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Study of Molecular Dynamics of Polymeric Systems using TDR

S. A. Ingole[1], P. M. Kokne[2], R. S. Bankar[3], A.N.Ardad[4] N. P. Barde[5]
School of Physical Sciences, SRTM University Nanded[1]
Dr. Badrinarayan Barwale College Jalna[2]
Mahatma Fule Mahavidyalaya Warud, Amravati[3]
Deogiri College, Aurangabad[4]
shitalpatil96231@gmail.com, rambankar9192@gmail.com, kokne2005@gmail.com

Abstract

The Complex permittivity spectra of aqueous polymer at variant temperatures (0°C–25°C) have been determined by Time Domain Reflectometry (TDR) technique in the frequency range 10 MHz to 50 GHz. The complex permittivity spectra for aqueous polymer system were fitted in the Cole-Davidson model. The Static dielectric constant (ε_0), Relaxation time (τ) and thermodynamic parameters (activation enthalpy and activation entropy) have been calculated by non-linear least square fit method. The intermolecular interaction between polymer-Water binary mixtures suggests the non-linear behavior of dielectric parameters. The nature of chemical reaction and disorderness of the system is suggested by thermodynamic parameter.

Keyword: *Time Domain Reflectometry, Binary mixture, Polymers, Thermodynamic Parameter*

1. Introduction

Polymers are large macromolecular compounds composed of Carbon and hydrogen molecules by multiplex repetition of one or more kinds of atoms coupled to each other. The linkage of repeating molecules is in an adequate proportion to provide a set of physicochemical characteristics that do not differ significantly with the addition of two or more repeating units. The small molecules or units from which polymers are synthesized are called monomers. The polymer designates an unspecified number of monomer units. Mostly natural and synthetic polymers are made up of two or more different types of monomers, such polymers are known as copolymers. Molecules with only a few constitutional repetitions of units are called an oligomer [1,2]. Tetraethylene glycol (TTEG) is one of the oligomers of ethylene glycol. The electrical and physicochemical properties of polymers change by changing its surrounding physical parameters. Because of their extensive range of properties both synthetic and natural polymers play an essential and pervasive role in everyday life [3,4].

Tetraethylene glycol (TTEG) [HO-(CH2CH2O)4-H] is a synthetic polymer having two -OH groups at the ends of their molecular chain. Due to these hydroxyl groups, the molecules can enter into intra- and intermolecular hydrogen bonding giving rise to a number of structures in water mixture [5–7]. TTEG is an industrial chemical especially useful in polyester resins, drying agents for natural gas in industry, solvent in the production of inks and dyes, solvent in hydrocarbon purification processes, and coupling agents in the production of textile lubricants. It is also widely used in pharmaceutical, cosmetic preparations and cleaning agents. Sengwa et al. [8,9], Shiyanshiki et al. [10,11], and Sato et al. [12] extensively investigated the oligomers of ethylene glycol mixtures in different polar, non-polar and polymeric systems to get the information on the heterogeneous molecular interactions and their molecular structures. Watode et al. [13–15] and Hudge et al. [16] also studied ethylene glycol oligomers in the frequency range 10 MHz to 30 GHz [1]. The study of dielectric properties of polymers, in particularly the determination of the static and the high frequency dielectric constant can

provide a good deal of information about their molecular structure and the intermolecular interaction. The Time Domain Reflectometry is a powerful technique to measure the complex dielectric permittivity of polymers as well as binary mixtures over a wider frequency range [17–19].

In the present paper, we have obtained the outcomes of dielectric behavior of Tetraethylene glycol (TTEG) and water mixtures using Time Domain Reflectometry (TDR) at different temperatures by extending the frequency range from 10 MHz to 50 GHz. The least square fit method was undertaken to gain static dielectric constant, permittivity at high frequency, dielectric relaxation time.

2. Materials and methods

2.1. Material: Tetraethylene Glycol [TTEG] was obtained from Sigma-Aldrich, USA and used without further purification (99% purity). Water was obtained from HPLC grade, Fisher Scientific India Pvt. Ltd. used as a solvent for preparing mixtures. The binary mixture of TTEG and Water were prepared at different concentrations by volume fraction.

2.2. Measurement: The dielectric spectra were obtained by the time domain reflectometry (TDR) technique. The Tektronix Digital Serial Analyzer model no. DSA8300 sampling mainframe along with the sampling module 80E10B has been used. Sampling oscilloscope monitors change in step pulse after reflection from the end of line. The Fourier transformation of the pulses and data analysis were done to determine complex permittivity spectra ε□(ω) using nonlinear least square fit method [20].

3. Results and discussion

3.1. Complex permittivity spectra:

Frequency dependant complex permittivity spectra of TTEG-Water mixture at different concentrations is shown in Fig 1. It is observed from the plot that values of dielectric permittivity (ε′) decreases and dielectric loss peak (ε″) shifted towards lower frequency side as the concentration of TTEG in Water increases. The shifting of loss peak towards lower frequency side with increasing concentration of TTEG in Water indicated increased relaxation time.

The dielectric relaxation parameters of TTEG-Water mixture are obtained by non-linear least square fit method [21] suggested by Havriliak-Negami equation [22].

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

Where $\varepsilon^*(\omega)$ is the complex permittivity having angular frequency (ω), ε_o is the static dielectric constant, ε_∞ is the permittivity at high frequency, τ is the dielectric relaxation time, α and β are the empirical fitting parameters having the values in between 0 and 1.

The current study of TTEG-Water mixture reveals Cole-Davidson type dispersion. Therefore the complex permittivity spectra are fitted in Cole-Davidson model to attain the dielectric parameters by non-linear least square fit method. The values of static permittivity (ε_o), relaxation time (τ) and β at various concentrations and temperatures are reported in Table 1. From the Table 1 it is seen that, values of static dielectric constant are decreasing with the reducing concentration of TTEG in Water whereas relaxation time is increasing with decreasing concentration of TTEG in Water. Also, the values of ε_o and τ are increasing with decreasing temperature. It is also observed from Table 1 that the values of concentration of TTEG-Water mixture lie between the isolated values of pure TTEG and water. One of the findings in our experiment is that, binary mixture of TTEG-Water after interacting with each other shows a non-linear variation [23,24]. This stipulates the existence of molecular association between the TTEG and water molecule.

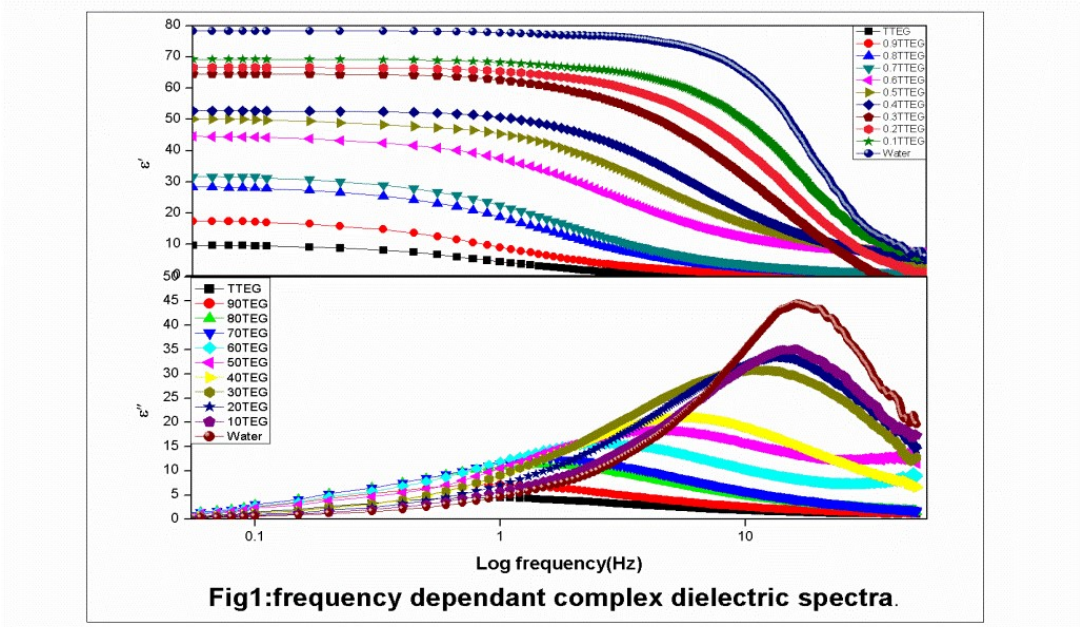

Fig1:frequency dependant complex dielectric spectra.

Fig 1 : Frequency Dependant complex permittivity spectra of TTEG-water mixture at 25ºC.

Table 1. Dielectric relaxation parameters for TTEG-Water mixtures at different temperatures.

Vol. Fract. of TTEG	25°C		15°C		10°C		0°C	
	ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)
0.0	10.12	156.49	10.88	196.96	12.05	247.98	11.68	330.94
0.1	17.99	163.40	18.71	205.96	20.61	254.42	19.54	374.14
0.2	28.77	111.75	30.57	132.63	32.98	155.52	35.05	221.55
0.3	32.09	97.03	33.84	107.34	35.14	155.76	37.54	169.62
0.4	45.07	58.12	48.82	66.51	51.55	77.41	52.70	116.69
0.5	50.47	35.04	53.15	40.03	55.48	43.33	57.98	65.44
0.6	53.25	26.97	54.37	30.95	56.11	33.24	60.30	44.15
0.7	64.58	16.38	66.78	17.40	68.63	17.75	73.64	22.65
0.8	66.44	12.88	68.37	15.84	72.06	14.32	77.34	17.10
0.9	68.72	10.17	70.83	10.77	72.76	11.03	79.17	13.82
1.0	79.03	8.74	81.68	9.30	86.75	10.12	99.84	13.68

3.2. Thermodynamic properties:

The thermodynamic energy parameters for TTEG-Water mixture is determined by using Eyring's rate equation [25]:

$$\tau = (h/kT)\exp(\Delta H/RT)\exp(-\Delta S/R) \qquad (2)$$

Where ΔH is the enthalpy of activation in kJ/mole, ΔS is the entropy of activation in J/mole, τ is the relaxation time in ps, T is the temperature in degree Kelvin, h is the plank's constant, R is the gas constant and k is the Boltzmann's constant.

For binary mixtures, the activation energy presents vital information of change in structure of different molecules [26]. The values of enthalpy of activation ΔH and entropy of activation ΔS are reported in Table 2. As the concentration of TTEG in water increases the ΔH value increases. The reaction is endothermic for all concentrations of TTEG-Water mixture that is why the ΔH values become positive. The values of ΔS for TTEG-Water mixture at different

concentrations are also found to be positive and the positive values of entropy suggest the random orientation in solute-solvent complex [27].

Table 2. Thermodynamic parameters for TTEG-water mixtures.

V_W	ΔH(kJ/mol)	ΔS(J/mol)
0.0	19.97(1)	0.239(6)
0.1	21.10(1)	0.243(4)
0.2	16.28(1)	0.230(4)
0.3	12.56(2)	0.219(7)
0.4	16.60(2)	0.237(7)
0.5	13.97(2)	0.232(7)
0.6	10.27(1)	0.221(4)
0.7	5.68(1)	0.210(5)
0.8	4.72(1)	0.209(3)
0.9	6.71(1)	0.218(6)
1.0	9.76(1)	0.229(6)

19.97(1) means 19.97 ± 0.01 and 0.239(6) means 0.239 ± 0.006

4. Conclusion

The temperature dependent complex permittivity spectra of Tetraethylene glycol [TTEG]-Water mixture have been studied using Time Domain Reflectometry technique in the frequency range 10 MHz to 50GHz. The dielectric permittivity spectra of TTEG-water are described by Cole-Davidson model. The thermodynamic parameter reveals the disorderness of the endothermic reaction.

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