

Molecular Correlation Study of 2-Pentenenitrile with 1, 2 Dichloroethane at 25⁰C Temperature using TDR

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Abstract

The dielectric relaxation study of 2-pentenenitrile (PN) with 1, 2 dichloroethane (DCE) mixture has been carried out 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 dielectric constant (ϵ_0) and relaxation time (τ) have been obtained by fourier transform and the least squares fit method. Kirkwood correlation factor (g_f) and effective Kirkwood correlation factor (g_f^{eff}) of the mixtures have been determined. In the mixtures the values of g_f^{eff} are less than one and it shows that there is antiparallel alignment of dipoles. In the mixtures the values of g_f are near to unity and it shows that there is weaker interaction between the constituent molecules.

Keywords: Dielectric, nitrile group, chloro group, Kirkwood Parameters.

I. INTRODUCTION

The dielectric relaxation study of solute-solvent mixture at microwave frequencies gives information about formation of monomers and multimers as well as interaction between the molecules of the mixture [1, 2]. 2-Pentenenitrile (PN) is non-associative liquids and 1, 2 dichloroethane (DCE) is associative liquid. One is of nitrile group and other with 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 molecular correlation between 2-pentenenitrile and 1, 2 dichloroethane mixture using TDR at 25⁰C temperature.

II. MATERIAL AND APPARATUS

A spectrograde 2-pentenenitrile (Fluka cheme GmbH-9471 Buchs, Steinheim, Swizerland) and AR grade 1, 2 dichloroethane (E-Merck) were used without further purification. The solutions were prepared at 11 different volume percentages of PN in DCE from 0 % to 100 % just before the measurements. Using these volume percents the mole fraction is calculated as

$$x_1 = (v_1\rho_1m_1) / [(v_1\rho_1m_1) + (v_2\rho_2m_2)]$$

where m_i , v_i , and ρ_i represent the molecular weight, volume percent, and density of the i^{th} ($i=1, 2$) liquids, respectively. The density and molecular weight of the liquids are as follows:

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

1, 2 Dichloroethane-density: 1.256gmcm⁻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 $R_1(t)$ 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.

III. 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, 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.

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, N is Avogadro's number. The dipole moments for PN and DCE in gas phase are taken as 4.12D 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

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

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.

IV. RESULTS AND DISCUSSION

The static dielectric constant (ϵ_0) and relaxation time (τ) obtained by fitting experimental data with the Debye equation are listed in Table 1. The values of static dielectric constant (ϵ_0) increases with the increase of concentration of PN in DCE and relaxation time (τ) values increases up to 40% then decrease for 50% and increases for 60% then it shows continuous decrease.

Table1: Static dielectric constant (ϵ_0) and relaxation time (τ) for 25⁰C temperature.

Volume % of PN in DCE	ϵ_0	τ (ps)
0	10.43	10.7
10	13.05	12.98
20	14.59	13.26
30	15.85	13.48
40	16.34	13.7
50	17.05	13.63
60	17.9	14.48
70	18.65	13.9
80	19.29	13.28
90	19.55	13.01
100		
	21	13

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 factors (g_f) which gives angular correlation between the constituent molecules of the system. The values of g^{eff} are less than one and it shows that there is antiparallel alignment of dipoles. The deviation of g_f values from unity is little. Small deviation in g_f shows that weaker interaction between the constituent molecules in the system.

The values of g_f^{eff} and g_f are calculated from equation (4) and (5) for the mixtures of the system. Temperature dependent g_f^{eff} and g_f for the system is shown in figure1.

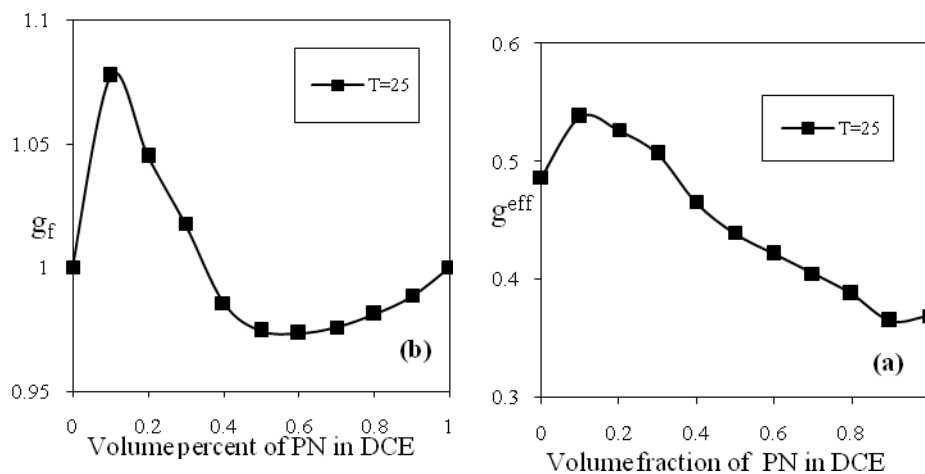


Figure1. (a) Kirkwood effective correlation factor g_f^{eff} and (b) Kirkwood correlation factor g_f , versus volume fraction (ϕ_2) of PN in DCE.

V. CONCLUSION

Dielectric relaxation parameters and Kirkwood parameters have been reported for DCE-PN mixtures at 25°C temperature and 11 concentrations. This data provide information regarding solute-solvent interaction in liquids. The g_f^{eff} value increases for 10% and then decreases linearly with increase in concentration of BN in the solution.

The values of Kirkwood correlation factor indicates the intermolecular interactions of the chloro group with the $C\equiv N$ bonded liquids. The deviation of g_f values from unity is little. Small deviation in g_f shows that weaker interaction between the constituent molecules in the system.

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