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Dielectric Spectral Analysis and Relaxation Dynamics of 3-Chloroaniline–1-Ethoxy-2-Propanol Binary Mixtures Using Time Domain Reflectometry

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Abstract

The dielectric behaviour of binary mixtures of 3-chloroaniline (3-CA) and 1-ethoxy-2-propanol (PGEE) was investigated at 25^0C across a frequency range of 10 MHz to 30 GHz for eleven volume fractions. Frequency-dependent complex dielectric permittivity spectra $\varepsilon^*(\omega)$ and complex dielectric loss spectra (ε'') were analyzed using the Havriliak-Negami model, which revealed Cole-Davidson-type relaxation. The static dielectric constant (ε_0) and relaxation time (τ) were determined. The dielectric response of all samples at 25^0C was satisfactorily explained by a single relaxation mechanism. Strong specific interactions were observed between the amino group ($-NH_2$) of 3-CA and the alcoholic group (-OH) of PGEE through hydrogen bonding, resulting in significant non-ideality in mixing. These findings demonstrate the effectiveness of dielectric spectroscopy in elucidating molecular interactions and relaxation phenomena in binary liquid mixtures.

Keywords: Time Domain Reflectometry (TDR), dielectric relaxation, 3-CA, PGEE, complex dielectric permittivity, complex dielectric loss.

1. Introduction

3-Chloroaniline (3-CA) is a chlorinated aromatic amine extensively utilized in the industrial production of dyes, cosmetics, pharmaceutical products and herbicides. As a result of its broad application, 3-CA has accumulated in industrial wastewater, sludge, agricultural soil, and sediments, leading to its widespread presence

in the environment [1]. Structurally, 3-CA contains both an electron-donating amino group (-NH2) and an electron-withdrawing chlorine substituent, which confer high polarity and enable participation in intermolecular interactions via dipole–dipole forces and hydrogen bonding.

1-Ethoxy-2-propanol (PGEE) is a glycol ether polar solvent characterized by the presence of hydroxyl (-OH) and ether (-O-) functional groups, which facilitate strong self-association and solvent-solute interactions [2]. Owing to these properties, glycol ethers are regarded as suitable scrubbing liquids [3]. They are also widely employed as detergents due to their ability to form stable homogeneous solutions with high water and oil content [4]. Additionally, glycol ethers are incorporated into lubricants, hydraulic fluids, greases and related products to enhance additive compatibility and address turbidity issues [5]. When combined, 3-CA and PGEE may form specific intermolecular complexes through hydrogen bonding between the amino group (-NH_2) of 3-CA and the hydroxyl group (-OH) of PGEE, which can significantly affect the dielectric relaxation behavior of the system.

Dielectric relaxation spectroscopy is a powerful technique for investigating molecular dynamics, dipolar orientation and intermolecular interactions in polar liquid mixtures. The frequency-dependent complex dielectric permittivity provides valuable information regarding molecular association, hydrogen bonding, and relaxation mechanisms occurring in liquid systems. Time Domain Reflectometry (TDR) has been widely employed to study dielectric relaxation processes in binary liquid mixtures over the microwave frequency region because of its high accuracy and broad frequency coverage. The dielectric parameters obtained from complex permittivity spectra, such as static dielectric constant, dielectric loss and relaxation time, are useful for understanding the structural and dynamical behavior of molecules in solution [6]. Several researchers have employed dielectric relaxation spectroscopy and TDR techniques to investigate intermolecular interactions in binary mixtures by determining dielectric constant, relaxation time, distribution parameters [7].

This study investigates the broadband complex dielectric spectra of binary mixtures of 3-chloroaniline (3-CA) and 1-ethoxy-2-propanol (PGEE) from 10 MHz to 30 GHz and at temperatures 25^{0}C using Time Domain Reflectometry (TDR). No previous dielectric relaxation studies have examined this binary system. The novelty of this work lies in identifying asymmetric non-Debye relaxation behavior (Cole–Davidson type), attributed to interactions between PGEE and 3-CA (-NH_2 and -Cl groups).

2. Materials and Methods

Sample preparation and mixing procedure

3-Chloroaniline (3-CA, 98% purity) was obtained from Sd. Fine Chem. Ltd., and 1-ethoxy-2-propanol (PGEE, 99% purity) from Tokyo Chemical Industry (India) Pvt. Ltd. Eleven binary mixtures were prepared with varying volume fractions of 3-CA and PGEE, each totaling 10 ml. Pure solute and solvent samples were also included. All eleven stoppered bottles were cleaned, dried with hot air, rinsed with acetone, and dried again. Mixtures were prepared in 1 mL increments, ranging from 10:0 to 0:10 mL of 3-CA to PGEE. After preparation, bottles were sealed and left undisturbed for 1 hour to ensure thorough mixing.

Measurement

We measured the complex permittivity of the solutions from 10 MHz to 30 GHz at temperatures 25^{0}C using time-domain reflectometry (TDR) [8]. A calibrated controller-maintained sample temperatures within ±0.10C. We used a Tektronix DSA8300 Digital Serial Analyzer with the 80E10B sampling module for TDR measurements. A fast-rising voltage pulse (18 ps incident, 20 ps reflected rise time) was applied through a coaxial line (inner diameter 0.28 mm, outer diameter 1.19 mm, 50-ohm impedance). The sampling oscilloscope monitored changes in the step pulse after reflection from the line end. We verified calibration using standard liquid methanol before dielectric characterization. Dielectric measurements were

performed at a fixed temperature, with uncertainties of ±1% for the dielectric constant (ε') and ±2% for dielectric loss (ε''). Repeatability was better than ±1%. As shown in Fig. 1, reflected pulses without the sample, $R_1(t)$, and with the sample, $R_x(t)$, were recorded in a 0.5 ns time window and digitized into 2000 points. The TDR rise time was 18 ps, corresponding to a bandwidth of 30 GHz (TDR bandwidth ≈ 1/(π × rise time)) [9]. Selecting the appropriate time window, sampling rate and the bilinear calibration method suggested by Cole et al. was essential for accurate complex permittivity measurements at higher frequencies [10]. A smaller time window results in signal loss, while a larger window introduces unwanted reflections. Therefore, proper time window selection is critical to minimize these effects. Fourier transformation and data analysis were previously performed to determine the complex permittivity spectra ε*(ω) using a nonlinear least squares fit method [10]. We maintained the sample temperature at 25.0 ± 0.10⁰C in a thermostatically controlled water bath. Samples were allowed to stabilize for 10–15 minutes before each reading. We kept the laboratory temperature constant during measurements.

Reproducibility

Reproducibility was confirmed by performing each measurement at least three times under identical conditions. Measurement reproducibility exceeded ±1%. Uncertainties were ±1% for the dielectric constant (ε') and ±2% for dielectric loss (ε'').

Data analysis

The static dielectric constant (ε_0), relaxation time (τ) and distribution parameters (α and β) were obtained by fitting complex permittivity $\varepsilon^*(\omega)$ data to the Havriliak-Negami expression using the nonlinear least-squares method [12]. The Havriliak-Negami (HN) model is a generalized dielectric relaxation model that characterizes the dielectric response of materials with complex relaxation behaviors. It is expressed as

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

Here, α and β are shape parameters that describe the symmetric and asymmetric broadening of the relaxation peak, respectively. The HN model encompasses several special cases, with, α, and β as fitting parameters. The Havriliak–Negami expression includes the Debye (α=0, β=1) [13], Cole–Cole (β=1) [14] and Cole–Davidson (α=0) [15] relaxation spectral functions as limiting forms. In this study, the binary mixture of 3-CA and PGEE exhibits Cole-Davidson type dispersion. Therefore, the complex permittivity spectra were fitted using a Cole-Davidson-type model and the nonlinear least-squares method to determine the dielectric relaxation parameters.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1+j\omega\tau)^\beta} \quad (2)$$

The close agreement between the experimental data and the fitted curves confirms that the Cole-Davidson model accurately describes the non-Debye dielectric relaxation behavior of the binary mixtures studied. These results validate the fitting procedure and confirm the reliability of the extracted relaxation parameters.

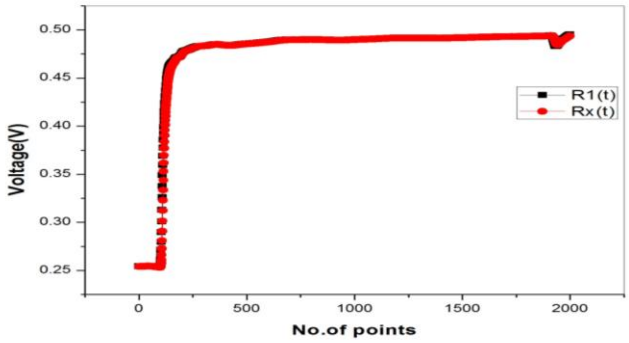

Figure. 1. $R_1(t)$ without and $R_x(t)$ with sample for 3-CA and PGEE

3. Results and Discussion

Complex dielectric spectra

Figure 2 presents the complex permittivity spectra for various concentrations of 3-CA in PGEE at 25⁰C. The real part of the complex permittivity decreases rapidly as the concentration of 3-CA increases. In pure PGEE, the peak position of dielectric loss occurs at a higher frequency, but shifts to a lower frequency as the 3-CA concentration increases. This shift is attributed to an increase in relaxation time toward the low-frequency side. Similar results were reported by Jeevanandham et al. [16].

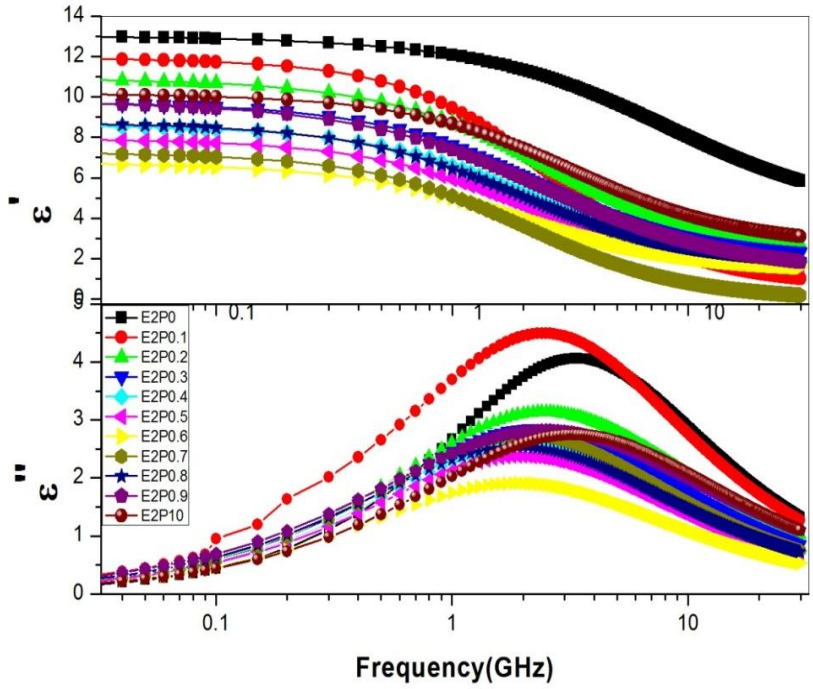

Figure 2. The complex dielectric permittivity spectra and dielectric loss spectra of 3-CA withPGEE binary mixtures at 25^{0}C

Table 1. The dielectric parameters (ε_0, τ and β) for 3-CA and PGEE binary system at 25^{0}C

Volume Fraction of 3-CA	**25^{0}C**		
	ε_0	τ	β
0.0	13.01(3)	20.68(4)	0.74(4)
0.1	11.94(1)	62.52(4)	0.85(1)
0.2	10.91(9)	64.87(7)	0.79(2)
0.3	9.74(2)	72.06(8)	0.80(2)
0.4	8.63(6)	76.31(1)	0.80(8)
0.5	7.95(4)	81.34(7)	0.80(2)
0.6	7.27(1)	83.81(1)	0.78(9)
0.7	6.76(6)	77.82(6)	0.80(7)
0.8	8.76(5)	83.57(3)	0.78(6)
0.9	9.81(3)	64.39(5)	0.73(1)
1.0	10.18(6)	48.82(4)	0.79(4)

Note: The bracketed term represents error in last digit (i.e., 13.01(3) means 13.01± 0.03 or 20.68(4) means 20.68 ± 0.04).

Table 1 presents the static dielectric constant, relaxation time and distribution parameter for the binary mixture of 3-CA and PGEE at 25^{0}C. The dielectric relaxation behavior was examined over a temperature 25^{0}C. Across all concentrations, relaxation time (τ) decreases as temperature increases. The relaxation time τ varies non-monotonically with composition. At low PGEE concentrations, τ increases due to hydrogen bonding between the –OH group of PGEE and the –NH_2 group of 3-CA, which restricts molecular reorientation. The

maximum τ at a 3-CA volume fraction of 0.5–0.6 suggests stronger intermolecular interactions and the formation of hydrogen-bonded aggregates. As PGEE concentration increases further, τ decreases, indicating changes in the hydrogen-bonding network and reduced molecular association. Additional factors, such as increased molar volume and effective dipole length at higher temperatures, also contribute to the decrease in τ, consistent with previous studies [17].

The dielectric constant (ε_0) also declines with increasing temperature for all concentrations, attributed to enhanced thermal agitation of dipoles. As the PGEE volume fraction increases, ε_0 decreases up to 0.7, then rises at higher PGEE concentrations, indicating shifts in molecular interactions and polarization mechanisms. These results suggest that the strongest heteromolecular interactions occur near a PGEE volume fraction of 0.7, where maximum τ and minimum ε_0 are observed [18]. The distribution parameter (β) from the Cole–Davidson model ranges from 0.70 to 0.87, aligning with the Cole–Davidson plots. Because $\beta<1$, the relaxation is non-Debye and shows an asymmetric distribution of relaxation times. Changes in β with composition and temperature indicate variations in the molecular environment and intermolecular interactions in the 3-CA–PGEE binary system [19].

4. Conclusion

The dielectric relaxation behavior of binary mixtures of 3-chloroaniline (3-CA) and 1-ethoxy-2-propanol (PGEE) at 25^0C demonstrates significant molecular associations and intermolecular interactions. A decrease in dielectric permittivity with increasing frequency indicates reduced dipole alignment with the electric field. Shifts in dielectric loss peaks with composition reflect changes in molecular relaxation dynamics. The amino group ($-NH_2$) of 3-CA and the hydroxyl group (–OH) of PGEE promote O–H···N hydrogen bond formation. Non-monotonic relaxation time (τ), with higher values at intermediate compositions, suggests restricted molecular reorientation due to hydrogen bonding and structural rearrangement. Relaxation time decreases with increasing temperature, indicating enhanced molecular mobility and reduced resistance to dipolar rotation. The Cole–Davidson parameter ($\beta < 1$) confirms asymmetric, non-Debye relaxation, reflecting a distribution of relaxation times across molecular environments.

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5. References

1. Ning M, Yao, J Kümmel, H, Li, S, Schaefer, T, Herrmann, H, Richnow, H, H. Carbon, hydrogen, nitrogen and chlorine isotope fractionation during 3-chloroaniline transformation in aqueous environments by direct photolysis, TiO_2 photocatalysis and hydrolysis. Water Research, 2025; 273: 122956.
2. Prajapati AN, Rana VA, Vyas AD. Microwave absorption and relaxation studies of binary mixtures of fluoro substituted anilines with some primary alcohols in benzene solutions. Indian Journal of Pure and Applied Physics, 2006; 44(8): 620-624.
3. Pal A, Gaba R. Speeds of sound and isentropic functions of n-alkoxypropanol with 1-butanol and 2-butanol at 298.15 K. Journal of Molecular Liquids, 2009; 144(1-2): 50-54.
4. Esteve X, Conesa A, Coronas A. Liquid densities, kinematic viscosities, and heat capacities of some alkylene glycol dialkyl ethers. Journal of Chemical & Engineering Data, 2003; 48(2): 392-397.
5. Liu YL, Chiou DR, Chen LJ. Liquid-liquid equilibria for the ternary system water + octane + diethylene glycol monobutyl ether. Journal of Chemical & Engineering Data, 2002; 47(2): 310-312.
6. Buchner R. Novel Approaches to the Structure and Dynamics of Liquids. Kluwer Academic Publishers, 2004: 133.
7. Chaudhari, Ajay, Prakash Khirade, Raghubar Singh, S. N. Helambe, N. K. Narain, and S. C. Mehrotra. Temperature dependent dielectric relaxation study of tetrahydrofuran in methanol and ethanol at microwave frequency using time

domain technique. Journal of molecular liquids. 82, no. 3 (1999): 245-253.

8. Kumbharkhane, A. C, S. N. Helambe, S. Doraiswamy, and S. C. Mehrotra. Dielectric relaxation study of hexamethylphosphoramide-water mixtures using time domain reflectometry. The Journal of chemical physics 99, no. 4 (1993): 2405-2409.
9. Lin CP. Frequency domain versus travel time analyses of TDR waveforms for soil moisture measurements. Soil Science Society of America Journal, 2003; 67(3): 720-729.
10. Cole, R. H, J. G. Berberian, S. Mashimo, G. Chryssikos, A. Burns, and E. Tombari. Time domain reflection methods for dielectric measurements to 10 GHz. Journal of applied physics 66, no. 2 (1989): 793-802.
11. Weingärtner, H, A. Knocks, Wilfried Schrader, and U. J. T. J. Kaatze. Dielectric spectroscopy of the room temperature molten salt ethylammonium nitrate. The Journal of Physical Chemistry A 105, no. 38 (2001): 8646-8650.
12. Havriliak S, Negami S. A complex plane analysis of α-dispersions in some polymer systems. Journal of Polymer Science Part C: Polymer Symposia, 1966; 14(1).
13. Kaatze U. Microwave dielectric properties of liquids. Radiation Physics and Chemistry, 1995; 45(4): 549-566.
14. Cole KS, Cole RH. Dispersion and absorption in dielectrics I. Alternating current characteristics. The Journal of Chemical Physics, 1941; 9(4): 341-351.
15. Davidson DW, Cole RH. Dielectric relaxation in glycerine. The Journal of Chemical Physics, 1950; 18(10): 1417-1418.
16. Jeevanandham, P., S. Kumar, P. Periyasamy, and A. C. Kumbharkhane. Dielectric Relaxation Studies of 2-Butoxyethanol with Aniline and Substituted Anilines Using Time Domain Reflectometry. Advances in Physical Chemistry 2014, no. 1 (2014): 659531.
17. Shinde RV, et al. Dielectric spectroscopy and hydrogen bonding studies of 1-chloropropane-ethanol mixture using TDR technique. Journal of Advanced Dielectrics, 2019; 9(2): 1950018.
18. Rana VA, Vyas AD, Mehrotra SC. Dielectric relaxation study of mixtures of 1-propanol with aniline, 2-chloroaniline and 3-chloroaniline at different temperatures using time domain reflectometry. Journal of Molecular Liquids, 2003; 102(1-3): 379-391.
19. Bhadane PA, Rander DN, Kanse KS, Joshi YS, Kumbharkhane AC. Exploring molecular interactions and cooperative dynamics of tripropylene glycol in ethanol solutions through dielectric relaxation techniques. Discover Chemistry, 2025; 2(1): 69.

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