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Dielectric Relaxation Study of 2-Nitrotoluene-Dmso Binary Mixtures Using TDR Technique

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ABSTRACT
The foremost objective is to determine and study the dielectric relaxation characteristics of 2-Nitrotoluene (2-NT) with DMSO binary mixtures at 25°Cfor 11 different concentrations in the 10 MHz to 50 GHz frequency range using technique of Time Domain Reflectometry (TDR). The dielectric relaxation factors that of Kirkwood correlation factor, static dielectric properties and excess parameters have been determined at 25°C. Negative excess parameters for entire system reveal weak molecular interactions.
Keywords: *Static dielectric parameters, Excess parameters, Kirkwood correlation factor, TDR technique.*

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INTRODUCTION

The concept of dielectrics in liquids and their mixtures is determined with the help of dynamics and deviations in structure of the liquid composite and is assessed by using TDR technique [1-5]. The properties of liquid dielectric materials are dependent on composition, structure of substance and on various external factors like temperature, humidity, intensity and changing frequency [6]. Effect of frequency and temperature on dielectric behavior of 2-NT-DMSO liquid mixture provides eminent information regarding the concept of hydrogen bonding, cooperative nature and intermolecular correlation between two heteromolecular entities in binary mixture [7-8]. 2-Nitrotoluene (2-NT) is an organic compound having formula as [$CH_3C_6H_4NO_2$]. It is pale yellow liquid also named as ortho-nitrotoluene. It is used in the production of antioxidant's, agricultural chemicals etc. It may be used as detection taggants for the explosive detection, in the synthesis of o-toludine and dyestuff industry [9-12]. Dimethyl sulfoxide (DMSO) [$(CH_3)_2SO$] is colorless polar liquid, watersoluble and in other solvents [13-15].
The effect of intermolecular exchanges in 2-NT with DMSO for 11 different concentrations is conveyed in the current work. Variations in the dielectric parameters using 10 MHz to 50 GHz of frequency range have been studied.

MATERIAL AND METHODS

2-NitroToluene (2-NT) and Dimethyl sulfoxide (DMSO) both were obtained from LobaChemie Pvt. Ltd Mumbai and s d fine-chem Ltd. with 99.00% of purityrespectively.
The static dielectric relaxation parameters were measured at 25°Cin 10 MHz to 50 GHz frequency rangeby means of TDR. The analysis of binary liquids under high frequency and procedure of TDR has been studied in previous articles thoroughly [16-18]

RESULTS AND DISCUSSION

Complex Permittivity Spectra
2-NT-DMSO complex permittivity spectra (CPS) for different mixtures at 25°C are shown in figure 1. Peak position shifting in the direction of lower frequency indicates decreasein relaxation time.Least squares fit method used to analyse raw data of CPS inHavriliak-Negami expression as [19-20],

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

where$\varepsilon_o$is static permittivity, ε_∞ is high frequency permittivity, τ is time of relaxation and α, β are parameters of distribution. Debye model ($\alpha = 0$, $\beta = 1$) [21] is used to fit the raw data.

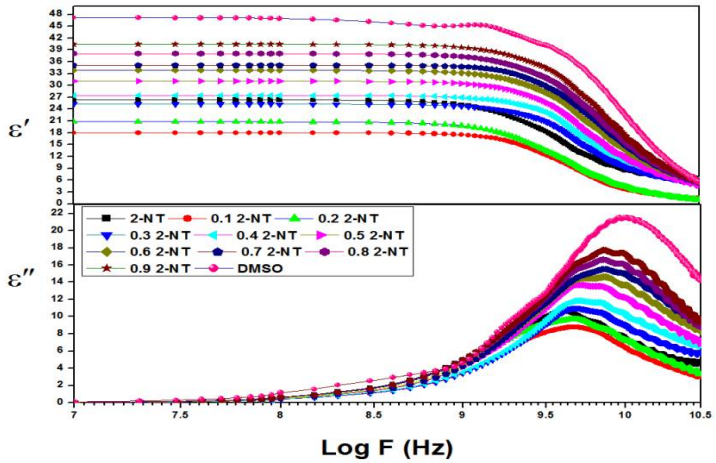

Fig. 1 CPS for**(a)** dielectric permittivity (ε′) and **(b)** dielectric loss (ε″) at 25° C.

Static dielectric parameters

As seen from the figure 2 (a) and (b) the heterogeneous interactions in binary mixture of 2-NT-DMSO direct dissimilarity in dielectric constant and relaxation time. Value of $\varepsilon_o$dropsupto 0.9 volume concentration and then it rises suddenly whereas value of τ surgesupto 0.8 and then reduces, it may be due to cluster formation and increase in size of molecule at these particular concentrations respectively[22-23]. Reduction in static permittivity designatescomprehensive connotation of 2-NT-DMSO binary solution.

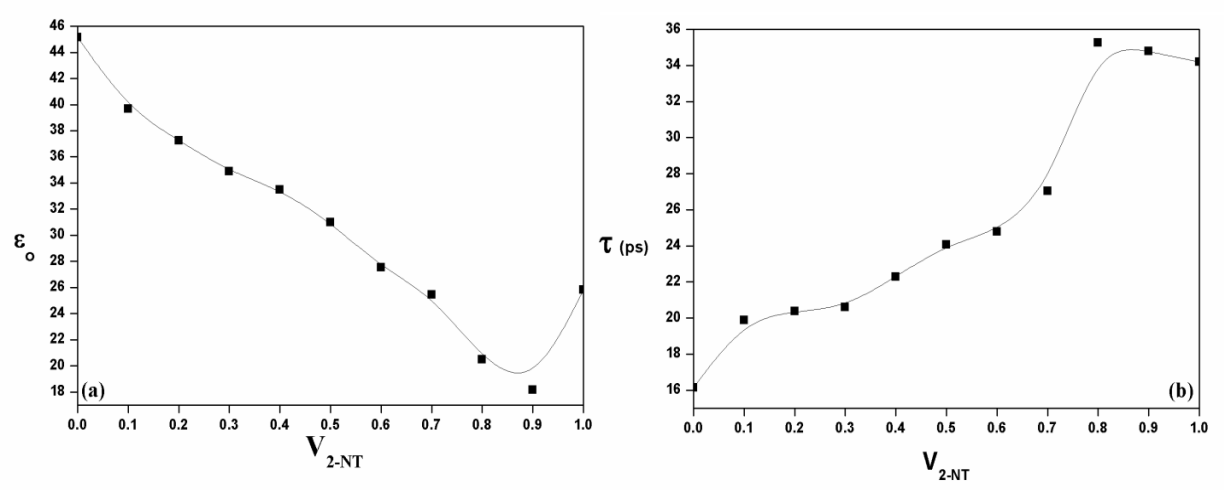

Fig. 2 (a) Static dielectric constant and **(b)**Relaxation time vs.$V_{2\text{-NT}}$ at 25 ºC

3xcess properties

The strength of hydrogen bonding interactions between different molecules is studied using excess permittivity $(\varepsilon_o)^E$and is calculated using the equation as [24-25],

$$\varepsilon_o^E = (\varepsilon_o)_m - [(\varepsilon_o)_2 V_2 + (\varepsilon_o)_1 (1 - V_2)] \quad (2)$$

Information associated to structural changes is studied by means of $(1/\tau)^E$and is evaluated by the equation as [26],

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 V_2 + \left(\frac{1}{\tau}\right)_1 (1 - V_2)\right] \quad (3)$$

where, suffix m, 1 and 2 denotes mixture, 2-NT and DMSO, $(\varepsilon_o)^E$ is excess permittivity, $(1/\tau)^E$ is the excess inverse relaxation time.

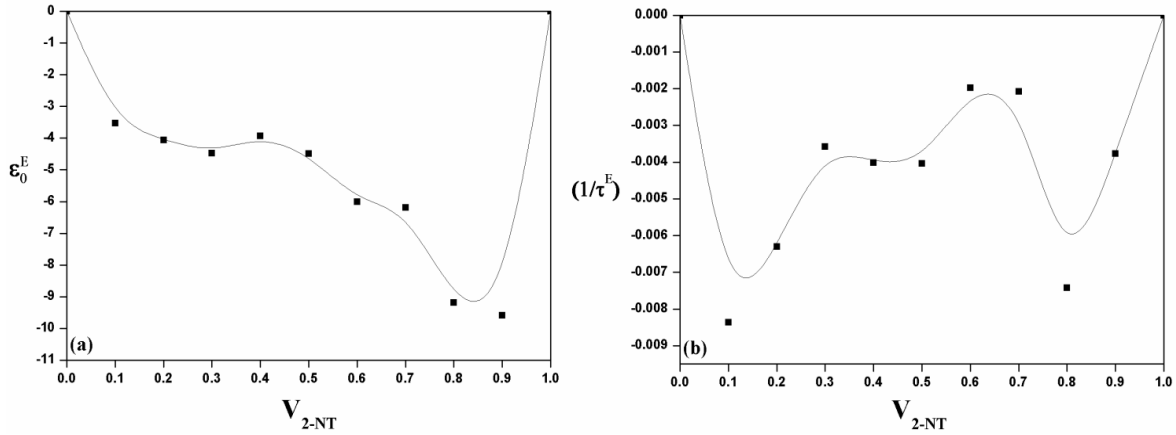

Fig. 3 (a) Excess permittivity **(b)** Excess relaxation vs. $V_{2\text{-NT}}$ at 25 ºC.

Excess permittivity, inverse relaxation values of 2-NT-DMSO binary blends are negative over complete range of concentration which stipulates formation of maximum complexes through H-bonding [27], such that structure of 2-NT is broken by DMSO [28] which concluded that the effective dipoles are reduced, are oriented in opposite direction with slower rotation and is may be because of polymeric makeup in composite [29-31].

Kirkwood correlation factor

The Kirkwood correlation parameter (g^{eff})for distinct molecules in the blend is evaluated using modified Kirkwood expression [32-33],

$$\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} = \frac{4\pi N}{9kT}\left[\frac{\mu_2^2\rho_2}{M_2}V_2 + \frac{\mu_1^2\rho_1}{M_1}(1-V_2)\right] \times g^{eff} \qquad (4)$$

where, g^{eff}, ε_{0m}, $\varepsilon_{0\infty}$, μ_1, μ_2, ρ_1, ρ_2,M_1, M_2, N, k, T has their usual meanings and V_2 is volume fraction of DMSO.

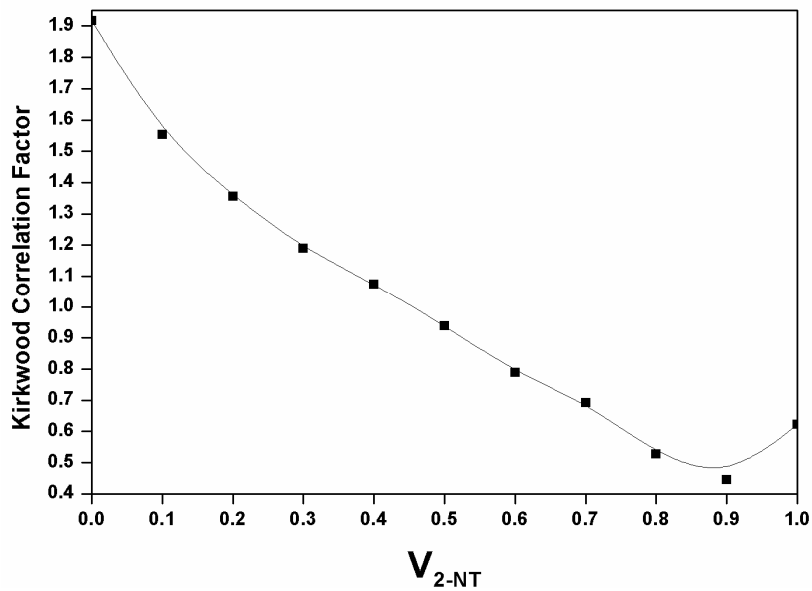

Fig.4 Kirkwood correlation factor (g^{eff}) vs.$V_{2\text{-NT}}$ at 25 ºC.

From figure 4, it is clear that the dipoles are oriented in antiparallel wayfrom 0.5 concentration such that g^{eff} value goes on decreasing below unity and are > 1 above 0.5 concentration indicating parallel orientation of dipoles [34].Theg^{eff} value for DMSO at 25 °C is 0.62 which is less than the value of 2-NT and is 1.91.

CONCLUSION

The dielectric characteristic study of 2-NT-DMSO binary mixtures has been revealed using TDR technique in the frequency range 10 MHz to 50 GHz. Reductioninε_o value and τ value progression in steps with rise

of $V_{2\text{-}NT}$ is studied. Strong intermolecular interactions with slower rotation of dipoles are thoroughly studied in excess parameters. g^{eff} values > 1 designatesthatthe dipoles oriented inparallelway.

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