of pure liquids were calculated by the following relation.²⁹

$$r = \left[\left\{ \left(\frac{3}{4\pi N} \right) \left(\frac{n^2 - 1}{n^2 + 2} \right) \right\} V_m \right]^{\frac{1}{3}}. \quad (5)$$

The well-known Buchler–Hirschfelder–Curtiss equation of state can be used to calculate the internal pressure of binary liquid mixtures.¹¹

$$P_{int} = \frac{2^{\frac{1}{6}} RT}{2^{\frac{1}{6}} V_m - 2rN^{\frac{1}{3}} V_m^{\frac{2}{3}}}. \quad (6)$$

where the variables T , V_m , r , N , and R represent the absolute temperature, molar volume, molecular radius, Avogadro's constant, and universal gas constant, respectively.

It is apparent from Table II that there is a considerable difference between the refractive index, density, and molar mass values of *n*-hexanol and DMF ($n_{HxoH} = 1.4126$, $n_{DMF} = 1.4246$, $\rho_{HxoH} = 0.7960$ g/cm³, $\rho_{DMF} = 0.9382$ g/cm³, $M_{HxoH} = 102.18$ g/mol, $M_{DMF} = 73.09$ g/mol). Therefore, the internal field in the pure state would be expected to differ significantly from the internal field in the mixed state. In

Table II Values of refractive index (n), density (ρ), molar volume (V_m), molar refraction (R_m), and atomic internal pressure (P_{int}) for the binary liquid mixtures of *n*-hexanol with *N,N*-dimethylformamide at 313.15 K

X_i	n	ρ (g/cm ³)	V_m (cm ³ /mol)	R_m (cm ³ /mol)	P_A (cm ³ /mol)	α Å ³	r Å	r_{ave} Å	P_{int} (MPa)
0.0000	1.4246	0.9382	77.9045	19.9037	2.1310	0.7894	1.99	1.9912	111.95
0.0639	1.4236	0.9270	81.1280	20.6845	2.1280	0.8204	2.01	2.0118	107.33
0.1331	1.4220	0.9190	84.6211	21.5038	2.1232	0.8529	2.04	2.0342	102.63
0.2084	1.4202	0.9130	88.4191	22.3849	2.1178	0.8878	2.07	2.0585	97.94
0.2905	1.4192	0.8990	92.5636	23.3852	2.1148	0.9275	2.10	2.0851	93.40
0.3805	1.4180	0.8920	97.1044	24.4708	2.1113	0.9706	2.13	2.1142	88.86
0.4795	1.4168	0.8640	102.1011	25.6652	2.1077	1.0179	2.16	2.1462	84.35
0.5890	1.4160	0.8390	107.6262	27.0085	2.1053	1.0712	2.20	2.1816	79.91
0.7107	1.4146	0.8230	113.7680	28.4653	2.1011	1.1290	2.24	2.2210	75.43
0.8468	1.4134	0.8060	120.6359	30.1069	2.0976	1.1941	2.28	2.2650	71.00
1.0000	1.4126	0.7960	128.3668	31.9818	2.0952	1.2685	2.33	2.3145	66.63

binary liquid mixtures, there is a wide range of possible molecular interactions between the constituents, including hydrogen bonding, molecular association, dipole–dipole, and dipole–induced dipole interactions, whereas in the case of *n*-hexanol and DMF, there is a small difference in the refractive index values. These interactions result in a deviation from the ideal behavior of the refractive index with the concentration of the mixture constituents. When DMF is added into the *n*-hexanol, the refractive index of the binary mixture decreases (Table II).

A close perusal of Table II reveals that the experimentally derived refractive index (n) and density (ρ) of the binary liquid mixtures decreases as the mole fraction of *n*-hexanol increases. This is possible because *n*-hexanol has a low packing density and an open structure. The molecules are connected to each other by H bonds that are formed by the molecules themselves. According to the refractive index, molar refraction (R_m) is an estimation of the volume occupied by an atom or molecule. It can be observed that the molar volume (V_m), molar refraction (R_m), polarizability (α), molecular radii (r), and average molecular radii (r_{ave}) increase as the mole fraction of *n*-hexanol increases in the binary liquid mixtures. The increased concentration of *n*-hexanol leads to an increase in the molecular radii because of the lower packing fraction of *n*-hexanol and reduction in the number of DMF molecules in the mixture system, while the opposite trend is observed for atomic polarization (P_A) and internal pressure (P_{int}). There is a large difference in internal pressure values of the pure components ($P_{int} = 66.63$ MPa [*n*-hexanol] and $P_{int} = 111.95$ MPa [MF]) that suggests a strong possibility of hetero interaction in molecular species.³⁰

Excess Parameters of Binary Liquid Mixtures

The excess function provides an idea of the amount of deviation of a given liquid mixture from ideality. The nature of molecular movement and intermolecular interactions in heteromolecules is fundamentally dependent on excess properties. In the present study, we calculated the excess refractive index (Δn), excess molar volume (ΔV_m), excess reduced molar free volume [$\Delta(V_m/R_m)$], excess atomic polarization (ΔP_A), excess molecular radii (Δr), and excess internal pressure (ΔP_{int}) of the binary mixtures. They are evaluated using the following equations^{11,15,29}:

$$\Delta n = n_m - (n_i X_i + n_j X_j), \quad (7)$$

$$\Delta V_m = V_m - (V_{mi} X_i + V_{mj} X_j), \quad (8)$$

$$\Delta \left(\frac{V_m}{R_m} \right) = \left(\frac{V_m}{R_m} \right) - \left[\left(\frac{V_{mi}}{R_{mi}} \right) X_i + \left(\frac{V_{mj}}{R_{mj}} \right) X_j \right], \quad (9)$$

$$\Delta P_{A_m} = P_{A_m} - (P_{A_i} X_i + P_{A_j} X_j), \quad (10)$$

$$\Delta r = r_m - (r_i X_i + r_j X_j), \quad (11)$$

$$\Delta P_{int} = P_{int m} - (P_{int i} X_i + P_{int j} X_j), \quad (12)$$

where X is the mole fraction of binary mixtures. The subscripts m , i , and j denote mixtures of molecular species *n*-hexanol and DMF, respectively. The deviations Δn , ΔV_m , (ΔP_{A_m}), $\Delta(V_m/R_m)$, Δr , and ΔP_{int} were fitted by the RK polynomial function²⁶:

$$A^E = (X_i X_j) \sum_k a_k (X_i - X_j)^k, \quad (13)$$

where a_k represents the polynomial coefficients obtained using the least squares regression approach to fit the equation to the experimental results. The standard deviations (σ) were calculated using the relation¹⁸

$$\sigma = \left[\frac{\sum (A_{\text{experimental}}^E - A_{\text{calculated}}^E)^2}{N - n} \right]^{\frac{1}{2}}, \quad (14)$$

where n is the number of coefficients and N is the number of experimental data points. The values of the coefficients (a_0 , a_1 , a_2 , a_3) and correlation constant (Δ) are shown in Table III.

Figure 1 shows the variation in the deviation and excess functions versus the mole fraction of *n*-hexanol. The solid line (curve) in Fig. 1 shows the calculated values (RK polynomial-fitted), and the round points represent the experimental values of deviation/excess functions. It can be observed from Fig. 1 that the values of Δn , ΔV_m , ΔP_A , and ΔP_{int} are

Table III Values of coefficients of the Redlich–Kister polynomial with correlation constant

Parameters	Δn	ΔV_m	$\Delta(V_m/R_m)$	ΔP_A	Δr	ΔP_{int}
a_0	−0.0077	−50.4624	0.0609	−0.0231	0.0507	−23.2274
a_1	0.0060	−0.0013	−0.0483	0.0180	−0.0003	6.5637
a_2	−0.0026	0.0050	0.0217	−0.0076	−0.0029	−1.8171
a_3	−0.0117	−0.0045	0.0968	−0.0354	−0.0182	−1.3186
Δ	0.9850	1.0000	0.9845	0.9855	0.9989	0.9999

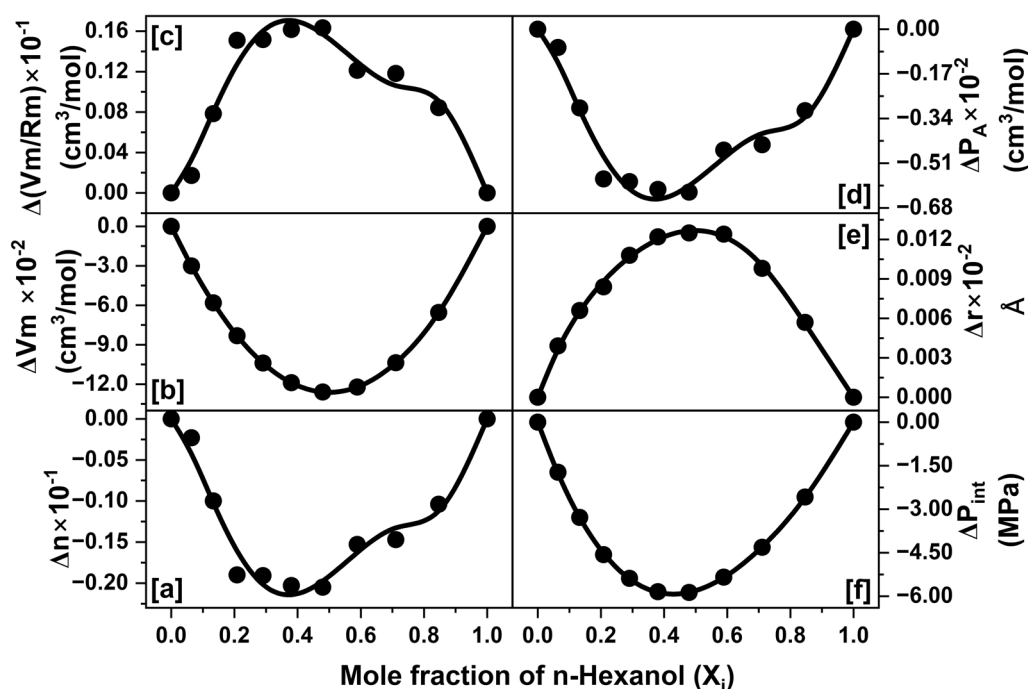


Fig. 1 Variation in excess functions (a) Δn , (b) ΔV_m , (c) $\Delta(V_m/R_m)$, (d) ΔP_A , (e) Δr , and (f) ΔP_{int} versus mole fraction of *n*-hexanol (X_1).

negative, while the values of $\Delta(V_m/R_m)$ and Δr show the reverse trend over the whole composition range (0.0 $\rightarrow$ 1.0).

The variation in the deviation of the refractive index versus mole fraction of *n*-hexanol is shown in Fig. 1a. Here, a negative deviation is seen over the entire composition range. The negative Δn values show a maximum at around 0.38 mole fraction of *n*-hexanol. It is observed that the variation in the refractive index is influenced by a number of different energetic and structural effects.³¹ The negative deviation (Δn) indicates a weak interaction between the mixture components.³²

The sign of ΔV_m of a system depends on the relative magnitude of the expansion and contraction upon mixing of two liquids. When the factors causing expansion outweigh the factors causing contraction, ΔV_m becomes positive, but if the contractive factors become more powerful than expansion factors, ΔV_m becomes negative. The factors causing positive ΔV_m include (i) the breaking of H bonds of one compound by another, or breaking up of links held together by weaker physical forces, such as dipole–dipole or dipole–induced dipole interactions, (ii) the geometry of the molecular structure which does not favor fitting of the molecules with each other, and (iii) steric hindrance, which opposes the proximity of the constituent molecular species. The factors causing negative ΔV_m include (i) chemical interactions between the components through H bonds, (ii) association through weaker physical forces, such as dipolar forces or any other forces of this kind, (iii) lodging of molecules of one component into the interstitials of the structural network

of molecules of another component, and (iv) geometry of molecular structures which favors fitting of the component molecules with each other.³³ The ΔV_m values for the binary mixture *n*-hexanol + DMF are found to be negative for the whole concentration range of *n*-hexanol. When *n*-hexanol is added to DMF, at least some proportion of *n*-hexanol (in the form of multimers in pure form) is dissociated into monomers, which results in volume expansion. The monomers so formed are thought to enter into the interstitial sites of DMF, causing volume contraction because $(V_m)_{DMF} > (V_m)_{n\text{-hexanol}}$. This contraction is believed to be larger than expansion; the net effect is therefore negative excess molar volume (ΔV_m). The other factors responsible for the volume contraction include the possible association between *n*-hexanol and DMF through H bonds and some weak association of DMF through physical forces such as dipolar types of interactions.

The excess reduced molar free volume is shown in Fig. 1c, and it is positive over the whole composition range at constant temperature. The refractive index deviation function must be computed on a volume fraction basis, whereas the molar refraction deviation function must be computed on a mole fraction basis.² This makes it possible for it to be directly understood as a measure of the expressed deviations of reduced free volumes from ideality. Figure 1d shows the negative behavior of excess atomic polarization which indicates the strong heteromolecular interaction between molecular species. The nonlinear positive trend of the deviation in molecule radii is seen in Fig. 1e. This suggests that the formation of a hetero complexion via hydrogen bonds between

dissimilar molecules is less important than the breaking of the chain of H bonds in *n*-hexanol. The negative deviation observed in internal pressure in Fig. 1f suggests that there are more repulsive forces than attractive forces.³⁴

Refractive Index Mixture Models

Several molecular interactions can be observed in binary mixtures since their constituents are composed of different types of compounds. In that sense, we test the applicability of the most important mixing rules suitable for predicting the refractive index in different physical situations to the binary mixtures under consideration. In the present work, the following mixing relations are evaluated.^{29,35}

Eyring–John (E–J) model:

$$n = n_i \varphi_i^2 + 2(n_i n_j)^{1/2} \varphi_i \varphi_j + n_j \varphi_j^2. \quad (15)$$

Gladstone–Dale (G–D) model:

$$n - 1 = [n_i - 1] \varphi_i + [n_j - 1] \varphi_j. \quad (16)$$

Arago–Biot (A–B) model:

$$n = n_i \varphi_i + n_j \varphi_j \quad (17)$$

Newton (Nw) model:

$$n^2 - 1 = [n_i^2 - 1] \varphi_i + [n_j^2 - 1] \varphi_j. \quad (18)$$

Lorentz–Lorentz (L–L) model:

$$\frac{n^2 - 1}{n^2 + 2} = \left[\frac{n_i^2 - 1}{n_i^2 + 2} \right] \varphi_i + \left[\frac{n_j^2 - 1}{n_j^2 + 2} \right] \varphi_j. \quad (19)$$

Weiner (Wi) model:

$$\left[\frac{n^2 - n_i^2}{n^2 + 2n_i^2} \right] = \left[\frac{n_j^2 - n_i^2}{n_j^2 + 2n_i^2} \right] \varphi_i. \quad (20)$$

Eykman (Ey) model:

$$\frac{n^2 - 1}{n + 0.4} = \left[\frac{n_i^2 - 1}{n_i + 0.4} \right] \varphi_i + \left[\frac{n_j^2 - 1}{n_j + 0.4} \right] \varphi_j. \quad (21)$$

Oster (Ost) model:

$$\frac{(n^2 - 1)(2n^2 + 1)}{n^2} = \left[\frac{(n_i^2 - 1)(2n_i^2 + 1)}{n_i^2} \right] \varphi_i + \left[\frac{(n_j^2 - 1)(2n_j^2 + 1)}{n_j^2} \right] \varphi_j. \quad (22)$$

The average percentage deviation (APD) is determined by

$$APD = \frac{100}{n} \sum_{i=n} \left(\frac{|\delta_{\text{expi}} - \delta_{\text{cali}}|}{\delta_{\text{expi}}} \right), \quad (23)$$

where n_m , n_i , and n_j indicate the refractive indices of the mixture, the solvent, and the solute, respectively, and φ_i and φ_j denote the volume fractions of the solvent and the solute, respectively.

The predicted and experimentally determined refractive indices of the binary mixtures at 313.15 K are compared, and the APD of the results for different models is shown in Fig. 2. A close perusal of Fig. 2 reveals that the Gladstone–Dale (G–D) and Arago–Biot (A–B) relations provide identical APD values. The APD values predicted by the Weiner (Wi), Eyring–John (E–J), Gladstone–Dale (G–D), Arago–Biot (A–B), Newton (Nw), Oster (Ost), and Eykman (Ey) relations are greater than those predicted by Lorentz–Lorentz (L–L), which is the best fit for the studied system. All theoretical mixture models perform well within the limits of experimental error.

FTIR Study of Binary Liquid Mixtures

FTIR spectroscopy is performed to provide an enhanced understanding of the interactions in specific binaries as predicted by refractive index study. The spectra are taken for pure liquid and liquid mixtures of *n*-hexanol + DMF for the entire composition range (0.0 → 1.0) at room temperature. The IR spectra of *n*-hexanol with DMF binary liquid mixtures for all the concentrations (0.0 → 1.0) are shown in Fig. 3. Here, an increase in the intensity of the O–H peak at 3500 cm^{−1} is observed as a function of *n*-hexanol concentration.^{36,37} The second peak of the carbonyl group (C=O) is characteristic of amides, for which a strong absorption

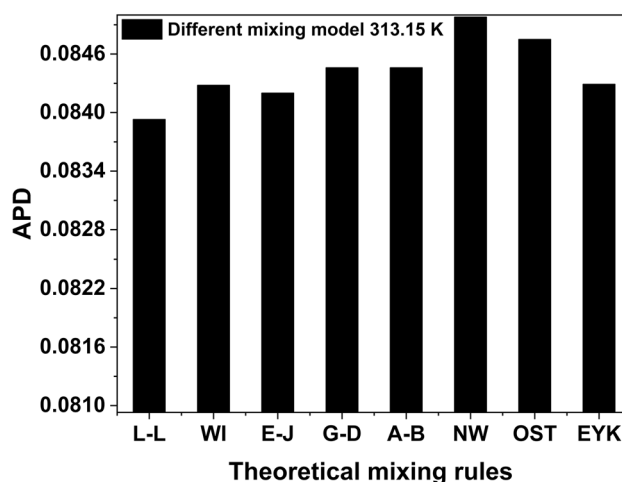


Fig. 2 Plot of APD as a function of different theoretical refractive index mixture models.

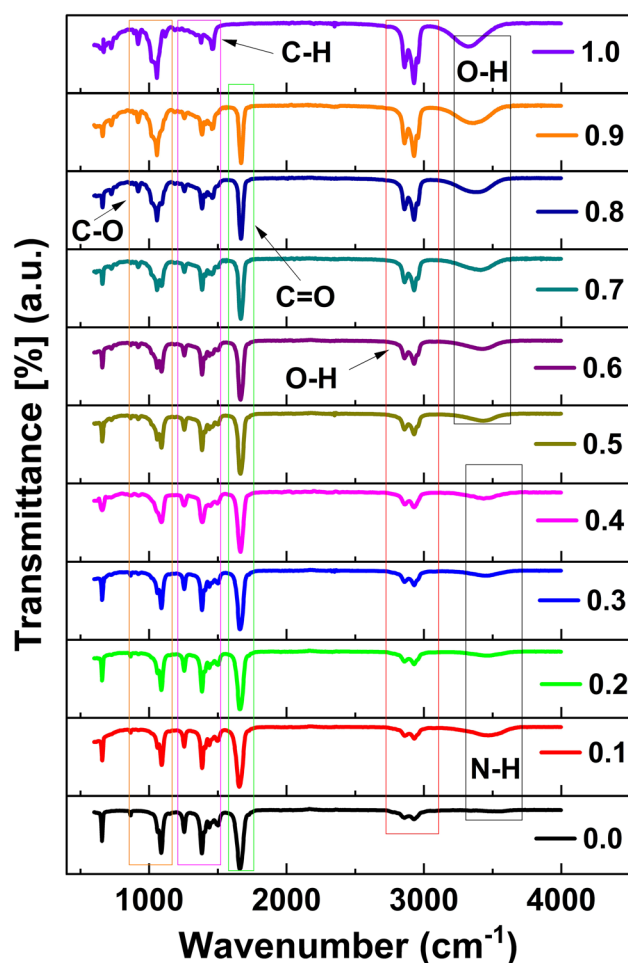


Fig. 3 Variation in IR spectrum for *n*-hexanol + DMF binary liquid mixtures.

band is observed in the region of $1500\text{--}1900\text{ cm}^{-1}$ due to the C=O stretching vibration. It is observed in Fig. 3 and supplementary data Table SI that in the concentration range $0.0 \leq X_1 \leq 0.4$, a small-magnitude N–H peak is present, whereas a broad O–H peak is clearly seen. The wavenumber of the stretching vibration increases if the surrounding groups increase the double-bond nature of the carbonyl group. The absorption spectra of these substances in solutions, therefore, contain characteristic bands of N–H and O–H vibrations of the monomer and the associated molecules.³⁸ The intensity of the C–O stretching peak at around $1000\text{--}1200\text{ cm}^{-1}$ and C–H stretching at around $1200\text{--}1400\text{ cm}^{-1}$ is decreased at lower DMF concentrations.

Conclusions

In the present study, the density and refractive index of binary liquid mixtures throughout the entire mixing composition range were considered. Good agreement was found

between the experimental and literature values for the refractive index and density of the *n*-hexanol and DMF mixture at 313.15 K. The atomic polarization of the binary mixtures decreased with the decreasing mole fraction of *n*-hexanol. The molar volume, polarizability, and molecular radii increased with increasing volume fraction of *n*-hexanol. A negative deviation in internal pressure indicated the appearance of complexation between molecular species. Values of Δn , ΔV_m , $\Delta(V_m/R_m)$, ΔP_A , Δr , and ΔP_{int} were calculated, and the results of deviation/excess functions were fitted to the RK equation. Various mixture models for the refractive index were tested for the system. For the refractive index (*n*), the L–L mixture model showed the smallest deviation among all models. The variations in position and intensity of the IR bands related to the functional groups indicated the molecular association in the liquid mixtures.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11664-024-11434-w>.

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Author Contributions N. A. Chaudhary: Conceptualization, Methodology, Software, Validation, Formal analysis, Writing—Original draft. S. P. Patel: Methodology, Validation, Formal analysis. M. K. Prajapati: Validation, Formal analysis. N. K. Acharya and A. N. Prajapati: Conceptualization, Writing—Review & editing, Supervision, Project administration.

Availability of Data and Materials Data and material will be made available on request.

Conflict of interest The authors declare that there are no competing interests as defined by Springer, or any other interests that might be perceived to influence the results and/or discussion reported in this paper.

Ethical Approval The authors confirm that the manuscript follows ethical guidelines.

Consent for Publication The authors agree with the publishing policy and submit this manuscript in accordance with this policy.

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Electrode polarization and ionic conduction relaxation in n-Hexanol and DMF Mixtures at 303.15 K: insights into molecular dynamics

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Abstract

Using a precision LCR meter, the real and imaginary components of the complex relative dielectric function ($\epsilon^*(f) = \epsilon'(f) - j\epsilon''(f)$) of the binary mixtures of n-Hexanol and N, N-Dimethylformamide were measured in the frequency range of 20 Hz to 2 MHz at a constant temperature of 303.15 K. Complex relative dielectric function $\epsilon^*(f)$, was then converted into various formalisms namely: complex electric modulus $M^*(f)$, complex electrical conductivity $\sigma^*(f)$, and complex impedance $Z^*(f)$ in order to explore the electric and dielectric characteristics of the liquid samples. Loss tangent ($\tan \delta = \epsilon''/\epsilon'$) was determined from the complex relative dielectric function $\epsilon^*(f)$. Further, $\epsilon^*(f)$ was fitted to the Cole–Cole relaxation model to determine different dielectric and electrical parameters. Relaxation time associated with various relaxation processes observed in the considered frequency range of applied ac electric field are determined. Measured dielectric data are used to gain information about the effect of electrode polarization relaxation and ionic conduction relaxation process in the given mixture. Various parameters, including Debye Length (λ_D), Ion Mobility (μ), Mobile Ion Concentration (P_0), and Ion Diffusivity (D) were computed for each binary mixture across constant temperature.

Keywords Binary Mixtures · Cole–Cole Model · Molecular Interaction · Precision LCR meter

Introduction

In order to probe the intermolecular structures of liquid mixtures and investigate their molecular dynamics, dielectric spectroscopy is a powerful technique widely used in the field. The dielectric spectroscopy involves analysis of the complex permittivity spectra measured by varying the frequencies of the electrical signals at varying temperatures or at a fixed temperature [1]. The dynamic electric and

dielectric behaviour of molecules present within a weakly conducting dipolar liquid system are easily studied using this experimental method. It has been a difficult task to study the dielectric properties of conducting materials for the research community. Some special technical measures need to be taken for getting reliable data from the experiments in such cases [2]. Various investigations on weakly conducting dipolar solvents have concluded that these solvents can be thermally activated through ionic impurities. However, this phenomenon is observed only at frequencies lower than that of the molecular reorientation relaxation frequency, usually lying below the microwave region [2–6].

In recent years, there has been a tremendous attention from the scientific community towards dielectric relaxation spectroscopy (DRS) studies on the dipolar liquids within static permittivity region, encompassing frequencies from a few Hertz to a few megahertz [2, 7–10]. Within this region, dielectric relaxation resulting due to dipolar rotation of molecules is absent, and the relaxation mechanism is mainly governed by the electrode polarization and ionic conductivity processes. In this frequency range, the polar liquids exhibit changes in their dielectric properties due to the ionic conduction processes and the electrode polarization. These

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changes are the result of the volatile ionic impurities or added ions in the liquid mixtures. Several researchers have concluded that even in their pure forms, highly polar liquids show presence of these impurities [7, 9, 11–13]. The combined effects of ionic conduction processes and electrode polarization (EP) shape the dielectric spectrum of polar liquids in the lower-middle frequency regions. The values of the complex dielectric function of such liquids are determined on these two phenomena [2, 14]. Due to the accumulation of ions at the interface between the electrode and dielectric, electric double layer (EDL) is formed resulting in the electrode polarization (EP). On the other hand, the transition from the direct current (DC) to alternating current (AC) for the transportation of the ions in the liquids results in the well-known ionic conduction process [4, 5, 14]. Moreover, the thickness (Debye length) of the ion layer at the electrode surface can be determined from the low-frequency complex permittivity data which is often influenced by electrode polarization [2, 10].

Alcohols and amides are the center of interest among the protic and aprotic solvents. Due to their ability of forming hydrogen bonds, the alcohols play a crucial role in all the scientific fields such as chemistry and biology. Alcohols, which are self-associated liquids, constitute a three-dimensional network of hydrogen bond due to which they can interact with other chemical groups having some degree of polar attractions. Hence, alcohols have demanded a noteworthy attention from many researchers due to its complex and interesting nature [1, 15–17]. Within the chemical industry, amides are an important class of solvents owing to their high polarity and strong solvating power. Because of its long-chained molecule and its wide use in petrochemical, agricultural and pharmaceutical industries [18], we have chosen n-Hexanol as one of the components of the binary liquid system to be investigated. The other component of the binary liquid mixture is DMF belonging to the amide group. A considerable interest has been subjected towards the study of various properties of DMF due to its association to the proteins and peptides [19–21].

The primary aim of the ongoing investigation is to explore the concentration-dependent dielectric properties of binary mixtures of polar liquids the n-Hexanol and the N, N-Dimethylformamide (DMF), across a frequency spectrum of 20 Hz to 2 MHz. We investigated the complex dielectric permittivity spectra $\epsilon^*(f)$, the complex electric modulus spectra $M^*(f)$, the complex impedance spectra $Z^*(f)$ and the complex ac electric conductivity spectra $\sigma^*(f)$ of the binary mixtures of different concentrations of n-Hexanol, and DMF at constant temperature (303.15 K).

Materials and methods

n-Hexanol and N, N-Dimethylformamide of analytical reagent (AR) grade were procured from Loba Chemie (India) and utilized without any further purification. These liquids were mixed with eleven different volume concentrations (X_A) ranging from 0.0 → 1.0 in hermetically sealed glass vials. Purity, Grade, CAS No, comparison of static permittivity (ϵ_0) of pure compound with literature values are tabulated in Table 1. The experiments were conducted at a constant temperature of 303.15 K. The complex dielectric spectra $\epsilon^*(f)$ of the liquid samples were determined using an Agilent E4980A precision LCR meter. A four-terminal liquid dielectric test fixture, Agilent 16452A model, was utilized for measuring capacitance and resistance within the frequency range spanning from 20 Hz to 2 MHz [22]. The capacitance and parallel resistance of the liquid dielectric test fixture were measured both with and without samples. The correction coefficient of the test fixture was also considered to eliminate the impact of stray capacitance when determining the value of the complex dielectric function. To determine the complex dielectric permittivity of the samples $\epsilon^*(f)$ we have used the following equation [23].

$$\epsilon^*(f) = \epsilon' - j\epsilon'' = \alpha \left(\frac{C_p}{C_0} - j \frac{1}{\omega C_0 R_p} \right) \quad (1)$$

In Eq. (1), the real part of the complex permittivity is a measure of the electrical energy storage capabilities of the dielectric material, and the imaginary part indicates an average energy loss per cycle due to the joules heating effect, $\omega = 2\pi f$ is the angular frequency, α is the correction coefficients of the cell, C_p is the capacitance of the test fixtures with sample, C_0 is the capacitance of the test fixture without sample, and R_p is the parallel resistance of the test fixtures with sample. The temperature of the binary liquid samples during measurement was carefully maintained using a constant temperature water bath supplied by MIC Fourtech, India. This water bath maintained a high level of accuracy, with a standard accuracy of ± 0.1 K.

Table 1 Chemicals used and their Purity, Grade, CAS No, and comparison of static permittivity (ϵ_0) of pure liquid with literature values at 303.15 K temperatures

Compound	Purity (%)	Grade	Cas No	Static Permittivity	(ϵ_0)
				Exp	Lit
N,N-Dimethylformamide	99.8	AR	68–12-2	36.22	36.65 ²⁰
n-Hexanol	99.0	AR	111–27-3	12.36	12.11 ²⁵

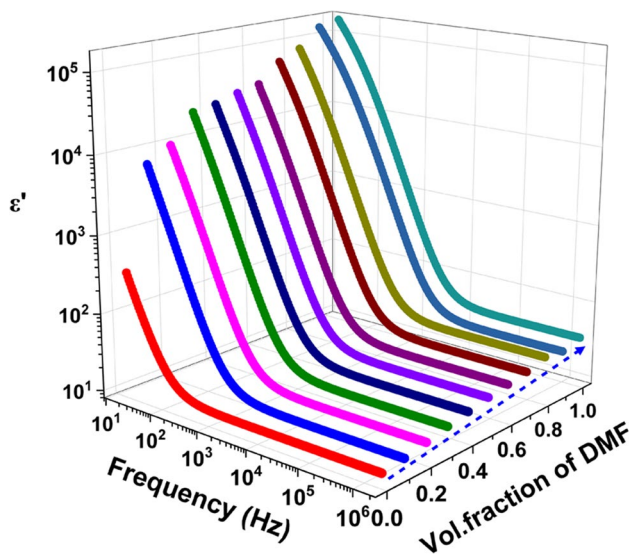


Fig. 1 Frequency dependent response of ϵ' against volume fraction of DMF

Results and discussion

Complex dielectric permittivity spectra

Figure 1 shows the frequency-dependent dielectric constant (ϵ') values of n-Hexanol + DMF binary mixtures of various volume fractions at constant temperature 303.15 K. It can be seen from the figure that the permittivity spectra ϵ' are divided into two different regions: higher frequency region (frequency independent plateau region), and lower frequency region (frequency dependent nonlinear region). In the higher frequency region above 10^3 Hz, the real part of permittivity spectra is independent of the frequency, providing static value of dielectric constant. In the lower frequency region below 10^3 Hz, there is an observed increase in the real part (ϵ') value with an increase in the volume fraction of DMF with an increase in frequency. High values of real part of permittivity (ϵ') observed at low frequencies regions are attributed to the EP (electron polarization) effect [5]. For these dielectric materials, the strength of the electric double layer (EDL) decreases with the increase of frequency, due to which the real part (ϵ') approaches the static permittivity (ϵ_0) above 10^3 Hz, as shown in Fig. 1. The inset in Fig. 1 indicates that static permittivity (ϵ_0) rises with an increase in DMF concentration, particularly at the spectral endpoints. At these frequencies, pure DMF exhibits a higher real part of the dielectric function ϵ' compared to pure n-Hexanol, pointing to an enhanced molecular polarization strength in the DMF system. The ϵ_0 values of n-Hexanol and DMF are tabulated in Table 1. It can be seen from Table 1 that experimental values of static dielectric constant (ϵ_0) of n-Hexanol and DMF are in good agreement with the literature values.

Figure 2 shows the imaginary part (ϵ'') for varying volume fractions of DMF within the n-Hexanol mixtures which reveal a strikingly consistent linear frequency dependence on log–log scale, with a slope of $-1.00 (\pm 0.02)$ for all mixture concentrations, in accordance with the equation $\epsilon'' = \frac{\sigma_{dc}}{\omega\epsilon_0}$. Very large values of imaginary part (ϵ'') at low frequency is due to ionic conduction loss. The dielectric constant, dielectric loss values, and AC conductivity at 303.15 K for n-Hexanol and DMF at various frequency points are presented in Table 2. This outcome verifies that n-Hexanol possesses a higher concentration of ionic impurities compared to DMF.

To address this, we utilized the Cole–Cole model [25] and specifically employed the Havriliak–Negami (HN) equation [26], which is given by

$$\epsilon^*(f) = \epsilon_\infty + \frac{\Delta\epsilon_{EP}}{[1 + (i\omega\tau_{EP})^\alpha]^\beta} \quad (2)$$

where $\Delta\epsilon_{EP} = \epsilon_{0(EP)} - \epsilon_0$, ϵ_0 is indicate the static dielectric constant, $\epsilon_{0(EP)}$ = low-frequency dielectric constant in the presence of EP and τ_{EP} = is the electrode polarization relaxation, α and β = the asymmetry and broadness parameters of the dielectric loss peaks.

A complex nonlinear least square (CNLS) fitting procedure, as described in reference [27] was executed to fit the experimental data to Eq. (1). During the complex nonlinear least squares (CNLS) fitting procedure, $\Delta\epsilon_{EP}$, ϵ_0 , and τ_{EP} were chosen as the fitting parameters. The fitted plots of complex dielectric spectra ($\epsilon^*(f)$) to the Cole–Cole model (using Eq. (1) set $\beta = 1$) for $X_A = 0.5$ volume fraction of DMF, alongside their corresponding experimental values,

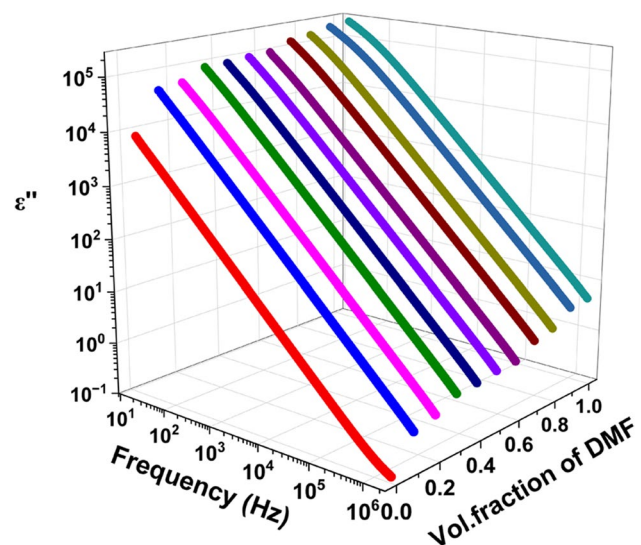
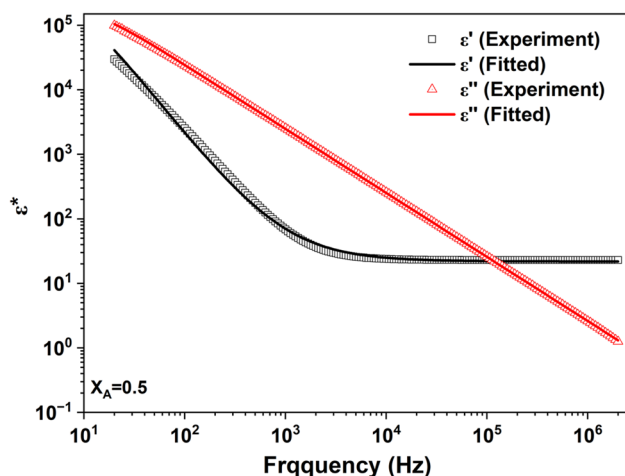


Fig. 2 Frequency dependent response of ϵ'' at different volume fractions of DMF

Table 2 Values of dielectric constant (ϵ'), dielectric loss (ϵ''), and AC conductivity (σ') of n-Hexanol and DMF at different frequencies at 303.15 K temperature

Frequency (Hz)	n-Hexanol			DMF		
	(ϵ')	(ϵ'')	(σ') (S/cm)	(ϵ')	(ϵ'')	(σ') (S/cm)
20	3.50E+02	8.75E+03	9.73E-06	1.56E+05	2.26E+05	2.52E-04
100	3.49E+01	1.77E+03	9.84E-06	2.46E+04	7.96E+04	4.44E-04
1000	1.29E+01	1.78E+02	9.93E-06	5.59E+02	9.67E+03	5.39E-04
10 K	1.24E+01	1.80E+01	1.00E-05	4.39E+01	9.93E+02	5.53E-04
50 K	1.23E+01	3.61E+00	1.01E-05	3.65E+01	2.00E+02	5.57E-04
100 K	1.23E+01	1.82E+00	1.01E-05	3.62E+01	1.00E+02	5.59E-04
500 K	1.23E+01	3.80E-01	1.06E-05	3.61E+01	2.01E+01	5.60E-04
1 M	1.23E+01	2.08E-01	1.16E-05	3.61E+01	1.00E+01	5.60E-04
1.5 M	1.24E+01	1.50E-01	1.30E-05	3.61E+01	6.27E+00	5.54E-04
2 M	1.24E+01	1.31E-01	1.45E-05	3.62E+01	4.93E+00	5.48E-04

**Fig. 3** Shows the experimental and fitted complex dielectric function (ϵ^*) data to the Cole–Cole model using CNLS for the concentration range ($X_A = 0.5$).

are depicted in Fig. 3. The Cole–Cole model exhibits an outstanding fit to the experimental results. Similar fitting results were obtained across the concentration range of $0.0 \leq X_A \leq 1.0$. The best-fit values of the fitting parameters for all concentrations ($0.0 \rightarrow 1.0$) are tabulated in Table 3. It indicates that the static permittivity value increases with increased volume fraction of DMF. Furthermore, electrode polarization relaxation time values undergo an anomalous change with increasing concentration of the mixture.

Figure 4 shows the loss tangent ($\tan \delta = \epsilon''/\epsilon'$) spectra at low frequencies serve as a useful tool for separating the dielectric properties of the bulk material from the frequency regime affected by electrode polarization (EP) [1, 5, 7, 10]. The $\tan \delta$ spectra has a peak value corresponding to the electrode polarization (EP) relaxation frequency f_{EP} . The $\tan \delta$ plot of n-Hexanol, DMF, and n-Hexanol + DMF binary mixtures, illustrated in Fig. 4, exhibit peaks in the frequency range approximately from 10^2 to 10^4 Hz, representing the EP relaxation process (EDL dynamics) at the frequency f_{EP} . The value of f_{EP} for n-Hexanol is found to be at 112.46 Hz, and it gradually shifts toward the higher frequency side with increasing DMF concentration in these

Table 3 Values of fitted parameters ϵ_0 , $\Delta\epsilon_{EP}$, τ_{EP} , relaxation time (τ_{EP}) and ionic polarization relaxation time (τ_σ) and dc conductivity (σ_{dc}) for mixtures of n-Hexanol and DMF

X_A	ϵ_0	$\Delta\epsilon_{EP}$	τ_{EP} (ms)	τ_{EP} (μ s)	τ_σ (μ S)	σ_{dc} (μ S/m) (From Fig. 9)	σ_{dc} (μ S/m) (Using Eq. 7)
0.0	12.20	2.53E+05	227.20	1415.83	10.62	1.01E-05	1.01E-05
0.1	13.18	3.23E+05	50.65	266.69	2.00	5.87E-05	5.78E-05
0.2	14.90	3.18E+05	39.24	199.99	1.78	7.73E-05	7.58E-05
0.3	17.11	3.42E+05	26.38	141.58	1.26	1.23E-04	1.21E-04
0.4	19.32	3.16E+05	23.55	133.66	1.42	1.29E-04	1.27E-04
0.5	21.82	3.14E+05	20.90	126.19	1.42	1.45E-04	2.03E-04
0.6	24.11	2.85E+05	18.46	119.13	1.50	1.49E-04	2.15E-04
0.7	26.30	3.30E+05	13.26	79.62	1.00	2.45E-04	2.41E-04
0.8	27.99	2.49E+05	4.900	75.16	1.00	2.94E-04	2.91E-04
0.9	31.39	3.24E+05	10.83	35.56	0.53	5.14E-04	5.08E-04
1.0	33.44	3.02E+05	53.72	39.90	0.56	5.59E-04	5.53E-04

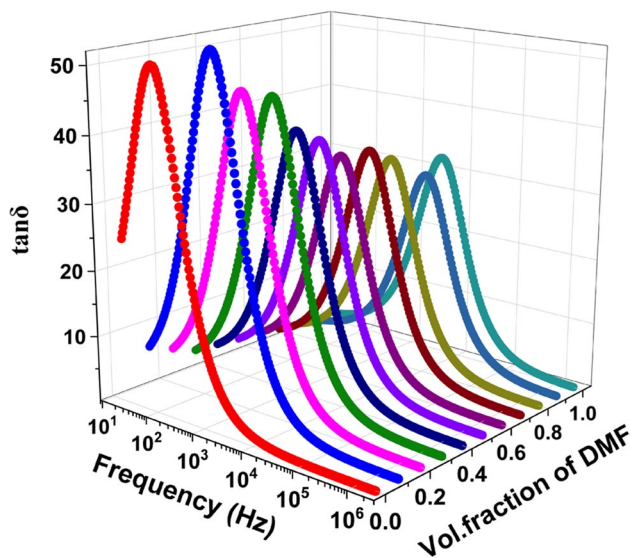


Fig. 4 Frequency dependent response of $\tan \delta$ against volume fraction of DMF

binary mixtures. The EP relaxation time (τ_{EP}), reflecting the charging and discharging time of the electric double layer (EDL) in these binary mixtures was calculated using the formula ($\tau_{EP} = (2\pi f_{EP})^{-1}$) and tabulated in Table 3

Complex electrical modulus spectra study

The dynamics of the ionic conductivity relaxation process in ion-conducting materials can be investigated by suppressing the dynamics of electric double layers (EDLs) through the conversion of dielectric spectra into electric modulus [28]. Electric modulus spectra were also analyzed to investigate the behavior of the conductivity relaxation mechanism. The frequency-dependent real (M') and imaginary (M'') parts of the complex electric modulus values for liquid mixtures were obtained using the equation [28–30].

$$M^*(f) = M' + jM'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} + j \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (3)$$

where ϵ' and ϵ'' represent the real and imaginary parts of permittivity, respectively.

Figure 5 represents 3D plot of the real part of complex electric modulus spectra for all mixtures across a range of frequencies at a temperature of 303.15 K. The values of M' over the EP-dominated low-frequency range (below 10^4 Hz) were found to be relatively small and nearly constant. This behavior is attributed to the suppression of high capacitance phenomena in the modulus formalism at these frequencies [10]. It has been observed that as the frequency range in which the ϵ' values gradually approach a steady state (as shown in Fig. 1), the M' values exhibit dispersion. These

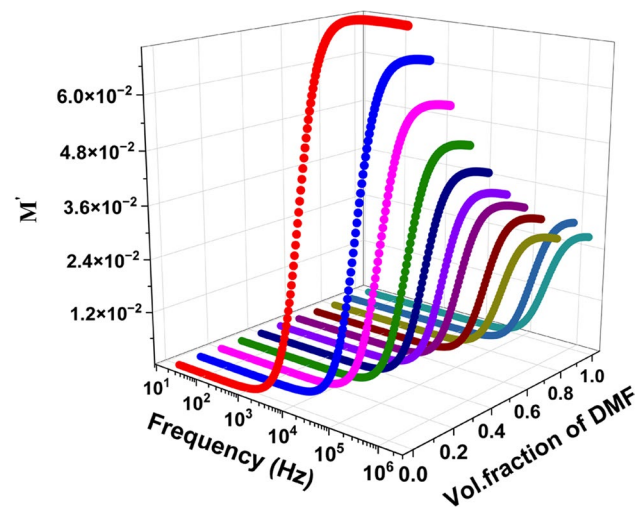


Fig. 5 Frequency dependent response of M' against volume fraction of DMF

spectra eventually reach a steady state in the higher frequency region [29, 30]. In the higher frequency region, M' values exhibit an increase as the frequency increases. In the mid-frequency region, for higher concentrations of DMF, the value of M' increases with an increase in frequency, approaching a constant level in the MHz range of frequency.

Figure 6 depicts 3D plot of the M'' for all mixtures across a range of frequencies at a temperature of 303.15 K. The M'' spectra exhibit dispersion in the frequency region between the frequencies f_{EP} and f_{σ} , which correspond to the $\tan \delta$ peak and M'' peak, respectively. A peak is observed for all the binary mixtures in the imaginary part of the electric modulus. The peak is observed in the higher frequency

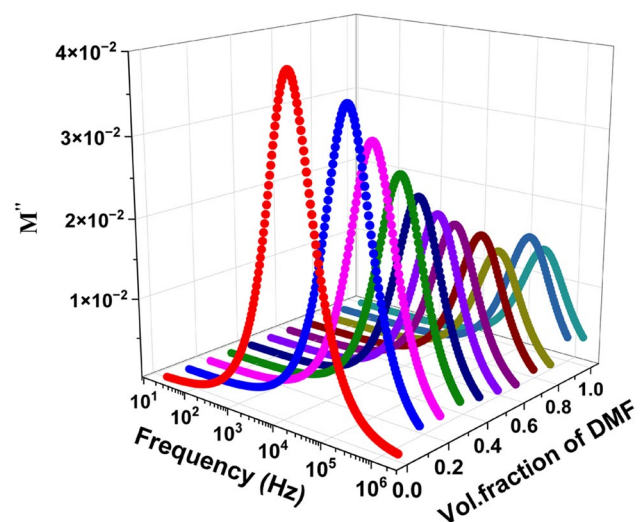


Fig. 6 Frequency dependent response of M'' against volume fraction of DMF

region for higher concentrations of DMF, and as the concentration of DMF decreases, the peak shifts towards lower frequencies. The frequency f_{σ} corresponding to the peak value of M'' is related to the ionic conductivity relaxation time $\tau_{\sigma} = (2\pi f_{\sigma})^{-1}$ [28–30]. The values of the ionic conductivity relaxation time, τ_{σ} , for various concentrations are reported in Table 3. The conductivity relaxation time for n-Hexanol is 10.60 μ S, which is 19 times higher than the relaxation time of DMF (0.56 μ S). From the observations, it can be concluded that the EDL relaxation process requires more time than the conductivity relaxation process. This is evident as the values of τ_{σ} are smaller than the values of τ_{EP} by two orders of magnitude.

Figure 7 illustrates the complex modulus plot (M'' vs. M') for mixtures of n-Hexanol and DMF at 303.15 K, varying the volume fraction of DMF. The observed Debye-type behavior in the complex modulus plot indicates a characteristic relaxation process in the ionic conductivity [1]. Furthermore, this behavior permits the scaling of the master curve for the electric modulus spectra in the binary system. The intercept of the M'' versus M' arc on the M' axis, specifically on the higher frequency side, yields the value of static permittivity ($\epsilon_0 = (M_{\infty})^{-1}$). The determined values of the static permittivity of the mixture samples (n-Hexanol + DMF) obtained from the M'' versus M' plots align with the static permittivity measured at a frequency of 2 MHz.

The correlation between the three relaxation times τ_{EP} , τ'_{EP} and τ_{σ} presents an intriguing avenue for exploration. Figure 8 shows the frequency-dependent variations of ϵ'' (dielectric loss), $\tan \delta$ (dissipation factor), and M'' (imaginary part of the complex modulus) for liquid samples at 303.15 K with compositions $X_A = 0.0$, $X_A = 0.5$, and $X_A = 1.0$. Various relaxation time is obtained like τ_{EP} is determined dielectric

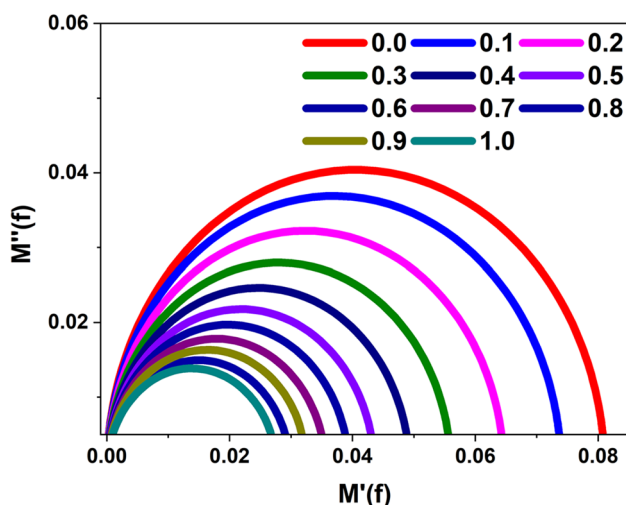


Fig. 7 Complex electric modulus plane plots ($M''(f)$ vs. $M'(f)$) for the binary mixtures of n-Hexanol and DMF

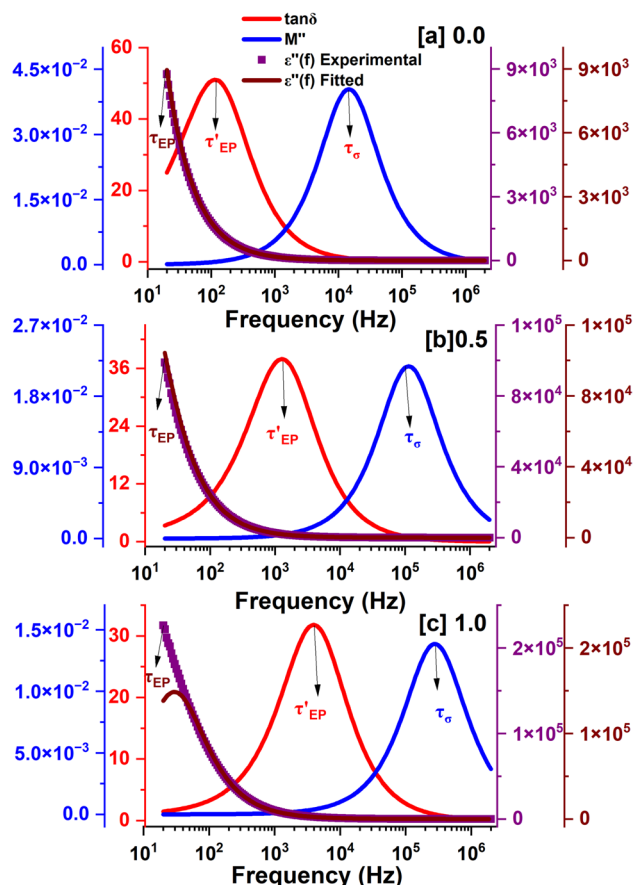


Fig. 8 Relationship between τ_{EP} , τ'_{EP} and τ_{σ} for $X_A = 0.0$, $X_A = 0.5$, and $X_A = 1.0$

loss spectra, τ'_{EP} is determined with the tangent ($\tan \delta$) spectra and τ_{σ} is evaluated with imaginary modulus (M'') spectra and can be related by relation $\tau'_{EP} = (\tau_{EP} \times \tau_{\sigma})^2$ [28, 29]. It can be seen from the graph that for all the concentration ranges the peak is shifting towards the higher frequency region as the concentration of the mixture increases. The relaxation frequency associated with electrode polarization in the ϵ'' plot is lower than the relaxation frequency observed in the $\tan \delta$ plots. Consequently, the electrode polarization relaxation time (τ'_{EP}) has a higher value compared to the relaxation time (τ_{EP}). All different relaxation time values anomalous behavior is observed in Table 3.

Complex electric conductivity spectra

The AC electrical conductivity values, including the real part (σ') and imaginary part (σ''), are obtained across frequencies spanning from 20 Hz to 2 MHz for n-Hexanol + DMF binary mixtures. This analysis relies on the relationship between complex conductivity and complex permittivity, as expressed in Eq. 4.

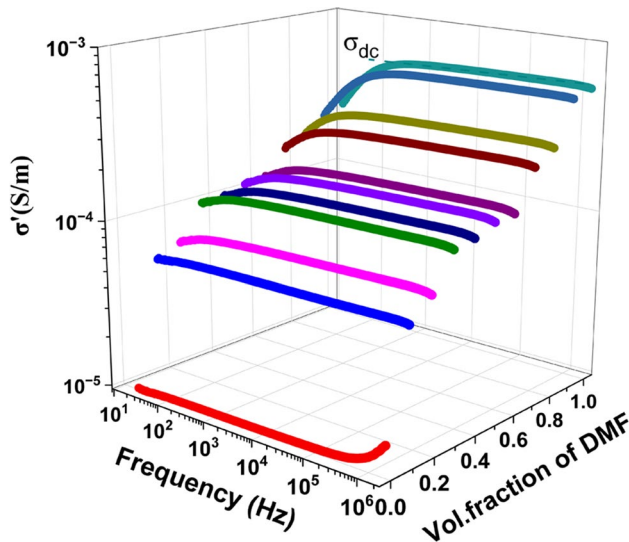


Fig. 9 Frequency dependent response of σ' against volume fraction of DMF

$$\sigma^*(f) = \sigma' + j\sigma'' = \omega\epsilon_0\epsilon'' + j\omega\epsilon_0\epsilon' \quad (4)$$

In the equation, ω represents the angular frequency, ϵ_0 is the permittivity of free space (8.854×10^{-12} F/m), ϵ' is the real part of permittivity, and ϵ'' is the imaginary part of permittivity, respectively.

Figure 9 illustrates the frequency-dependent σ' for n-Hexanol, DMF, and their binary mixtures. In this plot we observe two distinct regions: a dispersion part at low frequencies and a frequency-independent plateau at higher frequencies. These characteristics are noticeable within the low and mid-concentration range of DMF ($0.1 \leq X_A \leq 1.0$). The observed dispersion in the low-frequency region is attributed to interfacial impedance or space charge polarization [31]. As the frequency decreases, the density of accumulated charges at the electrode and material interface gradually increases. This accumulation results in a decrease in the number of mobile ions, eventually leading to a drop in conductivity at low frequencies. In the high-frequency region, the mobility of charge carriers is high, leading to an increase in conductivity with frequency [32]. Furthermore, In Fig. 9, the solid line represents the DC conductivity (σ_{dc}) within the σ' spectra. Initially, σ' shows a nonlinear increase with frequency, stabilizing beyond 2 kHz. These σ_{dc} values are derived from the frequency-independent plateau region of σ' values, painted by the straight line (using DMF concentration). Table 3 presents both calculated (from Eq. 7) and experimental σ_{dc} values for the n-Hexanol + DMF mixtures at this temperature. Notably, the σ_{dc} values for pure DMF (5.59×10^{-04} μ S/m) are approximately one order of magnitude higher than those of n-HxOH (1.01×10^{-05} μ S/m), consistent with the higher static dielectric constant (ϵ_0) of DMF.

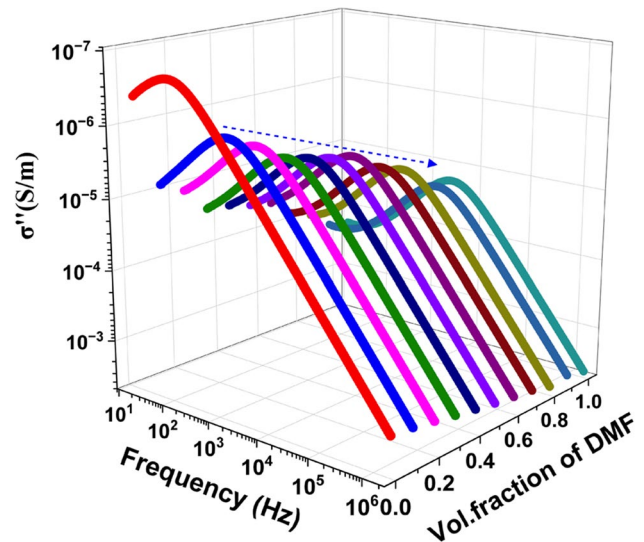


Fig. 10 Frequency dependent response of σ'' against volume fraction of DMF

Figure 10 shows the σ'' against volume fraction of DMF and their mixture in the frequency range 20 Hz to 2 MHz at constant temperature (303.15 K). In Fig. 10, the imaginary part of conductivity shows a clear segmentation into two separate regions. Within the initial region, spanning up to 10^3 Hz, the peak of σ'' exhibit a linear decline for both DMF and higher concentrations of DMF. In the intermediate frequency range, σ'' peak values reach a minimum. The frequency at which σ'' reaches its minimum matches precisely with the frequency of the peak in $\tan \delta$ shown in Fig. 4. This alignment implies that analyzing σ'' spectra can provide insights into the dynamics of electric double layers (EDLs) in dipolar liquids. In the higher frequency range (second region), above 10^3 Hz, the values of $\sigma''(\omega)$ exhibit a linear decrease when plotted on a log–log scale for concentrations ranging from 0.0 $\rightarrow$ 1.0.

Figure 11, Illustrates the variation of $\ln(\sigma_{dc})$ for DMF, n-Hexanol, and their mixture against $1000/T$. These changes follow the Arrhenius-type behavior, indicating that the dc conductivity follows an exponential relationship with temperature. The activation energy (E_a) for conductivity can be calculated using the Arrhenius equation [1].

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where A_0 is the pre-exponential factor, is the E_a activation energy, T is the absolute temperature, and R is the gas constant. The concentration-dependent activation energy (E_a) using DC conductivity (σ_{dc}) are tabulated in Table 4. It has been observed Table 4 that $E_{a \text{ n-Hexanol}} > E_{a \text{ DMF}}$. For the mixture concentration E_a values show the anomalous behaviour.

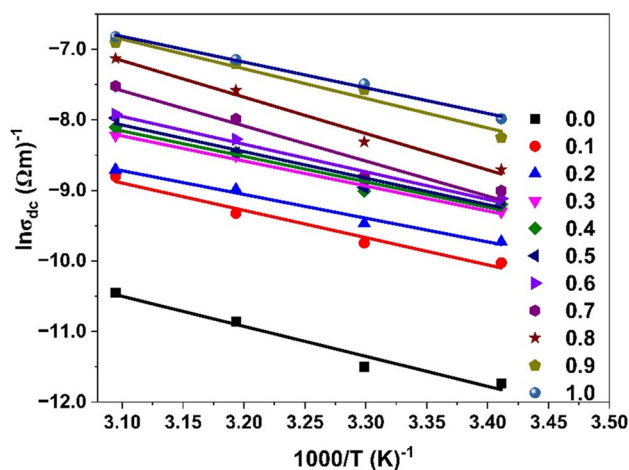


Fig. 11 Arrhenius plots of dc conductivity (σ_{dc}) for the binary mixture of DMF and n-Hexanol

Complex impedance spectra

In lower-frequency dielectric spectroscopy, polar liquid materials commonly exhibit two phenomena: electric double layer (EDL) and conductivity relaxation processes. These processes are typically identified by examining the imaginary part of the complex impedance spectra [12]. The real (Z') and imaginary part (Z'') of impedance plots are common methods for discerning bulk material properties and phenomena associated with electrode surface polarization. Dielectrics with DC conductivity typically exhibit a discontinuity at the electrode/dielectric interface, characterized by distinct polarization properties compared to the bulk material. The frequency-dependent Z' and Z'' components of the complex impedance ($Z^*(f)$) can be determined using Eq. (6) [29].

$$Z^*(f) = Z' - jZ'' = \frac{\epsilon''}{\omega C_0(\epsilon'^2 + \epsilon''^2)} - j \frac{\epsilon'}{\omega C_0(\epsilon'^2 + \epsilon''^2)} \quad (6)$$

In this Eq., ω stands for angular frequency, C_0 represents the electric capacity of the empty measuring cell, ϵ' indicates the real part of permittivity, and ϵ'' represents the imaginary part of permittivity.

Figure 12 shows the real part of the complex impedance spectra Z' for n-Hexanol + DMF binary mixture at constant temperature (303.15 K). It is observed that Z' exhibits a rapid decrease across the entire frequency range for the concentration range of $0.0 \leq X_A \leq 1.0$. The frequency-dependent

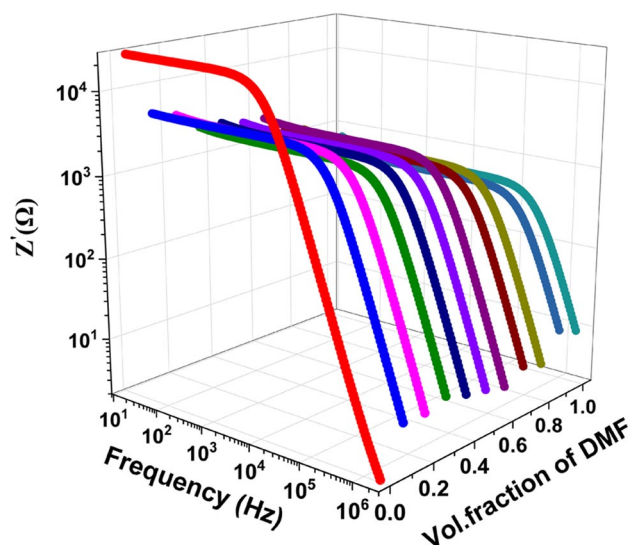


Fig. 12 Frequency dependent response of Z' against volume fraction of DMF

Z' values for n-Hexanol (with low static permittivity) are observed to be higher compared to those of DMF (with high static permittivity). Furthermore, the values for binary mixtures of n-Hexanol and DMF fall in between these two extremes [30].

Figure 13 depicts the Z'' exhibits both minima and maxima, indicated as f_{EP}' and f_{σ} respectively. f_{EP}' signifies the frequency at which the static dielectric constant (ϵ_0) begins to increase as the frequency decreases, indicating the onset of the Electric Double Layer (EDL) relaxation process [28]. Furthermore, f_{σ} corresponds to the conductivity relaxation process and coincides with the peak in the imaginary part of the electric modulus ($M''(f)$) Fig. 7). The derived values of f_{EP}' and f_{σ} were utilized to compute the respective relaxation times, τ_{EP} and τ_{σ} , employing the general relation $\tau = \frac{1}{2\pi f}$. These calculated relaxation times are reported in Table 3.

Figure 14 exhibits the complex impedance plot ($Z'' \rightarrow Z'$) for the concentration range $0.0 \leq X_A \leq 1.0$ for the binary mixtures of n-Hexanol + DMF. The plot indicates semi-circular Debye type arc for all concentration range (the inset represents the same figure for the concentration range $0.1 < X_A < 1.0$). The size of semi-circular arc decreases as the concentration of DMF increases in n-Hexanol. At higher frequencies, the arc represents the bulk behavior of the material. As frequency decreases, an inclined straight line emerges at lower

Table 4 Values of Activation energy (E_a) using dc conductivity (σ_{dc}) for the binary mixture of DMF and n-Hexanol

X_A	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
E_a (kJ/mol)	35.34	32.14	27.97	29.46	30.01	31.33	32.59	41.4	42.92	34.88	30.24

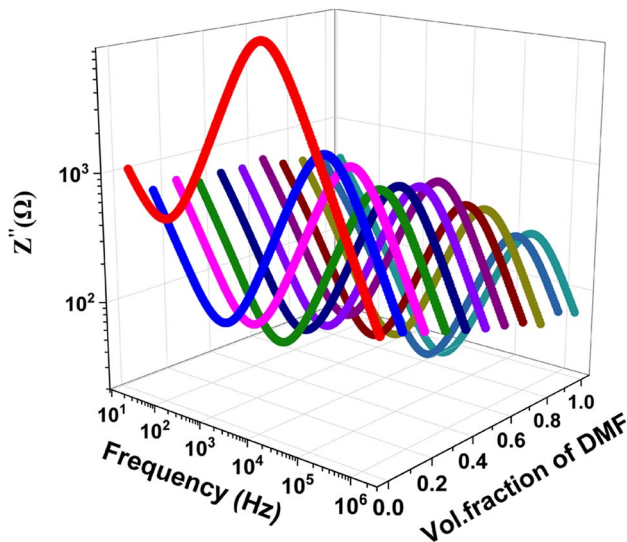


Fig. 13 Frequency dependent response of Z'' against volume fraction of DMF

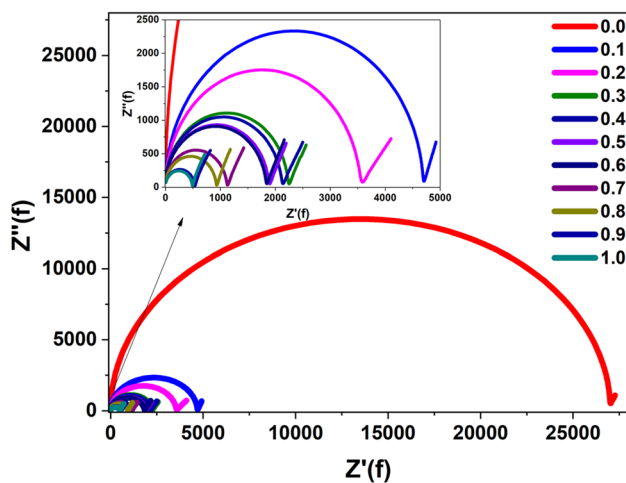


Fig. 14 Complex impedance plot ($Z'' \rightarrow Z'$) for n-Hexanol + DMF binary mixture in the frequency range 20 Hz to 2 MHz

frequencies, indicating the prevalence of the Electric Polarization (EP) effect [33]. The size of the semicircular arc changes depending on the concentration of DMF. By intersecting this arc with the Z' axis, we obtain direct current resistance (R_{dc}) values for the dipolar liquids. Notably, there's an inverse relationship between R_{dc} and ϵ_0 for pure n-Hexanol, DMF, and their mixtures, consistent with a determined correlation [1].

$$\sigma_{dc} = \frac{\epsilon_0 \epsilon_v}{\tau_\sigma} = \frac{t_g}{R_{dc} A} \quad (7)$$

Here, ϵ_0 represents the static dielectric constant, ϵ_v is the permittivity of vacuum, τ_σ is the relaxation time for ionic

conductivity, t_g is the gap between the parallel plates, and A is the surface area of the capacitance cell plate. The direct current resistance (R_{dc}) values were then used to calculate the direct current conductivity (σ_{dc}) using Eq. (4), with the results presented in Table 3.

Complex impedance plane plots are further analyzed using Electrochemical Impedance Spectroscopy (EIS), an important technique for studying relaxation processes in liquids [3].

The impedance data of the studied samples were fitted to a six-element equivalent circuit, which represents the measuring capacitive cell. The equivalent circuit for its impedance is depicted as an inset in Fig. 15. Experimental impedance data for all mixture concentrations were best fitted to the equivalent circuit model. Figure 15 presents representative plots depicting both experimental and fitted data points for concentration is $X_A = 0.0$, $X_A = 0.5$ and $X_A = 1.0$.

The EC-Lab software was instrumental in identifying the components of the equivalent circuit that represents the dielectric measurement cell. By utilizing Eq. (8) [3] to fit experimental data points, which corresponds to the Randles Cell Circuit model, the software facilitated the analysis of complex impedances.

$$Z(f) = R_1 + \frac{R_2}{1 + i\omega R_2 C_2} + \frac{R_3}{1 + i\omega R_3 C_3} + \frac{\sqrt{2\sigma_4}}{\sqrt{i\omega}} \quad (8)$$

Here, R_1 represents the dielectric measurement cell's resistance, the second term indicates the electrode polarization effect, the third term indicates the conduction process, and σ_4 indicates the Warburg element (a constant phase element, or CPE, with a phase of 45°), which is corresponding

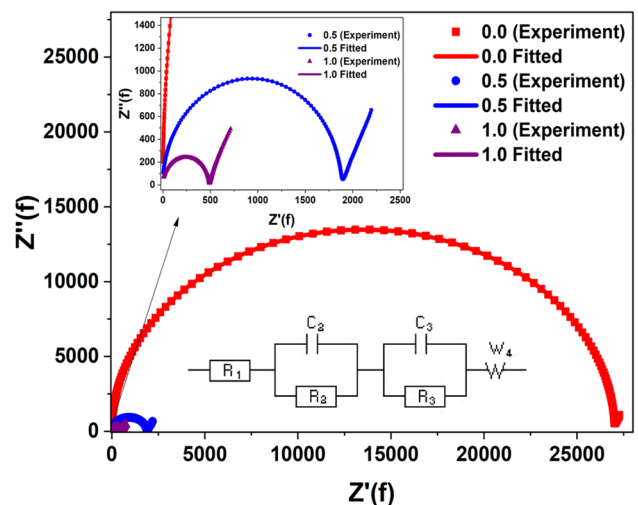


Fig. 15 The graphical representation of experimental data points along with fitted data points of complex impedance spectra plot (Z'' vs Z') using an equivalent RC circuit. The concentrations represented are $X_A = 0.0$, $X_A = 0.5$, and $X_A = 1.0$

to the Warburg impedance (W_4) in the Randles cell circuit model. The Warburg element is used to interpret the mechanism of the diffusion process in the low frequency region.

Table 5 presents the parameters obtained from fitting the equivalent circuit, providing crucial insights into the electrical behavior of the system. These parameters enable the examination of multiple relaxation behaviors for all concentrations. Additionally, the relaxation times, including the electric double layer formation time constant (τ_{EDL}) and the geometric relaxation time constant (τ_g), are calculated using Eqs. (9) and (10) respectively for all concentrations.

$$\tau_{EDL} = R_2 C_2 \quad (9)$$

$$\tau_g = R_3 C_3 \quad (10)$$

It can be observed from Table 5 that the volume fraction of DMF increase with a decrease in bulk resistance values (R_{dc}). It is clearly observed that the R_3 value and bulk resistance for all concentrations are nearly equal and observed geometric relaxation time (τ_g) and ionic conduction relaxation time (τ_σ) (In Table 3) for all the concentrations are almost equal. The value of electric double layer formation time constant (τ_{EDL}) and the geometric relaxation time constant (τ_g) anomalous behavior for all concentrations.

Figure 16 indicates the $\tan \delta$, Z'' (Imaginary part of impedance), M'' (Imaginary part of modulus), σ'' (Imaginary part of conductivity) on the same frequency scale for both pure n-Hexanol + DMF and volume fraction $X_A = 0.5$. This master plot is important because it helps us understand the various relaxation processes in dipolar liquids. It also guides us in choosing the right spectrum to study a particular relaxation process effectively [10, 29]. Vertical dotted lines in the master curve mark the locations of Electric Double Layers (EDLs) and conductivity relaxation processes. In the Z'' spectra, we see both relaxation processes clearly with peaks and valleys, while the other spectra only show one of the two relaxation processes. This analysis suggests

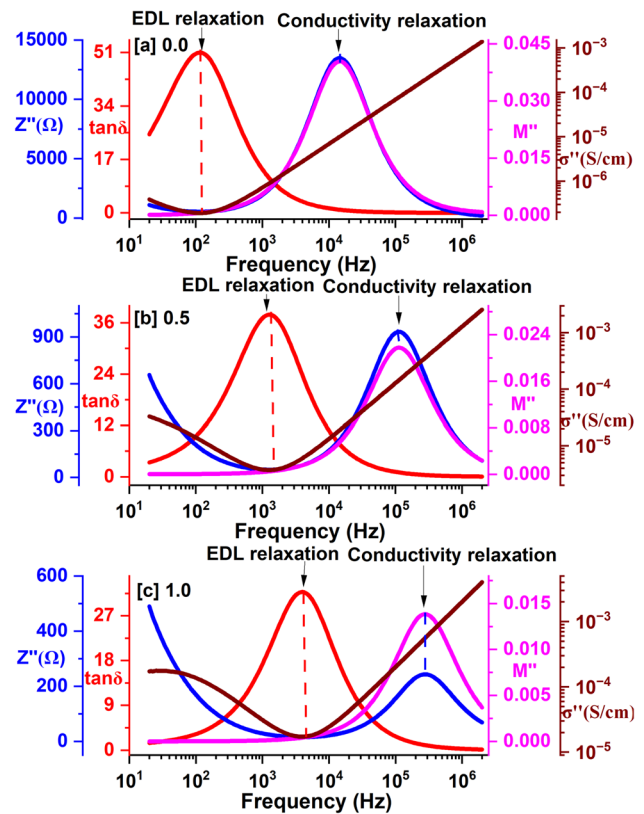


Fig. 16 Master curves showing EDL and conductivity relaxation processes for $X_A = 0.0$, $X_A = 0.5$, and $X_A = 1.0$

that when studying the relaxation processes caused by ionic charge impurities in pure dipolar liquids and their mixtures, impedance spectroscopy is more useful than dielectric and modulus spectroscopies [28].

Klein et al. [34] introduced a model to determine the thickness of ion buildup, ion mobility, mobile ion concentration, and ion diffusivity. These parameters were computed within the concentration range ($0.00 \leq X_A \leq 1.0$) using the

Table 5 Fitted parameters of four element equivalent RC circuit for all concentration, double layer relaxation time constant (τ_{EDL}) and geometric relaxation time (τ_g)

X_A	$R_{dc} (\Omega)$	$R_1 (\Omega)$	$C_2 (\mu F)$	$R_2 (\Omega)$	$C_3 (nF)$	$R_3 (\Omega)$	$\sigma_4 (\Omega s^{-1/2})$	$\tau_\sigma (\mu sec)$	$\tau_{EDL} (s)$
0.0	27,034.89	0.522	6.82	4281	0.402	26,982	965.5	10.8468	0.0292
0.1	4705.09	0.307	9.32	1791	0.435	4699	4462	2.0441	0.0167
0.2	2249.55	0.940	18.30	625	0.505	3525	4088	1.7801	0.0114
0.3	3586.68	0.745	17.44	2220	0.579	1311	2453	0.7591	0.0387
0.4	2137.64	0.913	17.71	2103	0.662	1188	3075	0.7865	0.0372
0.5	1336.69	0.957	17.57	1865	0.749	1760	2780	1.3182	0.0328
0.6	1261.91	1.049	15.71	1813	0.829	2038	2876	1.6895	0.0285
0.7	1129.81	0.741	18.51	1326	0.911	1107	2432	1.0085	0.0245
0.8	933.78	0.803	18.27	915	1.091	1797	2080	1.9605	0.0167
0.9	534.74	1.369	18.03	1347	0.991	521.1	2271	0.5164	0.0243
1.0	491.50	1.109	19.10	1474	1.167	480.8	1661	0.5611	0.0282

Klein model. The thickness of ions built up at the electrode surface was derived using Eq. (11).

$$\lambda_D = \frac{g}{2M} \quad (11)$$

where, λ_D represents the thickness of ions built up at the electrode surface, and g indicates the electrode gap and a ratio $M = \frac{\tau_{EP}}{\tau_\sigma}$. The thickness of the Debye layer varies, with n-Hexanol having the largest thickness at 70.10 nm, while DMF has the lowest at 15.74 nm. For the mixtures, the thickness falls between these two values as tabulated in Table 6. Ion mobility (μ) is calculated using Eq. (12),

$$\mu = \frac{qg^2}{4kTM\tau_{EP}} \quad (12)$$

where q represents the electron charge, k is the Boltzmann constant, T is the absolute temperature, and τ_{EP} denotes the electric double layer formation time. Mobile ion concentration (P_0) and diffusivity (D) are determined using Eqs. (13) and (14), respectively.

$$P_0 = \frac{\sigma_{dc}}{q\mu} \quad (13)$$

$$D = \frac{\mu KT}{q} \quad (14)$$

In the equation, μ , K , T , q is representing the ion mobility, Boltzmann constant, absolute temperature (303.15 K), charge of the electron.

Specific values for mobile ion concentration and diffusivity in DMF and n-Hexanol are tabulated in Table 6.

Table 6 indicates an anomalous trend in ion mobility, notably observed in pure n-Hexanol, where it jumps from

$1.77 \times 10^{-11} \text{ (m}^2 \text{ Vs}^{-1}\text{)}$ to $6.71 \times 10^{-11} \text{ (m}^2 \text{ Vs}^{-1}\text{)}$ at $X_A = 0.1$ before declining with further increases. This behavior is attributed to n-Hexanol larger molecular size and higher viscosity. Furthermore, the volume fraction of DMF increases the ion diffusivity anomalous behaviour observed. These observations suggest that ion mobility is not only affected by molecular structure and interactions but also by the viscosity of the medium. The viscosity of the liquid, plays a crucial role in controlling ion movement within the system.

Conclusions

This report investigates the concentration-dependent dielectric and electrical properties of n-Hexanol, N, N-Dimethylformamide (DMF), and their binary mixtures at a temperature of 303.15 K in the frequency range 20 Hz to 2 MHz. The complex dielectric function of these binary mixtures in lower frequency region is governed by ionic conduction and electrode polarization phenomenon. In the low frequency region, ionic conduction and electrode polarization have a dominant influence, leading to the large values of dielectric constant (ϵ') and dielectric loss (ϵ'') in the mixtures. The loss tangent peak systematically shift for all the binary mixtures. Experimentally determined values of complex permittivity of mixtures of n-Hexanol + 1-DMF can very well be fitted into the Cole–Cole model (with α values ≈ 1) for all concentration, in which EP is represented by a simple Debye relaxation. The M' spectra show a dispersion in the frequency region between f_{EP}' and f_σ frequencies. M'' spectra show a peak in the intermediate frequency region and peak is shifted to the lower frequency as the concentration of DMF increases. Complex modulus spectra show a Debye type semicircular arc for all the concentration range. The electrode polarization relaxation time τ_{EP} and the ionic conduction relaxation time τ_σ are found to vary significantly with concentrations of DMF in the binary mixture. DC conductivity of the liquid samples calculated using complex impedance (CI) and complex ac conductivity (CC) formalisms are found to be in good agreement. Complex impedance data is fitted to the equivalent circuit model to obtain six different components. Equivalent circuit elements signify various electrical processes in the bulk sample as well as at the electrode surface and are confirmed by the Bode plot analysis of the complex impedance data. Z'' spectra exhibit EDL and ionic relaxation processes in the considered frequency region while $\tan \delta$, M'' and σ'' exhibit either EDL process or ionic relaxation process. Anomalous type of behavior is observed in the Ion Mobility, Debye Length, Mobile Ion concentration, and Ion Diffusivity. This type of study on dielectric properties and relaxation processes induced by ionic conduction in n-Hexanol + DMF binary mixtures over the static permittivity frequency regime could contribute in the design

Table 6 Determined value of Debye length (λ_D), ion mobility (μ), mobile ion concentration (P_0) and ion diffusivity (D) for the mixtures of n-Hexanol and DMF

X_A	λ_D (nm)	$\mu \text{ (m}^2 \text{ Vs}^{-1}\text{)}$	$P_0 \text{ (m}^{-3}\text{)}$	$D \text{ (m}^2\text{/s)}$
0.0	70.10	1.77E-11	3.55E+24	4.47E-13
0.1	59.23	6.71E-11	5.38E+24	1.69E-12
0.2	68.14	9.96E-11	4.75E+24	2.52E-12
0.3	71.75	1.56E-10	4.84E+24	3.94E-12
0.4	90.18	2.20E-10	3.62E+24	5.55E-12
0.5	101.6	2.79E-10	4.56E+24	7.05E-12
0.6	121.8	3.79E-10	3.55E+24	9.57E-12
0.7	113.3	4.90E-10	3.06E+24	1.24E-11
0.8	307.1	3.60E-09	5.05E+23	9.09E-11
0.9	73.70	3.90E-10	8.14E+24	9.86E-12
1.0	15.74	1.68E-11	2.06E+26	4.25E-13

of suitable mixed solvents for the use in liquid electrolytes and many more related fields of industrial and technological interest.

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Authors' contributions 1-N. A. Chaudhary: Conceptualization, Methodology, Software, Validation, Formal analysis, Writing—Original Draft. 2-K. N. Shah: Methodology, Validation, Formal analysis. 3-C. R. Vaja: Validation, Formal analysis. 3-V. A. Rana: Conceptualization, Writing—Review & Editing, Supervision, Project administration. 4-Deepak Kumar: Conceptualization, Writing—Review & Editing, Supervision, Project administration. 5- A. N. Prajapati: Conceptualization, Writing—Review & Editing, Supervision, Project administration. All authors reviewed the manuscript.

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Data Availability No datasets were generated or analysed during the current study.

Declarations

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Competing interests The authors declare no competing interests.

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Dielectric spectroscopic study of the binary mixtures of N-Hexanol with N,N-Dimethylformamide in the frequency range of 20 Hz to 2 MHz

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A precision LCR meter with a liquid dielectric cell was used for complex dielectric function $\varepsilon^*(f) = \varepsilon'(f) - \varepsilon''(f)$ of binary mixtures of N-Hexanol ($n\text{-HxOH}$) and N,N-Dimethylformamide (DMF) in the frequency range of 20 Hz to 2 MHz at 293.15 K temperature. The data were utilized for various formalisms such as complex modulus spectra ($M^*(f)$), complex impedance spectra ($Z^*(f)$), and complex conductivity spectra ($\sigma^*(f)$). Complex permittivity data were fitted to the Cole–Cole Model. Different relaxation times like electrode polarization (τ_{EP}), relaxation time (τ'_{EP}), and ionic conduction relaxation time (τ_σ) were calculated and reported. Parameters like Debye Length (λ_D), Ion Mobility (μ), Mobile Ion Concentration (P_0), and Ion Diffusivity (D) were determined. The study is used to determine the effect of concentration dependent on different dielectric and electrical properties of the binary mixtures.

Keywords: Cole–Cole model; bode plot representation; n -Hexanol; N,N-Dimethylformamide.

PACS numbers: 66.10.Ed, 77.22.-d, 77.22.Ch, 77.22.Gm, 78.20.Ci, 78.40.Dw

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1. Introduction

The molecular interactions among the different polar liquids have produced an immense amount of attention within the scientific community recently. Dielectric spectroscopy is used to investigate the various short-range and fluctuating molecular interactions to understand the properties of these molecules. Our investigation of the dielectric properties of liquid mixtures incorporates various relaxation processes and molecular interactions providing valuable information about the molecules of the mixtures.¹ Dielectric relaxation spectroscopy has been utilized to probe the relaxation processes, mechanism of polarization in dielectric material, interaction between inter-intra molecules, and electrical conduction present within the studied mixtures. The detailed insights regarding the charge dynamics and electrical conduction mechanisms of the liquids, which are directly linked with the molecular structure and the polarization strength, are obtained from the low-frequency dielectric dispersion study.² Frequency-dependent dielectric properties have found their benefit in understanding the fundamental properties of liquids such as structure persistence, dynamics, and their practical applications.³ The lower frequency region of an applied electric field (A few tens of hertz to several megahertz) has found a significant interest in the research of dielectric and electrical properties of the various liquid molecular systems since this region lacks the dipolar relaxation.⁴⁻⁸ The detailed investigation on the dielectric characterization of solutions as a function of the concentration of *N*-Hexanol (*n*-HxOH) in *N,N*-Dimethylformamide (DMF) has been carried out in the frequency range 20 Hz to 2 MHz. Valuable insights into molecular interactions of liquid mixtures are obtained through the study of binary polar liquid mixtures having one associative and other non-associative liquid constituents.⁹⁻¹¹ Alcohol is one of the important centers among the associative liquids. Due to its associative nature, hydrogen bonding in various liquid systems has played an outstanding role in applied sciences. The hydroxyl group in alcohols is easily able to interact with any other chemical group with some degree of polar attraction.¹²⁻¹⁵ Among the alcohols, *n*-Hexanol (*n*-HxOH) is a relatively long-chained molecule widely used in petrochemical, agricultural and pharmaceutical industries for various applications.^{16,17}

On the other hand, non-associative liquids like amides possess strong solvating power and high polarity making them one of the highly sought-after solvents in chemical industries. For this study, *N,N*-Dimethylformamide (DMF) has been selected owing to its characteristic properties which have been the subject of significant interest because of its relationship with peptides and proteins.¹⁸ This solvent has found its applications in polymer and pharmaceutical industries¹⁹ as well. DMF has a highly aprotic polar nature and a significantly large dipole moment with a higher value of relative permittivity (Dielectric constant).

In this study, we have reported the different processes related to the relaxation time, phenomena of polarization, dielectric behavior, and DC conductivity of *n*-HxOH mixture with DMF. LCR meter was employed to measure complex

permittivity spectra $\varepsilon^*(f)$ of the binary mixtures at 293.15 K temperature. The dielectric and electrical properties of the studied liquid mixtures have been discussed with respect to variations in the concentration. Such studies also have great potential to design and verify appropriate theoretical models that might accurately describe the experimental data, making them more necessary from a purely academic perspective as well.²⁰

2. Experimental and Theoretical Details

N-Hexanol (*n*-HxOH) and *N,N*-Dimethylformamide (DMF) both the analytical grades were obtained from Loba Chemie Pvt Ltd., India, and used without any purification. Eleven different combinations with varying volume fractions (X_A) of *n*-HxOH in DMF were precisely prepared. Complex permittivity ($\varepsilon^*(f) = \varepsilon' - j\varepsilon'' = \alpha(\frac{C_P}{C_0} - j\frac{1}{\omega C_0 R_P})$) of *n*-HxOH and DMF with the help from capacitance and resistance with and without sample was determined using an Agilent E4980A precision LCR meter. For this purpose, a four-terminal liquid dielectric test fixture (Agilent 16452 A) was utilized, allowing capacitance and resistance measurement over a frequency range of 20 Hz to 2 MHz. The test fixture correction coefficient was taken into account when evaluating the complex dielectric function values to minimize the effect of stray capacitance. The experimental method for determining complex dielectric permittivity spectra, as well as its measurement with an accuracy of 0.04, is discussed in the stated references.^{21,22} The temperature of the binary liquid samples throughout measurement was controlled by constant temperature water bath (Supplied by MIC Fourtech, India) with an standard accuracy of ± 0.1 K.

3. Results and Discussion

3.1. Complex dielectric spectra

Figure 1 presents the (a) ε' and (b) ε'' spectra of the *n*-HxOH + DMF binary mixtures for various volume fractions, at constant temperature 293.15 K. Figure 1(a) shows that the permittivity spectra are divided into two different regions, in higher frequency region (it is independent of frequency) and lower frequency regions (it depends upon the frequency). In the higher frequency region above 10^4 Hz, the real part of permittivity spectra is independent of the frequency, and it attenuates to the steady region. It is observed in the lower frequency region below 10^4 Hz, the real part (ε') value increases with an increase in the volume fraction of DMF. The higher value of the real part of the permittivity in the lower frequency region predominates the effect of the electron polarization (EP).^{23,24} As frequency increases, ε' decreases linearly until reaching a steady state at specific frequencies. Steady-state values for pure *n*-HxOH and DMF occur at approximately 9 kHz and 50 kHz, respectively. Beyond these frequencies, ε' becomes frequency-independent, so-called as is static permittivity (ε_0). A noteworthy feature of dipolar liquids is the dependence of steady-state frequency on static permittivity, where higher static permittivity liquids

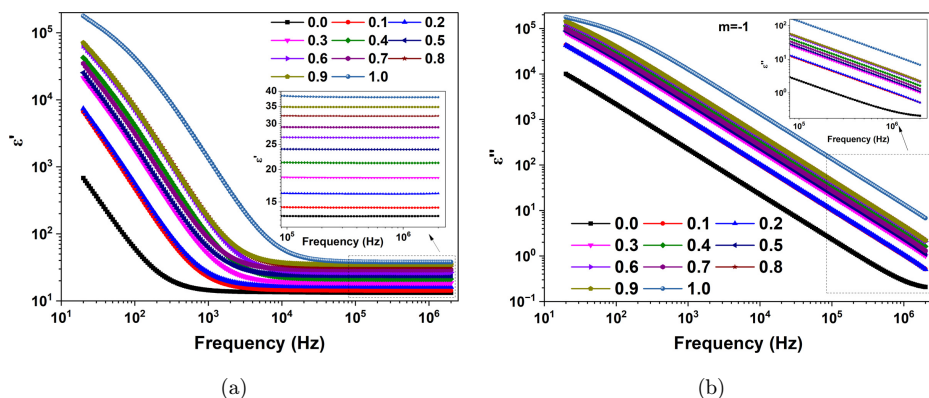


Fig. 1. (Color online) (a) ϵ' and (b) ϵ'' spectra of DMF, n -HxOH, and their binary mixtures in the frequency region 20 Hz to 2 MHz at 293.15 K.

achieve steadiness at higher frequencies compared to those with lower static permittivity values.²⁵ The inset in Fig. 1(a) indicates that static permittivity (ϵ_0) rises with an increase in DMF concentration, particularly at the spectral endpoints. At these frequencies, pure DMF exhibits a slightly higher real part of the dielectric function ϵ' compared to pure n -HxOH, pointing to an enhanced molecular polarization strength in the DMF system. The static permittivity (ϵ_0) for n -HxOH (13.23) and DMF (37.00) is in good agreement with the literature value for n -HxOH (13.05)²⁶ and DMF (37.69)²⁷ at the same temperature.

Figure 1(b) shows dielectric loss spectra (ϵ'') for varying volume fractions of DMF within the N-Hexanol mixtures which reveal a strikingly consistent linear frequency dependence spanning 20 Hz to 2 MHz. The logarithmic scale slope of -1.00 (± 0.02) underscores the manifestation of an Ohmic-type ionic conduction mechanism intrinsic to these liquid dielectric mixtures. This empirical behavior aligns with established patterns observed in diverse dipolar liquids and their binary compositions.^{25,28,29} Notably, the ϵ'' values for n -HxOH-DMF mixtures, initially in the order of six logarithmic magnitudes at 20 Hz, exhibit a systematic linear decline with increasing frequency, suggestive of an asymptotic approach to zero at higher frequencies, surpassing the experimental ceiling of 2 MHz.

The experimentally obtained complex permittivity data in the frequency range ($< 10^4$ Hz) for the studied mixtures are influenced by the electrode polarization (EP) effect.³⁰ To model this effect, we employed the Cole–Cole model and specifically utilized the Havriliak–Negami (HN) equation,³¹ which is given by

$$\epsilon(f) = \epsilon_{\infty} + \frac{\Delta\epsilon_{EP}}{[1 + (i\omega\tau)^{\alpha}]^{\beta}}, \quad (1)$$

where $\Delta\epsilon_{EP} = \epsilon_{0(EP)} - \epsilon_0$, ϵ_0 is the static dielectric constant, $\epsilon_{0(EP)}$ is the low-frequency dielectric constant in the presence of EP and τ_{EP} is the electrode

polarization relaxation, and α and β are the asymmetry and broadness parameters of the dielectric loss peaks.

The Complex Nonlinear Least Square (CNLS) fitting procedure, as detailed in Ref. 31, was employed to fit our experimental data to Eq. (1). The fitting parameters included $\Delta\varepsilon_{EP}$, ε_0 , and τ_{EP} . In Fig. 2, we present the fitted plots of $\varepsilon^*(f)$ to the Cole–Cole model (Eq. (1)) for concentration range ($X_A = 0.5$) alongside their corresponding experimental values. This fitting procedure allows us to determine and understand the key parameters governing the complex permittivity, providing a more accurate representation of our experimental results.

The Cole–Cole model provides an excellent fitting to experimental results. Similar fitting results were obtained for the concentration range $0.0 \leq X_A \leq 1.0$. The best-fit values of the fitting parameters for all concentrations are tabulated in Table 1.

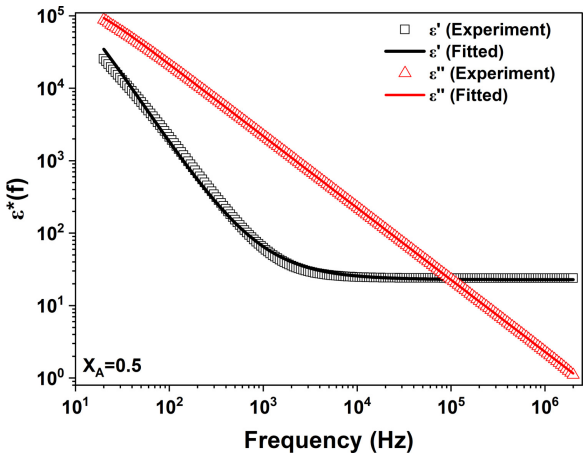


Fig. 2. (Color online) Experimental and fitted ($\varepsilon^*(f)$) to the Cole–Cole model by CNLS for the concentration range ($X_A = 0.5$).

Table 1. Fitted parameters ε_0 , $\Delta\varepsilon_{EP}$, τ_{EP} and α using the Cole–Cole model for the volume fraction of DMF at 293.15 K temperature.

X_A	ε_0	$\Delta\varepsilon_{EP}$	τ_{EP} (ms)	α
0.0	13.05	1.86E+05	134.68	0.99
0.1	13.87	2.79E+05	46.84	0.99
0.2	15.63	2.56E+05	41.89	0.99
0.3	17.79	2.96E+05	24.45	0.99
0.4	19.99	2.92E+05	15.44	0.99
0.5	22.81	2.96E+05	22.35	0.99
0.6	24.86	2.54E+05	10.58	0.99
0.7	27.57	2.72E+05	17.55	0.99
0.8	30.07	2.65E+05	10.14	0.98
0.9	32.75	2.69E+05	10.39	0.99
1.0	34.24	2.21E+05	3.010	0.98

Values' electrode polarization relaxation time changes anomalously as the concentration of the mixture increases.

The dielectric loss tangent ($\tan \delta = \varepsilon''/\varepsilon'$) spectra, commonly used in the study of dipolar liquids and liquid electrolytes at low frequencies, help separate the bulk dielectric properties from the electrode polarization (EP) effects on the frequency scale.^{25,28,32} In Fig. 3, $\tan \delta$ spectra for DMF, *n*-HxOH, and their binary mixtures show relaxation peaks in the frequency range around 10^2 Hz to 10^4 Hz, indicating symmetrical distribution characteristic of the EP relaxation process. These peaks reflect the dynamics of charging and discharging of electric double-layer (EDL) capacitances.³² The observed relaxation time (τ'_{EP}) values were derived from the frequency corresponding to the $\tan \delta$ peak ($\tau'_{EP} = (2\pi f_{EP})^{-1}$).

3.2. Complex modulus spectra

A suitable method for examining the features of ionic conductivity relaxation processes while reducing the impact of Electric Double Layers (EDLs) dynamics in ion-conductive materials is the conversion of dielectric spectra into electric modulus. Values of M' and M'' of the electric modulus for liquid DMF were determined using Eq. (2).⁷ These spectra are used to eliminate the material's electrode double layer (EDL) process. The inverse of the dielectric function M is denoted by the symbol $M^*(f) = \frac{1}{\varepsilon^*(f)}$.⁷

$$M^*(f) = M' + jM'' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}, \quad (2)$$

where ε' and ε'' show the real and imaginary parts of permittivity.

Figures 4(a) and 4(b) show the graph of M' and (b) M'' spectra for the binary mixtures of DMF and *n*-HxOH. As shown in Fig. 4(a), suppression of high

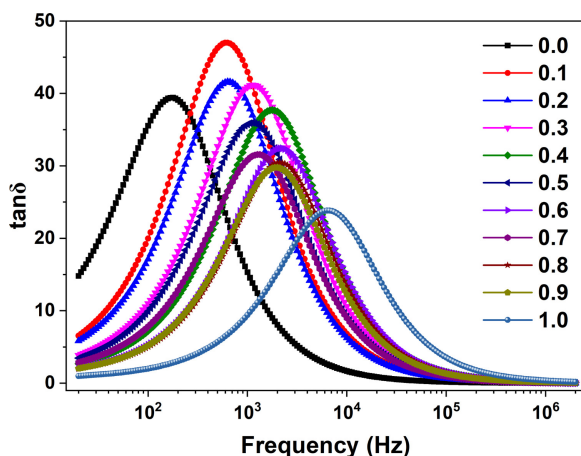


Fig. 3. (Color online) Dielectric loss tangent ($\tan \delta$) spectra of *n*-HxOH-DMF binary mixtures at various volume fractions of DMF at 293.15 K temperature.

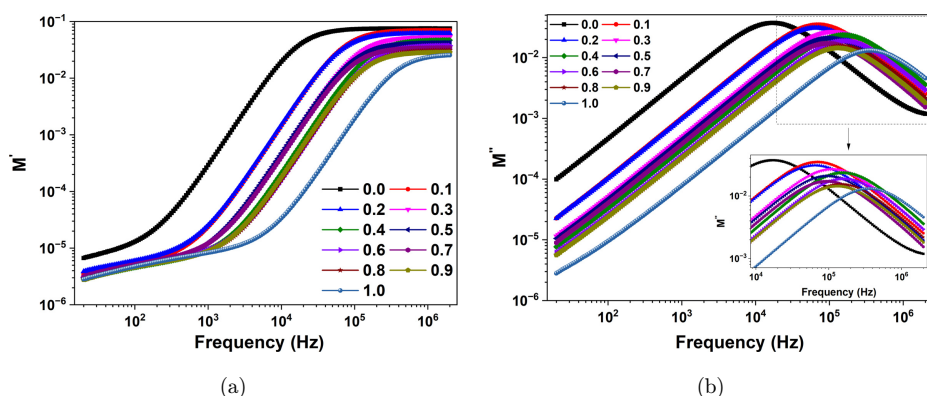


Fig. 4. (Color online) (a) M' and (b) M'' spectra for the binary mixtures of DMF and *n*-HxOH.

capacitance phenomena in modulus formalism results in relatively low M' values over the EP-dominated frequency range, with a minimal increase. In contrast, ε' values in the same frequency range are very high (Fig. 1(a)). But above this range, M' increases by a large magnitude with an increase in frequency and finally approaches the steady state at the high-frequency end. The M'' spectra in the logarithm scale have shown a linear increase over the low and intermediate-frequency regions and show peaks in the high-frequency region. These peaks correspond to the conductivity relaxation process as observed earlier for several dielectric liquids.^{28,29} Furthermore, Fig. 4(b) observed the magnitudes of these M'' peaks increase gradually and also shift toward the high-frequency side as the volume fraction of DMF increases. The frequency f_σ corresponding to the maximum value of M'' is related to the relaxation time of ionic conductivity, $\tau_\sigma = \frac{1}{2\pi f_\sigma}$.¹ Values of ionic conductivity relaxation time (τ_σ) with the change in the volume fraction of DMF at constant temperatures are tabulated in Table 2.

In Fig. 5, M'' versus M' plots for *n*-HxOH-DMF binary mixtures at 293.15 K are shown, exhibiting behavior conforming to the Debye function observed in other dipolar liquids.²⁸ The absence of a low-frequency spike in the electric modulus plane confirms that $M^*(f)$ spectra remain unaffected by the EP effect. Notably, the size of the Debye semicircle for DMF in the electric modulus is relatively small. A decrease in DMF concentration within the mixtures results in a gradual increase in semicircle size, attributed to higher $\varepsilon^*(f)$ values of DMF. This trend is consistent with the relationship between $M^*(f)$ and the inverse of $\varepsilon^*(f)$. The findings focus on the precision of modulus plots in evaluating static permittivity (ε_0) values for dipolar liquids.

Figure 6 shows the different relaxation phenomena on a single-frequency scale. The variation of τ_{EP} , τ'_{EP} and τ_σ for concentration $X_A = 0.5$ for the constant temperature ranges is shown in Fig. 6. The relaxation time (τ_{EP}) is obtained from the imaginary part of permittivity spectra (ε''), τ'_{EP} is derived from loss tangent ($\tan\delta$) and τ_σ is derived from Imaginary part of modulus (M'') spectra. It can be seen from

Table 2. Values of electrode polarization relaxation time (τ'_{EP}), ionic conductivity relaxation time (τ_σ), DC resistance (R_{dc}), and DC conductivity (σ_{dc}) for various concentrations of DMF at 293.15 K.

X_A	τ'_{EP} (μ s)	τ_σ (μ S)	R_{dc} (Ω)	σ_{dc} (μ S/m) (Fig. 7(a))	σ_{dc} (μ S/m) (Eq. (5))
0.0	893.33	9.46	10732.97	1.25E-05	1.01E-05
0.1	251.78	2.24	4942.19	5.53E-05	5.50E-05
0.2	251.78	2.52	4763.40	5.75E-05	5.70E-05
0.3	141.58	1.42	2377.03	1.14E-04	1.14E-04
0.4	89.33	1.00	1499.63	1.82E-04	1.81E-04
0.5	141.58	1.68	2155.14	1.27E-04	1.26E-04
0.6	75.16	1.00	1156.81	2.34E-04	2.35E-04
0.7	126.19	1.68	1811.08	1.51E-04	1.50E-04
0.8	75.16	1.06	1050.30	2.58E-04	2.59E-04
0.9	79.62	1.19	1070.81	2.53E-04	2.54E-04
1.0	25.18	0.45	364.85	7.41E-04	7.45E-04

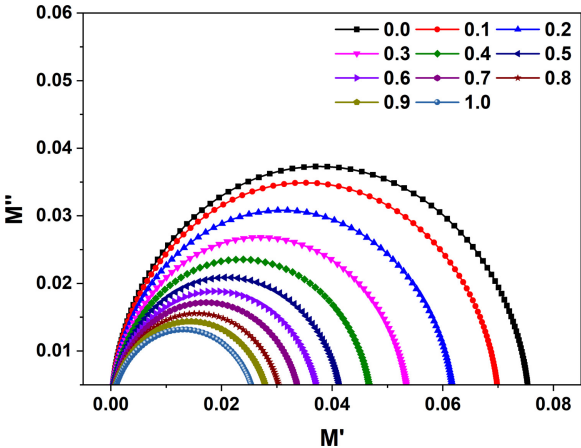


Fig. 5. (Color online) Complex electric modulus plane plots (M'' versus M') for the binary mixtures of n -HxOH and DMF at 293.15 K.

the graph that for all the concentration ranges the peak is shifting towards the higher frequency region as the concentration of the mixture increases. Three different relaxation times in the studied system are correlated by relation $\tau'_{EP} = (\tau_{EP} \times \tau_\sigma)^{\frac{1}{2}}$.³³ Many researchers observed a similar type of relation in the binary mixture.^{1,4,34}

3.3. Complex conductivity spectra

The frequency-dependent complex electric conductivity ($\sigma^*(f)$) for the liquid mixtures was determined by the following equation:

$$\sigma^*(f) = \sigma' + j\sigma'' = \omega\varepsilon_0\varepsilon'' + j\omega\varepsilon_0\varepsilon', \tag{3}$$

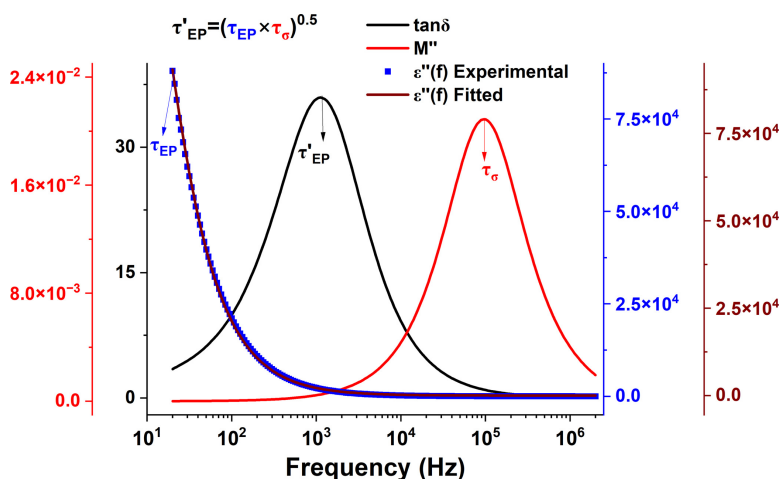


Fig. 6. (Color online) Relationship between τ_{EP} , τ'_{EP} and τ_{σ} for $X_A = 0.5$.

where ω is the angular frequency, ϵ_0 is the permittivity of the free space, ϵ' is the real part of permittivity, and ϵ'' is the imaginary part of permittivity, respectively.

The frequency-dependent real part (σ') and imaginary part (σ'') of the complex electric conductivity ($\sigma^*(f)$) for *n*-HxOH-DMF binary mixtures at various concentrations are presented in Figs. 7(a) and 7(b). The solid line in the σ' spectra denotes the DC conductivity, represented as σ_{dc} . In Fig. 7(a), it is observed that the σ' spectra initially exhibit a nonlinear increase with frequency, reaching a steady state shortly after. Beyond 2 kHz, the σ' values remain constant, representing the direct current electrical conductivity (σ_{dc}) values of these mixtures. The σ_{dc} values are determined from the frequency-independent plateau region of σ' values, as

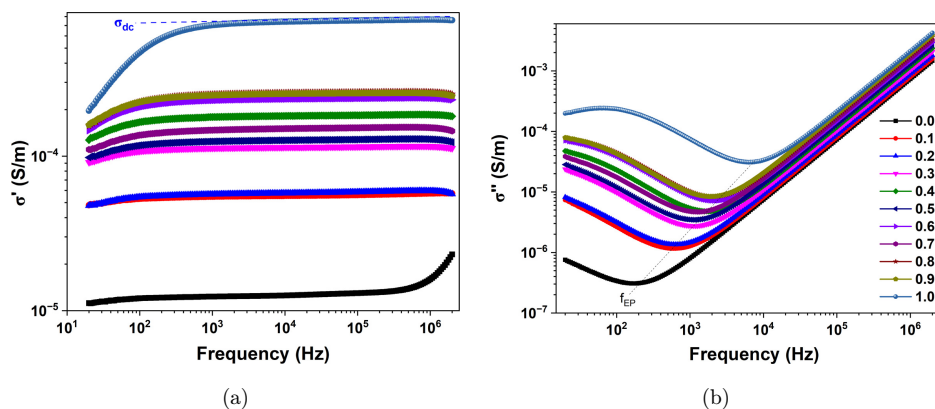


Fig. 7. (Color online) The frequency-dependent behaviors of (a) real part σ' and (b) imaginary part σ'' of the complex AC conductivity for *n*-HxOH-DMF binary mixtures are illustrated at different volume fractions of DMF at 293.15 K.

illustrated by the straight line (using a concentration of DMF) in the figure. The calculated σ_{dc} values (from Eq. (5)) and experimental (Fig. 7(a)) σ_{dc} values for the *n*-HxOH-DMF mixtures at 293.15 K are provided in Table 2. The σ_{dc} values for pure DMF ($7.41 \times 10^{-04} \mu\text{S/m}$) are approximately one order of magnitude higher than that of *n*-HxOH ($1.01 \times 10^{-05} \mu\text{S/m}$), consistent with the higher static dielectric constant (ϵ_0) of DMF. In Fig. 7(b), it is observed that initially, the σ'' values decrease with an increase in frequency from 20 Hz, reaching a minimum in the intermediate frequency region, corresponding to the Electric Double Layer (EDL) relaxation process, which is also evident from the peaking of $\tan\delta$ values in Fig. 3.

3.4. Complex impedance spectra

In the dielectric spectra of polar liquid materials, the Electric Double Layer (EDL) and conductivity relaxation processes are observed at lower frequencies. Revealing of these processes is facilitated by analyzing the imaginary part of the complex impedance spectrum.⁷ The complex impedance spectra $Z^*(f)$ are determined using the following equation:

$$Z^*(f) = Z' - jZ'' = \frac{\epsilon''}{\omega C_0(\epsilon'^2 + \epsilon''^2)} - j \frac{\epsilon'}{\omega C_0(\epsilon'^2 + \epsilon''^2)}, \quad (4)$$

where ω represents angular frequency, C_0 denotes the electric capacity of the empty measuring cell, ϵ' is the real part of permittivity, and ϵ'' is the imaginary part of permittivity.

In Fig. 8(a), it is observed that the Z' values remain relatively constant up to 10^4 Hz, after which there is a sudden decrease. Additionally, the Z' values for *n*-HxOH are notably higher than those for DMF. In Fig. 8(b), the graph of complex impedance (Z'') exhibits minima and maxima, corresponding to f'_{EP} and f_{σ} . f'_{EP} represents the frequency at which the static dielectric constant (ϵ_0) begins to increase

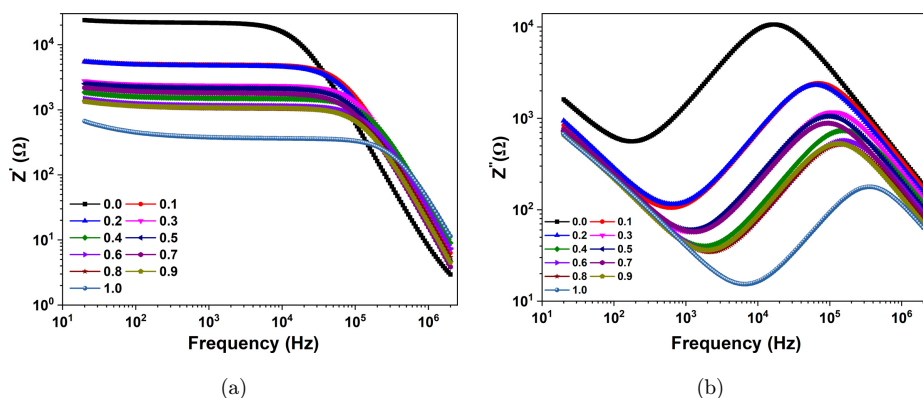


Fig. 8. (Color online) Frequency dependent of (a) real part of the impedance (Z') (b) imaginary part of the impedance (Z'') of DMF, *n*-HxOH and their binary mixtures at 293.15 K.

with decreasing frequency, indicating the onset of the Electric Double Layer (EDL) relaxation process.³⁵ Conversely, f_σ is associated with the conductivity relaxation process and aligns with the maximum in the imaginary part of the electric modulus (M'').⁶ The derived values of the f'_{EP} and f_σ were employed to calculate the respective relaxation times, f'_{EP} and f_σ , using the general relation $\tau = (2\pi f)^{-1}$ and are reported in Table 2. The EDL relaxation time (τ'_{EP}) signifies the duration for the charging/discharging of the electric layer capacitance associated with the dynamic behavior of adsorbed ions on electrode surfaces in response to varying electric fields.³⁶

In Fig. 9(a), the complex impedance plot (Z'' versus Z') exhibits a Debye-type semicircular arc³⁴ for varying concentrations ($0.0 \leq X_A \leq 1.0$) of *n*-HxOH and DMF mixtures. This arc, observed at higher frequencies, represents the bulk behavior of the material. As the frequency decreases, an inclined straight line emerges at lower frequencies, indicating the prevalence of the Electric Polarization (EP) effect.²⁹ The radius of the semicircular arc changes with DMF concentration. The intersection of this arc with the Z' axis provides direct current resistance (R_{dc}) values for the dipolar liquids, as detailed in Table 2. The observed inverse relationship between R_{dc} and ε_0 for pure *n*-HxOH, DMF, and their mixtures align with a known correlation.³⁶

$$\sigma_{dc} = \frac{\varepsilon_0 \varepsilon_v}{\tau_\sigma} = \frac{t_g}{R_{dc} A}. \quad (5)$$

Here, ε_0 represents the static dielectric constant, ε_v is the permittivity of vacuum, τ_σ is the relaxation time for ionic conductivity, t_g is the gap between the parallel plates, and A is the surface area of the capacitance cell plate. The direct current resistance (R_{dc}) values were subsequently employed to compute the direct current conductivity (σ_{dc}) using Eq. (3) and the results are detailed in Table 2. Impedance spectroscopy proves to be a particularly effective method for comprehending the lower-frequency

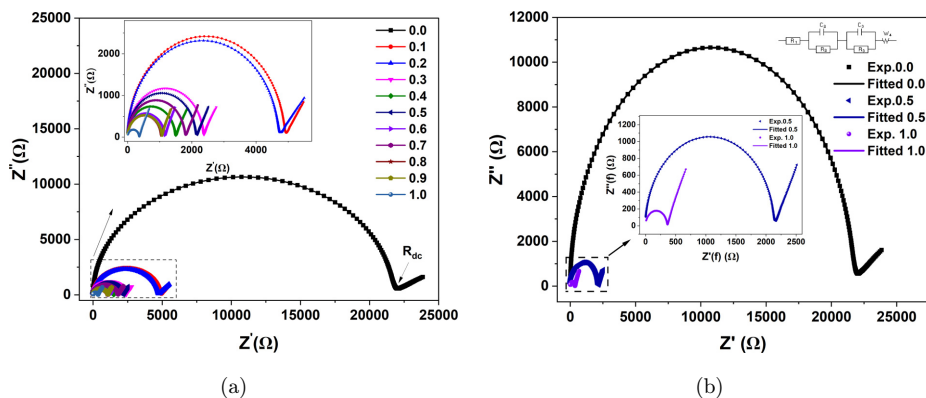


Fig. 9. (Color online) (a) Z'' versus Z' for binary *N*-Hexanol-DMF mixtures, and (b) experimental data points with fitted data points of complex impedance spectra (Z'' versus Z') using an equivalent RC circuit for $X_A = 0.0$, $X_A = 0.5$, and $X_A = 1.0$ at 293.15 K.

dynamics of a system. To analyze the impedance spectra of our investigated system, various equivalent circuit models were employed. Remarkably, the experimental data exhibited optimal fitting to a six-element equivalent circuit as illustrated in Fig. 9(b). The impedance data points for all binary mixtures were exceptionally well-matched to this equivalent circuit model. The graphical representation of the experimental and fitted data points for different concentration ranges 0.0, 0.5, and 1.0 are shown in Fig. 9(b).

In Fig. 10, the graph shows $\tan\delta$, Z'' , M'' , and σ'' spectra for an n -HxOH-DMF binary mixture with the concentration of $X_A = 0.5$, all plotted on the same frequency scale. This combined representation allows us to observe both the Electric Double Layer (EDL) and conductivity relaxation processes. Interestingly, the Z'' spectra display both relaxation processes with distinct minima and maxima peaks, while the other spectra exclusively show either the EDL or conductivity relaxation process.¹ This analysis shows that for examining the relaxation processes generated by ionic charge impurities in pure dipolar liquids and their binary mixes, impedance spectroscopy is a more useful method than dielectric and modulus spectroscopies. The calculation of Debye Length (λ_D), ion mobility (μ), mobile ion concentration (P_0), and ion diffusivity (D) within the concentration range ($0.0 \leq X_A \leq 1.0$) was conducted utilizing the model equation proposed by Klein *et al.*³⁷ The results of these calculations are tabulated in Table 3. Equation (6) applied to measure the thickness of ions deposited at the electrode surface. This analysis contributes valuable insights into the electrochemical characteristics of the system under investigation. Determining the thickness of the ions buildup at the electrode surface is given by

$$\lambda_D = \frac{g}{2M}, \quad (6)$$

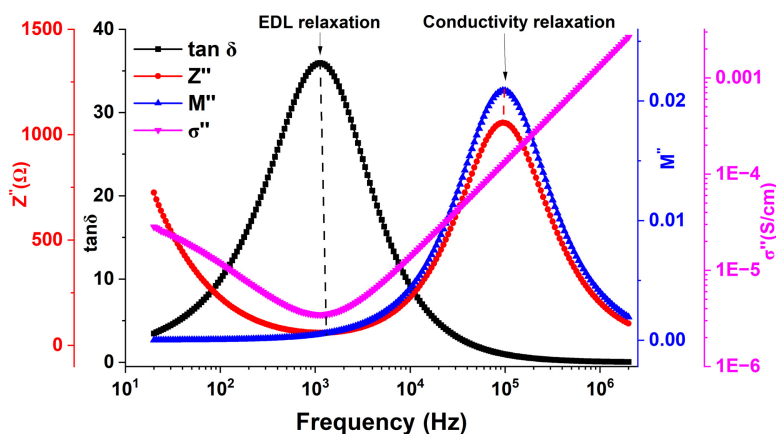


Fig. 10. (Color online) Master curves showing EDL and conductivity relaxation processes of n -HxOH-DMF binary mixtures of $X_A = 0.5$ at 293.15 K.

Table 3. Determined value of Debye length (λ_D), ion mobility (μ), mobile ion concentration (P_0) and ion diffusivity (D) for the mixtures of *N*-Hexanol and DMF at 293.15 K.

X_A	λ_D (nm)	μ (m ² Vs ⁻¹)	P_0 (m ⁻³)	D (m ² /s)
0.0	105.39	4.64E-11	3.41E+24	1.170E-12
0.1	71.86	9.10E-11	3.78E+24	2.299E-12
0.2	90.16	1.28E-10	2.79E+24	3.225E-12
0.3	86.85	2.11E-10	3.39E+24	5.322E-12
0.4	97.40	3.74E-10	3.03E+24	9.455E-12
0.5	112.92	3.00E-10	2.63E+24	7.571E-12
0.6	142.05	7.96E-10	1.84E+24	2.011E-11
0.7	143.81	4.86E-10	1.93E+24	1.228E-11
0.8	157.04	9.19E-10	1.76E+24	2.321E-11
0.9	172.03	9.83E-10	1.61E+24	2.482E-11
1.0	223.15	4.40E-09	1.06E+24	1.111E-10

where the gap between the electrodes (g), the thickness of the layer where ions gather on the electrode surface (λ_D), and a ratio $M = \frac{\tau_{EP}}{\tau_\sigma}$. The thickness of the Debye layer for *n*-HxOH is the smallest at 105.39 nm, for DMF it is the largest at 223.15 nm, and for the mixtures, it is somewhere in between these two values, as shown in Table 3. Ion mobility is calculated using the following equation:

$$\mu = \frac{qg^2}{4kTM\tau_{EP}}, \quad (7)$$

where q is the electron charge, k is Boltzmann constant and T is Temperature, respectively.

Mobile ions (P_0) and diffusivity (D) are done using the following equations:

$$P_0 = \frac{\sigma_{dc}}{q\mu}, \quad (8)$$

$$D = \frac{\mu KT}{q}, \quad (9)$$

where μ represents ion mobility, K is the Boltzmann constant, T is the absolute temperature, and q denotes the charge of the electron, specific values for mobile ion concentration and diffusivity in DMF and *n*-HxOH at a temperature of 293.15 K are provided in Table 3.

It is observed from Table 3 that the anomalous behavior of ion mobility for various concentrations is observed. The ion mobility of pure *n*-HxOH is 4.64×10^{-11} m²/Vs. For $X_A = 0.1$ ion mobility value leaps to 9.10×10^{-11} m²/Vs and then after, with an increase in X_A it decreases, this is due to the large molecular size and higher viscosity of *n*-HxOH. Furthermore, there is a decrease in ion diffusivity as the increase in concentration of DMF. The ion concentration is high for pure *n*-HxOH and changes as the concentration of *n*-HxOH decreases in DMF.

These observations indicate that, in addition to the molecular structure and inter-molecular interactions, the ion mobility is influenced by the viscosity of the medium. The viscosity, or thickness, of the liquid, plays a significant role in governing the movement of ions in the system.

4. Conclusions

This study explores the concentration-dependent dielectric and electrical properties of *n*-Hexanol (*n*-HxOH), N,N-Dimethylformamide (DMF), and their binary mixtures within the frequency range of 20 Hz to 2 MHz at 293.15 K. The lower frequency complex dielectric behavior is mainly governed by ionic conduction and electrode polarization phenomena of concentration dependent behavior are observed in the ionic conduction and electrode polarization processes within the studied binary mixtures. The experimental complex permittivity values align well with the Cole-Cole model. Evaluated values of Electrode polarization relaxation time (τ_{EP}), relaxation time (τ'_{EP}) and ionic relaxation time (τ_{σ}) are using various formalisms to demonstrate good agreement with experimental values of ϵ'' . Impedance data fitting with a six-element equivalent RC circuit confirms various electrical processes in the bulk sample and at the electrode surface. The observed perfect scaling in $\tan \delta$, M'' , and Z'' with concentration variation indicates potential for tuning the electrical and dielectric properties of *n*-HxOH through mixing with DMF. Furthermore, the determination of the thickness of ion accumulation at the interface between the electrode and the dielectric medium, which is composed of polar liquids such as *n*-HxOH, DMF, and their mixtures, adds to a thorough comprehension of their electrochemical behavior.

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Refractive indices, density and their related properties for several binary mixtures of n-Hexanol with N, N-Dimethylformamide at constant temperature 303.15K

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Abstract

In the present study, refractive index (n), and density (ρ) have been experimentally determined for binary liquid mixtures of n-Hexanol with N, N-Dimethylformamide over varying concentration of both mixture composition in the range (0.0 $\rightarrow$ 1.0) at constant temperature 303.15K. The experimental values of refractive index and density have been used to compute various refractometric parameters namely, molar volume (V_m), molar refraction (R_m), atomic polarization (P_A), molecular radii (r), reduce molar free volume (V_m/R_m), polarizability (α) and internal pressure (P_{int}). The excess of all computed parameters are obtained from the difference between experimentally determined values and values evaluated using additive mixing rules. The excess parameters are fitted in Redlich-Kistler polynomial. The variations of these parameters with composition at constant temperature of the mixtures are discussed in light of physical, chemical and structural effects between the unlike molecules. The refractive index (n) of binary mixtures are predicted using various mixing models. A comparison of various mixing models with experimental values of refractive indices are expressed in terms of Average Percentage Deviation (APD).

Keywords: Binary mixture, Density, Refractive index deviations, Molecular interaction

1. Introduction

In the past few years physicochemical properties of pure liquids such as Refractive index (n) and Density (ρ) and their binary mixtures are essential for accurate design and optimal operation of many industrial processes (Navarkhele et al., 2022). In the recent year theoretical and experimentally determined values of refractive index of binary liquid mixtures under varying conditions of concentration and temperature have been widely used as tools for investigation of the physical properties of pure components and the nature of intermolecular interaction between the liquid mixture constituents (De Cominges et al., 2001). The refractive indices measurements are also used to estimate the different properties of the molecule from which the type of molecular interaction can be very well understood. (Prajapati et al., 2012; De Cominges et al., 2001; Navarkhele et al., 2022). Among the associating liquids, alcohol is undoubtedly the centre of interest, because of its outstanding rule in chemistry and biology, hydrogen bonding in liquid system has been intensively studied to a lively scientific debate.

(Aleksandar 2. Tadd et al., 1992; Nain, 2010; Prajapati, 2016; Prajapati & Limberkar, 2014; Rozycka-Roszak et al., 2013). Much attention has been also directed towards the physiochemical properties of alcohol not only due to their widespread use as solvent but also because of their fascinating features. Since molecule with -OH groups form associative liquid due to hydrogen bonding, the effect of presence of molecules with other functional group on their molecules is very important to understand the behavior of hydrogen bonding. N, N Dimethylformamide (DMF) is as an industrially important solvent with low evaporation rate (Marcheselli, et al., 1992). DMF is used in the production of acrylic fibers and plastics, also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, films, and surface coatings. DMF swells most plastics. Because of this property DMF is suitable for synthesis and as a component of paint strippers. It is also used in the manufacturing of solvent dyes as an important raw material (Prajapati, et al., 2022). This particular system (n-Hexanol + DMF) was chosen for study because both the liquid are common solvents and are widely used in pharmaceutical industry and chemical industry, the present study reports the experimentally values of refractive index (n) and Density (ρ) of pure n-Hexanol and DMF and their binary liquid mixtures over the entire volume concentration range (0-1) at 303.15 K.

2. Materials and Methods

n-Hexanol and N, N-Dimethylformamide of A R grade was procured from Loba Chemie (India). Both chemicals were used without further purification. Using these polar liquids, binary mixtures systems were prepared in hermetically sealed glass vials at eleven volume concentrations over the entire mixing range (0.0 $\rightarrow$ 1.0) at constant temperature (303.15 K).

2.1. Methods

Refractive index of the binary mixtures was measured using Abbe's refractometric with a Sodium D-line source (Wavelength 589 nm). The maximum measurement error in the value of n was 0. 0001. Density of liquid and liquid binary mixtures are measured using the standard specific gravity bottle. All measurement were carried out at constant temperature 303.15 K. The temperature was controlled thermostatically using constant temperature bath.

2.2. Evaluated Parameters

Table 1 shows the densities and refractive indexes of the n-hexanol + DMF mixture measured at constant temperature 303.15 K.

Table 1 Comparison of experimental and literature values of pure compounds.

Compound	Refractive index (Expt.)	Refractive index (Lit.)	Density (Expt.) (gm/cc)	Density (Lit.) (gm/cc)
n-Hexanol	1.4168	1.4175 [1]	0.8158	0.8185[4]
N, N-Dimethylformamide	1.4286	1.4266 [2]	0.9425	0.9461[3]

Ref:- (1- A. Prajapati & S. Patel, 2019.), (2 - Aklima Jahan et al., 2018), (3- Prajapati et al.,

2022), (4- Iloukhani et al., 2007)

Using experimental densities (d) of pure substances and mixtures, we calculated the molar volume (V_m) (A. N. Prajapati et al., 2012).

$$V_m = \frac{(X_A M_A + X_B M_B)}{\rho} \quad (1)$$

In this equation, X_A and X_B are the volume fractions of n-hexanol and DMF, M_A and M_B are their molecular masses, and ρ is their density of the solution. The experimental molar refractions (R_m) are obtained by the relation given as (Dragoescu, 2015).

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2} \right) V_m \quad (2)$$

where n is the refractive index of the liquid and $V_m = M/\rho$ is molecular volume, in this M and ρ is the molecular weight and the density of the pure liquids respectively. The molar refraction (R_m) gives information about the presence of specific intermolecular interactions in the binary liquid mixture.

The atomic polarization (P_A) was calculated from the refractive indices (n) of pure substances and mixtures by the equation. (Prajapati, et al., 2014)

$$P_A = 1.05 n^2 \quad (3)$$

Using the Lorentz formula, the experimental densities and refractive indices of pure substances and mixtures were used to determine the molecular polarizability (α) (Rana et al., 2023).

$$\alpha = \frac{3V_m}{4\pi N} \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad (4)$$

Where N is the Avogadro's constant and V_m is molar volume. Using the values for the refractive index, one can properly calculate the molecular radii of pure liquids theoretically: (Ali et al., 2008)

$$r = \left[\left\{ \left(\frac{3}{4\pi N} \right) \left(\frac{n^2 - 1}{n^2 + 2} \right) \right\} V_m \right]^{\frac{1}{3}} \quad (5)$$

The well-known Buchler- Hirschfelder-Curtiss equation of state, which is provided as following, can be used to calculate the internal pressures of binary liquid mixtures. (Srivastava et al., 2019)

$$P_{int} = \frac{\frac{1}{26}RT}{\frac{1}{26}V_m - 2rN^{\frac{1}{3}}V_m^{\frac{2}{3}}} \quad (6)$$

Where R is universal gas constant and T is absolute temperature and V_m is the molar volume and r is the molecular radii and N is the Avogadro's constant respectively.

2.3. Excess Parameters

The deviation in refractive index, molar volume, internal pressure, and excess molecular radii of the binary mixtures are evaluated. (Ali et al., 2008; Ali & Traiq. 2008; Srivastava et al., 2019)

$$\Delta n = n_m - (n_A X_A + n_B X_B) \quad (7)$$

$$\Delta V_m = V_m - (V_{m_A} X_A + V_{m_B} X_B) \quad (8)$$

$$\Delta P_{int} = P_{int m} - (P_{int A} X_A + P_{int B} X_B) \quad (9)$$

$$\Delta r = r_m - (r_A X_A + r_B X_B) \quad (10)$$

$$\frac{\Delta V_m}{\Delta R_m} = \left(\frac{V_m}{R_m} \right) - \left[\left(\frac{V_{mA}}{R_{mA}} \right) X_A + \left(\frac{V_{mB}}{R_{mB}} \right) X_B \right] \quad (11)$$

Where X the volume fraction of binary mixtures. The subscripts m, A, and B, denote mixtures of molecular species n-Hexanol and DMF respectively. The deviations (Δn), (ΔV_m), ($\Delta V_m/\Delta R_m$) and (ΔP_{int}) have been fitted to the Redlich-Kister polynomial equation. (Ali & Mohammad, 2007)

$$A^E = (X_A X_B) \sum_i a_i (X_A - X_B)^i \quad (12)$$

A_i is the polynomial coefficients obtained by using the least squares regression approach to fit the equation to the experimental results. The standard deviations (σ) were calculated using the relation. (A. N. Prajapati et al., 2012)

$$\sigma = \left[\frac{\sum (A_{\text{experimental}}^E - A_{\text{calculated}}^E)^2}{N-n} \right]^{\frac{1}{2}} \quad (13)$$

Where, N is the number of experimental data points and n is the number of coefficients. The values of coefficients A_i ($i=0,1,2,3$) and standard deviations against deviations are tabulated in Table 3.

2.4. Refractive index mixing models

There are a lot of theoretical mixing rules that can predict the refractive index. A number of different workers have examined and verified these mixing rules, and they have also done studies on the relative benefits of using these mixing rules (Adrian Crisciu et al., 2014; Franchini et al., 2001; Iglesias et al., 1996; Pietro Baraldi et al., 2002; Prajapati, 2017; Wilfried Heller, 1965). In present work we tested following mixing relations.

Eyring-John (E-J):

$$n = n_A \varphi_A^2 + 2(n_A n_B)^{1/2} \varphi_A \varphi_B + n_B \varphi_B^2 \quad (14)$$

Gladstone-Dale (G-D):

$$n - 1 = [n_A - 1] \varphi_A + [n_B - 1] \varphi_B \quad (15)$$

Arago-Biot (A-B):

$$n = n_A \varphi_A + n_B \varphi_B \quad (16)$$

Newton (Nw)

$$n^2 - 1 = [n_A^2 - 1] \varphi_A + [n_B^2 - 1] \varphi_B \quad (17)$$

Lorentz-Lorentz (L-L)

$$\frac{n^2 - 1}{n^2 + 2} = \left[\frac{n_A^2 - 1}{n_A^2 + 2} \right] \varphi_A + \left[\frac{n_B^2 - 1}{n_B^2 + 2} \right] \varphi_B \quad (18)$$

Weiner (Wi):

$$\left[\frac{n^2 - n_A^2}{n^2 + 2n_A^2} \right] = \left[\frac{n_B^2 - n_A^2}{n_B^2 + 2n_A^2} \right] \varphi_B \quad (19)$$

Eykman (Ey):

$$\frac{n^2 - 1}{n + 0.4} = \left[\frac{n_A^2 - 1}{n_A + 0.4} \right] \varphi_A + \left[\frac{n_B^2 - 1}{n_B + 0.4} \right] \varphi_B \quad (20)$$

Oster (Ost):

$$\frac{(n^2-1)(2n^2+1)}{n^2} = \left[\frac{(n_A^2-1)(2n^2+1)}{n_A^2} \right] \varphi_A + \left[\frac{(n_B^2-1)(2n^2+1)}{n_B^2} \right] \varphi_B \quad (21)$$

APD is determined,

$$APD = \frac{100}{n} \sum_{i=n} \left(\frac{|\delta_{expi} - \delta_{cali}|}{\delta_{expi}} \right) \quad (22)$$

In the formula given, the variables n_m , n_A , and n_B indicate the refractive indices of the mixture, the solvent, and the solute, respectively. The variables φ_A and φ_B denote the volume fractions of the solvent and the solute, respectively.

3. Results and Discussions

The experimental values of refractive index and density of pure organic liquids used in the present study along with their literature value are presented in table-1. It can be shown that the experimental values obtained in this study are in good agreement with the values that have been observed in prior study. It is apparent from table-2 that there is a considerable difference between refractive index, density and molar mass values of n-Hexanol and DMF (n_{HxOH} -1.4168, n_{DMF} -1.4286, ρ_{HxOH} -0.8158, ρ_{DMF} -0.9425, M_{HxOH} -102.18, M_{DMF} -73.09 (Lide et al., 2004).

Table 2 - Values of refractive index(n), density (ρ), molar volume (V_m), molar refraction (R_m), atomic polarization (P_A), Polarizability (α), molecular radii(r) and internal pressure (P_{int}) for the binary liquid mixtures of n-Hexanol with N, N-Dimethylformamide at 303.15K temperature.

X	n	ρ (gm/cm ³)	V_m (cm ³ /mol)	R_m (cm ³ /mol)	P_A (cm ³ /mol)	α $\text{\AA}^3$	r $\text{\AA}$	P_{int} (MPa)
0.0000	1.4286	0.9425	77.5491	19.9759	2.1429	0.7923	1.9936	109.58
0.0556	1.4275	0.9350	80.2013	20.6128	2.1396	0.8176	2.0145	105.77
0.1344	1.4255	0.9176	83.9602	21.4906	2.1337	0.8524	2.0427	100.71
0.2102	1.4242	0.9061	87.5761	22.3562	2.1298	0.8867	2.0698	96.35
0.2928	1.4230	0.8907	91.5163	23.3042	2.1262	0.9243	2.0986	92.02
0.3831	1.4220	0.8768	95.8238	24.3506	2.1232	0.9658	2.1296	87.74
0.4823	1.4210	0.8604	100.5559	25.5000	2.1202	1.0114	2.1626	83.48
0.5917	1.4196	0.8513	105.7745	26.7452	2.1160	1.0608	2.1972	79.18
0.7130	1.4184	0.8385	111.5608	28.1375	2.1125	1.1160	2.2347	74.93
0.8482	1.4178	0.8244	118.0101	29.7267	2.1107	1.1790	2.2760	70.77
1.0000	1.4168	0.8158	125.2513	31.4845	2.1077	1.2488	2.3200	66.57

A close perusal of table-2 indicates that as the mole fraction of n-HxOH increase in the mixture, the refractive index and density decreases. This is possible because n-HxOH has a low packing density and an open structure. The molecules are connected to each other by H-bonds that are formed by the molecules themselves. It has been observed that molar volume, molar refraction, polarizability and molecular radii increases as the mole fraction of n-HxOH increase in mixtures. While the opposite trend is observed for atomic polarization and internal pressure. There is a vast difference in values of internal pressure of pure components (P_{int} = 109.58 Mpa

and $P_{\text{int}} = 66.57$ Mpa) suggests strong possibility of hetero interaction in molecular species (Prajapati, 2017;). The increased concentration of n-HxOH raises the molecular radii because of lower packing fraction of n-HxOH and reduction of number of DMF molecules in mixture system. Deviation of experimental measurements from ideal values for refractive index, molar volume, reduce molar free volume, molecular radii, and internal pressure of binary mixtures are determined and fitted in Redlich–Kister Polynomial. Table-3 shows the values of coefficients (A_0, A_1, A_2, A_3) and correlation coefficients (δ).

Table 3 - Values of Coefficients of Redlich–Kister Polynomial with correlation constant.

Parameter	Δn	ΔV_m	$\Delta V_m/\Delta R_m$	Δr	ΔP_{int}
A_0	-0.0084	22.1603	0.0619	0.0448	-21.3677
A_1	0.0019	-3.3493	-0.0133	-0.0058	5.3276
A_2	-0.0024	2.7028	0.0185	-0.0017	-1.6821
A_3	0.0003	-7.3803	-0.0026	0.0046	0.6976
δ	0.9843	0.9968	0.9831	0.9986	0.9999

Figure 1 shows the variation of deviation of refractive index against mole fraction n-HxOH. Figure 1 shows negative deviation over the entire composition range. The negative (Δn) value shows maxima around 0.29 mole fraction of n-HxOH. It is well information that the variation in the refractive index is influenced by a number of different energetic and structural effects (Casas et al., 2005). The negative deviation (Δn) indicates a weak interaction between the mixture's contributing components (Pandey et al., 1994).

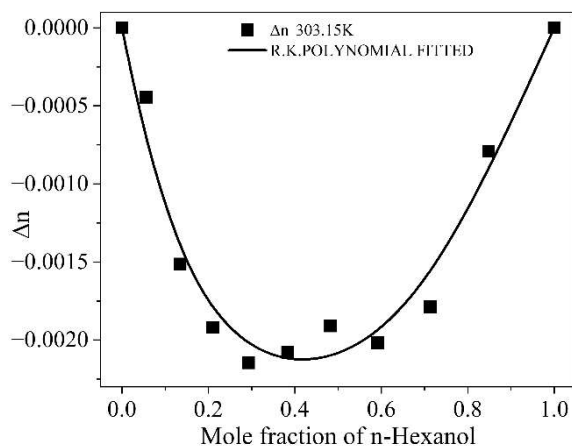


Figure-1. Plot of (Δn) vs mole fraction of n-Hexanol

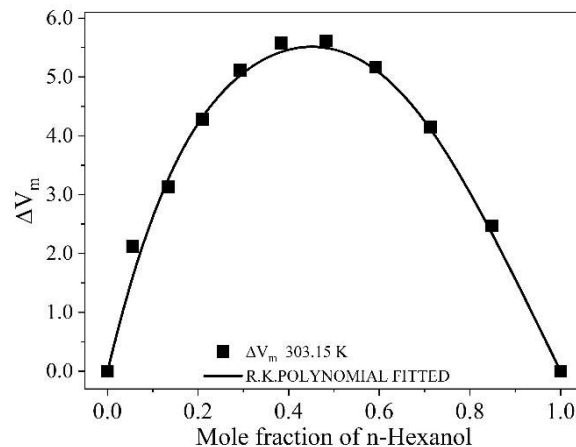


Figure-2. Plot of (ΔV_m) vs mole fraction of n-Hexanol

Fig. 2 indicates that the excess molar volume has a positive value over the whole range of concentrations for n-HxOH-DMF mixtures. Positive values of (ΔV_m) show that the volume of a mixture of two liquids has grown (n-HxOH with DMF). As the combination is less compressible than the ideal mixtures, the presence of weak dispersive forces is confirmed by this expansion (Navarkhele et al., 2022). The positive behavior may be due to specific interactions, such as the formation of hydrogen bonds, charge transfer complexes, and other complex forming interactions, including strong dipole–dipole interactions between the

component molecules in the mixture, which may lead to positive values of excess molar volume.

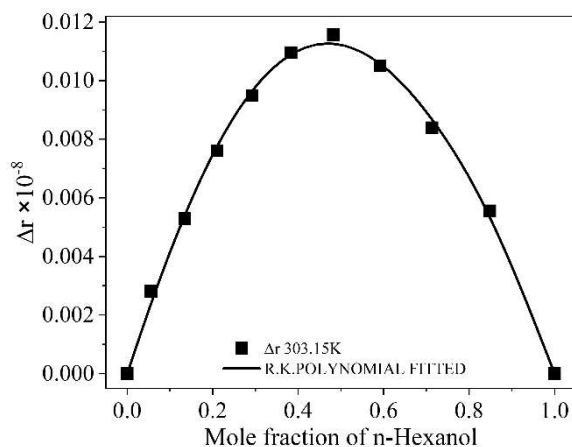


Figure-3. Plot of (Δr) vs mole fraction of n-HxOH

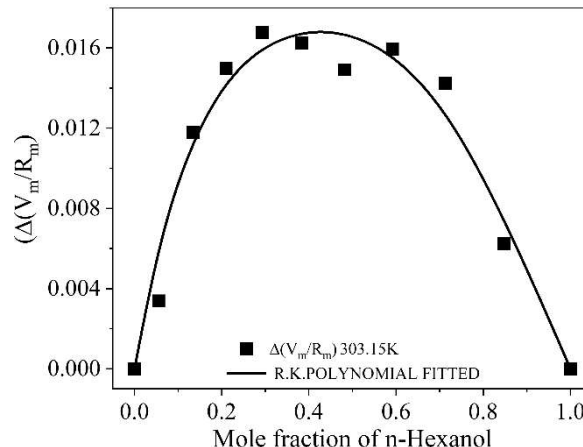


Figure-4. Plot of ($\Delta V_m/R_m$) vs mole fraction of n-HxOH

The non-linear positive trend of the deviation in molecule radii is seen in Figure 3. It means the formation of a hetero complexation via hydrogen bond between dissimilar molecules is less important than the breaking of the chain of hydrogen bonds in n-HxOH. Excess reduced molar free volume is shown in Fig. 4 to be positive over the whole composition range at constant temperature. According to (Brocos et al., 2003), the molar refraction deviation function must be calculated on a mole fraction basis, while the refractive index deviation function must be calculated on a volume fraction basis. This enables it to be directly understood as a measure of the deviations of reduced free volumes from ideality with a sign that is reversed.

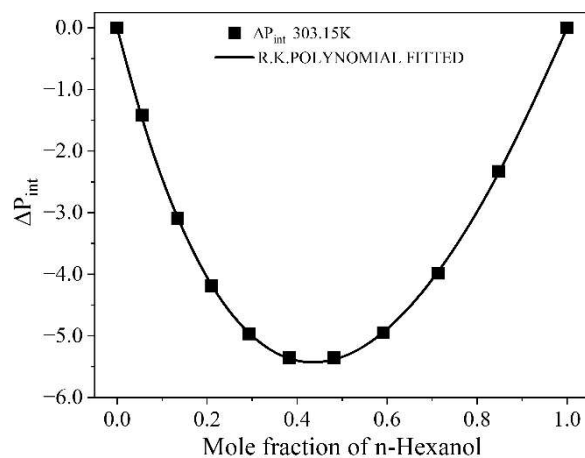


Figure-5. Plot of (ΔP_{int}) vs mole fraction of n-HxOH

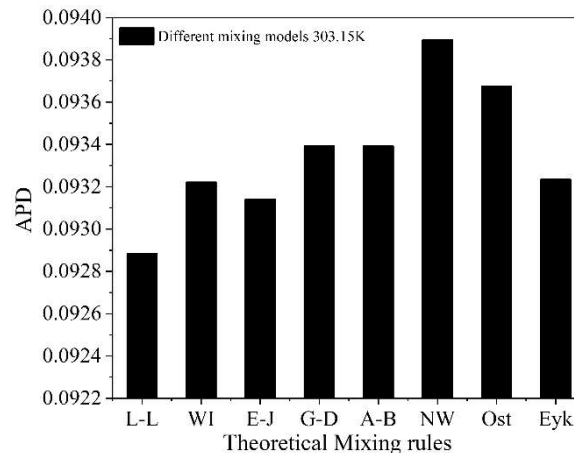


Figure-6. Plot of APD vs theoretical models

Fig. 5 exhibits the negative trends in internal pressure deviation across the entire composition range. Due to the fact that the internal pressure has a negative deviation, it may be concluded that the attractive forces are less than the repulsive forces. According to a report published by

(Prajapati et al., 2012) the concept of internal pressure is the amount of energy needed to vaporize a unit volume of a material. Internal pressure of pure alcohols decreases as chain length increases (Begona Garcia et al., 2002). The predicted refractive indices of the binary mixtures at each constant temperature (303.15K) studied were compared with the experimentally measured values and the results are presented in terms of Average percentage deviation (APD). The APD values for Lorentz-Lorentz (L-L), Weiner (W), Eyring-John (E-J), Gladstone-Dale (G-D), Arago-Biot (A-B), Newton (Nw), Oster (Ost) and Eykman (Eyk) relations are presented with their APD values in Figure 6. A close perusal of figure 6 reveals the Gladstone-Dale (G-D) and Arago-Biot (A-B) relations provided in figure 6 have identical APD values. The APD values predicted by Weiner (W), Eyring-John (E-J), Gladstone-Dale (G-D), Arago-Biot (A-B), Newton (Nw), Oster (Ost), and Eykman (Eyk) relationship are relatively greater than those predicted by Lorentz-Lorentz (L-L), which has the best fit for studied system. Since the observed that various types of liquid mixtures and their widely different molecular sizes, a given relation may yield excellent agreement in one position while deviating in another. The results of this research indicate that all theoretical mixing rules are quantitatively related in a simple manner and work properly within the experimental error limitations.

4. Conclusions

In this work, Refractive index and Density of binary mixture composition are measured over the entire range of mixing range at 303.15K. A good agreement has been found between the experimental and literature value of refractive index and density of n-HxOH with DMF. The atomic polarization of the binary mixtures decreases with decreasing volume fraction of n-HxOH. Molar volume, Polarizability and molecular radii increase with increasing volume fraction of n-HxOH. Negative deviation internal pressure indicates formation of complexion between molecular species. (Δn), ($\Delta \rho$), ($\Delta(V_m/R_m)$), (ΔP_{int}) values have been computed and the results of deviation/excess functions have been fitted to the Redlich–Kister equation. Various mixing models for refractive index have been tested for the studied system. For refractive index (n) the L-L mixing model shows least deviation among all.

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