

DIELECTRIC PARAMETERS OF LIQUID POLYMERS USING DIELECTRIC RELAXATION SPECTROSCOPY

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Abstract

The dielectric relaxation measurement on the binary mixture of polymers with water have been carried out over entire concentrations and at temperature 250C using picoseconds time domain reflectometry techniques in the frequency range of 10 MHz to 30 GHz. The complex permittivity spectra of polymer and water mixtures were fitted using Havriliak-Negami equation. The static dielectric constant, dielectric loss and relaxation time for all concentrations were obtained using least square fit method. The results are interpreted in terms of heterogeneous interaction between unlike molecules due to hydrogen bonding.

Keywords: Polymer, Time domain reflectometry, Relaxation time, Dielectric constant, Dielectric loss etc.

1.INTRODUCTION:

Dielectric relaxation studies are very useful in understanding the structure of polymers [1]. Dielectric relaxation studies involve measurements of permittivity and dielectric loss. Time domain reflectometry (TDR) is powerful technique to measure the complex permittivity of materials [1-6]. The molecules of polymers of ethylene glycol have two -OH groups at the ends of their molecular structure, due to which the molecules of these liquids can enter into intra and intermolecular hydrogen bonding giving rise to different conformations in water mixture [7, 8]. Polymers of ethylene glycol have large pharmaceutical applications as excipients, cosmetic preparations, industrial solvents, food additives, plasticizers etc.

The microwave dielectric relaxation behavior of pure ethylene glycols were investigated by Sengwa in the frequency range 200 MHz- 20 GHz to confirm the chain flexibility and coiling with increasing molecular chain length and its effect on the dielectric constant and molecular reorientation relaxation time [7]. Shinyashiki et al [9,10], Sato et al [11] and Sengwa et al [12, 13] have extensively investigated the mixtures of ethylene glycol in different non-polar, polar and polymeric systems to get the information on the heterogeneous molecular interactions, molecular dynamics and their structure.

In the present paper, the detailed dielectric relaxation study of polymers of ethylene glycol in water solutions at different concentrations and at temperature $25 \,^{0}$ C have been carried out using TDR from 10 MHz – 30GHz. The values of static dielectric constant, dielectric loss and relaxation time were determined for each concentration of polymers of ethylene glycol in water solutions has been evaluated.

2. EXPERIMENTAL:

2.1 MATERIAL:

Polymers of ethylene glycol like triethylene glycol (TEG) was obtained commercially from Aldrich. The double distilled water is used to prepare mixtures. The solutions were prepared at different weight fractions of water in triethylene glycol. The dielectric spectra have been obtained by time domain reflectometry (TDR) technique. The Tektronix model no.DSA8200 Digital Serial Analyzer sampling oscilloscope along with sampling module80E08 has been used for the measurement. A repetitive fast rising voltage pulse with 18 picoseconds incident rise time was fed through coaxial line system of impedance of 50 Ω . Reflected pulse without sample R₁ (t) and with sample R_x (t) were recorded in time window of 2 nanosecond and digitized in 2000 points. The Fourier transformation of pulses and data analysis were done earlier to determine the complex permittivity spectra $\varepsilon^*(\omega)$ using non linear least squares fit method [5, 14].

3. RESULTS AND DISCUSSION:

The frequency dependent values of dielectric permittivity (ϵ') and dielectric loss (ϵ'') of Triethylene glycol-water mixtures at 25^oC are shown in Fig.1.It is observed from the plot that the values of dielectric permittivity (ϵ') decreases with increase in the concentration of triethylene glycol and dielectric loss (ϵ'') peak shifts from higher to lower frequency.

In general dielectric loss spectrum of the aqueous solutions of polymers of ethylene glycol exhibits an asymmetrical shape and described by the Havriliak-Negami expression. We performed the non linear least square fitting procedure for polymers of ethyle glycol-water mixtures, in order to extract dielectric relaxation parameters with the following equation [15].

$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{0} - \varepsilon_{\infty}}{\left[1 + (j\omega\tau)^{1-\alpha}\right]^{\beta}}$$

Where ε_0 is static dielectric constant, ε_∞ is dielectric constant at high frequency, τ is dielectric relaxation time, α and β are the distribution parameters. The value of α is kept zero and β is varied such that $0 \le \beta \le 1$. The values of $\varepsilon_{0,\varepsilon_\infty}$ and τ over entire concentrations range studied here are reported in Table 1.

3.1 STATIC DIELECTRIC CONSTANT:

The value of static dielectric constant depends upon number of dipoles per unit volume of given liquid system. As weight fraction of water in polymer-water mixtures increases, the number of dipoles per unit volume of mixture increases. Hence the value of static dielectric constant increases by increase in weight fraction of water in polymer-water mixtures.

3.2 DIELECTRIC RELAXATION TIME (τ):

The dielectric relaxation time depends upon volume of molecule and hydrogen bonding between the molecules. As weight fraction of water in polymer-Water increases, the bonds between polymer molecules breaks and molecules can rotate freely within mixture. Hence relaxation time decreases by increases in weight fraction of water in TEG-water mixtures.

4. CONCLUSIONS:

The temperature dependent complex permittivity spectra of triethylene glycol in aqueous solution have been studied using time domain reflectometry technique in the frequency range 10 MHz to 30 GHz. The variation in dielectric constant and relaxation time with concentrations of water in TEG-water mixtures indicates heterogeneous interactions in TEG-water molecules.

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Fig.1 Frequency dependent dielectric permittivity (ϵ') and dielectric loss (ϵ'') for TEG-Water at 25^oC.

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Table 1: Dielectric Relaxation parameters for TEG-Water mixtures at 25° C.

Wt.Fra. ε_0 of Water		τ (ps)
0.0	21.87(2)	221.36(56)
0.1	30.08(2)	174.08(33)
0.2	37.53(3)	136.60(26)
0.3	43.74(3)	101.26(13)
0.4	49.95(2)	65.92(10)
0.5	54.93(7)	45.78(20)
0.6	58.70(2)	34.69(7)
0.7	62.47(2)	26.32(9)
0.8	67.42(2)	19.03(3)
0.9	72.37(2)	12.68(2)
1.0	78.32(2)	8.21(1)

Numbers in bracket denotes uncertainties in the last significant digits obtained by the least square fit method.

e.g. 21.87(2) means 21.87 \pm 0.02 and 8.21(1) means 8.21 \pm 0.01.

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