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HYDROGEN BOND INTERACTION STUDY OF DMSO-WATER BINARY MIXTURES

A. D. Bokhare[1]*, M. P. Lokhande[1] and A. C. Kumbharkhane[2]

[1]Govt. Vidarbha Institute of Science and Humanities, Amravati-444604, MS, India.

[2]School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431606, MS, India.

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***Corresponding Author**
A. D. Bokhare
Govt. Vidarbha Institute of Science and Humanities, Amravati-444604, MS, India.

ABSTRACT

The complex permittivity spectra for Dimethylsulphoxide(DMSO)-Water mixtures, in the frequency range 10 MHz -30 GHz has been measured, over the entire concentration range using time domain reflectometry (TDR) method. The complex permittivity spectra has been fitted to the Cole –Davidson relaxation model. The least squares fit method has been used to determine the static dielectric constant(ε_0), relaxation time(τ) from complex permittivity spectra in order to study hydrogen-bond interactions. The formation of hydrogen bonds between Dimethylsulphoxide(DMSO) and water has been studied by an analysis of their dielectric parameters. Luzar theoretical model is used to computeaverage number of hydrogen bond for Water–Water and Water–DMSO molecules.

KEYWORDS: Dielectric permittivity, Relaxation time, Time domain reflectometry (TDR).

INTRODUCTION

The hydrogen bond is an intermolecular interaction that appears between electron-deficient hydrogen and a region of high electron densitywhich significantly affects a material's viscosity, melting point, and other physical parameters.[1] The study of H-bond interactions, dipolar alignments, and hydrogen bond connectivity can all benefit greatly from dielectric characterization. Dielectric relaxation spectroscopy was proved to be an effective tool for an investigation of H-bond rearrangement dynamics.

DMSO contains a strongly polar sulfoxide (S=O) group and two hydrophobic methyl groups (CH_3). The sulfoxide group group can form hydrogen bonds with water molecules.[2] The findings of Bo Yang , Xianwen Cao et al are helpful for the research of hydrogen bonding and solvation of DMSO in life science and chemical industry.[3] The binary mixtures of DMSO with water have large number of applications in Pharmacology, organic chemistry and biology.[4-6] Luzar has discovered a hydrogen bonding model to study DMSO-Water system theoretically.[7] Although numerous investigations have been carried out on the aqueous solution of DMSO, the specifics of hydrogen bond modifications in DMSO-water remain unknown.

In the Present study, a dielectric study was conducted, in an effort to understand how hydrogen bonds form and how the pure water structure changes across the full concentration range of DMSO- Water.

EXPERIMENTAL

2.1. MATERIALS

Dimethylsulphoxide(DMSO) was obtained commercially from s d fine-chem limited company (AR Grade 99%). and used without further purification (99% purity). Water was obtained from HPLC grade, Fisher Scientific India Pvt. Ltd., and used as a solvent for preparing mixtures. The binary mixture of DMSO and Water was prepared at different concentrations by volume fraction.

2.2. Measurements

The time domain reflectometry (TDR)technique was implementedin the frequency region of 10 MHz to 30 GHzin order to understand the complex permittivity spectra and dielectric relaxation measurements of the DMSO-water mixture.

The Tektronix Digital Serial Analyzer model no. DSA8300 sampling mainframe oscilloscope along with the dual channel sampling module 80E10B has been employedfor time domain reflectometer. Fig. 1 shows the block diagram of TDR. The sampling module provides a 12 ps incident and 15 ps reflected rise time pulse. These pulses are reflected pulse without sample $R_1(t)$ and with sample, $R_x(t)$ were recorded in a time window of 5ns and digitized in 2000 points and are shown in Fig. 2. Coaxial cable used to feed the pulse which has 50-ohm impedance, inner diameter of 0.28 mm and outer diameter of 1.19 mm.

The addition *[q(t) = R1(t) + Rx(t)]* and subtraction *[p(t) = R1(t) – Rx(t)]* of these pulses are done in oscilloscope memory. These subtracted and added pulses are transferred to computer for further analysis.

The Fourier transformation of the pulses and data analysis was done earlier to determine the complex permittivity spectra in the frequency range 10 MHz to 30 GHz using the nonlinear least squares fit method.

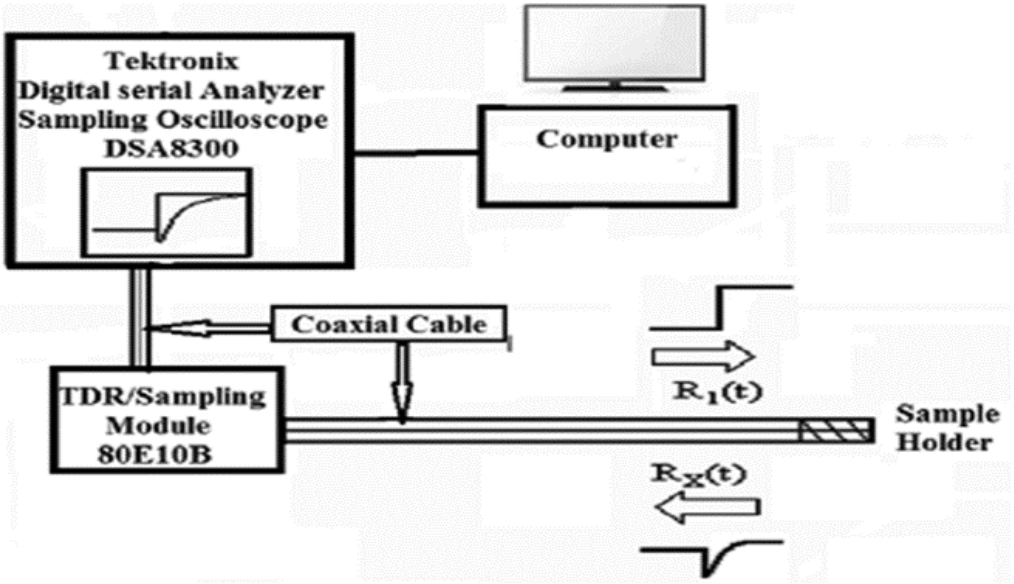

Fig. 1: Block Diagram of Time Domain Reflectometry (TDR).

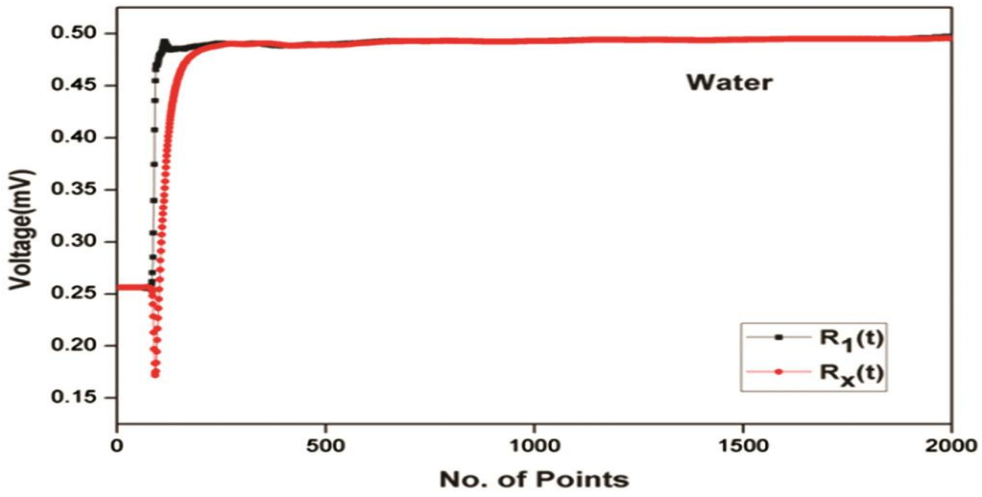

Fig. 2: TDR Waveform: Reflected pulses with & without Sample.

3 RESULTS AND DISCUSSION

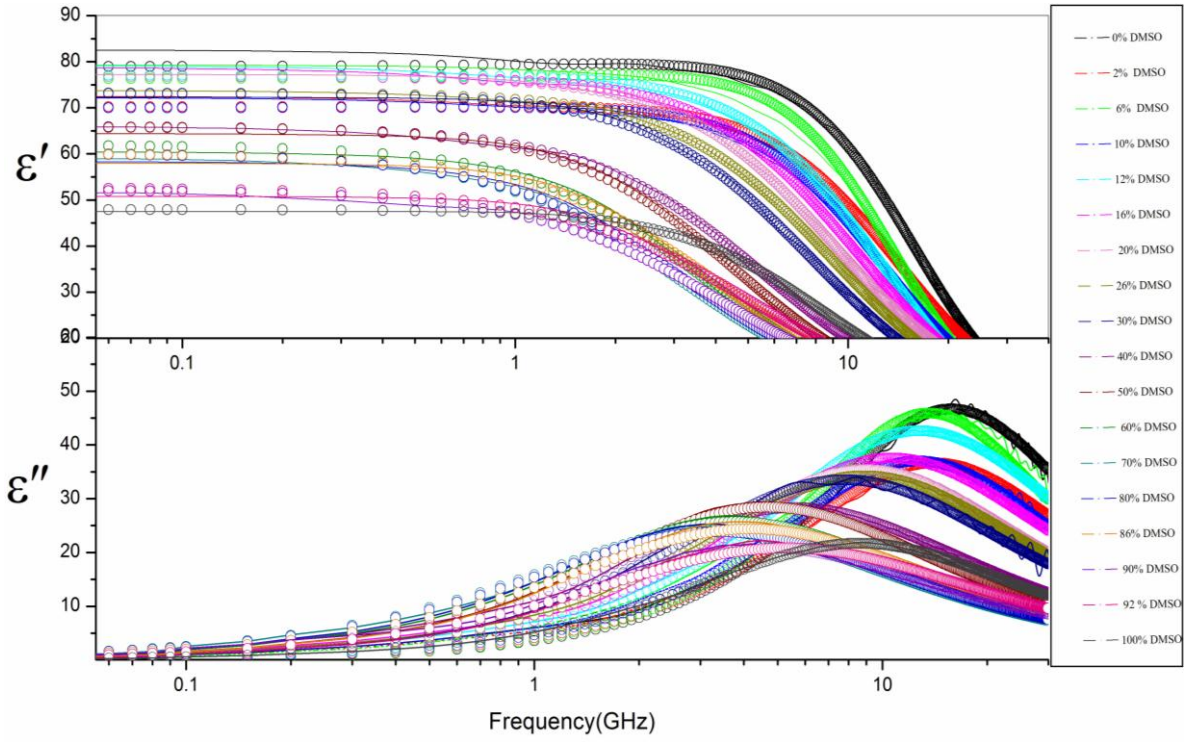

Fig. 3: Frequency dependence dielectric complex permittivity spectra for DMSO + Water mixture for various concentrations at 25 °C.

3.1 Static Dielectric Constant and Dielectric relaxation time

The complex permittivity spectra measured using TDR is fitted by the non-linear least squares fit method to the Havriliak - Negami expression.[8, 9]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1+(j\omega\tau)^{1-\alpha}]^\beta} \quad (1)$$

where ε_0 is the static dielectric constant , ε_∞ is the permittivity at high frequency which represents the instantaneous behaviour, τ is relaxation time and α and β are the distribution parameters.

Equation (1) includes the Debye (α =0, β = 1)[10], Cole-Cole ($0 \leq \alpha \leq 1$ and β = 1)[11] and Davidson – Cole (α = 0 and $0 \leq \beta \leq 1$).[12]. The static dielectric constant (ε_0) and relaxation time (τ) for DMSO-Water mixtures at different temperatures are given in table 1. Generally, the static dielectric constant for DMSO-Water mixtures decreases from the value for pure waterto that of pure DMSO. But low concentration of DMSO shows a peculiar behaviour as shown in Fig 4. As the concentration of DMSO increases, static dielectric constant decreases

which indicates that the hydrogen bond between DMSO and water molecule gradually brakes.

A plot of the principal dielectric relaxation time as a function of the composition of solutions given in Fig 5 indicates thatdielectric relaxation time decreases with increase in temperature in DMSO-Water mixture. Mixture's relaxation time is high at 70% DMSO concentration. However, the dielectric relaxation time reduces from 70% DMSO to pure DMSO.

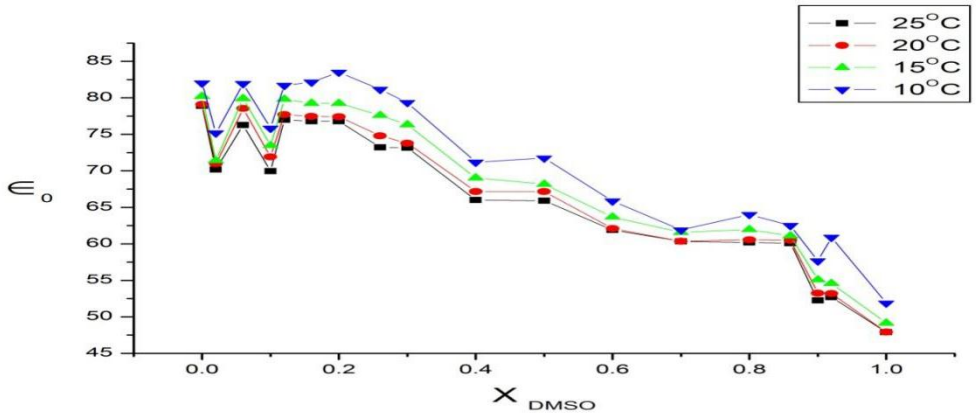

Fig. 4 Static dielectric constant vs volume fraction of DMSO for DMSO+Water system at different temperatures.

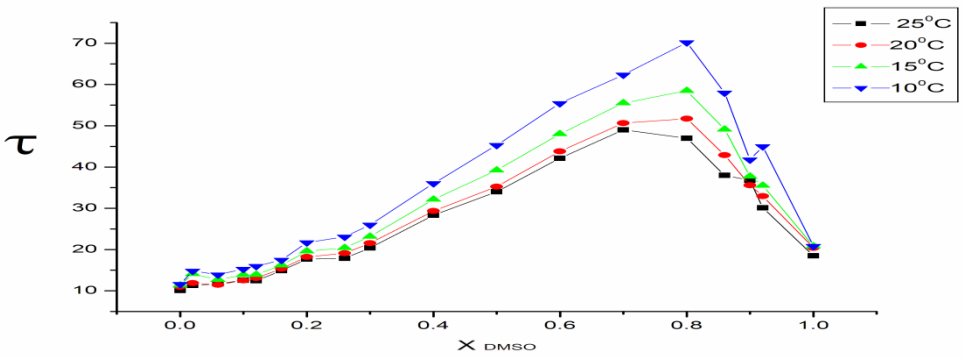

Fig. 5: Dielectric Relaxation time (τ) vs Volume fraction of DMSO (X_{DMSO}) at different temperature.

Table 1: Dielectric parameters: a) Dielectric constant (ε_0) b) relaxation time (τ) for DMSO-Water mixture.

Temp.→	25^0C		20^0C	
X_{DMSO}	ε_0	τ(ps)	ε_0	τ(ps)
0.00	78.92(13)	10.07(2)	79.1(11)	10.98(2)
0.02	70.19(9)	11.29(2)	70.96(8)	11.89(2)
0.06	76.29(20)	11.68(4)	78.55(11)	11.46(2)
0.1	69.96(11)	12.56(3)	71.91(5)	12.55(1)
0.12	76.99(8)	12.44(1)	77.7(8)	13.09(1)
0.16	76.8(7)	14.92(2)	77.47(13)	15.36(3)
0.2	76.79(9)	17.7(3)	77.41(9)	18.23(3)
0.26	73.21(4)	17.9(19)	74.8(3)	19.11(1)
0.3	73.18(16)	20.39(7)	73.79(4)	21.55(2)
0.4	66.00(6)	28.31(5)	67.17(5)	29.35(4)
0.5	65.9(9)	34.00(9)	67.17(11)	35.25(11)
0.6	61.9(11)	42.13(16)	62.09(12)	43.82(17)
0.7	60.34(14)	49.00(24)	60.35(19)	50.64(35)
0.8	60.2(14)	46.97(25)	60.55(16)	51.71(31)
0.86	60.1(14)	38.0(19)	60.50(16)	42.9(25)
0.9	52.25(10)	36.77(15)	53.25(10)	35.59(14)
0.92	52.7(13)	30.11(15)	53.2(13)	32.93(17)
1	47.9(1)	18.50(1)	47.91(2)	20.42(1)

Temp.→	15^0C		10^0C	
X_{DMSO}	ε_0	τ(ps)	ε_0	τ(ps)
0.00	80.2(9)	11.35(1)	82.03(9)	11.61(1)
0.02	71.41(12)	14.08(3)	75.19(9)	14.82(3)
0.06	79.9(33)	12.68(6)	81.96(45)	13.9(8)
0.1	73.48(19)	13.86(5)	75.84(24)	15.3(6)
0.12	79.82(9)	13.89(2)	81.7(33)	15.98(8)
0.16	79.25(17)	16.21(5)	82.15(31)	17.47(9)
0.2	79.24(7)	19.61(3)	83.51(6)	21.72(3)
0.26	77.6(5)	20.42(2)	81.16(20)	23.07(9)

0.3	76.32(6)	23.17(3)	79.35(9)	25.98(5)
0.4	69.03(9)	32.13(8)	71.19(13)	36.06(13)
0.5	68.17(13)	39.22(15)	71.75(18)	45.29(23)
0.6	63.67(15)	48.01(24)	65.87(19)	55.42(36)
0.7	61.58(24)	55.49(50)	61.9(21)	62.34(49)
0.8	61.96(22)	58.48(48)	64.01(26)	70.18(71)
0.86	61.09(20)	49.10(36)	62.51(27)	57.99(60)
0.9	55.07(16)	37.74(24)	57.66(23)	41.79(39)
0.92	54.58(18)	35.49(26)	60.89(19)	45(0)
1.0	49.41(2)	20.81(2)	51.88(6)	20.83(5)

Numbers in bracket denotes uncertainties in the last significant digits obtained by the least square fit method. e.g. 78.92(13) means 78.92 ± 0.13.

3.2 Luzar Model

The Luzar model can be used to investigate the role of hydrogen bonds in the dielectric properties of a mixture.[7]

The average number of hydrogen bonds $\langle n_{HB}^{11} \rangle$, $\langle n_{HB}^{12} \rangle$ and $\langle n_{HB}^{21} \rangle$

Per water molecule for 1*i* pairs (*i* =1 or 2) has been determined using following relation.[10]

$$\langle n_{HB}^{1i} \rangle = n_{1i}\omega^{1i} / n_1 \tag{2}$$

where $\omega^{1i} = 1/[1+ \alpha^{1i} \exp(\beta E^{1i})]$ is the probability of hydrogen bond formation between Water and DMSO. n_1 is the number density of water 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 $\langle n_{HB}^{11} \rangle$ and $\langle n_{HB}^{12} \rangle$ depend on the number of densities of the hydrogen-bonded pairs between Water and DMSO (n_{12}) and between Water-Water molecules ($n_{11}= 2n_1 – n_{12}$), respectively. These can be calculated, during which Water– Water (11 pair) and Water – DMSO (12 pair) are formed[7]. Fig. 8 shows a plot of the average number of hydrogen bonds between Water – Water molecules (11 pairs) and Water – DMSO (12 pairs) against the volume fraction of water. It can be seen from the values that $\langle n_{HB}^{11} \rangle$ and $\langle n_{HB}^{12} \rangle$ depend on the concentration of DMSO in Water – DMSO mixtures.

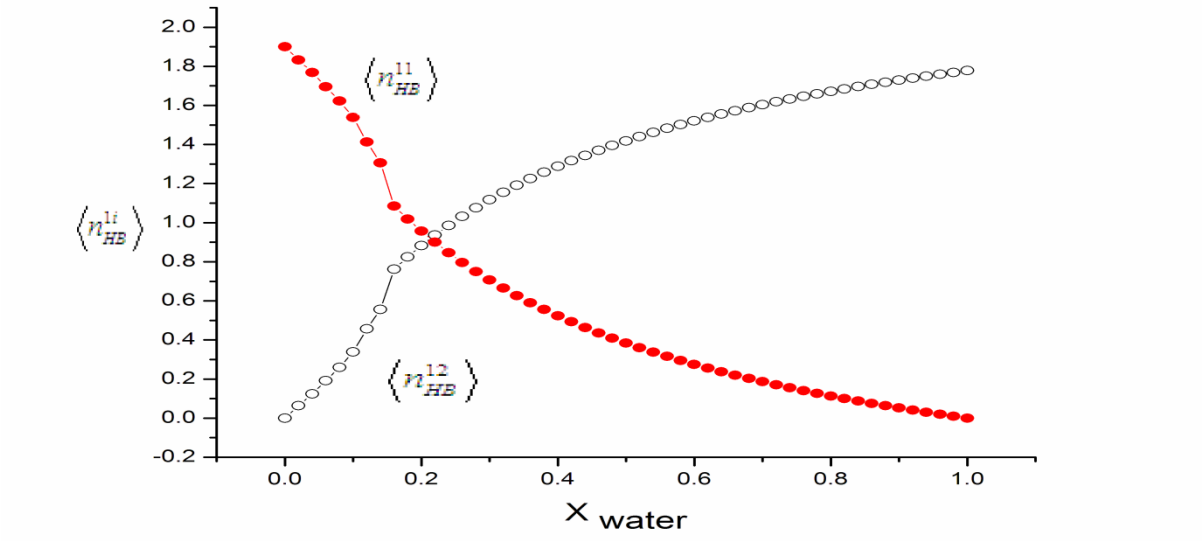

Fig. 6: Plots of the average number of hydrogen bonds between Water -Water molecule (n_{11} pair) and DMSO - Water (n_{12}pair) vs volume fraction of DMSO (X_{DMSO})

The different parameters required in the Luzar model are given in Table 2.

Table 2: Molecular parameters used in computation of the Static Dielectric Constant (ε_0).

Dipole moment[a] of Water	2.12
Dipole moment[a] of DMSO	4.22
Polarizibility[b] of Water	1.4
Polarizibility[b] of DMSO	7.97
Binding energy[c] of Water- Water	-13.40
Binding energy[c] of Water- DMSO	-16.5
Enthalpy[c] of DMSO -DMSO	28
Enthalpy[c] of Water-Water	41
Number of hydrogen bond	2

[a]Unit: Debye; [b]Unit : A^{03}; [c]Unit: kJ/mol

4. CONCLUSION

The hydrogen bond interaction between DMSO-Water binary mixtures was investigated by determining dielectric parameters dielectric constant(ε_0), relaxation time(τ). The dielectric parameters values of DMSO with water show that the DMSO molecules form Strong hydrogen bonds with water. Our findings support earlier research demonstrating that DMSO breaks down the H-bond networks in water.

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