IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Measurement of Microwave Dielectric Properties of Polar Liquids and Polyhydric Alcohols Using TDR

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Abstract: Microwave Dielectric properties of polar liquids (allyamine, benzylamine and pyrrolidine) and polyhydric alcohols (1,2,4-butanetriol, 1,2,5-pentaneriol and 1,2,6-hexanetriol) were carried out using time domain reflectrometry (TDR) technique at 250C in the frequency range from 10 MHz to 30 GHz. The relaxation behaviour of these system has been illustrated by using Debye model. The static dielectric constant (ε 0), dielectric constant at high frequency (ε ∞), relaxation time (τ) extracted from the complex permittivity spectra using least squares fit method.

Keywords: Dielectric Constant; Relaxation time; Time Domain Reflectometry.

I. INTRODUCTION

The dielectric properties of organic compounds, such as allylamine, benzylamine, and pyrrolidine, are vital for understanding their molecular interactions, polarity, and applications in various fields like chemistry, material science, and pharmaceuticals. Dielectric spectroscopy is one of the great tool for the study of co-operative and molecular dynamics of H-bonded systems [1-4]. In particular, fundamental information could be obtained from microwave dielectric studies. The present work deals with the dielectric relaxation study of amines (allyamine, benzylamine and pyrrolidine) and polyhydric alcohols (1,2,4-butanetriol, 1,2,5-pentaneriol and 1,2,6-hexanetriol) using pico-second Time Domain Reflectometry (TDR) technique. TDR developed by Cole et.al [5] studies dielectric relaxation behaviour over a wide frequency range.

TDR technique has been successfully used to obtain information of the structural behaviour and molecular dynamic parameters of liquids. The technique is used for the measurement of complex permittivity of polar liquids and its mixtures in the frequency range 10 MHz to 30 GHz.

The present work reports the dielectric parametrs of polar liquids (allyamine, benzylamine and pyrrolidine) and polyhydric alcohols (1,2,4-butanetriol, 1,2,5-pentaneriol and 1,2,6-hexanetriol) using pico-second Time Domain Reflectometry (TDR) technique in the frequency range 10 MHz to 30 GHz at 25^0C. From the complex permittivity spectra, the static dielectric constant (ε_0), and relaxation time (τ) were obtained by least square fit method. This study focuses on the dielectric behavior of these three amines and polyhydric alcohols at 25°C.

II. MATERIALS AND METHODS

Amines (Allyamine, benzylamine and pyrrolidine) and polyhydric alcohols (1,2,4-butanetriol, 1,2,5-pentaneriol and 1,2,6-hexanetriol) were obtained commercially from S. D. Fine Chemical Limited, India and was used without further purification. The dielectric measurements were carried out using TDR.[6,7].

The complex permittivity spectra were studied using TDR technique [8]. For the measurements, Tektronix model number DSA8200 digital serial analyzer with sampling module 80E08 have been used. A repetitive fast rising voltage pulse was fed through coaxial line system of impedance of 50Ω. All measurements are carried out in open load condition.Sampling oscilloscope monitors the changes in step pulse after reflection from the end of line. Reflected pulse without sample R_1 (t) and with sample R_x (t) were recorded in time window of 5 ns and digitized in 2000 points in the memory of the oscilloscope and transferred to the computer for further analysis. The selection of proper time window, sampling rate and bilinear calibration method suggested by Cole et al. were useful to measure the accurate complex permittivity at higher frequencies [5]. The smaller time window causes loss of signal while larger time window includes unwanted reflections. Thus selection of proper time window is important to minimize these effects. Further the Fourier transformation of the pulses and data analysis were done earlier to determine complex permittivity spectra using nonlinear least squares fit method [5, 9].

III. RESULT AND DISCUSSION

3.1. Complex permittivity:

The frequency and temperature dependent values of permittivity (ε′) and dielectric loss (ε″) for these molecules in their pure liquid state have been determined and compared with the number of OH group attached to the carbon atom. The values obtained are depicted in Fig. 1(a, b). It is found that the dielectric constant (ε′) for amines (allyamine, benzylamine and pyrrolidine) decreases with increasing the frequency. The dielectric losses (ε″) in all these systems are found to increase with increasing frequency and then decreases at higher frequencies. In all these molecules the values of (ε″) approach maximum in the frequency range from 0.1 GHz to 5 GHz.

The value of dielectric loss (ε''_{max}) peak goes lower with decreasing temperature. The complex permittivity spectra were fitted to a Havriliak-Negami(HN) equation using non linear least squares fit method to extract dielectric relaxation parameters with the following expression [10].

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

where, ε_0 is the static dielectric constant, ε_∞ is the permittivity at high frequency, τ is the relaxation time in pico-second. The exponents α and β describe the irregularity and broadness of the corresponding spectra. α and β are the empirical parameters for the distribution of relaxation times with values between 0 and 1.

Havriliak–Negami relaxation is an empirical modification of the Debye relaxation model, accounting for the irregular and broadness of the dielectric dispersion curve. The model was used to describe the dielectric relaxation of some polymers [10] by adding two exponential parameters to the Debye equation. The HN equation includes three relaxation models. The spectrum of complex permittivity has been fitted to theoretical model and determined dielectric properties. The dielectric properties for amines and polyhydric alcohols are as shown in Table.1 (a & b). The errors in these parameters have been given in the brackets which shows an uncertainty in the last significant digits e.g. the static dielectric constant of water 5.24 (17) means 5.24 ± 0.17.

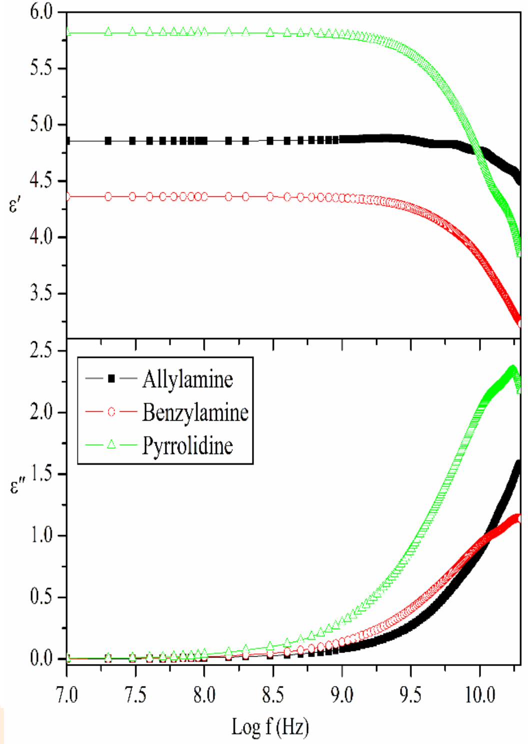

Fig. 1a. Frequency dependent complex permittivity spectra for amines (allylamine, benzylamine, pyrrolidine) at 25^{0}C.

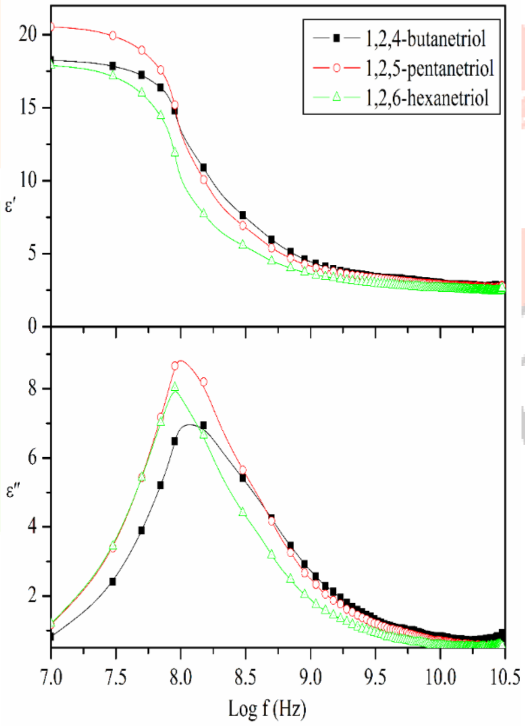

Fig. 1b. Frequency dependent complex permittivity spectra for amines (1,2,4-butanetriol, 1,2,5-pentanetriol and 1,2,6-hexanetriol) at 25^{0}C.

Table 1(a). Dielectric properties of allyamine, benzylamine and pyrrolidine at 25^0C.

Amines	ε_0	**τ(ps)**	ε_∞
Allyamine	5.24(17)	4.33(10)	2.05(5)
Benzylamine	4.33(2)	8.62(4)	2.15(1)
Pyrrolidine	5.77(8)	12.71(9)	2.23 (3)

Table 1(b). Dielectric properties of 1,2,4-butanetriol, 1,2,5-pentanetriol and 1,2,6-hexanetriol at 25^0C.

Polyhydric Alcohols	ε_0	**τ(ps)**	ε_∞
1,2,4-butanetriol	18.24(14)[a]	957.88(20)	2.86(1)
1,2,5-pentanetriol	21.97(18)	1221.88(20)	2.85(2)
1,2,6-hexanetriol	19.30(19)	1470.54(34)	2.58(2)

3.2 Dielectric Properties:

Dielectric constant of allylamine has higher dielectric constant compared to benzylamine, this due to strong polarity due to the presence of the -NH_2 group and the double bond in its structure. Benzylamine has a lower ε_0 compared to allylamine, likely due to the steric hindrance of the aromatic ring, which reduces its overall polarity. Pyrrolidine has the higher ε_0, than the allylamine and benzylamine, this may be due to the ring's flexibility and the ability of the -NH group to participate in hydrogen bonding. Allylamine has the lower value of relaxation time than the other amines, indicating faster molecular reorientation. This is consistent with its linear structure and strong dipole interactions. Higher value of relaxation time for benzylamine and pyrrolidine then allylamine, this is due to steric hindrance of the aromatic ring and slows down dipole reorientation. The study of dielectric properties of amines were useful for the application of organic synthesis and pharmaceutical formulations.

The variation in static dielectric constant (ε_0) of polyhydric alcohols were observed may due to increasing chain length. Shorter-chain triols like 1,2,4-butanetriol have more compact structures, allowing for stronger dipole interactions. The dielectric relaxation time (τ in ps) increases with chain length due to the greater steric hindrance and constrained molecular motion in longer-chain triols. This is consistent with the slower reorientation of dipoles in larger molecules.

IV. CONCLUSION

The complex permittivity spectra of polar liquids (allyamine, benzylamine and pyrrolidine) and polyhydric alcohols (1,2,4-butanetriol, 1,2,5-pentaneriol and 1,2,6-hexanetriol) have been studied using TDR technique in the frequency range 10 MHz–30 GHz. Using Havriliak–Negami equation, determined microwave dielectric constant (ε_0), relaxation time (τ in ps) and high frequency dielectric permittivity (ε_∞) for allyamine, benzylamine and pyrrolidine, 1,2,4-butanetriol, 1,2,5-pentaneriol and 1,2,6-hexanetriol. The dielectric properties of amines and polyhydric alcohols are strongly influenced by their molecular structures and intermolecular interactions. These findings provide valuable insights into the behavior of these amines and polyhydric alcohols, which can guide their applications in various scientific and industrial fields.

V. ACKNOWLEDGMENT

Authors are grateful to the Prof. A.C. Kumbharkhane, School of Physical Sciences, S.R.T.M. University, Nanded, India for their great support and guidance. Dr. M.B. Swami, Dept. of Physics and Electronics, M.U. Mahavidyalaya, Udgir, Maharashtra, India are greatly acknowledged.

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