

Dielectric relaxation study of N-methylformamide in 1, 4-dioxane solvent using time domain reflectometry technique up to 30 GHz

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Complex dielectric permittivity has been determined for the mixture of N- methylformamide (NMF) – 1, 4 –dioxane (DX) with various concentrations in the frequency range from 10 MHz to 30 GHz by time domain reflectometry (TDR) at different temperatures. The Luzar theory has been applied to compute Kirkwood correlation factors for the mixtures. It adequately reproduces the experimental values of static dielectric constants. The Bruggeman model for the non linear case has been fitted to the dielectric data of the binary mixture.

Keywords: Dielectric permittivity, Relaxation time, Time domain reflectometry (TDR), Dielectric relaxation

1 Introduction

The study of the dielectric properties of polar liquids, in particular the determination of the static and the high frequency dielectric constant can provide a good deal of information about their molecular structure and the intermolecular interaction. The remarkable interest in the study of dielectric relaxation behaviour of amide systems is to understand the role of hydrogen bonding and rotation of –NH₂ group. The dielectric relaxation study of solute – solvent mixtures in the microwave frequency range gives information about the molecular polarization of the system. This is related to formation of multimers in dipoles and their rotations. Temperature dependent dielectric parameters¹⁻⁴ have been reported on pure amide to understand hydrogen bonding limits. In case of N – methylformamide (NMF), Barthel *et al.*³ observed three dispersion steps up to 89 GHz and hence three relaxation times. The liquid structures and respective relaxation times suggest a relaxation process in NMF similar to that in alcohol⁵. There are many studies of the dielectric behaviour of amide in water, alcohol, acetone, ethylene glycol, dimethylsulphoxide, 1, 4 –dioxane (DX), 3- nitrotoluene⁶⁻¹⁶. The amide linkage (-CO–NH-) is an important functional group in chemistry, pharmaceutical and material science. Hydrogen bonds compose a very interesting class of intermolecular

interactions which has extreme importance in the fields of chemistry^{17,18}. The N-methylformamide is excellent proton donors as well as proton acceptor and hence it is strongly associated through intermolecular H-bonds¹⁹. The thermodynamic characteristics and intermolecular interaction of aqueous solution of N-methylformamide were calculated over the whole range of concentrations mixtures²⁰. The dielectric investigations of hydrogen bonded compounds (NMF) in non-polar solvent (1, 4-dioxane) provide valuable information regarding molecular complex formation in solution⁸.

The aim of present study is to investigate the dielectric spectra of NMF - 1, 4-dioxane mixtures using time domain reflectometry technique from 10 MHz to 30 GHz. Static dielectric constant, relaxation time, thermodynamic parameter and Kirkwood correlation factor have been evaluated for NMF - 1, 4-dioxane mixtures.

2 Experimental

N- methylformamide was obtained commercially of S D Fine-Chem Limited Company (AR Grade 99%). The solutions were prepared by mixing the 1, 4-dioxane and NMF in volume. The volume fraction of 1, 4-dioxane (V_{DX}) was calculated as follows:

$$V_{DX} = \frac{\text{Vol. of DX}}{[\text{Vol. of DX} + \text{Vol. of NMF}]} \quad \dots (1)$$

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The densities of solutions were measured using specific gravity bottle and weighting were carried out by using electronic balance. The uncertainties of the measured values of densities were $\pm 10^{-4}$ g/cm³. The dielectric complex permittivity $\epsilon^*(\omega)$ of the mixtures over the entire concentration range have been determined using TDR at a different temperatures, i.e., 0 °C to 25 °C with the interval of 5 °C. The temperature of sample under test has been maintained using calibrated temperature controller system with accuracy of ± 0.1 °C. The Tektronix DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 in the frequency range from 10 MHz to 30 GHz has been used. The details of the apparatus and data analysis procedures of the TDR have been reported previously^{21,22}.

3 Results and Discussion

Figure 1 (a,b) shows frequency dependent complex permittivity spectra for NMF – 1, 4-dioxane mixtures. The complex dielectric permittivity spectrum of a sample can be fitted by the non-linear least squares fit method using the models given by the Havriliak - Negami expression^{23,24}:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \quad \dots (2)$$

where α ($0 \leq \alpha \leq 1$) and β ($0 \leq \beta \leq 1$) are the shape parameters, ω is the angular frequency, ϵ_0 is the static dielectric constant, ϵ_∞ is the permittivity at high frequency, τ is relaxation time, and α and β is the

Cole-Cole and Davidson-Cole distribution parameter, respectively. The Debye ($\alpha = 0, \beta = 1$)²⁵ Cole-Cole ($0 \leq \alpha \leq 1$ and $\beta = 1$)²⁶ and Davidson – Cole ($\alpha = 0$ and $0 \leq \beta \leq 1$)²⁷ functions are the limiting cases of Eq. (2). The static dielectric constant (ϵ_0) and relaxation time (τ) for NMF – 1, 4-dioxane mixtures at different temperatures are given in Table 1. The static dielectric constant and relaxation time for NMF + 1, 4-dioxane mixture decreases with concentration of 1, 4-dioxane in NMF. The experimental value of dielectric constant and relaxation time are in good agreement with the literature values^{4,6,8}. The non linear behaviour of the static dielectric constant against X_{DX} of the binary mixtures suggests the formation of hydrogen bond complexes between NMF and 1, 4-dioxane molecule.

3.1 Kirkwood correlation factor

In the Kirkwood –Frohlich theory a way to calculate the static permittivity of a polar liquid accounting for molecular short range interaction is provided through the well known equation²⁸:

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{9\epsilon_0} = \frac{4\pi}{9kT} \sum_{i=1}^2 g_i \rho_i \mu_i^2 \quad \dots (3)$$

where ϵ_0 and ϵ_∞ are the static and high frequency permittivity, respectively, T is absolute temperature, k is Boltzmann constant, μ_i is the permanent dipole moment in the gas phase of the single molecule, ρ_i is the density and g_i is the Kirkwood correlation factor for the i^{th} liquid component, $i=1$ and 2 represent NMF

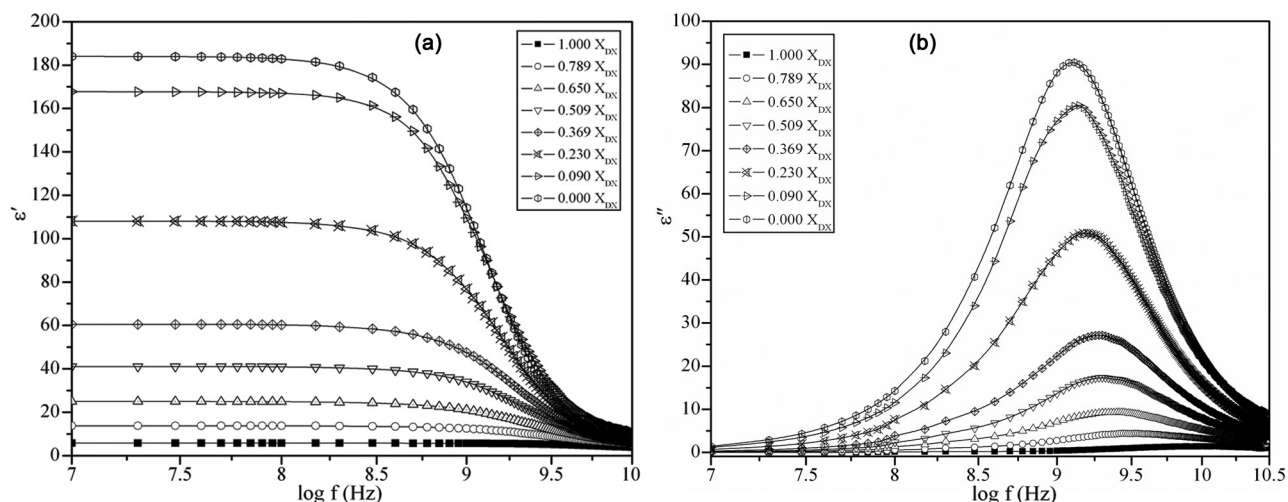


Fig. 1 — Frequency dependence dielectric permittivity (ϵ') and loss (ϵ'') for NMF - 1, 4-dioxane mixtures at various concentrations at 25°C. The solid line calculated from the Debye equation.

Table 1 — Temperature dependent dielectric relaxation parameters for NMF-1, 4-dioxane mixture.

25 °C					
V_{DX}	X_{DX}	ρ (g/cm ³)	ϵ_0	ϵ_∞	τ (ps)
1.000	1.000	1.0280	2.24(1)	2.31(2)	5.00(16)
0.955	0.931	1.0272	5.76(8)	2.38(3)	17.74(8)
0.905	0.858	1.0261	8.33(27)	2.61(4)	30.31(13)
0.855	0.789	1.0241	13.99(15)	2.78(5)	43.57(18)
0.800	0.717	1.0236	17.35(51)	3.12(16)	54.21(20)
0.745	0.650	1.0218	25.28(34)	3.30(18)	64.76(21)
0.685	0.580	1.0204	28.51(4)	3.34(9)	67.36(23)
0.620	0.509	1.0179	41.52(49)	3.30(8)	74.76(19)
0.550	0.437	1.0163	54.77(51)	3.52(19)	81.46(16)
0.480	0.369	1.0138	60.80(47)	3.48(8)	84.13(13)
0.400	0.297	1.0102	75.09(50)	3.76(9)	89.87(12)
0.320	0.230	1.0070	103.83(13)	3.70(17)	103.42(28)
0.230	0.159	1.0047	108.45(51)	6.70(22)	103.46(10)
0.135	0.090	1.0000	169.73(19)	6.50(30)	120.50(29)
0.075	0.049	0.9990	179.45(23)	6.41(30)	123.25(33)
0.000	0.000	0.9980	184.00(33)	2.99(2)	125.99(17)
20 °C					
V_{DX}	X_{DX}	ϵ_0	ϵ_∞	τ (ps)	
1.000	1.000	2.39(1)	2.83(4)	3.71(8)	
0.955	0.931	5.83(1)	3.12(10)	19.04(11)	
0.905	0.858	8.42(25)	4.17(19)	31.61(30)	
0.855	0.789	13.77(19)	4.19(2)	51.47(46)	
0.800	0.717	17.51(34)	4.58(2)	57.99(57)	
0.745	0.650	26.26(9)	4.54(2)	67.65(51)	
0.685	0.580	29.15(9)	4.53(2)	69.59(45)	
0.620	0.509	41.94(12)	4.00(2)	76.71(39)	
0.550	0.437	56.04(10)	4.05(2)	83.14(27)	
0.480	0.369	62.08(12)	4.26(3)	87.37(30)	
0.400	0.297	76.55(13)	4.39(2)	93.74(27)	
0.320	0.230	107.15(23)	3.10(6)	108.30(43)	
0.230	0.159	114.07(11)	4.10(5)	113.88(20)	
0.135	0.090	176.18(27)	3.70(3)	129.11(35)	
0.075	0.049	191.97(26)	3.55(4)	133.95(33)	
0.000	0.000	197.04(63)	2.84(11)	145.73(76)	
15 °C					
V_{DX}	X_{DX}	ϵ_0	ϵ_∞	τ (ps)	
1.000	1.000	2.68(1)	3.24(5)	3.22(8)	
0.955	0.931	6.31(12)	3.52(12)	20.39(15)	
0.905	0.858	9.04(90)	4.50(2)	32.50(35)	
0.855	0.789	14.44(95)	4.23(2)	51.99(50)	
0.800	0.717	17.95(46)	4.65(2)	58.23(62)	
0.745	0.650	26.71(11)	4.59(2)	68.25(62)	
0.685	0.580	29.89(13)	4.66(3)	71.49(61)	
0.620	0.509	44.48(16)	4.44(2)	83.85(54)	
0.550	0.437	57.76(14)	4.61(2)	89.43(38)	
0.480	0.369	65.96(14)	4.58(3)	97.64(39)	
0.400	0.297	80.47(15)	4.93(7)	102.50(34)	
0.320	0.230	112.23(28)	3.39(6)	117.59(55)	
0.230	0.159	118.77(14)	4.10(5)	122.29(25)	
0.135	0.090	184.13(31)	3.21(4)	140.60(43)	
0.075	0.049	199.24(29)	3.45(3)	143.75(38)	
0.000	0.000	206.53(45)	3.39(2)	162.14(21)	

(Contd...)

Table 1 — Temperature dependent dielectric relaxation parameters for NMF-1, 4-dioxane mixture.(Contd..)

10 °C				
V_{DX}	X_{DX}	ϵ_0	ϵ_∞	τ (ps)
1.000	1.000	3.22(1)	3.55(3)	----
0.955	0.931	6.80(15)	3.99(14)	20.70(18)
0.905	0.858	9.83(58)	4.88(2)	33.05(40)
0.855	0.789	15.34(94)	4.85(3)	52.37(62)
0.800	0.717	18.98(11)	4.86(6)	60.65(37)
0.745	0.650	27.21(14)	5.07(8)	69.21(72)
0.685	0.580	31.47(16)	5.30(3)	78.65(78)
0.620	0.509	46.85(18)	4.85(3)	91.51(66)
0.550	0.437	60.26(16)	4.92(2)	96.98(49)
0.480	0.369	68.39(17)	5.10(3)	105.37(48)
0.400	0.297	84.43(18)	4.35(5)	113.63(45)
0.320	0.230	118.92(19)	3.66(7)	133.18(44)
0.230	0.159	123.59(18)	3.40(6)	138.59(36)
0.135	0.090	193.05(36)	4.10(3)	156.10(54)
0.075	0.049	207.74(35)	5.01(4)	155.88(49)
0.000	0.000	215.87(13)	4.18(2)	181.97(21)
5 °C				
V_{DX}	X_{DX}	ϵ_0	ϵ_∞	τ (ps)
1.000	1.000	4.52(1)	3.67(4)	----
0.955	0.931	8.58(23)	4.87(10)	21.95(24)
0.905	0.858	11.46(15)	5.40(8)	34.76(47)
0.855	0.789	17.55(10)	5.15(3)	53.78(77)
0.800	0.717	20.60(13)	4.58(5)	61.11(86)
0.745	0.650	29.74(17)	4.80(7)	73.73(86)
0.685	0.580	33.11(19)	5.20(6)	80.46(29)
0.620	0.509	49.61(24)	4.75(2)	97.61(29)
0.550	0.437	62.94(20)	4.48(8)	106.39(62)
0.480	0.369	72.09(24)	4.85(6)	115.21(71)
0.400	0.297	87.57(23)	5.27(3)	123.03(60)
0.320	0.230	125.10(44)	5.31(3)	148.87(10)
0.230	0.159	130.74(28)	4.73(4)	150.40(61)
0.135	0.090	204.54(48)	4.94(5)	179.42(81)
0.075	0.049	218.74(43)	4.55(8)	177.23(67)
0.000	0.000	228.17(23)	4.27(6)	208.40(41)
0 °C				
V_{DX}	X_{DX}	ϵ_0	ϵ_∞	τ (ps)
1.000	1.000	5.73(1)	3.53(4)	---
0.955	0.931	10.29(27)	4.35(5)	23.52(30)
0.905	0.858	12.93(2)	5.24(7)	36.22(69)
0.855	0.789	18.86(12)	5.45(6)	54.04(91)
0.800	0.717	22.17(15)	5.10(4)	62.80(10)
0.745	0.650	31.54(22)	5.35(8)	77.29(14)
0.685	0.580	34.96(24)	6.10(3)	85.78(22)
0.620	0.509	53.06(30)	6.61(7)	111.08(27)
0.550	0.437	67.75(29)	6.61(7)	120.64(86)
0.480	0.369	76.42(31)	6.45(5)	130.96(10)
0.400	0.297	93.83(30)	7.10(6)	141.21(88)
0.320	0.230	133.08(55)	6.25(2)	173.74(44)
0.230	0.159	140.53(38)	5.65(3)	178.27(59)
0.135	0.090	221.87(69)	5.85(4)	218.09(38)
0.075	0.049	239.58(66)	6.41(11)	219.47(21)
0.000	0.000	254.14(49)	5.35(7)	248.93(79)

and DX, respectively. It is thus evident that, when there is no correlation between molecular orientations, one has $g = 1$; when molecules tend to align themselves with parallel dipole moments “ g ” will be larger than 1, while for antiparallel alignments one has $g < 1$. The interpretation of dielectric phenomena in terms of Kirkwood correlation factor is very difficult for a mixture of associated compounds. It is impossible to separate the average correlation factor g_1 and g_2 from single value of the static dielectric constant without any assumptions.

To understand the number of hydrogen bonds per NMF and DX molecules, we apply the Luzar model to the results of dielectric constant for NMF-DX mixtures. Luzar suggested theoretical model based on mean field approximation for hydrogen bonded mixture²⁹. The correlation factor ‘ g_1 ’ and ‘ g_2 ’ are calculated by following equations as follows:

$$g_1 = 1 + Z_{11} \cos\phi_{11} + Z_{12} \cos\phi_{12} (\mu_2/\mu_1) \quad \dots (4)$$

$$g_2 = 1 + Z_{21} \cos\phi_{21} (\mu_1/\mu_2) \quad \dots (5)$$

where $Z_{11} = 2 \langle n_{\text{HB}}^{11} \rangle$, $Z_{12} = \langle n_{\text{HB}}^{12} \rangle$, and $Z_{21} = \langle n_{\text{HB}}^{21} \rangle (1-X_{\text{DX}})/X_{\text{DX}}$ are the average number of hydrogen bond with NMF-NMF, NMF-DX pairs, respectively. ϕ_{11} , ϕ_{12} and ϕ_{21} are the average angles between neighboring dipoles of NMF and 1, 4-dioxane molecules. The values of g_1 and g_2 for NMF-DX mixtures are computed and are shown in Fig. 2. The values of g_1 and g_2 for this mixture have some deviation from ideality, which confirms that, the net change in dipolar ordering of the mixture constituents due to H-bond complication. Also it indicate that the tendency of dipoles to align themselves in parallel configuration.

The average number of hydrogen bonds $[n_{\text{HB}}^{11}]$, $[n_{\text{HB}}^{12}]$ and $[n_{\text{HB}}^{21}]$ per DX molecule for $1i$ pairs ($i=1, 2$) has been determined using following relation²⁹:

$$\langle n_{\text{HB}}^{1i} \rangle = n_{1i} \omega^{1i} / n_1 \quad \dots (6)$$

where $\omega^{1i} = 1/[1 + \alpha^{1i} \exp(\beta E^{1i})]$ is the probability of bond formation between NMF and DX. n_1 is the number density of NMF molecules, $\beta = 1/kT$, and α^{1i} are the statistical volume ratios of the two sub volumes of the phase space related to the non hydrogen-bonded and hydrogen bonded pairs. These hydrogen bonded pairs have only two energy levels, E^{11} and E^{12} , for 11 and 12 pair formed bonds,

respectively. The values of $[n_{\text{HB}}^{11}]$ and $[n_{\text{HB}}^{12}]$ depend on the number of densities of the hydrogen-bonded pairs between NMF and DX (n_{12}) and between NMF molecules ($n_{11} = 2n_1 - n_{12}$), respectively. These can be calculated, during which NMF– NMF (11 pairs) and NMF – DX (12 pairs) are formed²⁹. Figure 3 shows a plot of the average number of hydrogen bonds between NMF – NMF molecules (11 pairs) and NMF – DX (12 pairs) against the mole fraction of 1, 4-dioxane. It can be seen from the values that $[n_{\text{HB}}^{11}]$ and $[n_{\text{HB}}^{12}]$ depend on the concentration of DX in NMF – 1, 4-dioxane mixtures.

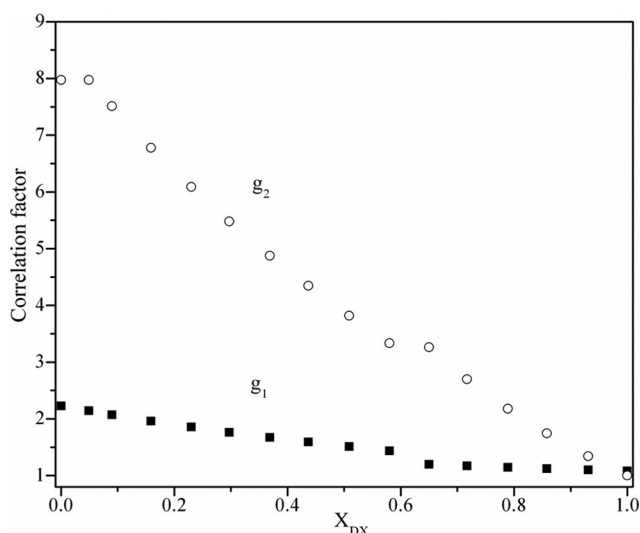


Fig. 2 — Plots of the correlation factor (g_1 and g_2) versus mole fraction of 1, 4 - dioxane (X_{DX}) at 25 °C.

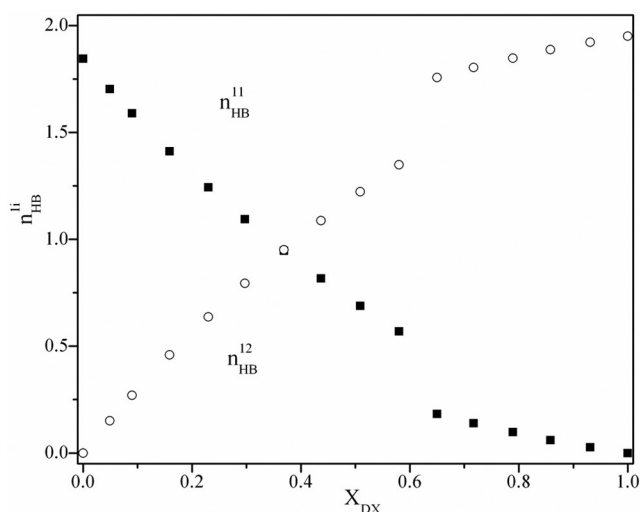


Fig. 3 — Plots of the average number of hydrogen bonds between NMF - NMF (n_{HB}^{11}) and NMF - DX (n_{HB}^{12}) versus mole fraction of 1, 4 - dioxane (X_{DX}) at 25 °C.

We calculated the average number of hydrogen-bonded NMF – NMF pairs $[n_{\text{HB}}^{11}]_{\text{V}}$ and NMF – DX pairs, $[n_{\text{HB}}^{12}]_{\text{V}}$ per unit volume ($/\text{cm}^3$) using³⁰⁻³²:

and

$$[n_{\text{HB}}^{11}]_{\text{V}} = \frac{C_{\text{NMF}} \rho_{\text{mix}} N_{\text{A}}}{M_{\text{NMF}}} n_{\text{HB}}^{11} (/ \text{cm}^3)$$

$$[n_{\text{HB}}^{12}]_{\text{V}} = \frac{C_{\text{NMF}} \rho_{\text{mix}} N_{\text{A}}}{M_{\text{NMF}}} n_{\text{HB}}^{12} (/ \text{cm}^3) \quad \dots (7)$$

where C_{NMF} is the weight fraction of NMF, ρ_{mix} (g/cm^3) is the density of mixture, N_{A} is the Avogadro number as 6.02×10^{23} ($/\text{mol}$) and M_{NMF} is the molecular weight of NMF. Figure 4 shows plots of $[n_{\text{HB}}^{11}]_{\text{V}}$ and $[n_{\text{HB}}^{12}]_{\text{V}}$ against X_{DX} . The value of $[n_{\text{HB}}^{11}]_{\text{V}}$ increases with increasing X_{DX} and that of $[n_{\text{HB}}^{12}]_{\text{V}}$ has a maximum at $X_{\text{DX}} = 0.37$. These results provide information regarding the intermolecular interaction of NMF-NMF and NMF-DX molecules.

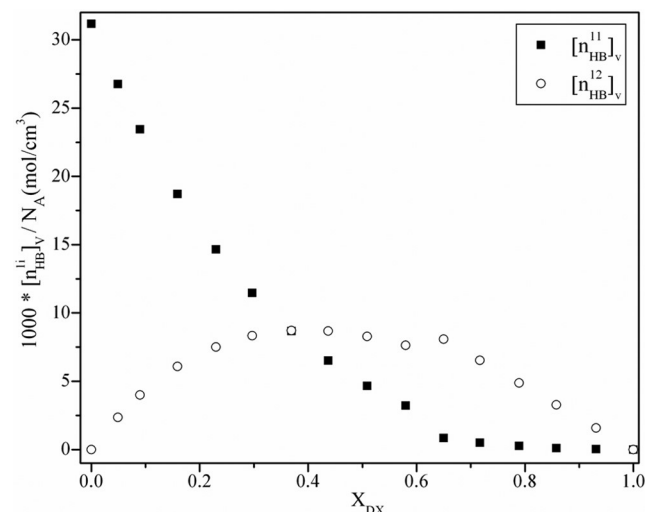


Fig. 4 – Plots of the number of hydrogen bonds per unit volume against mole fraction of 1, 4 - dioxane (X_{DX}) mixtures at 25 °C.

The concentration dependence of the dielectric permittivity is calculated using Eqs (3-6) and is compared with experimental data. The model gives a good qualitative account of the dielectric permittivity of the NMF- 1, 4-dioxane mixtures. In our analysis, best possible values of molecular parameters with which the theoretical dielectric permittivity values are in agreement with experiment values are given in Table 2. The theoretical values of static dielectric constants determined from hydrogen bonding model are found in good agreement with the experimental values obtained from TDR technique as shown in Fig. 5.

3.2 Bruggeman factor

The Bruggeman equation for binary mixture is given by the expression³³:

$$f_B = \left[\frac{(\epsilon_{0m} - \epsilon_{02})}{(\epsilon_{01} - \epsilon_{02})} \right] \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{1/3} = 1 - V_{\text{DX}} \quad \dots (8)$$

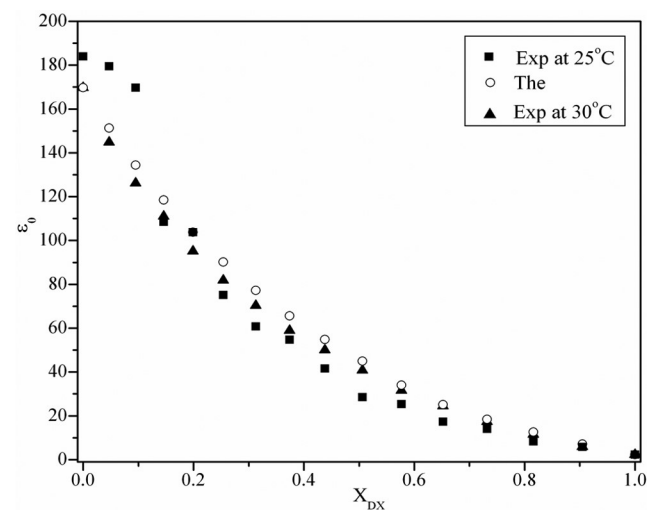


Fig. 5 – Theoretical and experimental static dielectric constant (ϵ_0) for NMF-DX mixtures as a function of mole fraction of DX (X_{DX}). – experimental at 25 °C ▲ – experimental at 30 °C (Ref. 8) ○ – theoretical.

Table 2 — Molecular parameters used in computation of the static dielectric constant (ϵ).

Molecular parameters	25 °C	20 °C	15 °C	10 °C	5 °C	0 °C
Effective dipole moment ^a of NMF	5.81	5.95	6.02	6.10	6.20	6.48
Effective dipole moment ^a of DX	0.75	0.82	0.94	1.11	1.44	1.67
Polarizability ^b of NMF	4.66	4.66	4.66	4.66	4.66	4.66
Polarizability ^b of DX	5.68	5.68	5.68	5.68	5.68	5.68
Binding energy ^c of NMF-NMF	-14.39	-14.39	-14.39	-14.39	-14.39	-14.39
Binding energy ^c of NMF-DX	-18.25	-18.25	-18.25	-18.25	-18.25	-18.25
Enthalpy ^c of NMF-NMF	28	28	28	28	28	28
Enthalpy ^c of DX-DX	40	40	40	40	40	40
Number of hydrogen bond	3	3	3	3	3	3

^aUnit: Debye; ^bUnit : A⁰³; ^cUnit: kJ/mol

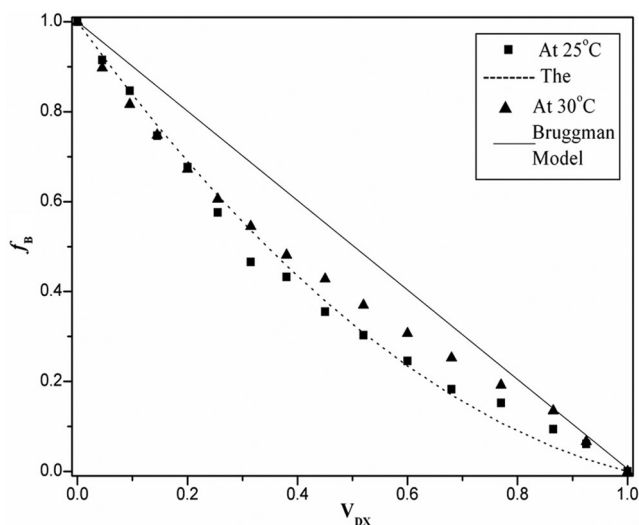


Fig. 6 — Bruggeman dielectric factor (f_B) versus volume fraction of 1, 4-dioxane (V_{DX}). Solid line represents theoretical curve according to Bruggeman model. Dashed line represents theoretical curve obtained from Eq. (8). ■ — experimental at 25 °C ▲ — experimental at 30 °C (Ref. 8)

where, (f_B) is the Bruggeman dielectric factor. The ϵ_{0m} , ϵ_{01} and ϵ_{02} are the static dielectric constants corresponding to mixture, NMF and 1, 4-dioxane, respectively. (V_{DX}) is the volume fraction of DX. The Bruggeman dielectric factor vs volume fraction of 1, 4-dioxane (V_{DX}) is given in Fig. 6. It can be seen from Fig. 6 that f_B is not a linear function of volume fraction on predicted by the Bruggeman equation. The Bruggeman equation may be written as³⁴:

$$f_B = \left[\frac{(\epsilon_{0m} - \epsilon_{02})}{(\epsilon_{01} - \epsilon_{02})} \right] \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{1/3} = 1 - [a - (a-1)V_{DX}]V_{DX} \quad \dots (9)$$

The value of $a=1$ implies the ideal mixture with no interaction between NMF and 1, 4-dioxane. In Fig. 6 solid line represents according to Eq. (8). Experimental values represent the deviation from ideality of mixture. It indicates the existence of hydrogen bonding interaction between NMF- 1, 4 - dioxane. The values of 'a' is determined by the least square fit method and are reported in Table 3.

3.3 Thermodynamic properties

The thermodynamic parameters evaluated using Eyring equation is as follows³⁵:

$$\tau = (h/k_B T) \exp(\Delta H/RT) \exp(-\Delta S/R) \quad \dots (10)$$

where ΔS is the entropy of activation in $\text{J mol}^{-1} \text{K}^{-1}$, ΔH is the activation energy in kJ/mole . τ is the

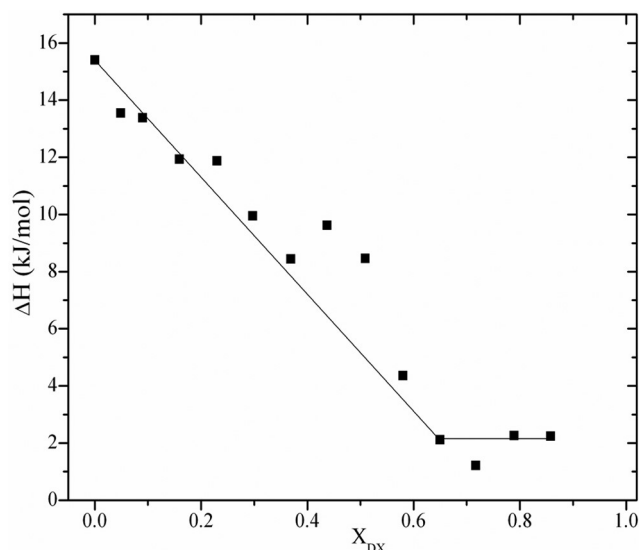


Fig. 7 — Activation energy versus mole fraction of 1, 4 - dioxane (X_{DX}).

Table 3 — Bruggeman factor for NMF - 1, 4 - dioxane mixture at different temperature.

Temperature (°C)	'a' value
25	1.69
20	1.75
15	1.76
10	1.77
5	1.79
0	1.87

relaxation time in ps, k_B is the Boltzmann constant, R is gas constant, T is the temperature in degree Kelvin and h is the Planck's constant. The resulting values of activation energy as obtained by the least square fit method are reported in Fig. 7. It indicates the positive values of enthalpies for all concentrations. The activation energy decreases with increasing concentration of 1, 4-dioxane (X_{DX}) in NMF.

4 Conclusions

The temperature dependence of the dielectric relaxation parameters of NMF-DX mixtures has been determined over the whole composition range using time domain reflectometry technique in the frequency range 10 MHz to 30 GHz. The static dielectric constant for the mixtures can be explained using hydrogen bonded model by assuming the formation of hydrogen bond between NMF-NMF and NMF-DX pairs. The activation energy decreases with increasing concentration of 1, 4-dioxane in NMF. The significant degree of hydrogen bonding leading to a strong

intermolecular correlation is due to ether oxygen's acceptor group available in 1, 4-dioxane and NMF molecules.

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