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Molecular interaction of butanenitrile-1,2-dichloroethane mixtures at microwave frequency

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ABSTRACT

The dielectric spectra have been studied for butanenitrile(BN) with 1,2 Dichloroethane(DCE) mixture at temperature 45^{0}C 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 study shows that the antiparallel alignment of the dipoles and strong interaction between the constituent molecules of the BN-DCE mixture.

Keywords: Dipole alignment, Nitrile group, Chloro group, Time Domain Reflectometer, Molecular Interaction.
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INTRODUCTION

The Dielectric studies 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 1, 2 Dichloroethane (DCE) is associative liquid. BN is C≡N group and DCE 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 report the interaction between molecules of butanenitrile and 1,2 Dichloroethane mixture at 45^{0}C temperature by using Kirkwood and Bruggeman models.

MATERIALS AND METHODS

A spectrograde butanenitrile 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 DE 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:

Butanenitrile-density - 0.8329gm cm^{-3}; mol. wt. - 67.09
1, 2 Dichloroethane -density: 1.256 gm cm^{-3}; mol.wt.-98.96

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 $R_l(t)$ 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

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

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 $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method [4].

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

$$\varepsilon^*(\omega) \quad = \quad \varepsilon_\infty + \frac{\varepsilon_0-\varepsilon_\infty}{1+j\omega\tau} \qquad (2)$$

With $\varepsilon_{0,}$ 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

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

where μ is dipole moment in gas phase, ρ is density at temperature T, M is molecular weight, k is Boltzman constant, N is Avogadro's number. The dipole moments for BN and DCE in gas phase are taken as 3.91D and 2.06 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

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

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

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

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.

In equation (4), 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. The values of g^{eff} are less than one; it shows that there is an antiparallel alignment of dipoles. The values of g_f are more deviated from one in DCE rich region, it indicates that stronger interaction between the constituent molecules. But in BN rich region the values are near to unity and it indicates that weaker interaction.

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

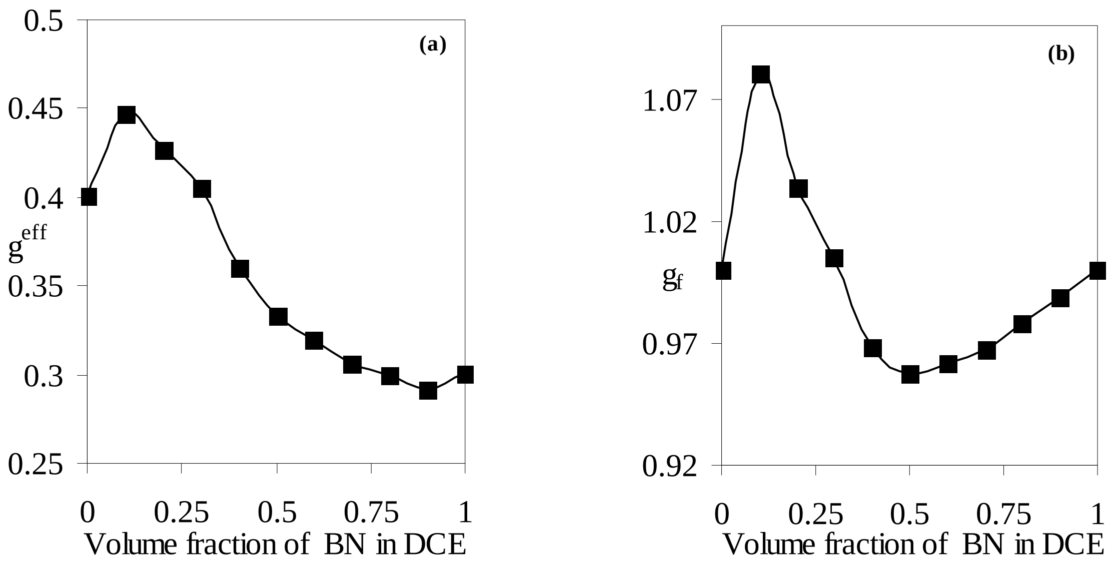

Figure 1. (a) Kirkwood effective correlation factor g^{eff} and (b) Kirkwood correlation factor g_f, versus volume fraction (ϕ_2) of BN in DCE.

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,

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

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 BN at 45°C is given in Figure 2.

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

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

Where 'a' is numerical fitting parameter.

The parameters ‘a’ has been determined by the least squares fit method and it is found to be 0.502. 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 DCE molecules of the mixture.

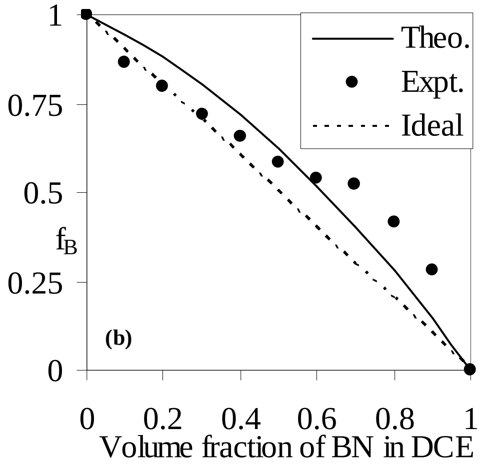

Figure 2.The Bruggeman plot for BN-DCE mixture at 45°C. Dashed line denote original model (equation 6).

Continuous line is the theoretical curve obtained from equation (7).Experimental points shown by the symbol •.

CONCLUSION

The Kirkwood correlation factors have been reported for BN-DCE mixtures at 45^0C temperature for 11 different concentrations. The interaction of the chlorine group with the nitrile group liquids is discussed. One observes significant deviation from the various models. The values of effective Kirkwood parameter (g^{eff}) are less than one; it indicates that the antiparallel alignment of the dipoles of the system. The values of Kirkwood parameter g_f are deviated from unity and it shows that the stronger interaction between the constituent molecules. The deviation of Bruggeman parameter 'a' from unity is also large and it indicates that stronger interaction between the molecules of the BN-DCE mixture.

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