



## TDR approach towards Dielectric relaxation studies of binary mixtures of organic compounds in polar solvents at room temperature

R.K.Pardeshi<sup>a\*</sup>, Megha Rai<sup>b</sup>, Shivaji Jadhav<sup>b</sup> and Mazahar farooqui<sup>b</sup>.

<sup>a</sup>Sant Ramdas College, Ghansawngi, Jalna, (M S).India

<sup>b</sup>Dr. Rafiq Zakaria College for Women, Aurangabad.(M.S).India

\*E-mail: dr.shivaji1985@gmail.com

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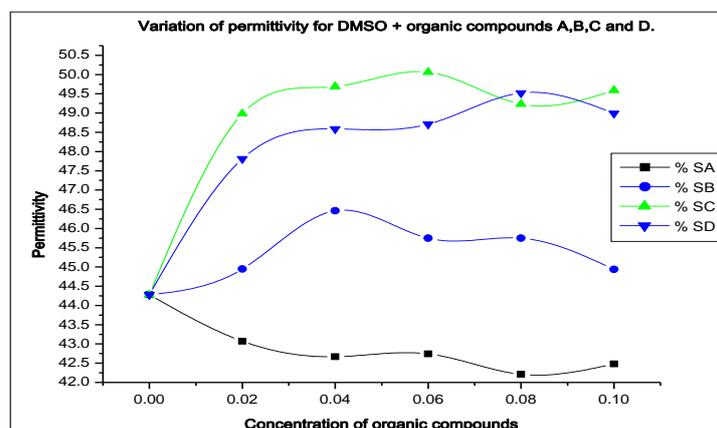
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### • Novelty and Highlights:

1. Static permittivity ( $\epsilon_0$ ) of organic compounds + polar solvent binary mixture has been evaluated.
2. The static permittivity ( $\epsilon_0$ ) of DMSO + organic compounds first increases and then slowly decreases.
3. Static permittivity ( $\epsilon_0$ ) of organic compounds in DMF indicates formation of bigger structure with less dipole moment.
4. Relaxation time ( $\tau$ ) indicate the formation of smaller structure in DMSO and larger in DMF than those in pure solvent.

### • Graphical Abstract:

Static permittivity ( $\epsilon_0$ ) of binary mixture varies with size of organic compounds.





## TDR approach towards dielectric relaxation studies of binary mixtures of organic compounds in polar solvents at room temperature.

R.K.Pardeshi,<sup>a\*</sup> MeghaRai,<sup>b</sup> ShivajiJadhav,<sup>b</sup> Mazaharfarooqui<sup>b</sup>

<sup>a</sup>SantRamdas College, Ghansawngi, Jalna, (M.S).India

<sup>b</sup>Dr. RafiqZakaria College for Women, Aurangabad.(M.S).India

\*E-mail: dr.shivaji1985@gmail.com

**Abstract:** A dielectric static permittivity and relaxation study of binary mixtures of organic compounds has been carried out at different concentrations at room temperatures in polar solvents using Time Domain Reflectometry (TDR) technique. By A non-linear Least Squares fit method has been used to obtain the dielectric parameters (the static dielectric constant ( $\epsilon_0$ ) and relaxation time ( $\tau$ ) using these parameters, excess permittivity and excess inverse relaxation time were determined and discussed to yield information on the molecular structure and dynamics of the mixture. Relaxation time ( $\tau$ ) indicates the size of newly formed structures decreases with increase in size of organic compounds added to polar solvent (DMSO as well as DMF).

**Keywords:** TDR, Dielectric constant, Relaxation time, Polar solvents.

### Introduction

Dielectric static permittivity and relaxation studies of binary mixtures of organic compounds are important for understanding the hydrogen bonding and intermolecular interactions in the mixtures. Dielectric relaxation study deals with ability of material to store electrical energy in the form of polarization. Relaxation time is reciprocal of frequency at which dielectric loss is a maximum. The fall in permittivity is proportional to square of the molecular dipole moment whereas relaxation time is related to size of the microscopic particles in the system. Dielectric relaxation measurements of binary mixture are used as spectroscopic method to study molecular interaction between solute and solvent. TDR [1-2] method serves as experimental tool to understand structural changes in liquid state. This method is used to determine dielectric parameter of various types of liquids, which includes binary mixtures of polar-polar systems [3-4] including Schiff bases [5], non-polar systems [6-7], electrolytes<sup>8-9</sup> and biological samples [10-11].

The TDR study of binary mixture of organic compounds is also carried out in Dioxane media. As Dioxane is non-polar solvent, the measurements of dielectric parameters do not show any significant changes in this media. Hence the study of these parameters has been carried out in polar solvents. TDR method is used for measurements of dielectric parameters of binary mixtures of organic compounds in polar solvents such as DMSO and DMF at room temperature. The TDR measurements provide wide band frequency dependant variation in complex permittivity parameters. This method is suitable for measurements since it requires very less amount of sample and single measurement

provide variations in complex permittivity over frequency range from 10 MHz to 20 GHz. The aim of present work is to report a dielectric study of binary mixtures of organic compounds in polar solvents conducted using TDR for the frequency range from 10 MHz to 20 GHz. The dielectric static permittivity  $\epsilon_0$  and relaxation time ( $\tau$ ) were determined. Excess inverse relaxation times were also obtained in order to obtain structural information about the mixtures.

### Experimental

The basic TDR setup consists of broadband sampling oscilloscope, TDR module and coaxial transmission line and sample cell. The Hewlett-Packard HP 54750 sampling oscilloscope with 20 GHz bandwidth HP 54754A TDR plug-in module was used. A 200 mV step pulse with 40ps rise time and 250 KHz repetition rate passes through flexible coaxial 50 $\Omega$  line, of 1 meter length, to standard military application sample cell. Sampling oscilloscope monitors changes in step pulse after reflection from sample cell. Reflected sample pulse without sample  $R_1(t)$  and with sample  $R_x(t)$  were recorded in time window of 5ns and digitized in 1024 points.

#### Data analysis:

The step pulses recorded without sample  $R_1(t)$  and with sample  $R_x(t)$  are subtracted and added to get

$$P(t) = [R_1(t) - R_x(t)] \dots \dots \dots (1)$$

$$q(t) = [R_1(t) + R_x(t)] \dots \dots \dots (2)$$

Reflection coefficient spectra  $p^*(\omega)$  over frequency range from 10 MHz to 20 GHz is obtained as,

$$p^*(\omega) = [c/(j\omega d)] [p(\omega)/q(\omega)], \text{ where } j = \sqrt{-1} \dots \dots \dots (3)$$

Where  $p(\omega)$  and  $q(\omega)$  are Fourier transforms of  $p(t)$  and  $q(t)$  obtained using Summation and Samulon methods [12-13].

The experimental values of  $\epsilon^*(\omega)$  were fitted to Debye [14-15] equation

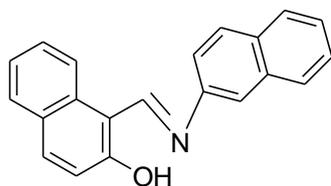
$$\epsilon^*(\omega) = \epsilon_0 + [\epsilon_\infty - \epsilon_0 / (1 + j\omega\tau)] \quad (4)$$

Where  $\epsilon_0$  and  $\tau$  as fitting parameters, A non-linear least-squares fit method<sup>16</sup> was used to determine the values of dielectric parameters.

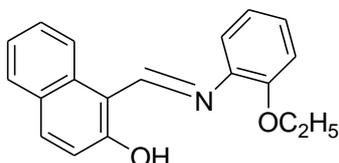
## Results and discussion

The static permittivity ( $\epsilon_0$ ) and relaxation time ( $\tau$ ) were obtained by fitting experimental data to Debye equation. The value of ( $\epsilon_\infty$ ) is kept fix in fitting procedure, since values of dielectric parameters obtained are very less sensitive to changes in ( $\epsilon_\infty$ ). The values of dielectric parameters are obtained for binary mixtures of organic compounds A,B,C and D in DMF and DMSO.

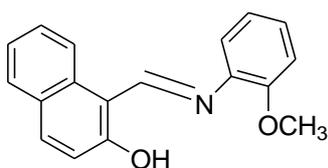
Where,



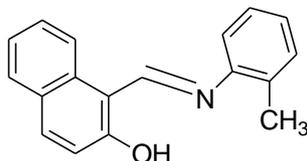
A: N-[2-hydroxy-1-naphthalidene]-2-naphthylamine.



B: N-[2-hydroxy-1-naphthalidene]-2-ethoxyaniline.



C: N-[2-hydroxy-1-naphthalidene]-2-methoxyaniline.



D: N-[2-hydroxy-1-naphthalidene]-2-methylaniline.

The measurements are done in concentration range  $0 \leq X \leq 0.1$  at 30°C and frequency range from 10 MHz to 20 GHz.

**Static permittivity ( $\epsilon_0$ ):** The variation in static permittivity ( $\epsilon_0$ ) for binary mixtures of organic compounds A,B,C and D in DMSO is shown in fig.1. The size of organic compounds decreases as  $D < C < B < A$  because the size of newly formed

structures decreases with decrease in bulky group of ligand molecules. Furthermore, organic compounds B and C have substituted groups containing highly electronegative oxygen atoms. The static permittivity of binary mixtures A, B and C in DMSO increases with increase in mole fraction of organic compounds. The increase in permittivity indicates increase in effective polarization of mixture molecules. While with addition of D to DMSO, decrease in static permittivity indicating decrease in polarization of mixture molecules. The increase in static permittivity more for bulky group with oxygen (B & C) as well as without oxygen (A & D).

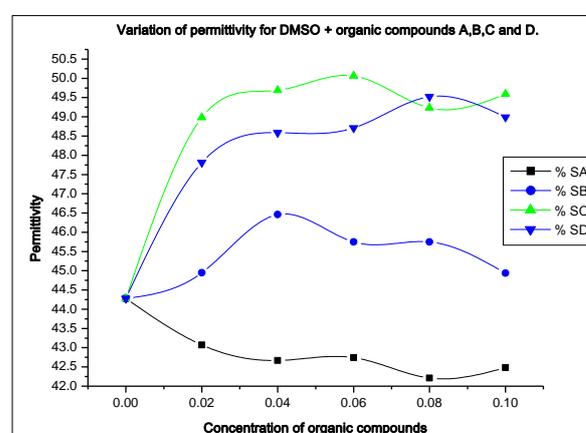


Fig.1. Variation of permittivity ( $\epsilon_0$ ) with variation in concentration of organic compounds in DMSO.

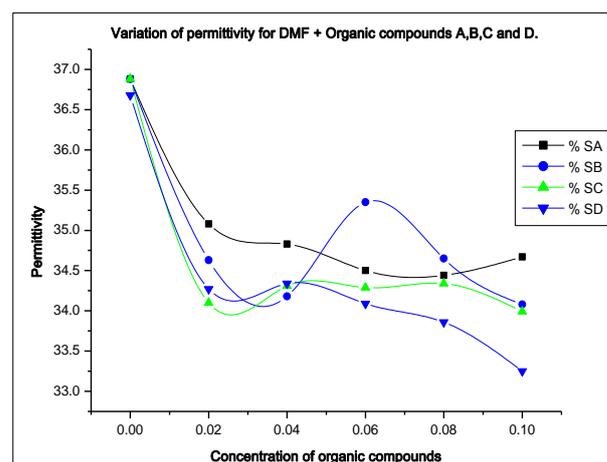


Fig.2. Variation of permittivity ( $\epsilon_0$ ) with variation in concentration of organic compounds in DMF.

The variation in static permittivity ( $\epsilon_0$ ) for binary mixtures of organic compounds A,B,C and D in DMF is shown in fig.2. The decrease in static permittivity with addition of organic compounds ligands in DMF is observed for all organic compounds. This fall of static permittivity can be

related to formation of bigger structures with less effective dipole moment.

**Relaxation Time ( $\tau$ ):** The sudden fall in relaxation time ( $\tau$ ) for binary mixtures with addition of organic compounds, A,B,C and D in DMSO is shown in fig.3, in DMSO indicates formation of structures smaller that present in pure solvent. The size of newly formed structures decreases with increase in size of organic compounds added to DMSO.

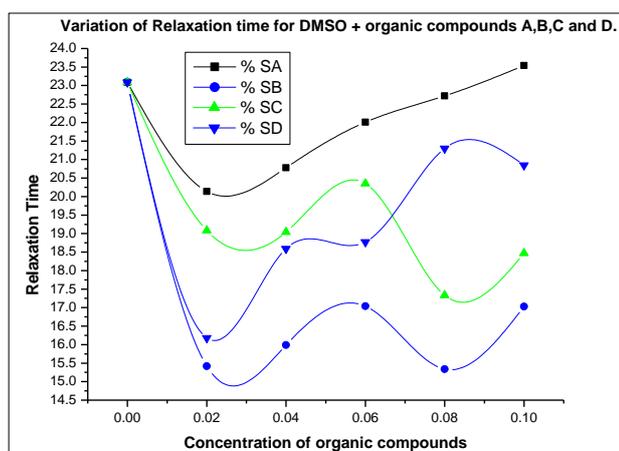


Fig.3: Variation of relaxation time ( $\tau$ ) with variation in concentration of organic compounds in DMSO.

The relaxation Time ( $\tau$ ) for binary mixtures of organic compounds A,B,C and D in DMF is suddenly increases shown in fig.4, at 0.02 mole fraction of ligand, for all organic compounds indicating formation of structures larger than those present in pure solvent. It is interesting to note that size of newly formed structure decreases with increase in size of compounds.

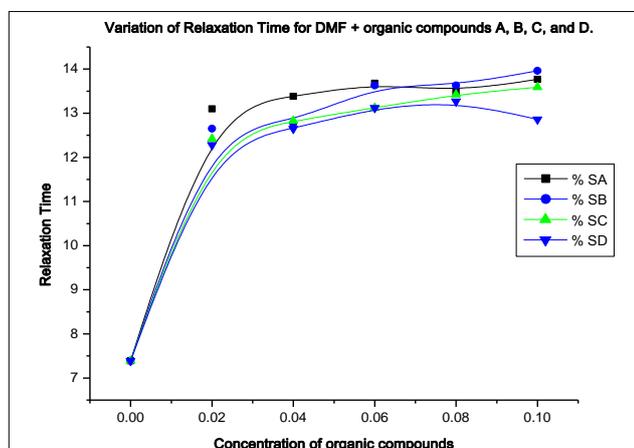


Fig.4: Variation of relaxation time ( $\tau$ ) with variation in concentration of organic compounds in DMF.

**Excess properties:** The useful information regarding structural changes in binary mixture can access by studying excess<sup>17</sup> dielectric properties. The information related to qualitative information about multimer formation in the mixture and dynamics of the solute-solvent interaction may be obtained by excess properties related with permittivity ( $\epsilon_0$ ) and relaxation time ( $\tau$ ) in the mixtures

**Excess permittivity ( $\epsilon^E$ ):** The excess permittivity is defined as

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_A X_A + (\epsilon_0 - \epsilon_\infty)_B X_B] \dots \dots \dots (5)$$

Where X is mole fraction and subscripts m, A and B represents mixture, solvent and solute respectively. The excess permittivity ( $\epsilon^E$ ) provides qualitative information about multimer formation in the mixture as follows:

- (i)  $\epsilon^E = 0$ : Indicate solute and solvent do not interact at all.
- (ii)  $\epsilon^E < 0$ : Indicate solute and solvent interact in such a way that the effective dipole moment get reduced. The solute and solvent may form multimers leading to less effective dipoles.
- (iii)  $\epsilon^E > 0$ : Indicate solute and solvent interact to form structures with increased dipole moment. There may be formation of monomers or dimers.

The excess permittivity is positive with addition of organic compounds A, B and C in DMSO indicate formation of structure with increased dipole moment. This may be due to breaking of hydrogen bonds in solvent, which leads to form monomers or dimers, Negative values of excess permittivity for D in DMSO mixture indicates formation of multimers. The variation excess permittivity ( $\epsilon^E$ ) for organic compounds + DMSO is shown in Fig.5

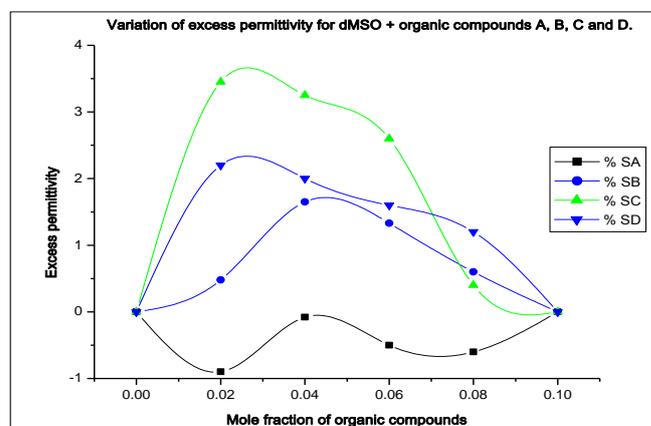


Fig.5: Variation of excess permittivity ( $\epsilon^E$ ) with mole fraction of organic compounds in DMSO.

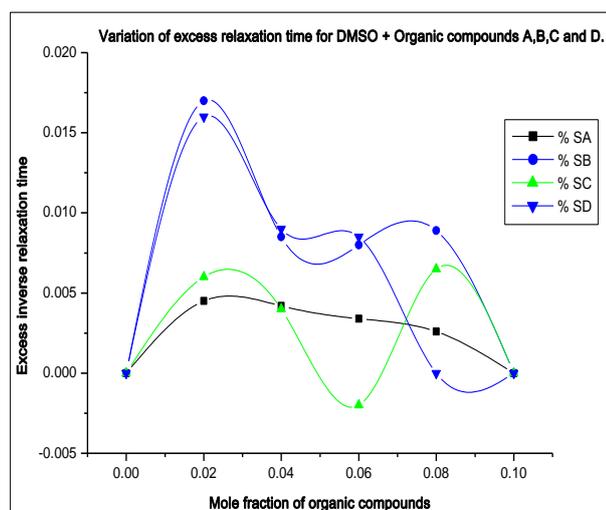
**Excess relaxation time  $(1/\tau)^E$ :** The excess relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A - (1/\tau)_B X_B] \dots \dots \dots (6)$$

Excess inverse relaxation time  $(1/\tau)^E$  provide information related dynamics of the solute-solvent interaction as follows:

- (i)  $(1/\tau)^E = 0$  : There is no change in the dynamics of the solute-solvent interaction.
- (ii)  $(1/\tau)^E < 0$  : The solute-solvent interaction produces a field such that the effective dipoles rotate slowly..
- (iii)  $(1/\tau)^E > 0$  : The solute-solvent interaction produces a field such that the effective dipoles rotate faster i.e. the field co-operate in rotation of dipoles.

The values of Excess inverse relaxation time  $(1/\tau)^E$  for organic compounds + DMSO mixture indicate faster rotation of dipole. The variation Excess inverse relaxation time  $(1/\tau)^E$  for organic compounds + DMSO is shown in Fig.6



**Fig.6. Variation of inverse relaxation time  $(1/\tau)^E$  with mole fraction of organic compounds in DMSO.**

## Conclusions

Dielectric relaxation parameters, excess permittivity and excess inverse relaxation time are reported in the present work for binary mixtures of organic compounds in polar solvents such as DMSO and DMF with various concentrations at room temperature by using TDR technique. These data provides qualitative information about multimer formation in binary mixtures, information regarding solute-solvent interaction in liquids. The increase in static permittivity is more for

bulky group present in organic compounds in DMSO. The decrease in static permittivity with addition of organic compounds in DMF can be related to formation of bigger structures with less effective dipole moment. Relaxation time indicates the size of newly formed structures decreases with increase in size of organic compounds added to DMSO as well as DMF.

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## Notes and references

- [1] R.H.Cole, J.G.Barbarian, S.Mashimo, G.Chryssikos, A. Burns, E.Tombari, *J.Appl.Physics*,1989,**66**,793.
- [2] S. M. Puranik, A.C.Kumbharkhane and S.C.Mehrotra, *J. Microwave Power, Electromag. Theory*,1991,**26**,196.
- [3] M.Davis, N.E.Hill, W.E.vaughan, A.H.Price, *Dielectric properties and molecular behevior*, London: Van Nostrand, 1969, 280-461.
- [4] S.M.Puranik, A.C.Kumbharkhane and S.C.Malhotra, *J. Chem. Soc. Faraday Trans*, 1992,**88**(3),433-435.
- [5] A.C.Kumbharkhane, S.N.Helambe, T.K.Chondekar and B.R.Arbad, *Indian J. Chem.*, 1994, **33A**,1011-1012.
- [6] S.P.Patil, A.S.Chaudhary, M.P.Lokhande, M.K.Lande, A.G.Shankrwar, S.N.Helambe, B.R.Arbad and S.C.Mehrotra, *J. Chem. Eng. Data*, 1999,**44**,875-878.
- [7] R.H.Fattepur, M.T.Hosamani, D.K.Deshpande and S.C.Mehrotra, *J.Chem Phys.*,1994,**101**,9556.
- [8] J.C.Lestrade, J.P.Badiali and H.Cachet, *Dielectric and related molecular processes*, London: The Chem. Soc.,1975, **2**,106-150.
- [9] D.V.Jahagirdar, B.R.Arbad, M.P.Lokhande and S.C.Mehrotra, *Indian J. Chem.*,1995,**34A**,462-465.
- [10] G.Schwarz, *Dielectric and related molecular processes*, London: The Chem. Soc.,1972,**1**,163-191.
- [11] A.C.Kumbharkhane, M.U. Patil and, S.C.Mehrotra, *Nat.Acd.Sci.Litt.*,1996,**19**(1&2),19-23.
- [12] C.E.shannon, *Proc.IRE*,1949,**37**,10.
- [13] H.A.Samulon, *Proc.IRE*,1951,**39**,175.
- [14] K.S.Cole and R.H.Cole, *J.Chem.Phys.*, 1941,**9**,341.
- [14] D.W.Davidson and R.H.cole, *J.Chem.Phys.*, 1950,**18**,1484.
- [14] P.R.Bevington, *Data reduction and error analysis for the physical sciences*, Mc. Graw Hill, New York, 1969,**104**.
- [15] J.B.Hasted, *Aqueous Dielectrics*, Chapman and Hall, London,1973.