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### Interaction Study of Butanenitrile with 1, 2 Dichloroethane Using Microwave at 45<sup>0</sup>C Temperature

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#### ABSTRACT

The complex permittivity spectra of butanenitrile(BN) with 1,2 Dichloroethane(DCE) mixture has been determined at temperature 45<sup>0</sup>C in the frequency range of 10 MHz to 20 GHz using time domain reflectometry (TDR) for 11 different concentrations of the system. 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 of the mixtures have been determined. In the mixtures excess permittivity is found to be positive in DCE rich region and negative in BN rich region. The excess inverse relaxation time is found to be negative. The investigation shows that there is systematic change in dielectric parameters of the system with change in concentration.

**Keywords:** Static Permittivity, Excess parameters, Relaxation time, Time Domain Technique.

**PACS:** 77.22

#### INTRODUCTION

The dielectric relaxation parameters of binary mixtures gives considerable information about solute-solvent interaction. Time Domain Reflectometry (TDR) was used to obtain the dielectric parameters of the system (1-3). It also provides the information about the charge distribution in a molecular system. The liquid BN is of C≡N group and DCE of chlorine group. It is interesting to see the effect of nitrile group with chlorine-group. The objective of the present paper is to report the detailed study of dielectric relaxation for butanenitrile and 1,2 Dichloroethane mixture using TDR at 45<sup>0</sup>C temperature at different 11 concentrations for the frequency range of 10MHz to 20GHz range. The dielectric parameters such as dielectric constant and relaxation time for the binary mixtures have also been determined.

#### MATERIAL AND APPARATUS

A spectrograde butanenitrile (Fluka cheme Gmbh-9471 Buchs,Steinheim,Switzerland) and AR grade 1,2 Dichloroethane (E-Merck) were used without further purification. The solutions were prepared at 11 different volume percentages of BN in DCE 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: Butanenitrile- density:  $0.8329 \text{ gm cm}^{-3}$ ; mol.wt.-67.09, 1,2Dichloroethane-density:  $1.256 \text{ gm cm}^{-3}$ ; mol.wt.-98.96. The complex permittivity spectra were studied using the time domain reflectometry [4] 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  $R_x(t)$  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 [5,6] as

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

Where  $p(\omega)$  and  $q(\omega)$  are Fourier transforms of  $[R_1(t)-R_x(t)]$  and  $[R_1(t)+R_x(t)]$  respectively,  $c$  is the 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 [4].

The experimental values of  $\epsilon^*$  are fitted with the Debye equation [7]

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

with  $\epsilon_0$ ,  $\epsilon_\infty$  and  $\tau$  as fitting parameters. A nonlinear least-squares fit method [8] 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 also increases upto 20% volume concentration of BN then there is continuous decrease with the increase the concentration of BN into DCE.

Figure 1(a) shows behavior of excess permittivity and (b) of excess relaxation time for the system as a function of volume concentration of BN in DCE at  $45^\circ\text{C}$  temperature.

The information related to liquids 1 and 2 interaction may be obtained by excess properties [9] related to the permittivity and relaxation times in the mixture. The excess permittivity  $\epsilon^E$  is defined as

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_1 x_1 + (\epsilon_0 - \epsilon_\infty)_2 x_2] \quad (3)$$

Where  $x$ - mole fraction and suffices  $m$ , 1, 2 represents mixture, liquid 1 (BN) and liquid 2 (DCE) 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 [10].

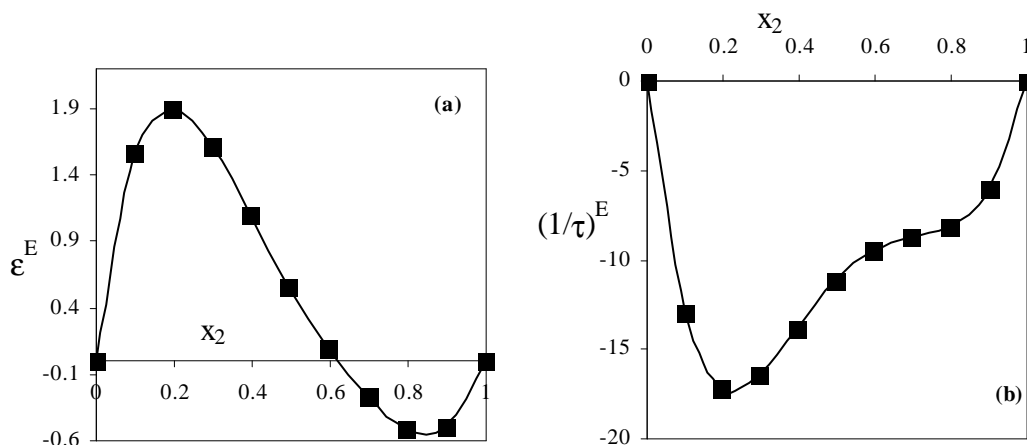


FIGURE 1.(a) The excess permittivity ( $\epsilon^E$ ) versus volume fraction of BN into DCE.  
(b) The excess relaxation time versus volume fraction of BN into DCE.

The experimental values of both the excess parameters were fitted to the Redlich-Kister equation [11, 12]

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

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

The excess permittivity ( $\epsilon^E$ ) increases sharply towards the peak values then decreases slowly up to pure BN. In the BN-DCE system excess permittivity ( $\epsilon^E$ ) curve, the peak value is noted at 0.1965 mole fraction of BN in DCE. Then it shows that there is a linear decrease. The value goes in negatives from concentration 0.6953. The  $\epsilon^E$  values are positive in DCE rich region. Hence there is formation of monomeric or polymeric structures. The total effective dipole increases. There is a parallel alignment of dipoles in DCE rich region. The values of excess permittivity are negatives in BN rich region. It indicates that there is decrease in dipole of the mixture. Hence there is anti parallel alignment of dipoles in BN rich region.

The excess inverse relaxation time values are negatives for all concentrations. It also shows that there is sudden increase in  $(1/\tau)^E$  from 0 to 0.1965 concentration of BN. The negative values of inverse relaxation time indicate that there is a opposing field in the molecules and there is slower effective dipole rotation of the molecules in the system.

Table1: Static dielectric constant ( $\epsilon_0$ ) and relaxation time ( $\tau$ ) for 45°C temperature.

Volume percentage of BN	$\epsilon_0$	$\tau$ (ps)
0	9.60(0)	9.80(0)
10	12.20(1)	10.97(10)
20	13.57(1)	10.40(10)
30	14.76(1)	10.26(9)
40	14.95(3)	9.33(11)
50	15.46(1)	8.95(12)
60	16.29(2)	8.54(13)
70	17.03(2)	7.95(15)
80	18.00(3)	7.64(19)
90	18.87(1)	7.48(4)
100	20.63(4)	6.83(1)

Number in bracket represent error in the corresponding value, e.g. means 14.95(3) means  $14.95 \pm 0.03$ .

## CONCLUSION

The dielectric constant, relaxation parameters, excess parameters are reported for butanenitrile and 1, 2 Dichloroethane system at 45°C temperature at 11 different concentrations. These data provide information regarding solute-solvent interaction. From the present study we can conclude that, the negative values of  $(1/\tau)^E$  indicates that there is a formation of hindering field in the molecules and the dipole rotation becomes slowly.

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