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Interaction Strength Between Pentanenitrile and Chlorobenzene Molecules at 25°C Temperature

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ABSTRACT

The dielectric spectra of butanenitrile(BN) with chlorobenzene(CBZ) mixture has analyzed at temperature 250C 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 (0) and relaxation time ( ) have been obtained by Fourier transform and the least squares fit method. The Kirkwood parameters have been determined from the dielectric parameters. The Bruggeman parameters have been also determined by fitting the dielectric parameters. The investigation shows that the effective dipoles of the system have strong interaction in CBZ region and it also shows that, antiparallel alignment of the dipoles in the mixture.

KEYWORDS : Molecular Interaction, Kirkwood Parameters, Bruggeman Parameters, Relaxation time, Time Domain Technique.

1. Introduction

The Kirkwood and Bruggeman parameters give considerable information about solute-solvent interaction. Time Domain Reflectometry (TDR) was used to obtain the dielectric parameters of the system [1]-[3]. 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 interaction strength between pentanenitrile and chlorobenzene molecules using TDR at 25°C temperature at different 11 concentrations for the frequency range of 10MHz to 20GHz range. The Kirkwood parameters and Bruggeman parameters are obtained by fitting dielectric parameters.

2. Material and apparatus

A spectrograde pentanenitrile (Fluka cheme Gmbh-9471 Buchs, Steinheim, Switzerland) and AR grade chlorobenzene (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 ρ_i represent the molecular weight, volume percent, and density of the ith (i=1, 2) liquids, respectively. The density and molecular weight of the liquids are as follows: Pentanenitrile- density: 0.795 gm cm^{-3}; mol.wt.-81.12,

Chlorobenzene-density : 1.1050gmcm^{-3};mol.wt.-112.56. 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.

Data analysis

The time dependent data were processed to obtain complex reflection coefficient spectra r*(w) over the frequency range from 10 MHz to 20 GHz using Fourier transformation [5], [6] as

$$r^*(w)=(c/jwd)[p(w)/q(w)] \quad (1)$$

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

The complex permittivity spectra e*(w) were obtained from reflection coefficient spectra r*(w) by applying bilinear calibration method [4].

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

$$e^*(w) = e_{¥} + \quad (2)$$

With $e_{0,}$ e□ and t as fitting parameters. A nonlinear least-squares fit method [8] was used to determine the values of dielectric parameters. In Eq.(2), e_0 is the static dielectric constant, e¥ is the limiting high-frequency dielectric constant and t is the relaxation time.

3. 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

$$\frac{4\Pi N\mu^2\rho}{9kTM}g_f = \frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2} \quad (3)$$

Where m is dipole moment in gas phase, r 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

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

with f_1 and f_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

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

Where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, with f_1 and f_2 as volume fractions of liquids 1 and 2 respectively.

The static dielectric constant (e_0) and relaxation time (t) obtained by fitting experimental data with the Debye equation for 25°C temperature is listed in Table 1. The values of static dielectric constant (e_0) increases with the increase of concentration of PN in CBZ and relaxation time (t) 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) gives angular correlation between the molecules of

the system. Temperature dependent g^{eff} and g_f for the system is shown in Figure (1)(a) and (b).

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

Table1: Static dielectric constant (e_0) and relaxation time (t) for 25°C temperature

Vol. % of PN in CBZ	e_0	t (ps)
0	5.54(2)	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 18.70(2) means18.70±0.02.

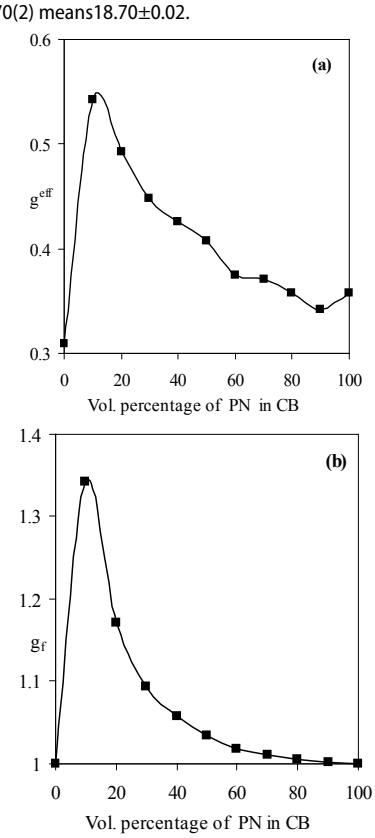

Figure 1. (a) Kirkwood effective correlation factor g^{eff} and (b) Kirkwood correlation factor g_f, versus volume fraction (f_2) of PN in CBZ.

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,

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

According to equation (6), a linear relationship is expected which will give a straight line when plotted f_B against f_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 f_2 of PN at 25°C is given in Figure 2.

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

$$f_B=1-[a-(a-1)f_2]f_2 \quad (7)$$

Where 'a' is numerical fitting parameter.

The parameters 'a' has been determined by the least squares fit method and it is found to be 0.281. 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 molecules of the mixture.

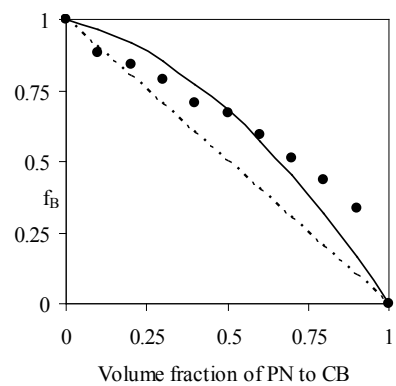

Figure 2.The Bruggeman plot for PN-CBZ mixture at 25°C. Dashed line denote original model (equation 6). Continuous line is the theoretical curve obtained from equation (7).Experimental points shown by the symbol

4. Conclusion

The analysis dielectric spectra give the dielectric parameters. The dielectric parameters are used to obtain the Kirkwood parameters and Bruggeman parameters. The Kirkwood effective correlation factors and Kirkwood angular correlation factors have been reported for PN-CBZ mixtures for 25°C temperature and different 11-concentrations. The correlation of the chlorine group CBZ with the CºN 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 parameter is more deviated from unity it indicates that; stronger interaction between the constituent molecules in the system. The Bruggeman parameter confirms the Kirkwood result.

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REFERENCES

[1] S.N. Helambe, M.P. Lokhande, A.C. Kumbharkhane and S.C. Mehrotra, Pramana-J. Phy, pp19; 1995. | [2] S.M. Puranik, A.C. Kumbharkhane and S.C. Mehrotra, J. Chem. Soc. Faraday Trans., pp1569; 1991. | [3] V.P. Pawar and S.C. Mehrotra, J. Sol. Chem., p.559-576; 2002. | [4] R.H. Cole, J.G. Berbarian, S. Mashimo, G. Chryssikos, A. Burns and E. Tombari, J. Appl. Phys., 793;1989. | [5] C.E. Shannon, Proc. IRE, p10; 1949. | [6] H.A. Samulan, Proc. IRE, p175; 1951. | [7] P. Debye, Polar molecules, Chemical Catalog, New York, 1929. | [8] P.R. Bevington, Data reduction and error analysis for the physical sciences, Mc-Graw Hill, New York, 1969 | [9] H. Frolhich, "Theory of dielectrics", Oxford University Press, London, 1949. | [10] R. C. Weast, "Handbook of Chemistry and Physics", 64th ed. CRC Press Boca Raton, Florida, 1983-84. | [11] A. C. Kumbharkhane, S. M. Puranik and S. C. Mehrotra, J. Sol. Chem., 219; 1993. | [12] A. G. Bruggeman, Ann. Phys. Leipzig., 636; 1935. | [13] S. M. Puranik, A.C. Kumbharkhane and S. C. Mehrotra, J. Chem. Soc. Faraday Trans., 1569; 1991. |