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Dielectric Studies of Acetonitrile with non-Polar Solvent

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ABSTRACT

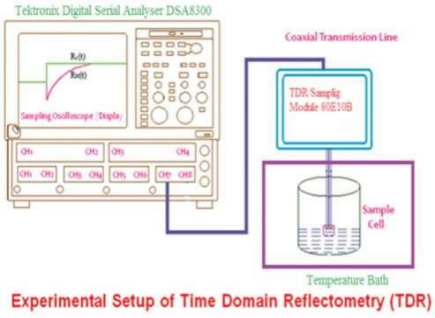
The Time Domain Reflecometry (TDR) method has been used to study dielectric relaxation in a binary solution of acetonitrile (ACN) and 1,4-dioxane(DX) in the frequency range of 10 MHz to 30 GHz. The complex permittivity spectrum of the acetonitrile-1,4-dioxane mixture reveals Debye-type relaxation processes. The dielectric relaxation time (τ) in picoseconds and the static dielectric constant (ε0) have been calculated using the least squares fit method. The interaction between ACN-1,4DX systems has been studied using the Bruggeman factor.
Keywords: complex permittivity spectra, Least squares fit method, Time domain reflectometry, relaxation time, static dielectric constant.

1. INTRODUCTION

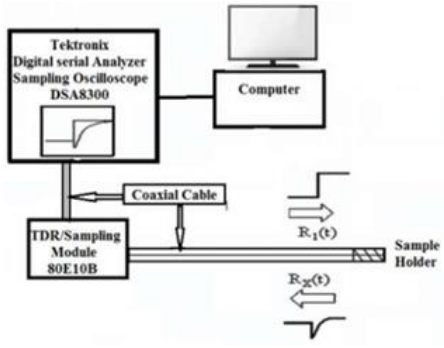
The different spectroscopic techniques are used to study the structural information of liquid molecules [1-4].Short-range molecular organisation that changes quickly over time is a characteristic of liquids. Dielectric spectroscopy has been employed to observe this arrangement and its thermal changes. The Broadband dielectric spectroscopy is a powerful technique for the electrical characterizations, charge distributions as naturally present in liquid and to understand intermolecular interaction between the binary mixtures of liquids. The intermolecular interaction of microscopic heterogeneous structure gives the information about relaxation process. In pharmaceutical and analytical sciences, the dielectric constant of mixed solvents is required to predict the solubility and chemical stability of the drug. TDR techniques are used to determine the various dielectric relaxation parameters such as dielectric permittivity, dielectric loss, static dielectric constant, and dielectric relaxation time. Understanding the non-hydrogen-bonded aprotic solute in a non-polar solvent is the primary goal of the study since it sheds light on how the systems' molecular multimer configurations disintegrate. Acetonitrile (CH_3CN) is the simplest organic nitrile. It is mostly produced as a by-product of acrylonitrile. Acetonitrile is used as a polar aprotic solvent in organic synthesis and purification of butadiene. It is widely used in battery applications due to its relatively high dielectric constant. The various literature surveys show the dielectric properties of acetonitrile with the polar and non-polar solvent [5-10].1,4-Dioxane($C_4H_8O_2$) is a heterocyclic organic compound, classified as an ether. It is a colorless liquid with a faint sweet odor similar to that of diethyl ether. There are number of research article in literature dealing with the dielectric study of dioxane as a solvent [11-15]. In present work, the complex dielectric spectra (CPS) were measured, and the least squares fit technique was used to get the static dielectric constant (ε_0) and relaxation time (τ). The Bruggeman factor has been also computed in order to study intermolecular interactions between ACN-DX molecules.

2. METHODS AND MATERIAL

S.D. Fine Chem. Ltd. supplied ACN and 1,4 DX in 99% purity. Ltd. The solutions were produced at various volume fractions of ACN in 1,4DX. To obtain the Complex permittivity spectra, the TDR technique was utilized [16, 17]. The experimental setup and block diagram of TDR technique is shown in Fig. 1(a,b). It shows the experimental setup and block diagram for the TDR method. Time domain reflectometry has been studied using the Tektronix DSA8300 sampling main frame oscilloscope sampling with the dual channel sampling module 80E10B. The sampling module outputs an incident time pulse of 12 ps and a reflected rising time pulse of 15 ps. The coaxial wire that feeds the pulse has an outer diameter of 1.19 mm, an inner diameter of 0.28 mm, and an impedance of 50 ohms. Following reflection from the end of the line, changes in pulse are monitored by sampling oscilloscopes. The reflected pulse was digitized into 2000 points and recorded within a 5 ns time window, both with and without sample R1(t) and Rx(t). Oscilloscope memory is used to add [q (t) = R1 (t) + Rx (t)] and subtract [p (t) = R1 (t) - Rx (t)] these pulses. The pulses that have been added and deleted are moved to a PC for further study. In order to find the complex permittivity spectra ε*(ω) using the nonlinear least square fit method, the Fourier transforms of the pulse and data analysis were completed earlier.



(a)



(b)

Fig. 1 (a) Experimental setup and (b) block diagram of TDR.

3. RESULTS AND DISCUSSION

3.1*Complex permittivity spectra*

The experimental CPS has been fitted to a Debye-relaxation model, which describes the dielectric relaxation parameters; using the nonlinear Least squares fit (LSF) method [18].

$$\varepsilon * (\omega) = \varepsilon_{\infty} + \frac{\varepsilon_o - \varepsilon_{\infty}}{[1+(j\omega\tau)^{1-\alpha}]^{\beta}} \quad (1)$$

where, ε∞, ε_0, τ, α and β as fitting parameters. The relaxation models for Debye (α = 0, β = 1), Cole-Cole (β = 1), and Davidson-Cole (α = 0) are shows in equation (1).The complex permittivity spectra (CSP) for the ACN-1,4,DX mixture in the 10MHz–30GHz frequency range are displayed in Fig. 2. The systematic

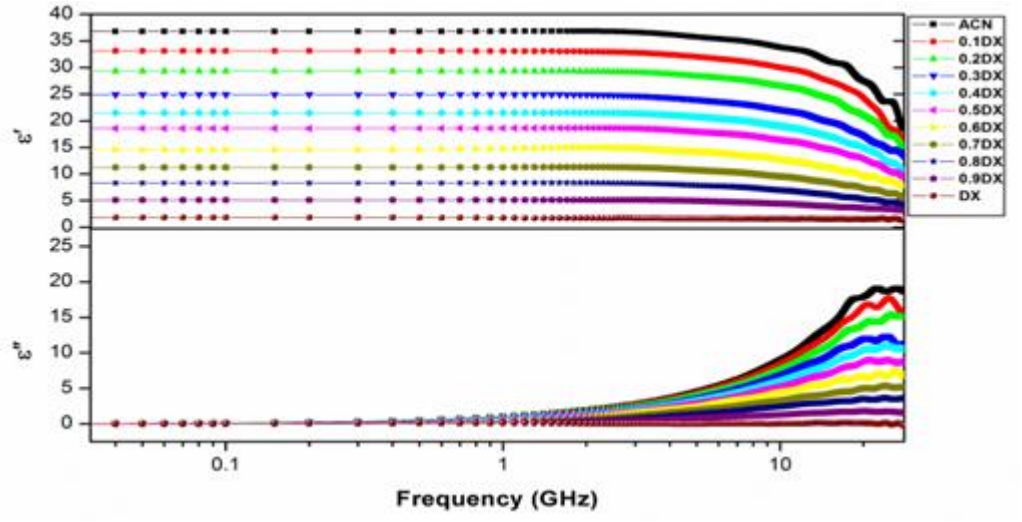


Fig. 2 Complex permittivity spectra for ACN-1, 4DX binary mixture at 25ºC

variations in dielectric permittivity (ε') and dielectric loss (ε") are displayed in this spectrum. Dielectric permittivity decreases with frequency at all concentrations of DX. From pure ACN to pure 1,4DX, the dielectric permittivity value changes linearly. When the DX in ACN solutions increases, the loss peak in the dielectric loss spectrum moves towards the lower frequency range.

3.2 *Static dielectric constant and relaxation time*:

Static dielectric constant values are depends on various factors such as temperature, the number of carbon atoms, the dipole moment, and intermolecular force [19]. The values of dielectric parameters static dielectric constant (ε_0) and relaxation time (τ) in picoseconds are obtained from equation (1) . The molecular size and functional group determine the relaxation time. The current study's calculated relaxation times at 25°C for DX and ACN are 3.95 and 4.33 ps, respectively. The non-linear relaxation behavior of the ACN-DX system is depicted in Table1. The maximum value is observed at 0.9 volume fraction of Dioxane which indicates that at these concentration molecular increases due stronger bonding in molecule's. This nonlinear change in relaxation time and dielectric constant indicates that intermolecular interaction is occurring in the system.

Table 1. Static dielectric constant (ε_0)and relaxation time (τ) of ACN-1,4DX mixture at 25ºC

Vol. frac.	ε_0	(τ)
0.0	36.62(2)	4.33(1)
0.1	32.82(2)	4.66(1)
0.2	29.17(2)	4.86(1)
0.3	25.46(2)	5.33(1)
0.4	22.05(2)	5.65(1)
0.5	18.63(1)	5.91(1)
0.6	14.77(1)	6.25(1)
0.7	11.24(1)	6.97(1)
0.8	8.32(1)	7.68(1)
0.9	5.21(1)	8.05(1)
1.0	2.21(1)	3.95(1)

3.*3 Bruggeman Factor*

The static dielectric constant of binary mixes can be determined using the Bruggeman factor, which can be computed as follows: [20]

$$f_B = \left(\frac{\varepsilon_m - \varepsilon_{DX}}{\varepsilon_{ACN} - \varepsilon_{DX}}\right)\left(\frac{\varepsilon_{ACN}}{\varepsilon_m}\right)^{1/3} = 1 - V_{DX} \qquad (2)$$

where, $f_B, \varepsilon_m, \varepsilon_{DX}, \varepsilon_{ACN}$ denotes Bruggeman factor, static dielectric constants of the mixture,1,4 DX and ACN respectively. V_{DX} is the volume fraction of 1,4-DX, respectively. Bruggeman's equation indicates a linear relationship (green line) between fB and $V_{DX,}$ however an experimental value (black point) deviates from this expectation, as seen in Figure 3. However, the following equation [21] describes the non-linear behavior of different kinds of molecules.

$$f_B = \left(\frac{\varepsilon_m - \varepsilon_{DX}}{\varepsilon_{ACRN} - \varepsilon_{DX}}\right)\left(\frac{\varepsilon_N}{\varepsilon_m}\right)^{1/3} = 1 - [a - (a-1)V_{DX}]V_{DX} \qquad (3)$$

where 'a' is a parameter that can be arbitrary and is always equal to 1 for the ideal mixture which indicates that there is no solute-solvent interaction. The green line in Figure 3 depicts the mixes' ideal behavior as determined by Equation (2), but the black point on the experimental values indicates the non-linear nature of the data. This shows a deviation from the mixture's ideal behavior and indicates the molecular interaction in ACN-1.4DX mixes.

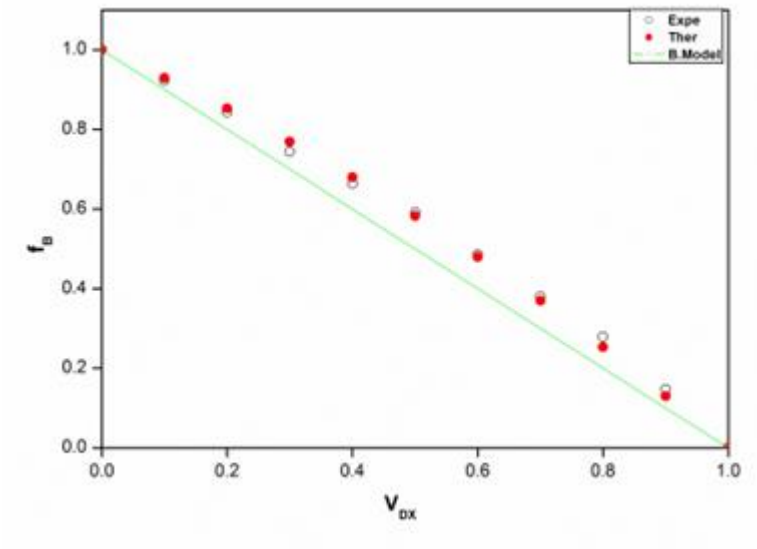


Fig.3 Bruggeman Factor for ACN-DX at 25°C

4. Conclusion

The Frequency dependent complex permittivity spectra for ACN-1,4DX mixture have been obtained in the frequency region 10 MHz -30 GHz. The nonlinear change in relaxation time and dielectric constant indicates that intermolecular interaction is occurring in the system. A modification of the Bruggeman Equation was used to provide a more accurate description of the dielectric behaviour of theACN-1,4DX mixture.

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