

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 12, Special Issue, December 2025
National Conference on Earth, Elements and Energy:
Interdisciplinary Perspectives (NC3EIP-2025)



ISSN: 2350-0328

Analysis of dielectric relaxation characteristics for propylene glycol—pyridine mixtures using time domain reflectometry at 25°C

Shakeel K. Khan*, Milind P. Lokhande, Ashok C. Kumbharkhane

Department of Physics, B.S. Patel Arts Commerce and Science College, Pimpalgaon Kale, 443403, Maharashtra Govt. Vidarbha Institute of Science and Humanities, Amravati-444604, MS, India School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431606, MS, India

ABSTRACT: The complex permittivity spectra of Propylene glycol-pyridine mixtures in the frequency range of 10 MHz to 30 GHz at 25°C were determined using a time domain reflectometry (TDR) technique over the whole concentration range. The complex permittivity spectra were fitted to the Cole-Davidson relaxation model, which accounts for the distribution of relaxation times often observed in polar mixtures. The Havriliak-Negami formula is used to investigate the frequency dependence of complex dielectric permittivity. The static dielectric constant and relaxation time were calculated using the nonlinear least squares fit method. Propylene glycol's hydrogen bonding overpowers pyridine's weaker polarity, increasing its responsiveness to electric fields and resulting in a higher dielectric constant. Propylene glycol's stickiness causes it to become more viscous, causing molecules like pyridine to take longer to re-orient after an electric field is removed, resulting in longer relaxation times.

KEYWORDS: Dielectric constant, Complex permittivity, Relaxation time, Time domain reflectometry (TDR)

I. INTRODUCTION

"The dielectric studies of propylene glycol provide valuable information for understanding its fundamental properties [1]." Propylene glycol, also known as 1,2-propanediol, has the chemical formula $C_3H_8O_2$. It's a simple alcohol with a three-carbon backbone, two hydroxyl groups (OH), and a single methyl group (CH₃). Propylene glycol, as a polar solvent, can solvate pyridine molecules to a certain extent, depending on the concentration and presence of other components in the mixture.

Propylene glycol has hydroxyl groups that can form hydrogen bonds, while pyridine has a nitrogen atom that can accept hydrogen bonds. The dielectric properties of the mixture can reveal the strength and nature of these interactions. A stronger interaction between the two components would be reflected in changes in the dielectric constant and relaxation times compared to the individual components [2]. By understanding the dielectric behavior of the propylene glycolpyridine mixture, researchers can gain valuable insights into the interaction between the components and predict the mixture's suitability for various applications.

This research uses time domain reflectometry (TDR) to analyze the complex permittivity spectra of propylene glycol-pyridine mixtures across various concentrations in the frequency range of 10 MHz to 30 GHz. Based on these spectra, they determine two key parameters: Static dielectric constant (ϵ_0) which reflects the mixture's overall response to an electric field at equilibrium.and Relaxation time (τ) which indicates how long it takes for the mixture's molecules to reorient themselves after the electric field is removed. The study then investigates how these parameters change with the increasing volume fraction of pyridine in the mixture.

II. RELATED WORK

Propylene glycol and pyridine were used to prepare solutions by volume fraction.

III. SIGNIFICANCE OF THE SYSTEM AND METHODOLOGY

Meticulously prepared solutions were held at a constant temperature for 10-15 minutes before TDR measurements [3-5] using a conventional setup with a signal source, a 50 Ω coaxial transmission line, and a high-speed Tektronix DSA 8300



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sampling oscilloscope equipped with a dual-channel 80E10B module. This module generated fast-rise time pulses (12 ps incident and 15 ps reflected) using a tunnel diode, launching them into the coaxial line. The reflected pulse response, $R_1(t)$ for the empty line and $R_1(t)$ for the sample-filled line, was captured within a 5 ns window and digitized with 2000 points by the sampling oscilloscope. Fourier transform and non-linear least squares analysis were then applied to extract the complex permittivity spectra $(\varepsilon^*(\omega))$ of pure solutions and binary mixtures for frequency dependence.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Complex permittivity spectra

The frequency dependent complex permittivity spectra for propylene glycol-pyridine at various concentrations produced by the time domain reflectometry technique (TDR) at 25 °C are shown in Fig. 1. These spectra show that Dielectric Permittivity decreases with increasing frequency. This happens because the material's polarizable components (dipoles) can't reorient themselves as quickly as the electric field changes at higher frequencies.

The complex permittivity spectra obtained with TDR are fitted to the Havriliak - Negami expression using the non-linear least squares fit method.

$$\varepsilon * (\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{[1 + (j\omega\tau)^{1-\alpha}]^{\beta}}$$
(1)

 $\varepsilon*(\omega) = \varepsilon_{\scriptscriptstyle \infty} + \frac{\varepsilon_0 - \varepsilon_{\scriptscriptstyle \infty}}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \ldots (1)$ where ε_0 is the static dielectric constant which represents the equilibrium behaviour, $\varepsilon_{\scriptscriptstyle \infty}$ is the permittivity at high frequency which represents the instantaneous behaviour, τ is relaxation time, α and β are the shape parameters describing symmetric and asymmetric distribution of relaxation time, respectively, and ω is the angular frequency. The Debye (α =0, $\beta = 1$)[6], Cole-Cole ($0 \le \alpha \le 1$ and $\beta = 1$) [7] and Davidson – Cole ($\alpha = 0$ and $0 \le \beta \le 1$) [8] relaxation models are the limiting cases of Havriliak - Negami expression. The static dielectric constant (ε_0) and relaxation time (τ) for propylene glycol-pyridine mixtures at different temperatures are shown in table 1.

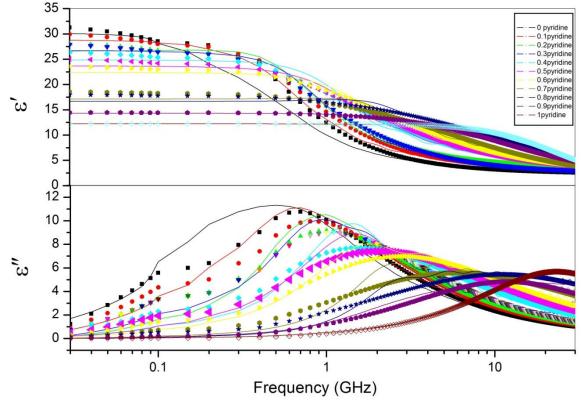


Figure 1 Complex permittivity spectra for Propylene Glycol+ pyridine mixtures at 25°C.



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Table 1. Dielectric parameters: a) Dielectric constant (ε_0) b) relaxation time (τ) for Propylene Glycol+ pyridine mixture.

Volume fraction of Pyridine	Static Dielectric constant (ε_0)	Relaxation time (τ) (ps)
00	31.70	333.67
0.1	30.28	253.16
0.2	28.28	198.15
0.3	28.15	182.65
0.4	26.63	115.24
0.5	25.27	88.19
0.6	23.72	61.54
0.7	18.64	27.50
0.8	18.04	14.82
0.9	14.45	13.84
1	12.23	6.879

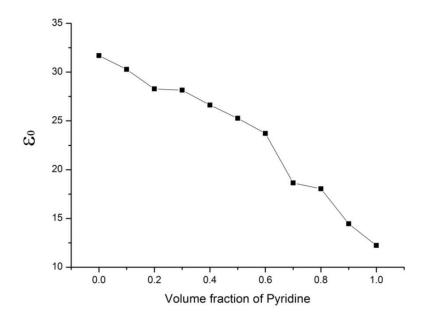


Figure 2: Static Dielectric constant versus Volume fraction of Pyridine for Propylene Glycol+ pyridine mixtures at 25°C

Figure 2 reveals that the static dielectric constant of the mixture decreases as the volume fraction of pyridine increases for propylene glycol+pyridine mixtures. At lower pyridine concentrations, the added pyridine molecules could interact with the propylene glycol molecules, influencing their orientation in the electric field and potentially increasing the dielectric constant. However, as the pyridine concentration increases, it might overwhelm the propylene glycol molecules, hindering their ability to align in the field and leading to a decrease in the overall dielectric constant. Figure 3 reveals that the relaxation time of the mixture decreases as the volume fraction of pyridine increases for propylene glycol+pyridine mixtures. it implies that the molecules are returning to their random orientations faster after the electric field is removed.



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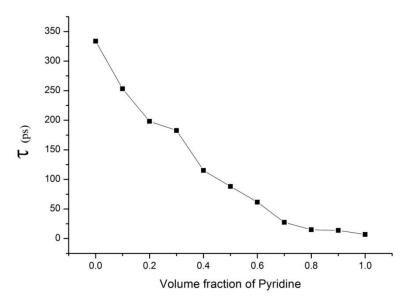


Figure 3: Relaxation time versus Volume fraction of Pyridine for Propylene Glycol+ pyridine mixtures at 25°C

V. CONCLUSION

A dielectric relaxation study using time domain reflectometry revealed that interactions between propylene glycol and pyridine in mixtures affect their response to electric fields. While propylene glycol's dominant hydrogen bonding initially increased the mixture's dielectric constant at lower pyridine concentrations, further addition of pyridine disrupted this alignment, leading to a decrease. Additionally, the presence of pyridine reduced the relaxation time, indicating that molecules re-oriented faster after the electric field was removed. This study highlights how intermolecular interactions influence the dielectric behavior of propylene glycol-pyridine mixtures.

VI.ACKNOWLEDGEMENT

Author Shakeel K. Khan is thankful to Director of Government Vidarbha Institute Of Science and Humanities, Amravati and School of Physical Sciences, SRT Marathwada University, Nanded (MS) For availing the laboratory facility. It is acknowledged that the Department of Science and Technology (DST), New Delhi, India, provided financial assistance for this project (Project number: DST PROJECT- SB/S2/LOP-032/2013).

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