Dielectric relaxation Study of butanenitrile and 1, 2-dichloroethane mixture at 35°C temperature

Ishwar G. Shere

Department of Electronics, Shri. Havagiswami Mahavidyalaya, Udgir, Maharashtra (India)
_____

ABSTRACT

The dielectric relaxation study of butanenitrile(BN) and 1,2 Dichloroethane(DCE) mixture has been carried out at 35^0C temperature 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 (ε_0) and relaxation time (τ) have been obtained by Fourier transform and the least squares fit method. The Excess parameters of the mixtures such as excess permittivity and excess inverse relaxation time have been determined. In the mixtures excess permittivity (ε^E) is found to be positive in DCE rich region and negative in BN rich region. The excess inverse relaxation time $(1/\tau)^E$ is found to be negative. It indicates that the effective dipoles produces hindering field in the mixture and dipole rotates slowly.

Keywords: Dielectric parameters, Excess permittivity, Excess Inverse relaxation time, Time Domain Technique.
PACS: 77.22
_____

INTRODUCTION

The information of molecular interaction between the constituent molecules of the mixture can be obtained by the study of dielectric spectra. Time Domain Reflectometry (TDR) was used to study the dielectric spectra of the system [1-2]. It also provides the information about the charge distribution in a molecular system. It is interesting to see the effect of BN as nitrile group with DCE as chlorine-group. The objective of the present paper is the detailed study of dielectric relaxation for butanenitrile and 1,2 Dichloroethane mixture using TDR at 35^0C temperature at different 11 concentrations for the frequency range of 10MHz to 20GHz range. The dielectric parameters such as dielectric constant and relaxation time for the binary mixtures have also been determined.

MATERIALS AND METHODS

A spectrograde butanenitrile (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 BN in DCE from 0 % to 100 % just before the measurements. Using these volume percents the mole fraction is calculated as

$x_1 = (v_1\rho_1/m_1) /[(v_1\rho_1/m_1) + (v_2\rho_2/m_2)]$

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:$0.8329 gmcm^{-3}$; mol.wt.-67.09, 1,2Dichloroethane-density:$1.256gmcm^{-3}$;mol.wt.-98.96

The complex permittivity spectra were studied using the time domain reflectometry [3] 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 [4, 5] as

$$\rho*(\omega)=(\chi/\varphi\omega\delta)[\pi(\omega)/\theta(\omega)] \tag{1}$$

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 [3].

The experimental values of ε^* are fitted with the Debye equation [6]

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

with $\varepsilon_0,\, \varepsilon_\infty$ and τ as fitting parameters. A nonlinear least-squares fit method [7] 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 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 and the relaxation time (τ) increases suddenly as the volume percentage of butanenitrile increases from 0 to 10% after that there is a continuous linear decrease up to pure BN.
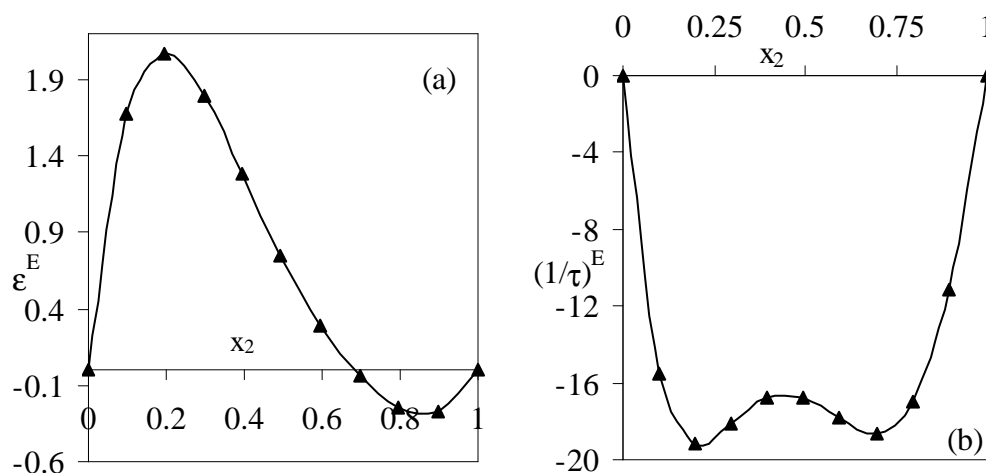

FIGURE 1. (a) The excess permittivity (ε^E) versus volume fraction of BN into DCE.
(b) The excess inverse relaxation time $(1/\tau)^E$ versus volume fraction of BN into DCE.

Figure 1, (a) shows behavior of excess permittivity for the system as a function of volume concentration of BN in DCE at 35^0C temperature and (b) shows behavior of excess inverse relaxation time for the system as a function of volume concentration of BN in DCE at 35^0C temperature.

The information related to liquids 1 and 2 interaction may be obtained by excess properties [8] related to the permittivity and relaxation times in the mixture. The excess permittivity ε^E is defined as

$$\varepsilon^E = (\varepsilon_0 - \varepsilon_{\infty m} - [(\varepsilon_0 - \varepsilon_\infty)_1 x_1 + (\varepsilon_0 - \varepsilon_\infty)_2 x_2] \tag{3}$$

Where x- mole fraction and suffices m, 1, 2 represents mixture, liquid 1 (BN) and liquid 2 (DCE) respectively. The excess permittivity may provide qualitative information about multimers formation in the mixture.

Similarly, the excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_1 \, x_1 + (1/\tau)_2 \, x_2] \tag{4}$$

where $(1/\tau)^E$ is excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is inverse of the relaxation time) in the resonant spectroscopy [9].

The experimental values of both the excess parameters were fitted to the Redlich-Kister equation [10, 11]

$$A^E = (x_1 \, x_2) \sum_n B_n \left(x_1 - x_2 \right)^n$$

Where A is either ε^E or $(1/\tau)^E$. By using these B_n values, A^E values were calculated.

The excess permittivity (ε^E) increases sharply towards the peak values then decreases slowly up to pure BN. In the BN-DCE system excess permittivity (ε^E) curve, the peak value is noted at 0.1965 mole fraction of BN in DCE. Then it shows that there is a linear decrease. The value goes in negatives from concentration 0.6953. The ε^E values are positive in DCE rich region. Hence there is formation of monomeric or polymeric structures. The total effective dipole increases. There is a parallel alignment of dipoles in DCE rich region. The values of excess permittivity are negatives in BN rich region. It indicates that there is decrease in dipole of the mixture. Hence there is anti parallel alignment of dipoles in BN rich region.

The excess inverse relaxation time values are negatives for all concentrations. It also shows that there is sudden increase in $(1/\tau)^E$ from 0 to 0.1965 concentration of BN and it decreases from 0.2957 to 0.5947 then for next concentration it increases to 0.6953 and then decreases to pure BN. The negative values of inverse relaxation time indicate that the effective dipoles produces an opposing field in the molecules and the slower effective dipole rotation of the molecules in the system.

Table1: Static dielectric constant (ε_0) and relaxation time (τ) for 35^0C temperature.

Volume percentage of BN in DCE	ε_0	τ (ps)
0	10.1	10.81
10	12.77	12.71
20	14.3	12.34
30	15.37	11.87
40	15.62	11.28
50	16.13	11.03
60	17.03	10.65
70	17.73	10.31
80	18.68	9.76
90	19.61	9.16
100	21.1	8

CONCLUSION

The dielectric constant increase as the concentration of BN increases in DCE. The values of excess permittivity and excess inverse relaxation time are reported for butanenitrile and 1, 2 dichloroethane system at 35^0C temperature for 11 different concentrations. The excess permittivity graph shows that in DCE rich region effective dipoles increases

105

and in BN rich region reduces. The negative values of $(1/\tau)^E$ indicates that there is a formation of hindering field in the molecules of the mixture and the dipole rotates slowly.

REFERENCES

[1] V.P. Pawar and S.C. Mehrotra*, J. Sol. Chem.,* **2002**, 31(7),.559-576.

[2] S. N. Helambe, A. S. Chaudhary and S. C. Mehrotra*, J. Mol. Liq.,* **2000**, 84, 235

[3] R.H. Cole, J.G. Berbarian, S. Mashimo, G. Chryssikos, A. Burns and E. Tombari*, J. Appl. Phys*., **1989**, 66,793.

[4] C.E. Shannon, Proc. IRE, **1949**, 37, 10.

[5] H.A. Samulan, Proc. IRE, **1951**, 39, 175.

[6] P. Debye, Polar molecules, Chemical Catalog, New York, **1929**.

[7] P.R. Bevington, Data reduction and error analysis for the physical sciences,Mc-Graw Hill, NewYork, **1969**

[8] M. Tabellout, P. Lanceleur, J.R. Emery, D.Hayward and R.A. Pethrick, *J.Chem.Soc.FaradayTrans*., **1990**, 86,1493.

[9] S.C. Mehrotra and J. E. Boggs*, J. Chem. Phys*., **1977**, 66, 5306.

[10] M.I. Aralaguppi, T.M. Aminabhavi, R.H. Balundgi and S.S. Joshi, *J. Phy. Chem*., **1991**, 95, 5299.

[11] S.F. Al-Azzawl, A.M. Awwad, A.M. Al-Dujaili and M.K. Al-Noori, *J. Chem. Engg. Data*, **1990**, 35, 463.