ISSN : 2393-8188 (print)
2393-8196 (online)
www.milliyasrcollege.org.journal.php

DIELECTRIC PROPERTIES OF BINARY MIXTURE USING TIME DOMAIN REFLECTOMETRY TECHNIQUE

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ABSTRACT:

The dielectric properties of binary mixture Glycerol (Gly) with N-Methylacetamide (NMA) has been carried out with varying concentrations at different temperatures in the frequency range between 10MHz-20GHz using time domain reflectometry (TDR) technique. Dielectric parameters namely static permittivity (ε0), relaxation time (τ) were obtained from complex permittivity spectra ε(ω), using nonlinear least squares fit method .These values are used for the calculation of Bruggeman factor. All the systems show a systematic change in dielectric parameters with temperature and concentration. On the basis of above parameters, intermolecular interaction and dynamics of molecules at molecular level are predicated. The dielectric behavior of this binary mixture is found to agree well with the modified Bruggeman equation.*

KEYWORDS: Dielectric parameters; Time domain Reflectometry; Bruggeman factor.

1. INTRODUCTION

The objective of the proposed work is to apply our Experimental data for Glycerol –N-Methylacetamide system to verify modified Bruggeman relation. Dielectric relaxation behavior of mixtures of polar molecules under varying conditions of composition have evoked considerable interest, because, it helps in formulating adequate models at liquid relaxation and in obtaining information about the relaxation process in mixtures. The dielectric relaxation study of binary polar liquids is important for understanding the hydrogen bonding & intermolecular dynamics of molecules at molecular levels. Glycerols (Gly), N-Methylacetamide (NMA), are polar liquids, one with hydroxyl group & other with amide group. It is interesting to see the effect of amide group in Glycerol. To study the dielectric properties of the mixture of polar liquids, the most reliable technique is time domain technique developed by Cole et.al. Time domain reflectrometry in reflection mode [1-4] has been used to obtain the dielectric parameters. With these parameters, the Bruggeman factor has also been determined. The measurements in the frequency range between 10 MHz to 20 GHz are interesting because the dielectric dispersion of these molecules occurs in the same frequency range. Further the frequency dependent complex permittivity measurements using TDR are more reliable because it is a powerful technique and a single measurement covers a wide frequency range in a very short time.

A systematic investigation of Dielectric relaxation in binary mixtures at various concentrations and temperature employing Time domain reflectometry (TDR) were studied by P. W. Khirade .et.al. [5-7]. Dielectric relaxation study of N- Methylacetamide with 1,4-dioxane mixture using Picoseconds Time domain Reflectometry technique were reported by G.R. Mahajan and A.C.Kumbharkhane [8]. Bruggeman factor-Tool to indicate the change in Volume through intermolecular Interaction were studied by G.M.Dharne and P.W.khirade, [9]. Static dielectric measurements on binary mixtures of the homogeneous series of monoalkyl ethers of ethylene glycol with polar solvents were carried out using LCR meter by R.J. Sengwa and co-authors [10].

2. EXPERIMENTAL SET UP AND DATA ACQUISITION:-

The chemicals, used in the present work are Glycerol and N- Methylacetamide (NMA), are of spectroscopic grade and used without further purification. The solution are prepared at eleven different volume fractions of N- Methylacetamide (NMA) from 0 to 1 in Glycerol in step of 0.1.These volume fractions are converted to mole fractions for further calculations.

The complex permittivity spectra of the samples are studied using time domain reflectrometry (TDR) method [11-15]. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug -in module is used. 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 Ω. 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 & 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) & with sample R_x (t) were digitized in 1024 points in the memory of the oscilloscope & transferred to a pc through 1.44 MB floppy diskette drive.

A temperature controller system with a water bath & thermostat has been used to maintain the constant temperature within the accuracy limit of + or - 273 k. **"Figure 1".** Shows Block Diagram of Experimental setup.

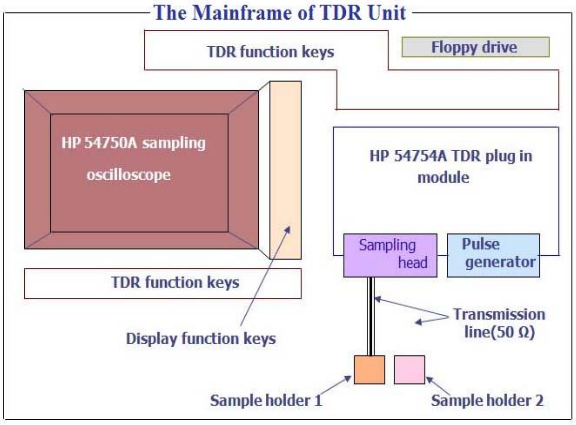

Fig .1 *Block Diagram of Dual Channel TDR Unit*

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

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

Where p (ω) and q (ω) are Fourier transforms of [R_1 (t) - R_x (t)] and [R_1 (t) +R_x (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 [1]. The experimental values of ε*(ω) are fitted the Debye equation [18].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \qquad (2)$$

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 [19] used to determine the values of dielectric parameters.

Bruggeman factor, help to depict intermolecular interaction among the liquids.

This formula states that static permittivity of binary mixture (ε_{0m}), Solute A (ε_{0A}), and solvent B (ε_{0B}), can be related to volume fraction of solvent (Φ_B) in mixture.

The Modified Bruggeman equation [20] for mixture is given by expression

$$f_B = \left(\frac{\varepsilon_{0m} - \varepsilon_{0B}}{\varepsilon_{0A} - \varepsilon_{0B}}\right)\left(\frac{\varepsilon_{0A}}{\varepsilon_{0m}}\right)^{1/3} = 1 - \Phi_B \qquad (3)$$

According to above equation linear relationship is expected which will give a straight line when f_B plotted against Φ_B. Any deviation from this linear relation indicates molecular interaction.

3. Results and discussion

The values of the dielectric parameters ε_0 and τ obtained from **"equation (2)"** for GLY-NMA system with the mole fraction of NMA at four different temperatures are recorded in **"Table 1".** From **"Table 1".** It can be observed that static permittivity ε_0 & relaxation time τ increase with increase in mole fraction of NMA in GLY. Same type of change has been observed at four temperatures under study.

In an ideal mixture of polar liquids, if the molecules are non-interacting linear variation in the values of static dielectric constant and relaxation time with concentration is expected.

Table 1 Dielectric parameters for binary mixture of Glycerol + NMA, X_{NMA} mole fraction of N-methylacetamide.

X_{NMA}	288 K		298 K	
	ε_0	τ (ps)	ε_0	τ (ps)
0	44.55	249.48	42.22	238.25
0.0968	48.50	360.79	42.21	320.90
0.1943	52.75	424.51	44.80	373.45
0.2925	56.77	476.88	49.40	420.14
0.3914	62.12	528.84	56.46	465.25
0.4910	70.90	574.49	64.48	507.47
0.5913	78.12	608.84	72.07	540.40
0.6924	88.14	629.73	80.47	566.12
0.7942	98.90	650.69	91.40	583.02
0.8967	110.32	666.90	104.20	591.65
1	122.18	674.00	120.51	586.12
	308 K		318 K	
	ε_0	τ (ps)	ε_0	τ (ps)
0	40.88	226.45	38.53	214.00
0.0968	37.30	289.55	32.68	256.20
0.1943	38.00	336.65	32.83	307.00
0.2925	44.80	373.30	37.30	348.70
0.3914	49.40	428.00	42.98	386.20
0.4910	56.90	456.36	48.23	415.60
0.5913	64.00	500.99	55.29	444.00
0.6924	74.04	524.36	64.16	460.60
0.7942	86.80	532.92	77.40	470.50
0.8967	97.91	545.15	90.50	470.50
1	117.89	516.60	115.95	458.20

However the relationship for dielectric constant and relaxation time is nonlinear with change in mole fraction of NMA in Glycerol. The non- linear variation in dielectric constant and relaxation time with change in mole fraction of NMA in Glycerol suggests weak intermolecular interaction due to shielded charge distribution in NMA molecules and exposed charged distribution in Glycerol i.e intermolecular association is taking place in all these systems [21].

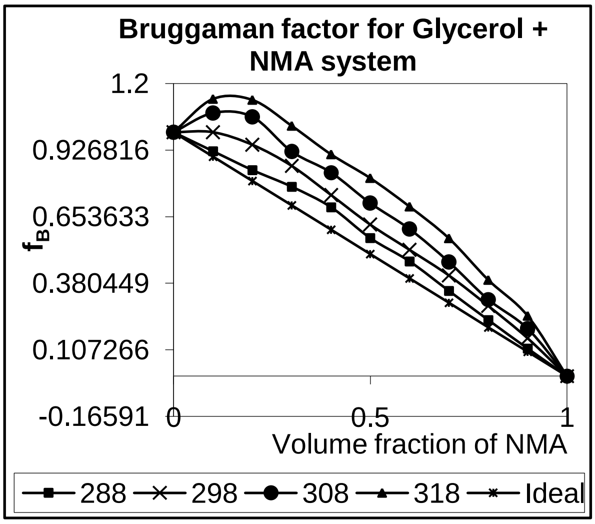

Fig.2 *Bruggeman factor for binary mixture of Glycerol (Gly) - N-Methylacetamide (NMA) system*

The experimental values with ideal values of Bruggeman factor plotted against volume fraction of NMA in the mixture as shown in **"Figure 2".** The values of f_B shows deviation above linearity from the ideal Bruggeman behavior for all concentrations in the temperature range 288 K to 318 K. This confirms the intermolecular interaction in the mixture. Several similar observations have been reported in the literature [4, 5, 9 and 22].

4. CONCLUSIONS

The study provides information that static permittivity, relaxation time and Bruggeman factor of binary mixture of Glycerol (Gly) - N-Methylacetamide (NMA) are depending on temperature and Concentration. Molecular interactions in Glycerol- N-Methylacetamide system were discussed in terms of Bruggeman factor. One observes significant deviation from the Bruggeman factor. The dielectric behavior of this binary mixture is found to agree well with the modified Bruggeman equation.

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