

Dielectric Relaxation of Acetonitrile and 1, 2 Dichloroethane at 35⁰c Temperature Using Tdr

Ishwar G. Shere¹

¹Department of Electronics, Shri. Havagiswami Mahavidyalaya, Udgir-413517 Maharashtra (India)

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ABSTRACT: The dielectric relaxation study of acetonitrile with 1,2dichloroethane mixture has been carried out at temperature 35⁰C. The dielectric relaxation study of solute-solvent mixture at microwave frequencies gives information about the formation of monomers and multimers as well as interaction between the molecules of the mixture. The dielectric parameters viz. static dielectric constant (ϵ_0) and relaxation time (τ) have been obtained by the least squares fit method. The static dielectric constant increases and relaxation time decreases with increase in concentration of acetonitrile in 1, 2-dichloroethane in the system. Excess properties of the mixtures have been determined. The time domain reflectometry (TDR) has been used for the study of dielectric relaxation spectra of acetonitrile (ACN) and 1,2 dichloroethane (DCE) binary mixtures. The frequency range has been used as 10 MHz to 20 GHz. The relaxation in this system can be described by a single relaxation time using the Debye model. The Excess parameters such as excess permittivity(ϵ^E) and excess inverse relaxation time ($1/\tau^E$) of the mixtures have been determined. In the mixtures excess permittivity (ϵ^E) and the excess inverse relaxation time ($1/\tau^E$) both are found negative.. The investigation shows that the effective dipoles of the system decreases. It also shows that due to the hindering field between the constituent molecules the dipole rotates slowly. **Keywords:** Dielectric, Static Permittivity, Excess permittivity, Excess inverse relaxation time, Time Domain Technique.

I. INTRODUCTION

The study of dielectric relaxation spectra at microwave frequencies have been carried out to understand intermolecular and intramolecular interactions. Time Domain Reflectometer (TDR) is used to obtain the dielectric parameters of the system [1-3]. The dielectric relaxation parameters of binary mixture give information about solute-solvent interaction. It also provides the information about the charge distribution in a molecular system.

The liquid ACN is of C≡N group and DCE of chlorine group. It is interesting to see the interaction of nitrile group with chlorine-group. The frequency dependent complex permittivity measurements using TDR is more powerful technique because a single measurement covers a wide frequency range in a very short time. Several workers have studied the temperature dependent dielectric relaxation parameters.

II. MATERIAL AND APPARATUS

A spectrograde acetonitrile(ACN) (Fluka cheme GmbH-9471 Buchs, Steinheim, Switzerland) and AR grade 1, 2 dichloroethane(DCE) (E-Merck) were used without further purification The solutions were prepared at 11 different volume percentages of ACN 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: Acetonitrile(ACN)- density:0.7857gcm⁻³; mol.wt.-41.05

1, 2 Dichloroethane(DCE)-density:1.256gcm⁻³;mol.wt.-98.96

The complex permittivity spectra were studied using the time domain reflectometry [4-5] 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 $\Gamma^*(\omega)$ over the frequency range from 10 MHz to 20 GHz using Fourier transformation [6, 7] as

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

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 $\Gamma^*(\omega)$ by applying bilinear calibration method [5].

The experimental values of ϵ^* are fitted with the Debye equation [8]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau}$$

with ϵ_0 , ϵ_∞ and τ as fitting parameters. A nonlinear least-squares fit method [9] 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.

IV. RESULTS AND DISCUSSION

The static dielectric constant (ϵ_0) and relaxation time (τ) obtained by fitting experimental data with the Debye equation are

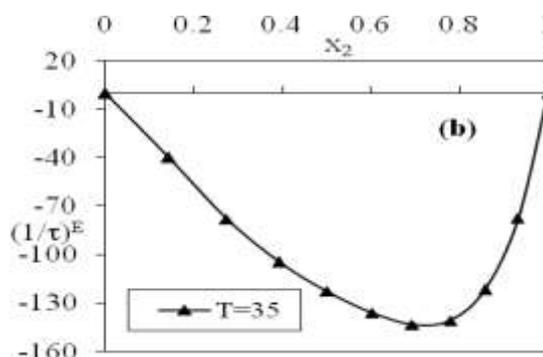
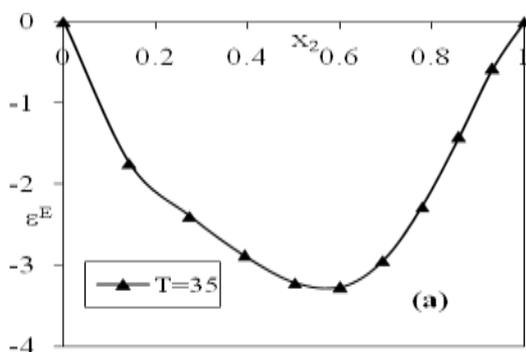


FIGURE1. (a) The excess permittivity (ϵ^E) versus volume fraction of ACN in DCE
 (b) The excess inverse relaxation time ($(1/\tau)^E$) versus volume fraction of ACN in DCE.

listed in Table 1. The values of static dielectric constant (ϵ_0) increases and relaxation time (τ) values increase at 10% and then it shows decreasing trend with the increase of concentration of ACN into DCE.

The information related to liquids 1 and 2 interaction may be obtained by excess properties [10] related to the permittivity and relaxation times in the mixture. The excess permittivity ϵ^E is defined as

$$\epsilon^E = (\epsilon_m - [\epsilon_1 x_1 + \epsilon_2 x_2]) \quad (3)$$

Where x - mole fraction and suffices $m, 1, 2$ represents mixture, liquid 1 (ACN) 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

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

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 [11].

The experimental values of both the excess parameters were fitted to the Redlich-Kister equation [12, 13]

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

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

Figure 1, shows behavior of excess permittivity and excess inverse relaxation time for the system as a function of volume concentration of ACN in DCE at 35°C temperature.

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

Vol. percentage of ACN in DCE	ϵ_0	τ (ps)
0	10.1	10.12
10	12.2	10.49
20	14.82	10.32
30	17.41	9.9
40	20.19	9.2
50	22.94	8.18
60	24.81	7.03
70	28.42	5.81
80	31.39	4.84
90	33.87	3.73
100	36.36	2.72

In the system of ACN-DCE, from the excess permittivity (ϵ'') curve we can see that the excess permittivity (ϵ'') values are negative for all concentrations. The negative peak is obtained at 0.6013 concentrations. From negative peak the values are gradually decreases. The negative values indicate that; there is formation of multimetric structures which leads to decrease in total number of dipoles in the system. It also shows antiparallel alignment of the dipoles.

The excess inverse relaxation time ($1/\tau''$) values are negatives for all concentrations. The negative peak is obtained at 0.6934 concentrations. From the peak point to pure ACN the values are decreases continuously. The negative values of ($1/\tau''$) indicates that; the effective dipoles in the system creates hindering field. It also represents that; the effective dipole rotation becomes slowly.

V. CONCLUSION

The dielectric parameters such as dielectric constant and relaxation time values of acetonitrile (ACN) and 1, 2 dichloroethane (DCE) mixtures are obtained by analyzing dielectric relaxation spectra. The excess permittivity and excess inverse relaxation time values are also reported at 35°C temperature for 11 different concentrations in the frequency range of 10 MHz to 20 GHz. This data provides information regarding solute-solvent interaction. From the present study we can conclude that; the total number of dipoles in the system decreases and shows the antiparallel alignment of the dipoles in the system. We also conclude that; the dipoles produces opposing field

to each other in the mixture and the dipoles in the system rotates slowly.

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