Journal of Advances in Applied Sciences and Technology
ISSN : 2393-8188 (print)
2393-8196 (online)
www.milliyasrcollege.org.journal.php

DIELECTRIC PROPERTIES OF BINARY MIXTURE ETHANOL WITH NITROTOLUENE USING TIME DOMAIN TECHNIQUE

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Abstract: Using TDR technique the dielectric properties of binary mixture of Ethanol with Nitrotoluene at over the frequency range of 10MHz-20GHz are investigated, at various temperatures from 283 K to 313 K. The static dielectric constant (ε_0) and relaxation time (τ) are obtained by fitting experimental data to the Debye equation. By using these dielectric parameters various dielectric properties such as excess properties, Kirkwood correlation factor are obtained. The static dielectric constant of mixture increases with increase in temperature. Relaxation parameter is very sensitive parameter related to molecular size as well as mobility of molecules in liquid. The decrease in effective angular correlation factor g^{eff} shows weak dipole-dipole interaction resulting formation of anti parallel alignment of dipoles. The decrease in correlation factor g_f shows the dipoles will be oriented in such a way that the effective dipole will be less than the corresponding values of pure liquid.

KEYWORDS: Dielectric properties, TDR, Kirkwood correlation factor

1. INTRODUCTION

Time Domain Reflectometry (TDR) for the frequency range 10 MHz to 10 GHz., the dielectric relaxation spectroscopy probes the interaction of a macroscopic sample with a time dependent electric field. The observed dielectric polarization yields information on structural aspects and dynamical process, which is only partly accessible with other methods. For pure liquids and liquid mixtures at ambient temperature, dynamical process in the time scale of Pico-to-nano seconds arise from the orientation of molecular dipole moment and from kinetic processes involved with intermolecular hydrogen bonding. Due to recent progress in microwave technology, determination of complex permittivity spectra in the gigahertz range is now a day fairly straightforward for non-conducting liquids [1-7].

The design and implementation of microwave heated processes, the availability of quantitative data on dielectric properties of solvent systems or methods for their prediction are essential. The dielectric relaxation behaviour of liquid mixtures has gained increasing interest in recent years. There have been several investigations on the dielectric behaviour of solvent and solvent mixtures in which dielectric relaxation spectra were used to examine molecular orientations and hydrogen bonded networks of these systems.

Dielectric relaxation studies on binary mixtures are important for understanding the hydrogen bonding and intermolecular interactions in the mixture. A dielectric study yields the Kirkwood correlation factor, which is strongly correlated with the solute-solvent interactions. Dielectric dimethylformamide, parameters for ethanol-tetrahydrofuran, ethanol-dimethylsulphoxide, ethanol- ethanol-2-ethoxyethanol, ethanol-anilin, and binary systems were reported earlier by Chaudhari et al., Khirade et al. All the above systems showed systematic change in the dielectric parameters with concentration and temperature.

The present work is to report a dielectric study on ethanol-nitrobenzene mixtures conducted using Time Domain Reflectometry (TDR) for the frequency range 10 MHz to 10 GHz. The dielectric parameters viz. the static dielectric constant to relaxation time and dielectric constant at high frequency were determined. The Kirkwood correlation factor, excess dielectric parameters and activation energy were also obtained for 283, 293, 303 and 313 °K in order to obtain structural information about the binary mixtures.

2. EXPERIMENTAL

Mixture of Ethanol and Nitrotoluene (E-Merck grade) were obtained and used without further purification. The solutions were prepared at different compositions in steps of 10% by volume within a 0.02% error limit.

The experimental set up for TDR technique consists of sampling oscilloscope HP 54750A; TDR module HP 54754A, a transmission line and sample cell. The complex permittivity spectra were studied using TDR (Cole et al., 1989). A 200 mv pulse from a tunnel diode pulse generator with a rise time of 25 ps and repetitive frequency of 1 kHz was transmitted along a 3.5 mm transmission line with a characteristic impedance of 50 ohms. The sample cell was placed at the end of the transmission line, after the sample head. The reflected pulse along with the incident pulse was sampled with the sampling head. The length of the transmission line [9] was about twice that of the transmission line [8], so that the incident pulse was well separated from the reflected pulse. The required cell was designed in such a way that its impedance matched the impedance of the transmission line (50 ohms).

A Tektronix 7854 sampling oscilloscope was used to sample the reflected pulse. The time window used for the experiment was kept at 5 ns. The reflected pulse was digitized with 1024 points in the selected time window. The oscilloscope interfaced with a personal computer through a IEEE-488 General Purpose Interfacing Bus (GPIB) card with handshaking software.

First, the reflected pulses Rl (t) and Rx (t) without and with a sample in the cell, respectively, were recorded. Time referencing was done by matching small reflections due to a particular discontinuity at the beginning of the cell in Rl (t) and Rx (t).Subtraction and addition of these pulses were done in the memory of the oscilloscope after proper time shifting. The subtracted pulse and added pulse were transferred to the computer for further analysis.

The temperature controller system with a water bath and a thermostat was used to maintain a constant temperature within an accuracy limit of ±1°C. The sample cell was surrounded by a heat insulating container, through which water obtained at a constant temperature using a temperature controller system was circulated. The temperature at the cell was checked using an electronic thermometer.

The dielectric properties of binary mixtures at over the frequency range of 10MHz-20GHz are investigated using TDR technique, at various temperatures from 10 °C to 40 °C. The static dielectric constant (ε0) and relaxation time (τ)are obtained by fitting experimental data to the Debye equation. By using these dielectric parameters various dielectric properties such as excess properties Kirkwood correlation factorare obtained.

3. OBSERVATIONS

3.1 Static Permittivity and Relaxation Time:

The values of static dielectric constant (ε_0) and relaxation time (τ) for concentrations at four temperatures are listed in Table 1. The variation of static dielectric constant and relaxation time with change in mole fraction at four different temperatures is shown in Fig. 1 and Fig. 2 respectively.

3.2 Kirkwood correlation factor:

The structural information about the liquids from the dielectric relaxation parameter may be obtained using the Kirkwood correlation factor g [14]. This factor is also a parameter for obtaining information regarding orientation of electric dipoles in polar liquids. The values of g^{eff} are given in Table 2 and shown in Fig. 3. The variation in gf with change in volume fraction of NT are given in Table 3 and shown in Fig.4. The amount of solute- solvent interaction can be accessed using these parameters.

Table:1: Temperature dependent dielectric parameters
for binary mixture of ETOH+NT

Mole Fraction of NT	283K		293K		303K		313K	
	ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)
0	27.76	218.5	26.97	173.6	24.87	131.5	22.77	111.8
0.06	24.19	194.4	23.35	155.7	22.17	120.4	20.76	104.5
0.125	23.62	134.4	22.81	107.5	21.5	85.55	20.77	67.24
0.196	23.47	122	22.4	101.7	21.31	78.74	20.52	62.78
0.275	23.46	117.9	22.12	98.54	21.2	75.23	20.04	58.31
0.363	23.68	74.79	22.43	62.45	21.78	52.25	21.01	49.78
0.461	23.88	65.39	22.55	59.26	22.01	48.86	21.69	42.3
0.571	24.44	62.54	23.2	55.57	22.27	46.53	21.81	41.02
0.695	24.73	63.3	24.42	57.53	22.61	51.09	22.5	46.76
0.837	24.89	70.71	24.49	63.86	23.5	53.27	22.84	49.58
1	25.02	83.48	24.71	67.77	23.62	57.51	23.29	51.86

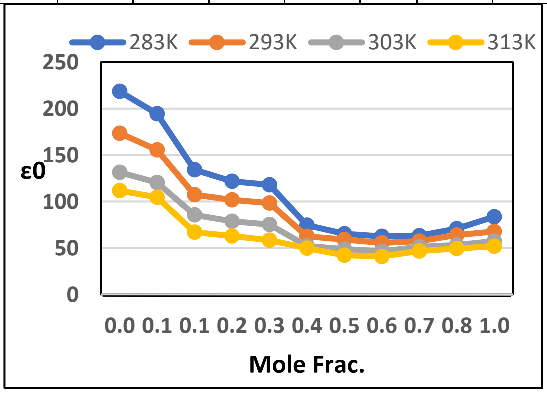

***Fig.1**. Variation of static dielectric constant (ε_0) as a function of mole fraction*

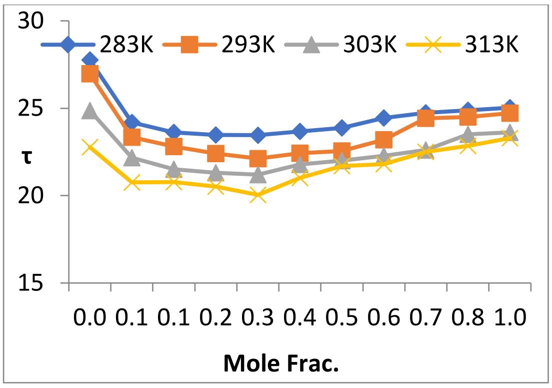

Fig.2. *Variation of relaxation time (τ) as a function of mole fraction of NT*

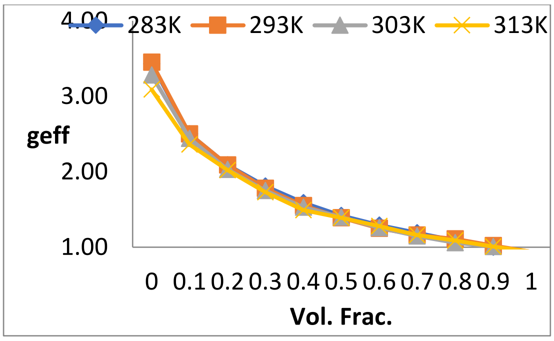

Fig.3. Variation of Kirkwood correlation factor

Table: 2: Kirkwood Correlation factor (g^{eff})

Volume Fraction of NT	283K	293K	303K	313K
0	3.43	3.45	3.28	3.09
0.1	2.50	2.50	2.44	2.36
0.2	2.09	2.09	2.03	2.02
0.3	1.81	1.78	1.75	1.73
0.4	1.59	1.55	1.53	1.49
0.5	1.42	1.39	1.40	1.39
0.6	1.29	1.25	1.26	1.28
0.7	1.19	1.16	1.15	1.16
0.8	1.09	1.11	1.06	1.09
0.9	1.00	1.02	1.01	1.01
1	0.92	0.94	0.93	0.94

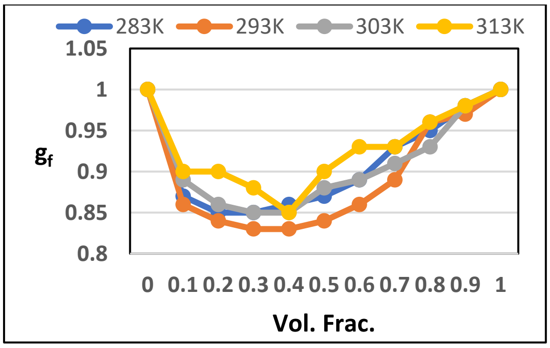

Fig.4. Variation of Kirkwood correlation factor (g_f)

Table :3 : Kirkwood Correlation factor (g_f)

Volume Fraction of NT	283K	293K	303K	313K
0	1	1	1	1
0.1	0.87	0.86	0.89	0.90
0.2	0.85	0.84	0.86	0.90
0.3	0.85	0.83	0.85	0.88
0.4	0.86	0.83	0.85	0.85
0.5	0.87	0.84	0.88	0.90
0.6	0.89	0.86	0.89	0.93
0.7	0.93	0.89	0.91	0.93
0.8	0.95	0.96	0.93	0.96
0.9	0.98	0.97	0.98	0.98
1	1	1	1	1

4. Result and Discussion:

4.1. Static Permittivity and Relaxation Time

The dielectric parameters for different temperatures and concentrations are given in Table 1 and shown in Fig.1 and 2 from these values it is observed that static dielectric constant (ε_0) for the mixture increases towards the dielectric constant of respective Alcohol. This is probably due to the lower dielectric constant of Nitrotoluene [1].

The relaxation time (τ) decreases with increase in temperature from 283K to 313K. This may possibly due to increase in molar volume and increase in the effective length of the dipole with increase in temperature and also due to increase in the thermal agitation and partly due to decrease in the viscosity [2,10,11]

4.2. Kirkwood correlation factor

The values of effective angular correlation factor g^{eff} are 3.43 at 283K and decreases 3.09 at 313K. The value confirms the formation of hydrogen bonding in pure ethanol. These values are greater than unity suggesting parallel orientation of electric dipoles. The corresponding value of NT is 0.93 and 0.88 respectively, indicating weak dipole-dipole interaction resulting formation of anti parallel alignment of dipoles in the pure system of NT. The variation of g^{eff} indicates intermolecular interaction in the mixture going to parallel orientation to anti parallel orientation of dipoles with increase in number of NT molecules.

The amount of solute solvent interaction is accessed by correlation factor g_f. For pure liquids these values are always equal to unity and deviates from unity for mixture. For this system, values of correlation factor for pure liquids are unity as expected and these values are less than unity at all concentration and temperatures. This indicates that the dipoles of mixture will be oriented in such a way that the effective dipole will be less than the corresponding values of pure liquid [13].

5. CONCLUSION

The static dielectric constant of mixture decreases slowly due to addition of Nitrotoluene. Relaxation parameter is very sensitive parameter related to molecular size as well as mobility of molecules in liquid. In this mixture relaxation time decreases with increase in temperature, this is due to the fact that with increase in temperature there is an increase in thermal agitation, which results in lowering down the values of relaxation time.

The decrease in effective angular correlation factor g^{eff} from ethanol to respective liquid of nitro group molecule shows weak dipole-dipole interaction in mixture resulting parallel alignment to of anti parallel alignment of dipoles. The decrease in correlation factor g_f shows the dipoles will be oriented in such a way that the effective dipole will be less than the corresponding values of pure liquid.

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