

THE CORRELATION OF 2-PENTENENITRILE AND CHLOROBENZENE MOLECULES AT 15⁰C TEMPERATURE BY USING MICROWAVES

Dr. Shere Ishwar Gurunathrao

Assistant Professor, Shri Havagiswami College, Udgir, Latur, India

Email: shereishwar@yahoo.in

ABSTRACT

The dielectric relaxation spectra of 2-pentenenitrile (PN) with chlorobenzene (CBZ) mixture has been studied at temperature 35⁰C. The mixture of PN and CBZ system has 11 different concentrations. The microwaves have been used of the frequency range from 10 MHz to 20 GHz. The experimental set up used for the study is time domain reflectometry (TDR). The dielectric parameters such as static dielectric constant (ϵ_0) and relaxation time (τ) have been obtained by Fourier transform and the least squares fit method and these are fitted in Kirkwood model. The Kirkwood correlation factor (g_f) and effective Kirkwood correlation factor (g^{eff}) of the mixtures have been determined by fitting static dielectric constant in the Kirkwood formula. Similarly, Bruggeman parameters are also obtained. In the mixtures the values of g^{eff} are less than one and it shows that; the antiparallel alignment of dipoles. The values of g_f are more deviated in CBZ rich region than PN rich region. The less deviation from one it represents weaker interaction between the constituent molecules of the system. The strong interaction between the constituent molecules in this system confirms by Bruggeman result.

Keywords: Dielectric permittivity, Molecular interaction, Kirkwood Parameters, Bruggeman parameters, Time Domain Reflectometer

INTRODUCTION

Dielectric relaxation study deals with ability of material to store electric energy in the form of polarization. Consider a system consisting of macroscopic charged particles. When this system is subjected to time dependent electric field, the particles will exhibit time delayed response termed as relaxation, if changes in applied field are fast compared to relaxation times of rearranging particles. Applied electrical energy causes charge redistribution in dielectric material, which will build-up induced polarization. Time Domain reflectometry (TDR) is a term used to describe a technique of observing the time dependant response of a sample of interest after application of time dependent electromagnetic field. The dielectric study of materials provides vital information about dielectric parameters and molecular interaction, which are of the direct technological importance. The interpretation of dielectric

behavior of a material in terms of its molecular structure is a scientific objective. The dielectric properties are essential and useful in vast area of physical and biological sciences; engineering technology etc. The dielectric study yields useful information on molecular structure, dynamic and kinetic of solutions. The information about interaction between the molecules of the mixture can be obtained by the study of dielectric spectra of the mixture of bipolar liquids at microwave frequencies ^[1, 2].

The objective of the present paper is to report the detailed study of molecular correlation and interaction strength between pentanenitrile and chlorobenzene mixture using time domain technique at 35^oC temperature.

MATERIAL AND APPARATUS

A spectrograde 2-pentenenitrile (Fluka cheme GmbH-9471 Buchs, Steinheim, Switzerland) and AR grade chlorobenzene (E-Merck) were used without further purification. The density and molecular weights of the liquids are as follows:

2-Pentenenitrile-density: 0.795 gm cm⁻³; mol.wt.-81.12.

Chlorobenzene-density: 1.105gmcm⁻³; 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. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. 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 $\rho^*(\omega)=(c/j\omega d)[p(\omega)/q(\omega)]$ (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, ω 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 ^[3].

The experimental values of ϵ^* are fitted with the Debye equation ^[7]

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

with ϵ_0 , ϵ_∞ , and τ as fitting parameters. A nonlinear least-squares fit method ^[8] was used to determine the values of dielectric parameters. In Eq.(2), ϵ_0 is the static dielectric constant, ϵ_∞ is the limiting high-frequency dielectric constant and τ 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 μ is dipole moment in gas phase, ρ is density at temperature T, M is molecular weight, k is Boltzman constant, and N is Avogadro's number. The dipole moments for PN and CBZ in gas phase are taken as 4.12D 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^{eff} such that the Kirkwood equation for the mixture can be expressed by

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

with ϕ_1 and ϕ_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^{eff} is the effective Kirkwood correlation factor for a binary mixture, with ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively.

The static dielectric constant (ϵ_0) and relaxation time (τ) obtained by fitting experimental data with the Debye equation for 35^oC temperature is listed in Table 1. The values of static dielectric constant (ϵ_0) increases with the increase of concentration of PN in CBZ and relaxation time (τ) values have no trend.

In equation (5), the values of g^{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. Temperature dependent g^{eff} and g_f for the system is shown in Figure (1)

The values of g^{eff} and g_f are calculated from equation (4) and (5) for the mixtures of the system. The values of g^{eff} are very less than one it indicates that; the antiparallel alignment of dipoles. The deviation of g_f values from unity is large in CBZ region means stronger interaction but little in PN rich region; it means that weaker interaction between the constituent molecules in the system.

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,

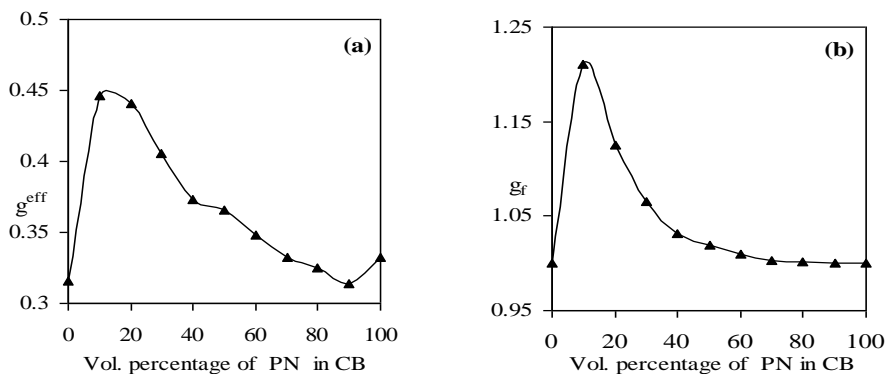


Figure 1. (a) Kirkwood effective correlation factor g^{eff} and (b) Kirkwood correlation factor g_f , versus volume fraction (ϕ_2) of PN in CBZ.

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

According to equation (6), a linear relationship is expected which will give a straight line when plotted f_B against ϕ_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 ϕ_2 of PN at 35°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 0.442. 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 PN and CBZ.

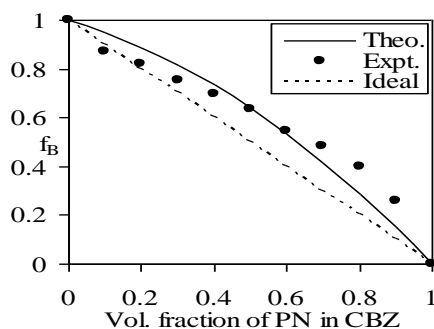


Figure 2. The Bruggeman plot for PN-CBZ mixture at 35°C

Table1. Static dielectric constant (ϵ_0) and relaxation time (τ) for 35⁰C temperature

Volume % of PN in CBZ	ϵ_0	τ (ps)
0	5.51(0)	13.09(0)
10	8.16(1)	16.59(10)
20	9.85(1)	14.79(14)
30	10.95(1)	15.29(22)
40	11.82(1)	14.64(15)
50	13.16(2)	15.05(23)
60	14.07(2)	13.70(18)
70	14.94(2)	14.06(13)
80	16.05(2)	13.77(14)
90	16.88(1)	12.53(7)
100	19.15(0)	12.36(0)

Note: Number in bracket represent error in the corresponding value, e.g. means 12.53(7) means 12.53 ± 0.07

CONCLUSION

The dielectric spectra analysis gives the dielectric parameters. The dielectric parameters are used to obtain the Kirkwood parameters. The Kirkwood correlation factors have been reported for PN-CBZ mixtures for 35⁰C temperature and different 11-concentrations. The correlation of the chlorine group CBZ with the C \equiv N bonded liquid PN is discussed. From the above investigation it shows that; the stronger interaction between the PN and CBZ molecules in CBZ region and weaker interaction in PN rich region. It also shows that; the antiparallel alignment of the dipoles in the system. The Bruggeman parameters are also reported. These Bruggeman Parameters represents that stronger interaction between the constituent molecules in the given system and it also confirms the Kirkwood result.

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