

Temperature Dependent Dielectric Relaxation Study of Butanenitrile with Chlorobenzene



Engineering

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Ishwar G. Shere

Department of Electronics, Shri. Havagiswami Mahavidyalaya, Udgir-413517 Maharashtra (India)

ABSTRACT

The complex dielectric permittivity spectra of butanenitrile(BN) with chlorobenzene(CBZ) mixture has been determined at temperature 50C 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 relaxation in this system can be described by a single relaxation time using the Debye model. The Excess parameters of the mixtures have been determined. In the mixtures excess permittivity is found to be negative. The excess inverse relaxation time is also found to be negative. The investigation shows that the effective dipoles of the system decreases and produces opposing field, so that dipole rotates slowly

1. Introduction

The dielectric relaxation parameters of binary mixture give considerable information about solute-solvent interaction. Time Domain Reflectometry (TDR) was used to obtain the dielectric parameters of the system [1]-[3]. It also provides the information about the charge distribution in a molecular system. The liquid BN is of C^oN group and CBZ 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 detailed study of dielectric relaxation for butanenitrile and chlorobenzene mixture using TDR at 5^oC 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.

2. Material and apparatus

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

$$x_1 = (v_1 r_1 / m_1) / [(v_1 r_1 / m_1) + (v_2 r_2 / m_2)]$$

where m_i , v_i , and r_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: Butanenitrile- density:0.8329 gm cm⁻³; mol.wt.-67.09, Chlorobenzene -density:1.1050gm cm⁻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

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

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 $\epsilon^*(w)$ were obtained from reflection coefficient spectra $r^*(w)$ by applying bilinear calibration method [4].

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

$$\epsilon^*(w) = \epsilon_\infty + \tag{2}$$

With ϵ_0 , ϵ_∞ and t 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 t is the relaxation time.

3. Results and Discussion

The static dielectric constant (ϵ_0) and relaxation time (t) obtained by fitting experimental data with the Debye equation are listed in Table 1. The values of static dielectric Constant (ϵ_0) increases and relaxation time(t) values increase up to 20% concentration then decreases with the increase of concentration of BN into CBZ.

Figure 1, shows behavior of excess permittivity for the system as a function of volume concentration of BN in CBZ and figure 2, shows behavior of excess inverse relaxation time of BN in CBZ at 50C temperature.

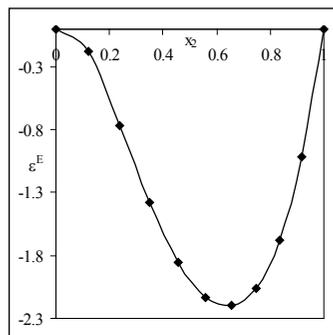


FIGURE 1. The excess permittivity (ϵ^E) versus volume fraction of BN in CBZ

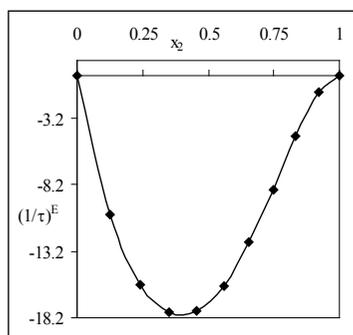


FIGURE 2. The excess inverse relaxation time $(1/t)^E$ versus volume fraction of BN in CBZ.

Vol. Percent of BN	ϵ_0	t (ps)
0	8.02	9.86
10	11	10.72
20	12.39	12.06
30	14.86	11.86
40	16.96	11.65
50	18.87	11.6
60	21	11.18
70	22.98	10.79
80	25.84	10.31
90	28.4	9.72
100	31.2	9.76

Table1: Static dielectric constant (ϵ_0) and relaxation time (t) for 5°C temperature

The information related to liquids 1 and 2 interaction may be obtained by excess properties [9] related to the permittivity and relaxation times in the mixture.

The excess permittivity e^E is defined as

$$e^E = (\epsilon_0 - \epsilon_{\psi})_m - [(\epsilon_0 - \epsilon_{\psi})_1 x_1 + (\epsilon_0 - \epsilon_{\psi})_2 x_2] \quad (3)$$

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

Similarly, the excess inverse relaxation time is defined as

$$(1/t)^E = (1/t)_m - [(1/t)_1 x_1 + (1/t)_2 x_2] \quad (4)$$

where $(1/t)^E$ 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 [10].

The experimental values of both the excess parameters were fitted to the Redlich-Kister equation [11],[12]

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

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

In BN-CB system excess permittivity (e^E) curve, the excess permittivity (e^E) values are negative. The negative peak is obtained at 0.6548 concentrations. Up to negative peak the values are increases then there is linear decrease up to pure BN. These negative values indicate that; there is formation of multimeric structures which leads to decrease in total number of dipoles in the system. There is an opposite alignment of dipoles.

The excess inverse relaxation time $(1/t)^E$ values are also negative. The negative peak is obtained at 0.3515 concentrations. All the negative values of $(1/t)^E$ indicates that there is a formation of hindering field in the molecules and the dipole rotation becomes slowly

4. Conclusion

The dielectric constant, relaxation parameters, excess parameters are reported for butanenitrile and chlorobenzene system at 5°C temperature at 11 different concentrations. These data provide information regarding solute-solvent interaction. From the present study we can conclude that, the negative values of the excess permittivity (e^E) indicates that there is decrease in total number of dipoles in the system and excess inverse relaxation time shows that molecular rotation slowly.

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