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Thermodynamic Properties of Binary Mixture Using Time Domain Reflectrometry Technique

By

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Abstract

In this paper we have reported, a dielectric relaxation study of Chlorobenzene (CB) – Diethylene Glycol Monomethyl Ether (DGME) binary mixtureof polar liquids with varying concentrations at different temperatures in the frequency range between 10MHz-20GHz using time domain reflectometry (TDR) technique in reflection mode.Dielectric parameters viz. dielectric constant (ε0)and relaxation time (τ) were obtained from complex permittivity spectra ε(ω), using nonlinear least squares fit method. Using these parameters, Thermodynamic properties like enthalpy change (ΔH) and entropy change (ΔS)are determined.The dielectric relaxation is use to estimate thermodynamic properties.Thermodynamic propertiesare helpful in accessing the states of dipoles under the influence of applied field.*

Keywords- *Dielectric relaxation, Time domain Reflectometry,Thermodynamic properties*

Introduction

In this paper, the values of static dielectric constant, relaxation time, thermodynamic parameters of (DGME) and (CB) mixtures for various temperatures are reported. The dielectric relaxation study of binary polar liquids is important for understanding the hydrogen bonding and intermolecular dynamics of molecules at molecular levels. Diethylene glycol Monomethyl ether (DGME), Chlorobenzene (CB), both is polar liquids, one with Glycol ether group and other with aromatic group. It is interesting to see the effect of aromatic group in glycol ether. To study the dielectric properties of the mixture of polar liquids, the most reliable technique is time domain technique developed by Cole et.al. [1-4]. Time domain reflectometry (TDR) technique can be used to study thermodynamic parameters by analyzing how electromagnetic waves reflect from a material as a function of time. TDR can provide perceptions into the molecular behavior and interactions within the material, which are related to thermodynamic properties like enthalpy and entropy of activation,by measuring the dielectric properties such as permittivity of a substance over a range of temperatures and concentrations.Thermodynamic propertieslike enthalpy change (ΔH) and entropy change(ΔS) helpus to determine whetherthe process is exothermic or endothermic and whether it occurs spontaneously. In binary mixture of polar liquids, there is a change in the energy of the system. This change in energy can be interpreted with thermodynamic properties such as free energy of activation (ΔG), molar enthalpy of activation (ΔH) and molar entropy of activation (ΔS).Complex and thermodynamic properties of polar liquids using time domain reflectometry has been studied by ShaguftaTabassum et.al., (2019)[5]. R.M Shirke (2023) [6] reported Thermodynamic Parameters in the Dielectric Study of Methyl Acetate + Alcohol Systems. Temperature variation of the relaxation time has been utilized to evaluate the thermodynamic parameters at microwave frequencies.by HD Purohitet.al., (1988,1989)[7,8] The molar energies of activation for dipole orientation in the pyridine – amide systems, at different concentrations were determined bySunil Ahire et.al.(1998) [9]. Thermodynamic parameter deals with the passing of a dipole across a potential barrier which separates the minima of energy and the values of molar entropy of activation (ΔS) of the system are negative for all concentrations. It means that the environmentof the system is cooperative resulting in the activated state, which is more ordered than the normal state has been studied by ShaguftaTabassumet.al., (2018) [10].The decrease of thermodynamic parameter in the mixtures can be attributed to changes in the hydrogen bond strength and a decrease in the

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average number of hydrogen bonds are reported by RavindraTalware (2024)[11].

Materials and Methods

The chemicals, used in the present work are Diethylene glycol Monomethyl ether, Chlorobenzene (CB), are of spectroscopic grade and used without further purification in the present work. The solutions are prepared at eleven different volume fractions of Chlorobenzenefrom 0 to 1 in step of 0.1. These volume fractions are converted to mole fractions for further calculations.

The complex permittivity spectra of the samples were studied using time domain reflectrometry (TDR) method in reflection mode[12,15].The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug -in module was used. Fig.1.Shows Block Diagram of Experimental setup.

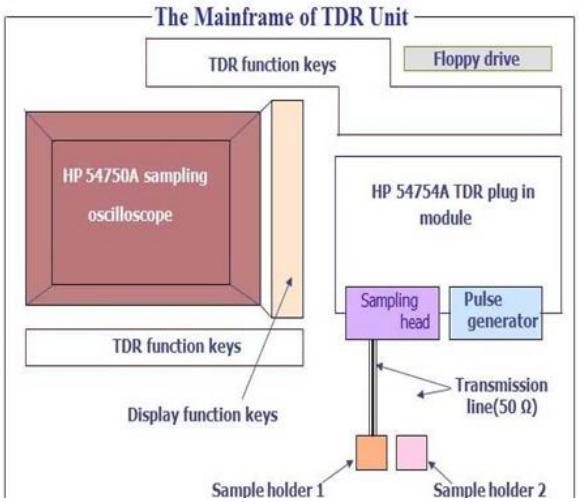

Fig 1: Block Diagram of Dual Channel TDR Unit

A fast rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance of 50 ohm. The transmission line system under test was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell connecter with 3.5mm outer diameter and 1.35 mm effective pin length .All measurements were done under open load conditions.

The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope .In this experiment, a time window of 5ns was used .The reflected pulses without sample R_1 (t) and with sample R_X (t) were digitized in 1024 points in the memory of the oscilloscope and transferred to a pc through 1.44 MB floppy diskette drive.

A temperature controller system with a water bath and thermostat has been used to maintain the constant temperature within the accuracy limit of ± 273 k .The sample cell was surrounded by a heat insulating container through which the water of constant temperature using a temperature controller system was circulated. The temperature at the cell is checked using the electronic thermometer.

The time dependent data were processed to obtain complex reflection coefficient spectra ρ*(ω) over the frequency range from 10 MHz to 20 GHz using Fourier transformation [16-17]as

$$\rho^*(\omega) = \left[\frac{c}{j\omega d}\right]\left[\frac{p(\omega)}{q(\omega)}\right] \text{----------} (1)$$

Where p(ω) and q(ω) are Fourier transforms of [R1 (t) - Rx (t)] and [R1 (t)+Rx (t)], respectively. C is the velocity of light, w is angular frequency and d is the effective pin length and j = root (-1)

The complex permittivity spectra ε*(ω) were obtained from reflection coefficient spectra ρ*(ω) by applying a bilinear calibration method.C.E. Shannon(1949)[16]. The experimental values of ε*(ω) are fitted the Debye equation [17].

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau} \text{----------} (2)$$

where, ε_0, ε_∞ and τ as fitting parameters. The value of $\varepsilon_\infty$was kept to be constant as the fitting parameters are not sensitive to ε_∞ .A non-linear least squares fit method[18]used to determine the values of these dielectric parameters.

Thermodynamic parameters

The thermodynamic parameters evaluated Using Eyring rate equation. [19] is as follows

$$\tau = (h/kT)\, e^{\Delta H/RT}\, e^{-\Delta S/R} \text{----------} (3)$$

Where, ΔH is molar enthalpy of activation and ΔS is molar entropy of activation for the dipole reorientation process. □, is relaxation time, T is temperature and h is Planck's constant.

The order of magnitude of the enthalpy of activation and entropy of activation can give some clue to the molecular energy and order of molecules in the relaxation process.

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Result and Discussion

The dielectric constant ε0 and relaxation time τ for the mixture obtained by fitting experimental data with the Debye equations (2) at four different temperatures are shown in Table. 1.

Table -1

Temperature Dependent Dielectric Parameters For DGME-CB system

Mole fraction of CB	288 K		298 K		308 K		318 K	
	ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)
0	14.62	31.9	13.99	29.85	13.44	28.68	13.02	26.33
0. 1135	13.69	31.58	13.19	29.26	12.79	26.94	12.42	24.45
0. 2237	12.58	30.83	12.18	27.76	11.74	24.78	11.43	22.8
0. 3307	11.52	29.5	10.64	26.41	10.75	23.89	10.46	21.69
0. 4346	10.56	27.65	11.15	24.65	9.84	22.32	9.57	21.26
0. 5355	9.75	25.82	9.39	23.05	9.09	20.69	8.86	20.06
0. 6336	8.95	23.37	8.65	21.29	8.39	19.03	8.17	18.52
0. 729	8.17	20.81	7.91	19.15	7.67	17.22	7.49	16.65
0. 8218	7.38	18.06	7.16	16.17	6.96	15.18	6.81	14.8
0. 9121	6.63	16.01	6.44	14.07	6.28	13.53	6.15	13.17
1	5.97	14.39	5.8	13.09	5.65	12.63	5.52	12.48

The static dielectric constant and relaxation time decreases with increasing concentration of CB in DGME for all temperaturesas well as with increase in temperature. This suggests that weak intermolecular interaction due to shielded charge distribution in CB molecules and exposed charge distribution in DGME molecules i.e. Intermolecular association is taking place in all these systems [13]. In an ideal mixture of polar liquids, if the molecules are non- interacting, a linear variation in the values of static dielectric constant and relaxation time with concentration is expected. However, the relationship for relaxation time is nonlinear with change in volume fraction of CB in DGME. This suggests that weak intermolecular interaction due to shielded charge distribution in CB molecules and exposed charge distribution in DGME molecules i.e. Intermolecular association is taking place in all these systems.[13].

Table. 2. Thermodynamic parameters (ΔH, ΔS)for DGME + CB system

Volume Fraction of CB	ΔH Enthalpy (J /mole)	ΔS Entropy (J /K)
0	2161	-36.20
0.1	3945	-29.95
0.2	5248	-25.17
0.3	5276	-24.71
0.4	4273	-27.56
0.5	4111	-27.54
0.6	3682	-28.24
0.7	3409	-28.25
0.8	2554	-29.93
0.9	2293	-29.76
1	1051	-33.25

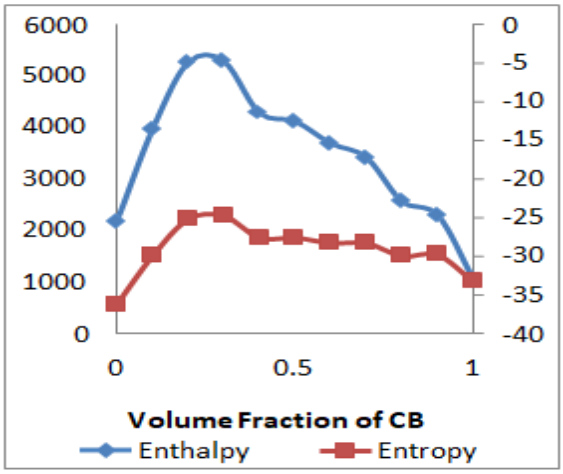

Fig.2. Thermodynamic Parameters for DGME + CB System

It has been observed from Table. 2. that molar enthalpy of activation (ΔH) increases up to30%volume fraction of CBin DGME from 2161 J/mole to 5276 J/mole. This means that more energy is needed for group dipole reorientation up to 30% volume fraction of CB in the mixture. Afterwards 40 to 100% concentration of CB in the mixture decreases up to 1051 J/mole(100%), means that less energy is needed for group dipole reorientation with increase in volume fraction of CB in the mixture. The values are positive for all concentrations, suggest endothermic interaction[22].

All negative value of molar entropy of activation (ΔS) with volume fraction of CB indicates relatively high ordered arrangement of molecules in the activated state is exists[23].

Conclusion

The dielectric relaxation parameters and thermodynamic properties show systematic change with concentration and temperature.The thermodynamic parameters like the enthalpy of activation related to the energy barrier for reorientation and entropy of activation related to the change in disorder can be determined by analyzing how relaxation time changes with temperature. A positive (ΔH) value indicates an endothermic process i.e.,heat is absorbed and a negative (ΔH) value indicates an exothermic process i.e.,heat is released. A positive (ΔS) value,suggests an increase in randomness at the interface, which can influence the adsorption process.

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