

## 2-pentanenitrile and chlorobenzene molecular relaxation at 25<sup>o</sup>c temperature

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### ABSTRACT

The time domain reflectometry (TDR) has been used for the study of dielectric relaxation spectra of pentanenitrile (PN) and chlorobenzene (CBZ) binary mixtures. The frequency range used for the study has been 10 MHz to 20 GHz. The system has been studied at 25<sup>o</sup>C temperature for 11 different concentrations. The dielectric parameters such as static permittivity ( $\epsilon_0$ ) and relaxation time ( $\tau$ ) have been obtained by Fourier transform and the least squares fit method. The relaxation in this system can be described by a single relaxation time using the Debye model. The Excess parameters such as excess permittivity and excess inverse relaxation time of the mixtures have been determined. In the mixtures excess permittivity ( $\epsilon^E$ ) is found to be positive but for 0.7064 concentrations it is negative. The excess inverse relaxation time ( $1/\tau^E$ ) is also found to be negative except 0.9027 concentrations. The investigation shows that the effective dipoles of the system increases. It also shows that due to the opposing field between the constituent molecules the dipole rotates slowly.

**Key words:** Static Permittivity, Nitrile group, Chlorine group, Excess permittivity, Excess inverse relaxation time, Time Domain Technique.

### INTRODUCTION

Time Domain Reflectometry (TDR) was used to obtain the dielectric parameters of the system (Helambe *et al.*, 1995). The dielectric spectra study at microwave frequencies have been carried out to understand intermolecular and intramolecular interactions. The dielectric relaxation parameters of binary mixture give considerable information about solute-solvent interaction. It also provides the information about the charge distribution in a molecular system. The liquid PN is of C≡N group and CBZ of chlorine group. It is interesting to see the effect of nitrile group with chlorine-group. The frequency dependent complex permittivity measurements using TDR are more powerful technique because a single measurement covers a wide frequency range in a very short time. Several workers have studied the temperature dependent dielectric relaxation parameters. The objective of the present paper is to report the detailed study of dielectric relaxation for pentanenitrile and chlorobenzene mixture using TDR at 25<sup>o</sup>C temperature at different 11 concentrations for the frequency range of 10MHz to 20GHz range. The dielectric parameters and

excess parameters for the mixtures have also been determined.

### MATERIALS AND APPARATUS

A spectrograde pentanenitrile (Fluka cheme GmbH-9471 Buchs, Steinheim, Switzerland) and AR grade chlorobenzene(CBZ) ( E-Merck) were used without further purification. The solutions were prepared at 11 different volume percentages of PN in CBZ from 0 % to 100 % just before the measurements. Using these volume percents the mole fraction is calculated as

$$x_1 = (v_1\rho_1/m_1) / [(v_1\rho_1/m_1) + (v_2\rho_2/m_2)]$$

Where  $m_i$ ,  $v_i$ , and  $\rho_i$  represent the molecular weight, volume percent, and density of the  $i^{\text{th}}$  ( $i=1, 2$ ) liquids, respectively. The density and molecular weight of the liquids are as follows: Pentanenitrile- density: 0.795gmcm<sup>-3</sup>; mol.wt.- 81.12 Chlorobenzene (CBZ) -density:1.1050 gm cm<sup>3</sup>; mol. wt. -112.56

The complex permittivity spectra were studied using the time domain reflectometry (Puranik *et al.*, 1994) method. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug in module has been used.

A fast rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance 50 Ohm. Transmission line system under test was placed at the end of coaxial line in the standard military applications (SMA) coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were carried out under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In the experiment, time window of 5 ns was used. The reflected pulse without sample  $R_1(t)$  and with sample  $R_2(t)$  were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through 1.44 MB floppy diskette drive.

### Data analysis

The time dependent data were processed to obtain complex reflection coefficient spectra  $\rho^*(\omega)$  over the frequency range from 10 MHz to 20 GHz using Fourier transformation (Shannon *et al.*, 1949) as

$$\rho^*(\omega) = (c/j\omega d)[p(\omega)/q(\omega)] \quad (1)$$

Where  $p(\omega)$  and  $q(\omega)$  are Fourier transforms of  $[R_1(t) - R_2(t)]$  velocity of light,  $\omega$  is angular frequency,  $d$  is the effective pin length and  $j = \sqrt{-1}$ .

The complex permittivity spectra  $\epsilon^*(\omega)$  were obtained from reflection coefficient spectra  $\rho^*(\omega)$  by applying bilinear calibration method (Cole *et al.*, 1989)

The experimental values of  $\epsilon^*$  are fitted with the Debye equation (Debye *et al.*, 1929).

$$\epsilon^*(\omega) = \epsilon_\infty + \quad (2)$$

With  $\epsilon_0$ ,  $\epsilon_\infty$  and  $\tau$  as fitting parameters. A nonlinear least-squares fit method (Bevington *et al.*, 1969) was used to determine the values of dielectric parameters. In Eq. (2),  $\epsilon_0$  is the static dielectric constant,  $\epsilon_\infty$  is the limiting high-frequency dielectric constant and  $\tau$  is the relaxation time.

### RESULTS AND DISCUSSION

The static dielectric constant ( $\epsilon_0$ ) and relaxation time ( $\tau$ ) obtained by fitting experimental data with the Debye equation are listed in Table 1. The values

of static dielectric constant ( $\epsilon_0$ ) increases and relaxation time ( $\tau$ ) values have no specific trend with the increase of concentration of PN into CBZ. The information related to liquids 1 and 2 interaction may be obtained by excess properties (Tabellout *et al.*, 1990) related to the permittivity and relaxation times in the mixture. The excess permittivity  $e^E$  is defined as

$$e^E = (e_0 - e_\infty)_m - [(e_0 - e_\infty)_1 x_1 + (e_0 - e_\infty)_2 x_2] \quad (3)$$

Where  $x$ - mole fraction and suffices  $m$ , 1, 2 represents mixture, liquid 1 (PN) and liquid 2 (CBZ) respectively. The excess permittivity may provide qualitative information about multimers formation in the mixture.

Similarly, the excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_1 x_1 + (1/\tau)_2 x_2] \quad (4)$$

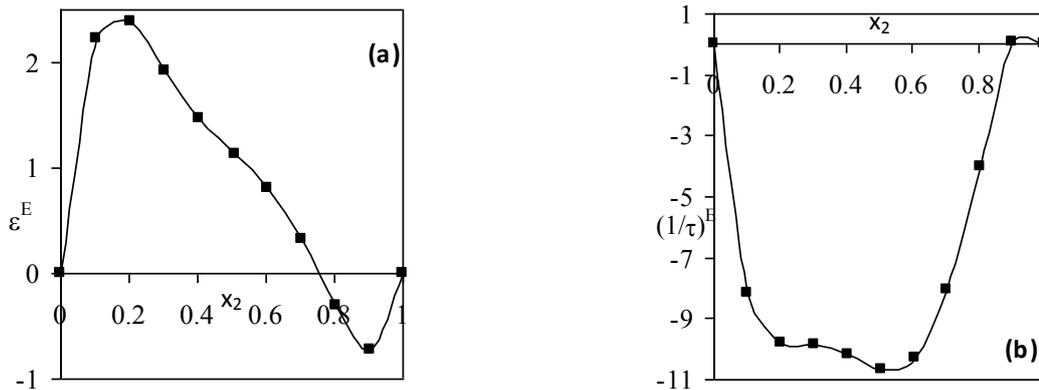
Where  $(1/\tau)^E$  is excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is inverse of the relaxation time) in the resonant spectroscopy (Mehrotra *et al.*, 1975).

The experimental values of both the excess parameters were fitted to the Redlich-Kister equation (Aralaguppi *et al.*, 1990)

$$A^E = (x_1 x_2) \sum_n B_n (x_1 - x_2)^n$$

Where  $A$  is either  $\epsilon^E$  or  $(1/\tau)^E$ . By using these  $B_n$  values,  $A^E$  values were calculated.

Figure 1, shows behavior of excess permittivity and excess inverse relaxation time for the system as a function of volume concentration of PN in CBZ at 25°C temperature. In the system of PN-CBZ, from the excess permittivity ( $\epsilon^E$ ) curve we have found that the excess permittivity ( $\epsilon^E$ ) values are positives up to at 0.7064 concentrations then the values goes into negatives. The positive peak is obtained at 0.2049 concentration. From positive peak the values are gradually decreases and goes to negative. The positive values indicates that; there is formation of monomeric or polymeric structures which leads to increase in total number of dipoles in the system. It also shows parallel alignment of the dipoles.



**Figure 1:** (a) The excess permittivity ( $\epsilon^E$ ) versus volume fraction of PN in CBZ  
 (b) The excess inverse relaxation time  $(1/\tau)^E$  versus volume fraction of PN in CBZ.

**Table1: Static dielectric constant ( $\epsilon_0$ ) and relaxation time ( $\tau$ ) for 25<sup>0</sup>C temperature.**

Vol. percentage of PN in CBZ	$\epsilon_0$	$\tau$ (ps)
0	5.54(0)	13.78(0)
10	9.51(3)	16.55(18)
20	10.95(3)	14.33(17)
30	12.12(3)	16.14(30)
40	13.48(4)	15.86(39)
50	14.76(6)	16.10(46)
60	15.40(3)	14.63(18)
70	16.87(5)	15.12(32)
80	17.89(4)	13.84(29)
90	18.70(2)	13.18(13)
100	21.05(0)	13.03(0)

Number in bracket represent error in the corresponding value, e.g. means 17.89(4) means  $17.89 \pm 0.04$ .

But the negative values indicate that, the formation of multimetric structures and the total number of dipoles in the system decreases. It also represents that antiparallel alignment of the dipoles. The excess inverse relaxation time  $(1/\tau)^E$  values are negatives for all concentration except 0.9027 concentration. The negative peak is obtained at 0.5076 concentrations. The values increases negatively up to peak value then there is continuous decrease. The negative values of  $(1/\tau)^E$  indicates that; the effective dipoles in the system creates hindering field so that, the effective dipole rotates slowly. But for 0.9027 concentrations the value is positive it represents that; for this particular concentration the effective dipoles produces favoring field so that the dipoles in the system rotates fastly. The dielectric parameters such as dielectric constant and relaxation time

values of 2-pentanenitrile (PN) and chlorobenzene (CBZ) mixture are obtained by analyzing dielectric relaxation spectra. The excess permittivity and excess inverse relaxation time values are also reported at 25<sup>0</sup>C temperature for 11 different concentrations in the frequency range of 10 MHz to 20 GHz. From the present study we can conclude that; the total number of dipoles in the system increases and shows the parallel alignment of the dipoles in the system. It also concludes that; the dipoles produces opposing field to each other in the mixture and the dipoles in the system rotates slowly.

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