



A COMPARISON OF THE DIELECTRIC RELAXATION BEHAVIOUR OF 2-NITROTOLUENE-DIMETHYL SULFOXIDE AND 1-NITROPROPANE-DIMETHYL SULFOXIDE MIXTURES USING TIME DOMAIN REFLECTOMETRY

Aniket D. Bokhare^{a*}, Haribhau M. Dhage^b, Milind P. Lokhande^a, Ashok C. Kumbharkhane^b

^a Govt. Vidarbha Institute of Science and Humanities, Amravati-444604, MS, India,

^b School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431606, MS, India

aniketbokhare13696@gmail.com, haribhau210@gmail.com,
mplokhande123@gmail.com, akumbharkhane@yahoo.co.in

Abstract— The complex permittivity spectra (CPS) of 2-nitrotoluene (2NT) –Dimethyl sulfoxide(DMSO) and 1-nitropropane(NTP) -Dimethyl sulfoxide(DMSO) mixtures in the frequency range of 10 MHz to 50 GHz were determined using a time domain reflectometry (TDR) technique over the whole concentration range. The CPS have been fitted to the Debye relaxation model. The static dielectric constant (ϵ_0) and relaxation time (τ) for both systems were calculated from the CPS using the nonlinear least squares fit method. The observation that 2NT-DMSO mixtures have a lower dielectric constant than 1-nitropropane-DMSO mixtures, despite the longer relaxation time, highlights the complex interplay of factors influencing dielectric properties in mixtures.

Index Terms— Dielectric constant, Complex permittivity, Time domain reflectometry (TDR), 2-nitrotoluene Relaxation time, 1-nitropropane

I. INTRODUCTION

The nitro group ($-\text{NO}_2$) can have a complex and multifaceted influence on the dielectric properties of a molecule, depending on the specific context and interactions within the material. The presence of other functional groups and atoms in close proximity to the nitro group can influence its electronic interactions and impact its contribution to the overall dielectric properties [1-4]. A dielectric study is

thus required to better understand the molecular interaction between the nitro group and other functional groups. Additionally, the orientation and spatial arrangement of the nitro group within the molecule can also play a significant role in calculating its effect on dielectric behaviour. Understanding these factors is crucial for predicting and manipulating the overall dielectric behaviour of a material. To understand this interaction, we have chosen 2 nitrotoluene(2NT) -DMSO and 1 nitropropane (NTP) -DMSO mixture.

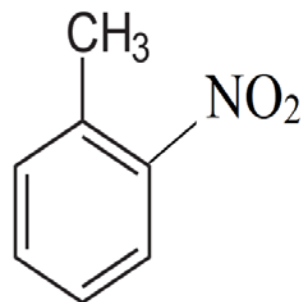


Fig. 1. Structure of 2-Nitrotoluene



Fig. 2. Structure of 1-Nitropropane

2NT has a benzene ring substituted with a nitro group ($-\text{NO}_2$) at the 2-position as shown in Fig. 1. The aromatic ring contributes to its overall polarity, but the presence of the methyl group ($-\text{CH}_3$) adds steric hindrance. Fig.2 shows structure of NTP. It is a straight-chain alkane with a nitro group ($-\text{NO}_2$) attached. It lacks the

aromaticity of 2NT but has a more linear structure. DMSO was chosen as the solvent because of its high polarity and ability to dissolve a wide range of compounds. Also, the interaction between the nitro group and the sulfoxide group in DMSO can lead to interesting chemical reactions. Overall, the differences in structure between 2NT and NTP contribute to variations in their reactivity and behaviour. The choice of DMSO as a solvent may also impact the outcome of chemical reactions involving these compounds.

Both NTP and 2NT can engage in dipole-dipole interactions with DMSO molecules, influenced by their respective dipole moments and geometric factors. These interactions can affect the overall orientation and mobility of molecules in the mixture, impacting the dielectric response. The nitro group can influence the dielectric properties of both NTP and 2NT. The nitro group affects the dielectric behaviour of these mixtures, but the specific outcome depends on the interplay of various factors. More research is needed to precisely quantify and understand this impact under different mixture compositions and measurement conditions.

The results of the current investigation demonstrate the effect of nitro group on 2NT-DMSO and NTP-DMSO mixtures at various concentrations. Variations in dielectric properties have been studied at frequencies ranging from 10 MHz to 50 GHz in order to gain a better knowledge of the relaxation mechanisms using time domain reflectometry. Understanding these mechanisms can provide insights into the dynamics of the nitro groups and their contribution to the dielectric relaxation process. To calculate the ϵ_0 and τ , the least squares fit method is used.

The results of the current investigation demonstrate the effect of nitro group on 2NT-DMSO and NTP-DMSO mixtures at various concentrations. Variations in dielectric properties have been studied at frequencies ranging from 10 MHz to 50 GHz in order to gain a better knowledge of the relaxation mechanisms using time domain reflectometry. Understanding these mechanisms can provide insights into the dynamics of the nitro groups and their contribution to the dielectric relaxation process.

To calculate the ϵ_0 and τ , the least squares fit method is used.

II. EXPERIMENTAL PROCEDURE

A. Materials

2NT and NTP were purchased commercially from Loba Chemie Pvt. Ltd., Mumbai, with 99.00% purity. DMSO was obtained from S. D. Fine-Chem Ltd. The binary mixture of NTP-DMSO and 2NT-DMSO was prepared at varying concentrations by volume fraction.

B. Measurements

The CPS were obtained using the TDR technique [5]. The Tektronix digital serial analyzer model no. DSA8300 sampling mainframe oscilloscope along with the dual channel sampling module 80E10B has been used for time domain reflectometer. The experimental setup and instrument calibration are carried out in accordance with the references [6, 7].

III. RESULTS AND DISCUSSIONS

Fig. 3 and Fig. 4 display the frequency-dependent CPS for NTP-DMSO and 2NT-DMSO at various concentrations respectively. The CPS obtained with TDR are fitted to the Havriliak - Negami expression using the non-linear least squares fit method [8-9].

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

Where ϵ_0 , τ , ϵ_∞ , α and β are the fitting parameters. ω is the angular frequency. The Debye ($\alpha = 0$, $\beta = 1$) [10], Cole-Cole ($0 \leq \alpha \leq 1$ and $\beta = 1$) [11] and Davidson - Cole ($\alpha = 0$ and $0 \leq \beta \leq 1$) [12] relaxation models are the limiting cases of Havriliak - Negami expression.

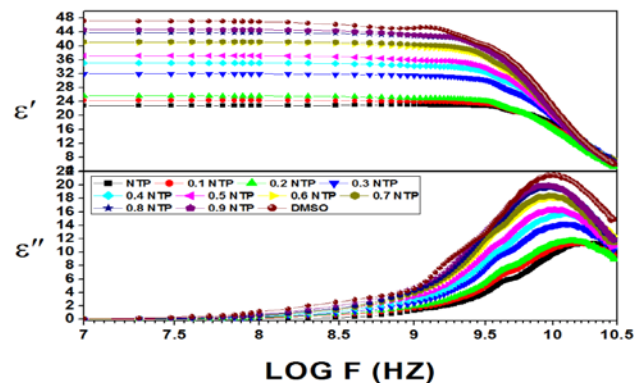


Fig. 3. Frequency dependent complex permittivity spectra for NTP-DMSO mixtures at 25 ° C

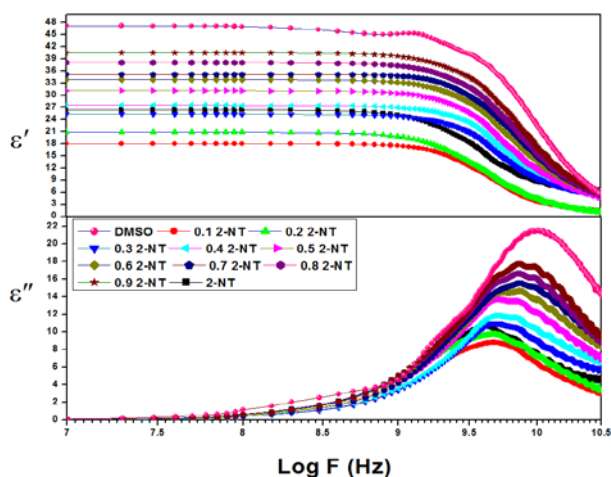


Fig. 4. Frequency dependent complex permittivity spectra for 2NT-DMSO mixtures at 25 ° C

The study compares ϵ_0 for 2NT-DMSO and NTP-DMSO mixtures at 25°C for different volume fraction of DMSO at 25 °C as represented in Fig. 5. It is found that, despite 2 NT having a higher dielectric constant than NTP, when DMSO interacts with both, the dielectric constant of 2 NT-DMSO is smaller than that of NTP-DMSO over different concentration ranges. The study by Dhage et al. reports that the interaction between 2NT and DMSO is weak [2], leading to negative excess parameters for the entire system, which indicates weaker molecular interactions. Also, the study of NTP-DMSO reports positive excess parameters [3], which indicate a stronger molecular interaction. Our observations are supported by these results.

The dielectric constant of 2-NT may be influenced by the aromaticity and the presence of the nitro group, leading to relatively higher values compared to NTP. NTP have a lower dielectric constant compared to 2-NT due to its linear structure and potentially lower polarity. Even 2-NT has a larger permanent dipole moment than NTP, its interaction with DMSO molecules found weaker compared to the interaction between NTP and DMSO. This weaker interaction can lead to a lower overall polarization of the mixture, resulting in a smaller dielectric constant. The seemingly contradictory trend in 2NT-DMSO vs. NTP-DMSO mixtures underscores how interactions beyond individual dipole moments significantly affect dielectric properties.

Comparison of relaxation time (τ in ps) for 2NT-DMSO and NTP-DMSO mixtures for

different volume fraction of DMSO at 25 °C is represented in Fig. 6. The value of τ of 2NT-DMSO mixtures found to be greater than NTP-DMSO mixtures over different concentration ranges. 2-NT has a larger aromatic ring compared to 1-NTP's linear structure. This bulkier size can create steric hindrance, making it harder for 2-NT to rotate in the applied electric field during TDR measurements. Slower rotation translates to longer relaxation times.

When the concentration of DMSO increases in 2-NT-DMSO mixtures, the relaxation time decreases. This suggests faster molecular reorientation as DMSO concentration increases. Higher DMSO content could dilute the 2-NT molecules, reducing their influence on reorientation and leading to faster overall movement. On the other hand the value of τ of NTP-DMSO mixtures increases with increasing DMSO concentration, resulting in increased viscosity and slower movement, which leads to longer relaxation times.

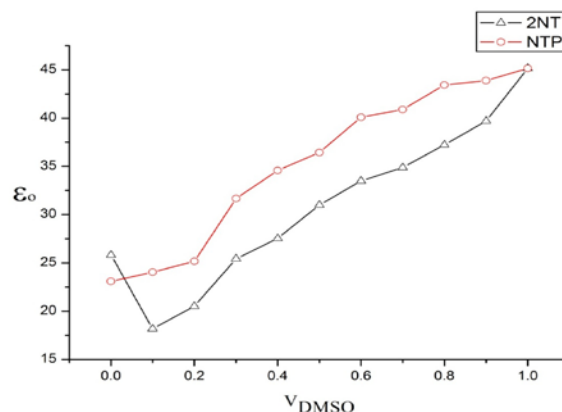


Fig. 5. Comparison of dielectric constant for 2NT-DMSO and NTP-DMSO mixtures for different volume fraction of DMSO at 25 ° C

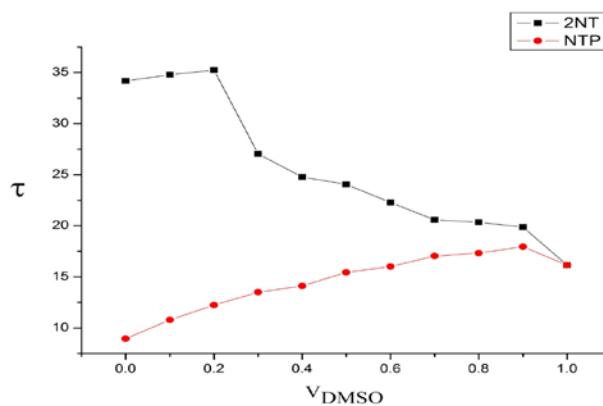


Fig. 6. Comparison of Relaxation time for 2NT-DMSO and NTP-DMSO mixtures for different volume fraction of DMSO at 25 ° C

IV. CONCLUSION

Both 2-NT and NTP contain nitro groups, their structural and chemical differences lead to variations in their ϵ_0 and τ when interacting with DMSO. These differences arise from factors such as molecular structure, polarity, and intermolecular interactions. These interactions can involve factors like dipole-dipole interactions and solvent dynamics, leading to complex behaviours [13-15].

V. ACKNOWLEDGEMENT

Author Aniket D. Bokhare expresses gratitude to the Director of the Government Vidarbha Institute of Science and Humanities, Amravati. The School of Physical Sciences at SRT Marathwada University in Nanded (MS) is also acknowledged by the author for providing the laboratory equipment. Author acknowledges the fellowship received from the Chhatrapati Shahu Maharaja Research, Training, and Human Development Institute (SARTHI), Pune (CMSRF-2021). It is acknowledged that the DST, New Delhi, India, provided financial assistance for this project (Project number: DST PROJECT- SB/S2/LOP-032/2013).

REFERENCES

- [1] Chaudhari, A., Chaudhari, H. and Mehrotra, S., 2002. Dielectric properties for the binary mixture of dimethylsulphoxide and dimethylacetamide with 2-nitrotoluene at microwave frequencies. *Fluid phase equilibria*, 201(1), pp.107-118.
- [2] Dhage, H.M., Deshmukh, A.R., Birajdar, S.S. and Kumbharkhane, A.C., 2022. Temperature dependent dielectric relaxation studies of 2-nitrotoluene-dimethyl sulfoxide mixture using time domain reflectometry.
- [3] Dhage, H.M., Bokhare, A.D., Garad, N.P., Lokhande, M.P. and Kumbharkhane, A.C., 2024. Dielectric relaxation studies of 1-nitropropane-dimethyl sulfoxide mixtures using a Time Domain Reflectometry. *Physics and Chemistry of Liquids*, pp.1-10.
- [4] Mohan, A. and Malathi, M., 2018. Dielectric relaxation and thermodynamic studies of binary mixtures of 2-nitrotoluene with primary and secondary alcohols at different temperatures. *Journal of Solution Chemistry*, 47, pp.667-683.
- [5] Cole, R.H., Berberian, J.G., Mashimo, S., Chryssikos, G., Burns, A. and Tombari, E., 1989. Time domain reflection methods for dielectric measurements to 10 GHz. *Journal of applied physics*, 66(2), pp.793-802.
- [6] Kadam, S.S., Kanse, K.S., Joshi, Y.S., Rander, D.N. and Kumbharkhane, A.C., 2018. Dielectric relaxation studies of 1, 3 and 1, 4-butanediol–water mixtures using time domain technique. *Indian Journal of Physics*, 92, pp.1367-1372.
- [7] Mehrotra, S.C., Kumbharkhane, A. and Chaudhari, A., 2017. *Binary polar liquids: structural and dynamic characterization using spectroscopic methods*. Elsevier.
- [8] Havriliak, S. and Negami, S., 1966. A complex plane analysis of α -dispersions in some polymer systems. In *Journal of Polymer Science Part C: Polymer Symposia* (Vol. 14, No. 1, pp. 99-117). New York: Wiley Subscription Services, Inc., A Wiley Company.
- [9] Kaatze, U., 1995. Microwave dielectric properties of liquids. *Radiation Physics and Chemistry*, 45(4), pp.549-566.
- [10] Debye, P., 1929. Polar molecules, the chemical catalog company. *Inc., New York*, 89.
- [11] Cole, K.S. and Cole, R.H., 1941. Dispersion and absorption in dielectrics I. Alternating current characteristics. *The Journal of chemical physics*, 9(4), pp.341-351.
- [12] Davidson, D.W. and Cole, R.H., 1950. Dielectric relaxation in glycerine. *The Journal of Chemical Physics*, 18(10), pp.1417-1417.
- [13] Bokhare, A.D., Garad, N.P., Lokhande, M.P. and Kumbharkhane, A.C., 2024. Dielectric relaxation and hydrogen bonding interactions study of aqueous D-sorbitol using time domain reflectometry. *Physics and Chemistry of Liquids*, 62(1), pp.1-8.
- [14] Bokhare, A.D., Patange, S.S., Garad, N.P., Kumbharkhane, N.A., Lokhande, M.P. and Kumbharkhane, A.C., 2024. Dielectric characterisation and intermolecular interactions in propionitrile-dimethyl sulphoxide mixtures using a time domain reflectometry. *Physics and Chemistry of Liquids*, pp.1-9.
- [15] Bokhare, A.D., Garad, N.P., Lokhande, M.P. and Kumbharkhane, A.C., 2024. Molecular interaction and dielectric relaxation study of DMSO-water binary mixtures using a TDR.