

**BUTANENITRILE – CHLOROBENZENE MOLECULAR  
CORRELATION STUDY BY USING TIME DOMAIN  
REFLECTOMETER AT 5°C TEMPERATURE**

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**Abstract**

*The dielectric parameters of butanenitrile(BN) with chlorobenzene(CBZ) mixture have been studied at 5<sup>o</sup>C temperature in the frequency range of 10 MHz to 20 GHz using time domain reflectometry (TDR) for 11 different concentrations of the system. The Kirkwood correlation factor ( $g_f$ ) and Kirkwood averaged effective correlation factor ( $g^{eff}$ ) of the mixture has been determined. The static dielectric constants for the mixtures have been fitted with the modified Bruggeman model. The investigation shows that the antiparallel alignment of the dipoles of the system. It also indicates that strong interaction between the constituent molecules of the BN and CBZ mixture.*

**Keywords:** Nitrile group, Dielectric parameters, Correlation factor, Bruggeman Parameter, Time Domain Reflectometer.

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## INTRODUCTION

The Dielectric spectra study at microwave frequencies have been carried out to understand intermolecular interactions and dynamics of the molecules of the liquid mixtures using time domain reflectometry [1-2]. Butanenitrile (BN) is non-associative liquids and chlorobenzene (CBZ) is associative liquid. BN is nitrile group and CBZ is of chlorine group. It is interesting to see the effect of nitrile group with chlorine-group. The objective of the present paper is to detail study the correlation between molecules of butanenitrile and chlorobenzene (CBZ) mixture at 5<sup>0</sup>C temperature by using Kirkwood. The strength of molecular interaction is studied by using Bruggeman model.

## MATERIAL AND APPARATUS

A spectrograde butanenitrile (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 BN 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:  
Butanenitrile- density:0.8329gmcm<sup>-3</sup>; mol.wt.-67.09  
Chlorobenzene-density:1.105gmcm<sup>-3</sup>;mol.wt.-112.56

The complex permittivity spectra were studied using the time domain reflectometry [3-4] 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  $R_i(t)$  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  $\epsilon^*(\omega)$  over the frequency range from 10 MHz to 20 GHz using Fourier transformation [5, 6] as

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

Where  $p(\omega)$  and  $q(\omega)$  are Fourier transforms of  $[R(t)-R_x(t)]$  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  $\epsilon^*(\omega)$  by applying linear calibration method [4].

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

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

With  $\epsilon_0$ ,  $\epsilon_\infty$  and  $\tau$  as fitting parameters. A nonlinear leastsquares 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 Kirkwood correlation factor  $g_f$  [9] is also a parameter for getting information regarding orientation of electric dipoles in polar liquids. The  $g_f$  for pure liquid may be obtained by the expression

$$\frac{4\pi N \mu^2 \rho}{9kTM} g_f = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (3)$$

where  $\mu$  is dipole moment in gas phase,  $\rho$  is density at temperature  $T$ ,  $M$  is molecular weight,  $k$  is Boltzman constant,  $N$  is Avogadro's number. The dipole moments for BN and CBZ in gas phase are taken as 3.91D and 1.69 D [10] respectively.

For the mixture of two polar liquids 1, 2 Eq. (3) is modified by ref.[11] with the following assumptions:

1. Assume that  $g$  for the binary mixture is expressed by an effective averaged correlation factor  $g^{\text{eff}}$  such that the Kirkwood equation for the mixture can be expressed by

$$\frac{4\pi N}{9kT} \left( \frac{\mu_1^2 \rho_1}{M_1} \phi_1 + \frac{\mu_2^2 \rho_2}{M_2} \phi_2 \right) g^{\text{eff}} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (4)$$

with  $\phi_1$  and  $\phi_2$  as volume fractions of liquids 1 and 2 respectively.

2. Assume that the correlation factors for molecules 1 and 2 in the mixture contribute to the effective  $g$  proportionality to their pure-liquid values  $g_1, g_2$ . Under this assumption the Kirkwood equation for the mixture can be written

$$\frac{4\pi N}{9kT} \left( \frac{\mu_1^2 \rho_1 g_1}{M_1} \phi_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} \phi_2 \right) g_f = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m} (\epsilon_{\infty m} + 2)^2} \quad (5)$$

where  $g^{\text{eff}}$  is the effective Kirkwood correlation factor for a binary mixture, with  $\phi_1$  and  $\phi_2$  as volume fractions of liquids 1 and 2 respectively.

In equation (4), the values of  $g^{\text{eff}}$  will change from  $g_1$  to  $g_2$  as concentration of molecule 2 will decrease from 100% to 0%. The Kirkwood correlation factor,  $g_f$ , which gives angular correlation between the molecules of the system.

The values of  $g^{\text{eff}}$  are less than one it shows that; an antiparallel alignment of dipoles. The values of  $g_f$  are more deviated from one in chlorobenzene region but deviation in BN region is small, it indicates that strong interaction in CBZ and weak interaction in BN region between the constituent molecules of the system.

The values of  $g^{\text{eff}}$  and  $g_f$  are calculated from equation (4) and (5) for the mixtures of the system. Temperature dependent  $g^{\text{eff}}$  and  $g_f$  for the system is shown in Figure (1).

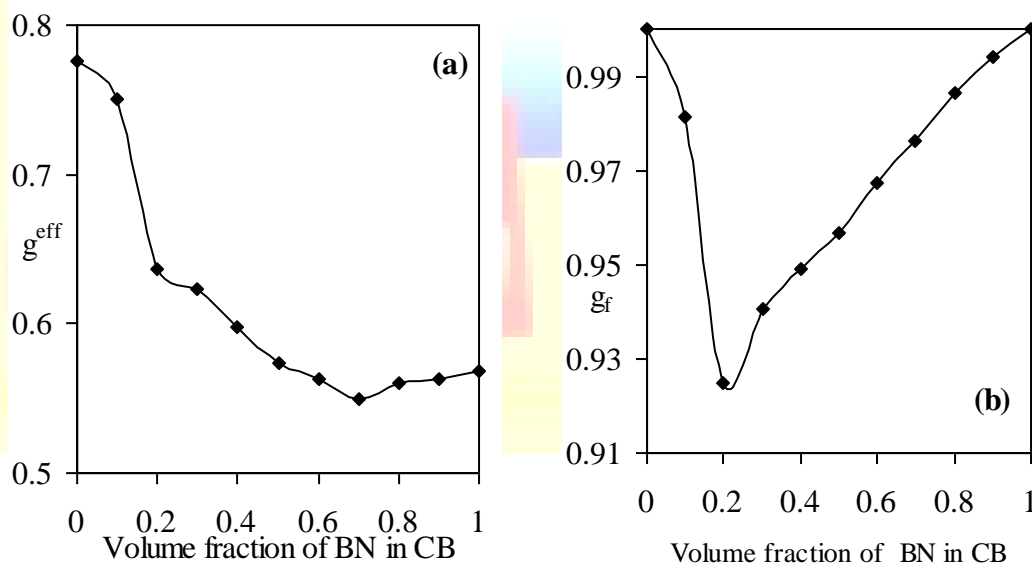


Figure 1. (a) Kirkwood effective correlation factor  $g^{\text{eff}}$  and (b) Kirkwood correlation factor  $g_f$ , versus volume fraction ( $\phi_2$  of BN in CBZ).

The modified Bruggeman equation [12] is another parameter, which may be used an indicator of liquid 1 and 2 interaction. The Bruggeman factor  $f_B$  is given by,

$$f_B = \left( \frac{\epsilon_{0m} - \epsilon_{02}}{\epsilon_{01} - \epsilon_{02}} \right) \left( \frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{1/3} = (1 - \phi_2) \quad (6)$$

According to equation (6), a linear relationship is expected which will give a straight line when plotted  $f_B$  against  $\phi_2$ . However, here the experimental values of  $f_B$  were found to deviate from the linear relationship. The Bruggeman dielectric factor  $f_B$  versus volume fraction  $\phi_2$  of BN at 5°C is given in Figure 2.

To fit the experimental data, Eq.(6) has been modified [13]

$$f_B = 1 - [a - (a-1)\phi_2]\phi_2 \quad (7)$$

Where 'a' is numerical fitting parameter.

The parameters 'a' has been determined by the least squares fit method and it is found to be 0.761. The value of 'a' = 1 corresponds to the ideal Bruggeman mixture formula. The deviation from 1 relates to interaction between corresponding liquids 1 and 2. The large deviation of "a" suggest that stronger interaction between BN and CBZ molecules of the mixture.

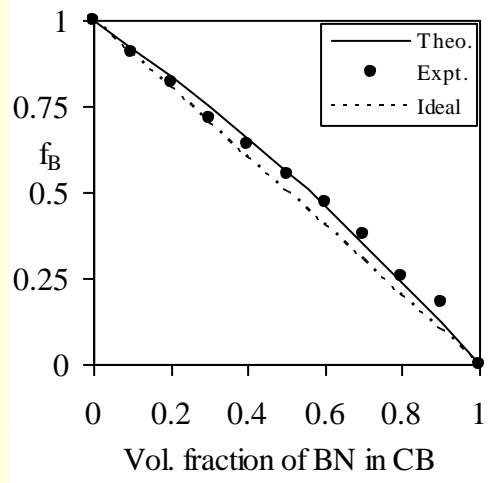


Figure 2. The Bruggeman plot for BN-CBZ mixture at 5°C

### CONCLUSION

The Kirkwood angular correlation factors and Kirkwood effective correlation factors have been reported for BN-CBZ mixtures at 5<sup>0</sup>C temperature for 11 different concentrations. The Bruggeman parameter is also reported. The values of effective Kirkwood parameter are less than one it indicates that; antiparallel alignment of the dipoles of the constituent molecules. The values of Kirkwood parameter  $g_f$  are deviated from unity it represents that; the stronger interaction between the constituent molecules in chlorobenzene region but weak interaction in butanenitrile rich region. The deviation of Bruggeman parameter 'a' from unity is also large and it indicates that; stronger interaction between the molecules of the BN-CBZ mixture and it confirms the Kirkwood result.

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