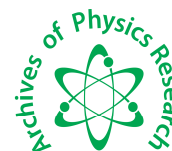




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Time domain reflectometry technique for study of thermodynamic parameters

Pradnya R. Maheshmalkar^a, Shafiyoddin B. Sayyad^b and Prakash W. Khirade*

^aMrs. K. S. K. College, Beed, India

^bMilliya College, Beed, India

*Microwave Research Laboratory, Dept. of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India

ABSTRACT

In this paper, a dielectric relaxation study on Bromobenzene (BB) - Diethylene Glycol Monomethyl Ether (DGME) binary mixtures has been carried out 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 (ϵ_0), relaxation time (τ) were obtained from complex permittivity spectra $\epsilon^(\omega)$, using nonlinear least squares fit method. Using these parameters, thermodynamic parameters are determined. All the systems show a systematic change in dielectric parameters with temperature and concentration. The dielectric relaxation is used to estimate thermodynamic Parameters. Thermodynamic properties are helpful in accessing the states of dipoles under the influence of applied field.*

Keywords: Time domain Reflectometry, Dielectric relaxation, Thermodynamic Parameters

INTRODUCTION

The objective of this paper is to report Thermodynamic Parameters in the Dielectric relaxation Study of polar liquids. 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), Bromobenzene (BB), both are 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].

RM Shirke [5] 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 by HD Purohit and RJ Sengwa [6, 7] at microwave frequencies. The molar energies of activation for dipole orientation in the pyridine – amide systems, at different concentrations were determined by Sunil Ahire et.al.[8].

MATERIALS AND METHODS

The chemicals, used in the present work are Diethylene glycol Monomethyl ether, Bromobenzene (BB), are of spectroscopic grade and used without further purification in the present work. The solutions are prepared at eleven different volume fractions of Bromobenzene from 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 reflectometry (TDR) method in reflection mode [9, 12]. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug-in module was used. Fig.1. Shows Block Diagram of Experimental setup.

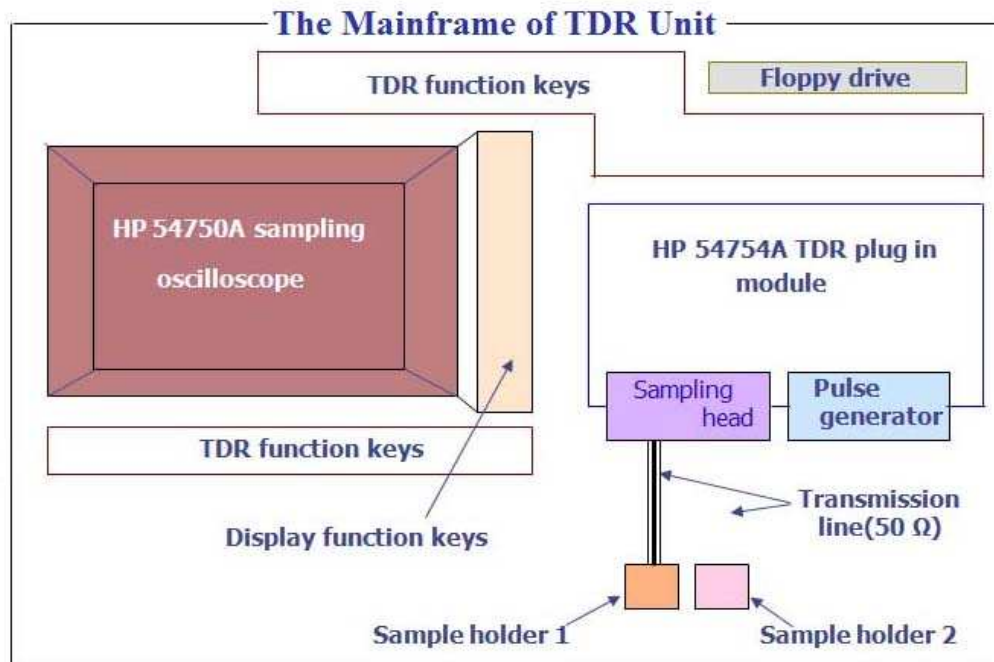


Fig 1: Block Diagram of Dual Channel TDR Unit

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 connector 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 $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz using Fourier transformation [13, 14] as

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

Where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_1(t) - R_x(t)]$ and $[R_1(t) + R_x(t)]$, respectively. C is the velocity of light, ω is angular frequency and d is the effective pin length and $j = \sqrt{-1}$

The complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method [15]. The experimental values of $\epsilon^*(\omega)$ are fitted the Debye equation [16].

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

where, ϵ_0 , ϵ_∞ and τ as fitting parameters. The value of ϵ_∞ was kept to be constant as the fitting parameters are not sensitive to ϵ_∞ . A non-linear least squares fit method [17] used to determine the values of these dielectric parameters.

Thermodynamic parameters:- The thermodynamic parameters evaluated Using Eyring rate equation [18] is as follows:

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

Where, ΔH is molar enthalpy of activation and ΔS is molar entropy of activation for the dipole reorientation process. τ Is relaxation time, T is temperature and h is planks 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.

RESULTS AND DISCUSSION

The dielectric constant ϵ_0 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- BB system

Mole fraction of BB	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
0.1102	13.16	31.4	12.69	29.24	12.32	27.56	11.96	25.4
0.2179	12.05	30.43	11.62	28.25	11.27	26.6	10.94	24.49
0.3232	11.01	29.93	10.64	27.4	10.31	25.68	10.01	24.01
0.4262	10.03	28.88	9.72	26.2	9.42	24.69	9.17	22.91
0.5270	9.13	27.26	8.85	25.09	8.6	23.51	8.32	22.02
0.6257	8.34	26.08	8.08	23.9	7.84	22.6	7.63	20.84
0.7222	7.51	24.69	7.28	22.6	7.03	21.23	6.88	19.95
0.8168	6.70	23.11	6.50	21.33	6.32	20.09	6.17	19
0.9093	5.99	21.33	5.80	19.4	5.72	18.6	5.56	17.47
1	5.48	18.63	5.28	17.33	5.16	16.63	5.03	16.25

The static dielectric constant and relaxation time decreases with increasing concentration of BB in DGME as well as with increase in temperature.

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 BB in DGME. This suggests that weak intermolecular interaction due to shielded charge distribution in BB molecules and exposed charge distribution in DGME molecules i.e. Intermolecular association is taking place in all these systems [10].

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

Volume Fraction of BB	ΔH (KJ /mole)	ΔS (KJ /mole)
0	2.161	-0.036
0.1	2.772	-0.034
0.2	2.897	-0.033
0.3	3.021	-0.033
0.4	3.235	-0.032
0.5	2.863	-0.032
0.6	3.035	-0.031
0.7	2.841	-0.032
0.8	2.424	-0.033
0.9	2.38	-0.032
1	0.944	-0.036

It can be seen from Table. 2. that molar enthalpy of activation (ΔH) increases with increase in volume fraction of BB in DGME from 2.161 KJ/mole to 3.235 KJ/mole. This means that more energy is needed for group dipole reorientation up to 40% concentration of BB in the mixture.

Afterwards 50 to 100% concentration of BB in the mixture decreases up to 0.944. KJ/mole means that less energy is needed for group dipole reorientation with increase in volume fraction of BB in the mixture. The values are all positive suggest endothermic interaction [19].

All negative value of molar entropy of activation (ΔS) with volume fraction of BB indicates relatively high ordered arrangement of molecules in the activated state is exists [20].

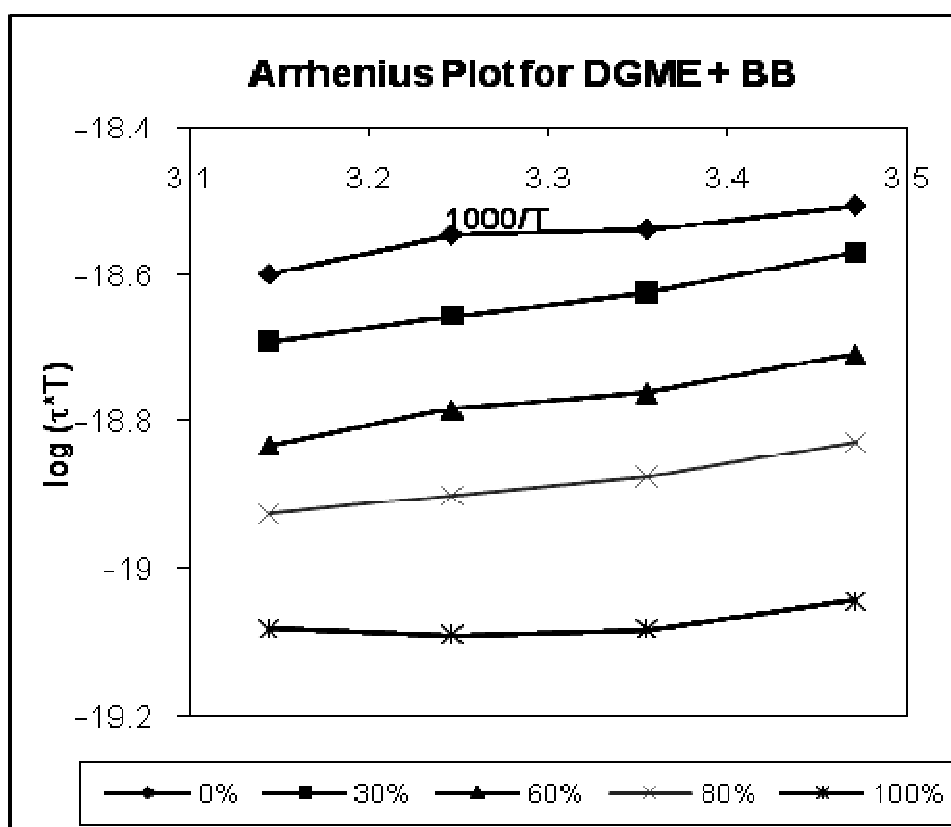


Figure 2. Arrhenius plot for DGME + BB system

The slope of Arrhenius plot changes with concentration. This shows the change in activation energy of the system. The temperature dependence of relaxation time follows Arrhenius behavior [20].

CONCLUSION

This paper provides information of the specific structure of mixtures in different concentration regions determined by the dielectric relaxation dynamics, obtained from the effect of temperature on the relaxation time. This study has been proved that TDR is an efficient tool for the study of molecular processes in solutions under the sufficiently wide frequency range. The dielectric relaxation parameters and thermodynamic parameters show systematic change with concentration and temperature.

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