Dielectric relaxation studies of Schiff bases in Dimethyl Sulfoxide (DMSO) using Time Domain Reflectometry(TDR)

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Abstract: Static permittivity and relaxation times have been determined for four Schiff bases derived from 2-hydroxy-1-naphthaldehyde with o-substituted anilines in Dimethylsulfoxide (DMSO) solution by using a Time Domain Reflectometry (TDR) technique. The observations are taken at room temperature (30°C) in frequency range 10 MHz to 20 GHz. Fourier transform and least squares fit methods have been used to obtain dielectric parameters. The excess dielectric parameters have also been determined for the system. In the present investigation it is observed that there is change in dielectric parameters of the system with change in concentrations

Keywords: Time Domain Reflectometer, Schiff Bases, Dielectric Relaxation Studies.

Introduction:

The Dielectric relaxation study of Schiff bases have been carried out by some workers[1]. The dielectric relaxation study of solute-solvent mixture at microwave frequency gives information about formation of monomers and multimers. It gives understanding of solute-solvent interactions and liquid structure. In the present investigation, Schiff bases are used as a solute and DMSO as a solvent. The picosecond Time Domain Reflectometry[2-6] in reflection mode has been used to obtain dielectric parameters. The excess dielectric constant and excess relaxation time is obtained by using dielectric constant and relaxation time.

Materials and Methods:

Preparation of Schiff bases

0.1 mole of 2-hydroxy-1-naphthaldehyde dissolved in ethanol was taken in a round bottomed flask. The ethanolic solution of corresponding substituted aniline (0.1M) was added slowly with constant stirring. The resulting mixture was refluxed on water bath for 3-4 hours. Then the mixture was allowed to cool at room temperature so as to separate out the solid product. The solidified Schiff base was then filtered, washed with ethanol and dried. These Schiff bases were recrystallised in ethanol, which gives fine, needle shaped yellow crystals. The purity was checked by melting points, TLC, elemental analysis and IR spectra.

The name of Schiff bases used and their notations are as below:

A = N-[2-hydroxy-1-naphthaledene]-2-naphthylamine.
B = N-[2-hydroxy-1-naphthaledene]-2-ethoxyaniline.
C = N-[2-hydroxy-1-naphthaledene]-2-methoxyaniline.
D = N-[2-hydroxy-1-naphthaledene]-2-methylaniline.

In the present study the basic TDR setup consists of broadband sampling oscilloscope,TDR module, coaxial transmission line and sample cell. Hewlett and Packard`s HP 54750A sampling oscilloscope with 18.2 GHz bandwith and TDR module HP 54754A with step generator and sampling head is used. A 200 mV step pulse with 40 ps rise time and 250 KHz repetition rate passes through flexible coaxial 50 Ω line, of one meter length, to SMA (standard millitary application) sample cell. All measurements were done in open load condition. Sampling oscilloscope monitors changes in step pulse after reflection from sample cell. Reflected pulse without sample $R_1(t)$ and with sample $Rx(t)$ were recorded in time window of 5 ns and digitized in 1024 points. All the observations were carried out at 30 ± 0.1^oC.

Data analysis:

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

$$p(t) = [R_1(t) - R_x(t)] \tag{1}$$

$$q(t) = [R_1(t) + R_x(t)] \tag{2}$$

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

$$\rho^*(\omega) = \frac{c}{(j\omega d)} \frac{p(\omega)}{q(\omega)} \qquad \text{(Where, } j = \sqrt{-1}\text{)} \tag{3}$$

Where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $p(t)$ and $q(t)$ obtained using Shannon[7] and Samulon[8] methodsrespectively. c is velocity of light, ω is angular frequency and d is effective pinlength. The complex reflection coefficient spectra for pure DMSO at 30^oC are shown in Figure 1.

The complex permittivity spectra $\varepsilon^*(\omega)$ is obtained from complex reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method suggested by Cole.

$$\varepsilon^*(\omega) - 1 = \frac{(1+A)\rho^*}{(1-B\rho^*)} \tag{4}$$

Where A and B are frequency dependant constants. The values of A and B are determined by using two calibrating liquids. In the present work pure DMSO and 0.1 molar solutions of Schiff bases, in each binary mixture, are used as calibrating liquids.
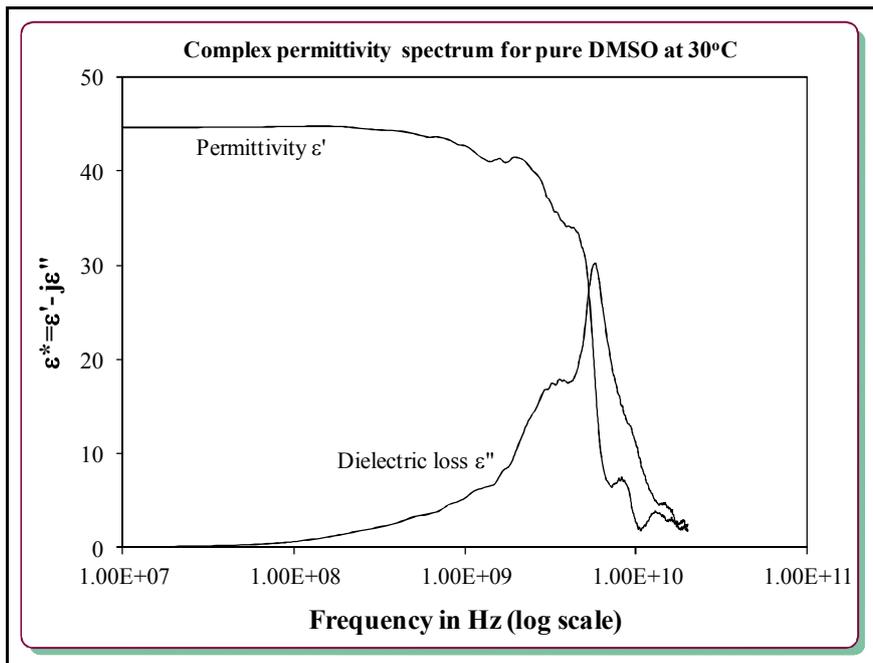

Figure 1: Typical plot showing variation in permittivity with frequency for pure DMSO at 30^oC

The experimental values of $\varepsilon^*(\omega)$ were fitted to Debye[9] equation

$$\varepsilon^*(\omega) = \varepsilon_o + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega\tau)} \qquad (5)$$

withε_o and τ as fitting parameters. A non-linear least square fit method[10] is used to determine the values of dielectric parameters. ε_o is static permittivity, τ is relaxation time and ε_∞ is limiting high frequency dielectric constant.

Results and Discussion:

The static permittivity (ε_o) and relaxation time (τ) were obtained by fitting experimental data to Debye equation. The values of static permittivity (ε_o) and relaxation time (τ) are listed in Table 1. Numbers in bracket denote uncertainties in least significant digits as obtained by least square fit method e.g. 44.28 (13) means 44.28 $\pm$ 0.13. The value of (ε_∞) is kept fix in fitting procedure, since values of dielectric parameters obtained are very less sensitive to changes in (ε_∞). The values of dielectric parameters are obtained for binary mixtures of ligands A, B, C and D in DMSO. The measurements are done in concentration range $0 \leq X \leq 0.1$ at 30°C and frequency range 10 MHz to 20 GHz.

Table 1: Static Permittivity and Relaxation time for binary mixtures of ligands A, B, C and D in DMSO.

Ligand A						
M	0	0.02	0.04	0.06	0.08	0.1
(ε_0)	44.28(13)	47.81(29)	48.59(26)	48.71(25)	49.52(23)	48.99(24)
(τ)	23.09(36)	16.18(71)	18.59(63)	18.77(60)	21.30(55)	20.85(60)
Ligand B						
M	0	0.02	0.04	0.06	0.08	0.1
(ε_0)	44.28(13)	48.98(30)	49.69(20)	50.06(20)	49.23(22)	49.59(25)
(τ)	23.09(36)	19.08(73)	19.04(49)	20.35(47)	17.33(52)	18.47(60)
Ligand C						
M	0	0.02	0.04	0.06	0.08	0.1
(ε_0)	44.28(13)	44.95(22)	46.46(19)	45.75(19)	45.75(28)	44.94(21)
(τ)	23.09(36)	15.42(56)	15.99(49)	17.04(50)	15.34(71)	17.03(56)
Ligand D						
M	0	0.02	0.04	0.06	0.08	0.1
(ε_0)	44.28(13)	43.07(06)	42.67(09)	42.74(13)	42.21(18)	42.48(18)
(τ)	23.09(36)	20.14(19)	20.78(25)	22.01(39)	22.72(52)	23.54(52)

M: Mole fraction of Ligand; (ε_0): Static Permittivity; (τ): Relaxation Time.

Static permittivity and relaxation time:

The variation in ε_o and τ for binary mixtures of A, B, C and D in DMSO is shown in **Figure 2 and 3**. The size of ligand molecules decreases as D < C < B < A. Furthermore, ligands B and C have substituted groups containing highly electronegative oxygen atoms. The static permittivity of binary mixtures of A, B and C in DMSO increases with increase in mole fraction of ligands. This 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 is more for bulky substituted group with oxygen (B and C) as well as without oxygen (A and D).

The sudden fall in relaxation time with addition of ligands, as shown in **Figure 3**, in DMSO indicates formation of structures smaller than that present in pure solvent. The size of newly formed structures decreases with increase in size of ligand molecules added to DMSO.
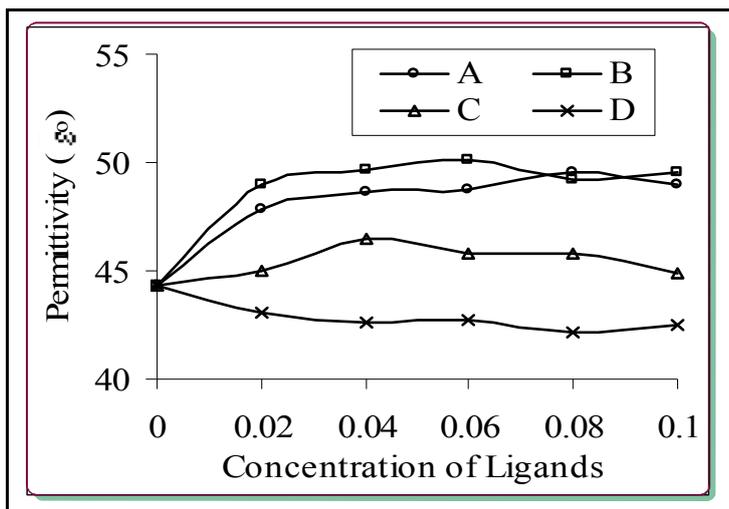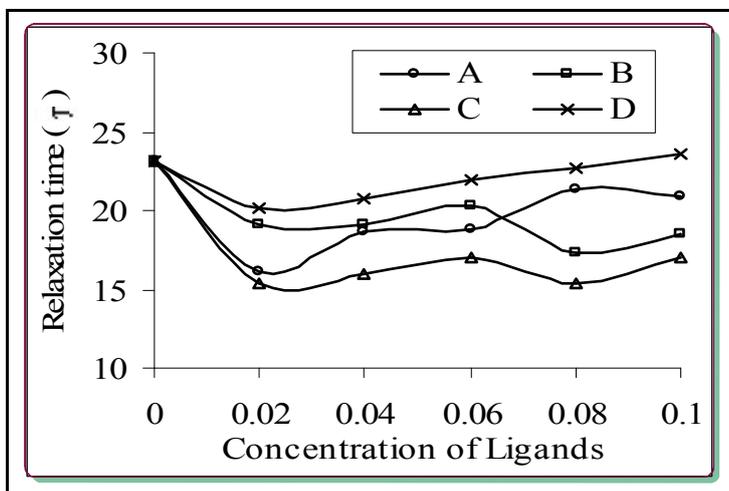
Figure 2: Static permittivity Vs Concentration of ligands.

Figure 3: Relaxation time Vs Concentration of ligands.

Excess properties:

The correlation between dielectric parameters and molecular interactions as well as structural changes in mixture can be explored to some extent by using various theories. In absence of exact theory exploring these quantities, available theories with some assumptions can provide trend regarding interactions and structural changes.

The useful information regarding structural changes in binary mixture accessed by tudying excess[11] dielectric properties. Let A and B are two molecular systems with measurable macroscopic properties P_A and P_B. If we prepare the mixture of A and B having mole fraction X_A and X_B ($X_B = 1- X_A$), the excess macroscopic property P^E corresponding to mixture is defined as

$$P^E = P_{AB} - (P_A * X_A + P_B * X_B) \hspace{4cm} (6)$$

Where P_{AB} is measured value of property P for mixture. The values of P^E provides information regarding interactions between A and B. $P^E = 0$ indicates no significant interaction between A and B. $P^E > 0$ indicates that interactions between A and B leads to increase in the value of property P. Similarly, $P^E < 0$ indicates decrease in macroscopic property P.

In the present system excess dielectric properties are determined corresponding to static permittivity and inverse relaxation time. The inverse relaxation time is taken instead of relaxation time, as it corresponds to broadening of spectral lines in resonant spectroscopy. The broadening of two levels are additive for two energy

levels. The analogy is taken here in dielectric spectroscopy. The excess permittivity (ε^E) and excess inverse relaxation time $(1/\tau)^E$ are defined as

$$\varepsilon^E = (\varepsilon_o - \varepsilon_\infty)_m - \left[(\varepsilon_o - \varepsilon_\infty)_A X_A + (\varepsilon_o - \varepsilon_\infty)_B X_B\right] \tag{7}$$

$$(1/\tau)^E = (1/\tau)_m - [\,(1/\tau)_A X_A + (1/\tau)_B X_B\,] \tag{8}$$

where X is mole fraction and subscripts m, A and B represent mixture, solvent and solute respectively.

The excess permittivity (ε^E) provide qualitative information about multimer formation in the mixture as follows:

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

Similarly, excess inverse relaxation time $(1/\tau)^E$ provide information regarding dynamics of solute solvent interaction as follows:

(i) $(1/\tau)^E = 0$: There is no change in the dynamics of 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-operates in rotation of dipoles.

The variation in excess permittivity (ε^E) and excess inverse relaxation time $(1/\tau)^E$ for ligands + DMSO is shown in Figure 4 and 5. The excess properties of systems presented here are evaluated with reference to 0.1 molar solutions of ligands in respective solvent.

The excess permittivity (ε^E) is positive with addition of ligands A, B and C in DMSO indicates formation of structures with increased dipole moment. This may be due to breaking of hydrogen bonds in solvent, which leads to form monomers or dimers. It is observed from absolute values of ε^E that ability of forming monomeric structures increases with increase in size of ligands. Negative value of ε^E for D+DMSO mixture indicates formation of multimers. The values of excess inverse relaxation time $(1/\tau)^E$ are positive for all DMSO + ligand mixtures indicate faster rotation of dipoles.
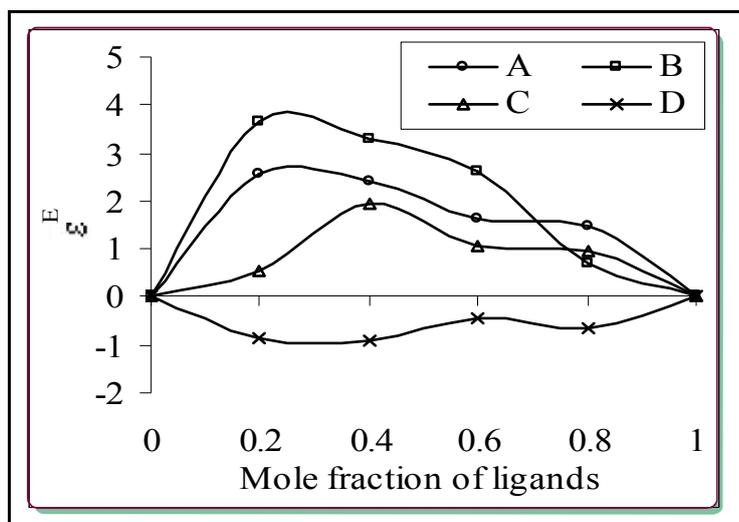

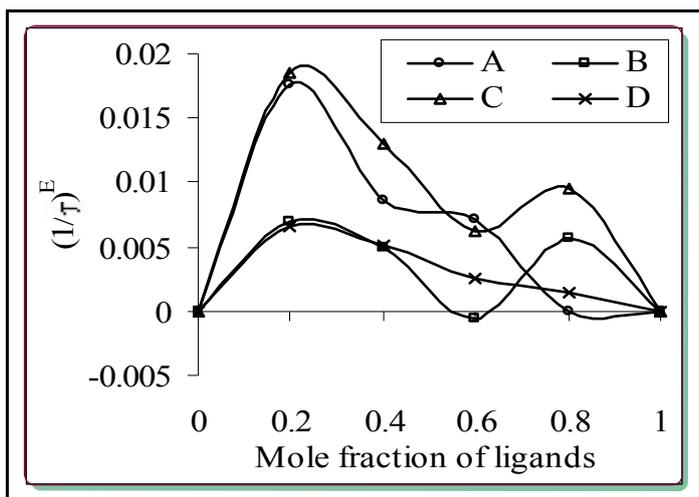**Figure 4: Excess permittivity ($\square^E$) Vs Mole fraction of ligands**

Figure 5: Excess inverse relaxation time $(1/\tau)^E$ Vs mole fraction of ligands

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