Structural Properties of Polar Liquids in Binary Mixture Using Microwave Technique

Shagufta Tabassum, V. P. Pawar

Abstract—The study of static dielectric properties in a binary mixture of 1,2 dichloroethane (DE) and n,n dimethylformamide (DMF) polar liquids has been carried out in the frequency range of 10 MHz to 30 GHz for 11 different concentration using time domain reflectometry technique at 10ºC temperature. The dielectric relaxation study of solute-solvent mixture at microwave frequencies gives information regarding the creation of monomers and multimers as well as interaction between the molecules of the binary mixture. The least squares fit method is used to determine the values of dielectric parameters such as static dielectric constant (ε_0), dielectric constant at high frequency (ε_∞) and relaxation time (τ).

Keywords—Excess parameters, relaxation time, static dielectric constant, time domain reflectometry.

I. INTRODUCTION

THE time domain reflectometry is very effective tool to identify inter and intra-molecular interaction between binary polar molecules [1]-[3]. The 1,2-dichloroethane (DE) is a colorless, oily, heavy non-associative polar liquid which is slightly soluble in water and has chloroform like odor. DE primarily used for the production of various chemicals such as vinyl chloride. It is also used as a wetting and penetrating agent for dispersant in rubber and plastics. It is an important binary liquid mainly used in chemical industries as in ore flotation, as a grain fumigant, as a metal degreaser, in textile and PVC (poly vinyl chloride) cleaning [4], [5].

The N,N-dimethylformamide (DMF) is a colorless liquid. It is very efficiently used in industries as a solvent, an additive, or an intermediate because of its extensive miscibility with water and also in peptide coupling, in the development, and production of pesticides, and in the manufacturing of adhesives, fibers, films etc. It is a polar aprotic solvent with high boiling point [5].

At microwave frequency the process associate to static dielectric properties of polar binary liquids mixture has been carried out using time domain reflectometry technique by many workers [6]-[10]. DE and DMF binary liquids have high polarity and strong solvating power, which makes them very effective in the industrial and technological applications. The DE and DMF linkage (-CH$_2$-CL) and (-NCH$_3$-C=O) respectively, are an important functional group in field of chemistry, biochemistry, pharmaceutical, and material science.

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The main objective of this paper is to report dielectric properties for DE and DMF liquid mixture at 10ºC.

II. EXPERIMENTAL

A. Materials

DE and DMF are polar liquids (AR grade, Qualigens fine chemical Pvt. Ltd, Bombay, India). Using DE-DMF system 11 different volume percentage of liquid mixture were prepared. Using volume percent mole fraction is calculated as

$$X_1 = \frac{v_1\rho_1/m_1}{[v_1\rho_1/m_1 + v_2\rho_2/m_2]} \tag{1}$$

where m_i, v_i and ρ_i represents the molecular weight, volume percent and density of the ith (i=1,2) liquids respectively.

B. Apparatus

The time domain reflectometry (TDR) technique [11]-[15] is used to determine the time dependent reflection response of the sample under test, after application of time dependent electromagnetic field. TDR setup contains Tektronix model number DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08. Dielectric measurements are carried out along the coaxial transmission line with the sample mounted in the sample cell that terminates the line. TDR dielectric measurement system consists of a step generator, which produce a fast-rising pulse of order of picoseconds. A suitable fast rising voltage pulse with 18ps incident rise time is made to incident on the sample cell through coaxial line of impedance 50 ohm. All measurements are following through in open load condition. Sampling oscilloscope monitors changes in step pulse after reflection from the sample cell at terminate line. Reflected electromagnetic pulse from sample cell without sample $R_1(t)$ and with sample Rx(t) were recorded in time window of 5ns and digitized in 2000 points. The nature of reflected pulse with and without sample for DE and DMF are observed.

The temperature controller system with water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of ±1°C. The temperature control system contains a heat insulating container through which water of constant temperature is circulated, which is surrounded around sample cell. The temperature at the cell is checked using the electronic thermometer.

The graphical representation of frequency dependent static permittivity (ε') and dielectric loss (ε'') for 11 concentrations is shown in Fig. 1.

C. Data Analysis

The time dependent data continued to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range of 10MHz to 30GHz using Fourier transformation [16], [17]

$$\rho^*(\omega) = \frac{c}{j\omega d} \cdot \frac{p(\omega)}{q(\omega)} \tag{2}$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of [$R_1(t)$ (reflection of pulse with sample)-$R_X(t)$(reflection of pulse without sample)] and [$R_1(t)+R_X(t)$] respectively, c is the velocity of light, ω is the angular frequency, d is the effective pin length and $j=\sqrt{-1}$.

The frequency dependent complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ through bilinear calibration method [18].

The experimental values of ε^* are obtained by Debye equation [19]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1+j\omega\tau} \tag{3}$$

where ε_0 (Static permittivity), ε_∞ (Permittivity at high frequency) and τ (Relaxation time) are fitting parameters. ω is the angular frequency and $j=\sqrt{-1}$.

A nonlinear least square fit method [20] was used to find out the values of dielectric parameters.

III. RESULTS AND DISCUSSIONS

A. Dielectric Parameters

We represent the static dielectric parameters values for 11 different concentrations after fitting the experimental data in the Debye equation. From Table I the static dielectric constant (ε_0) increases with the concentration of DMF in DE as expected, it is due to the presences of C=O in DMF. The relaxation time (τ) does not follow a linear pattern. The graphical representation of excess properties with respect to the mole fraction of DMF in DE is shown in Fig. 2.

B. Excess Parameters

The information related to liquid 1 (DE) and 2 (DMF) may be obtained by excess properties [21]. ε^E is defined as

$$\varepsilon^E = (\varepsilon_0 - \varepsilon_\infty)_m - [(\varepsilon_0 - \varepsilon_\infty)_1 x_1 + (\varepsilon_0 - \varepsilon_\infty)_2 x_2] \tag{4}$$

where x represents mole fraction and suffices m,1,2 represents mixture, liquid 1(DE) and liquid 2 (DMF) respectively.
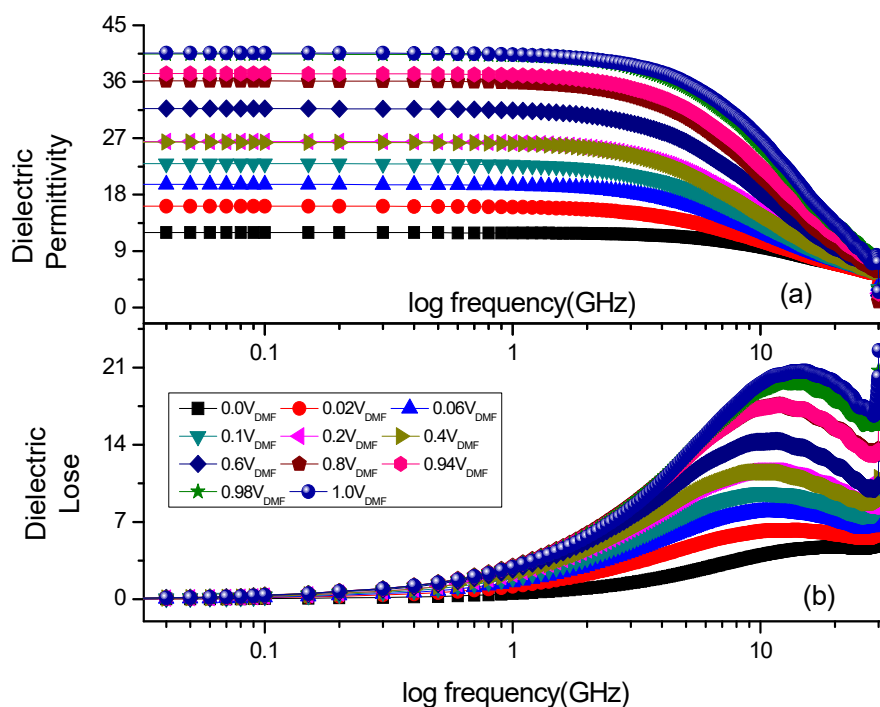

Fig. 1 (a) Frequency dependent static dielectric permittivity (ε'), (b) frequency dependent dielectric loss (ε'') with logarithmic frequency for DMF-DE system at 11 different concentrations

The excess permittivity may provide structural information about multimers formation in binary mixture as shown below

i) $\varepsilon^E = 0$ indicates the liquid mixture (DE-DMF) constituents do not interact at all.

ii) $\varepsilon^E < 0$ indicates the liquid mixture (DE-DMF) constituents interaction in such a way that the total number of effective dipoles contributed in the liquid mixture get reduced.

iii) $\varepsilon^E > 0$ indicates that the constituents of a mixture interact in such a way that is an increase in the number of effective dipoles contributed in the mixture.

From Fig. 2 (a), it is clear that the ε^E values are negative in DE rich region and are positive in DMF rich region. The

negative value indicates that the effective dipole values got reduce and positive value shows that the effective dipole values increases in DE-DMF system. Similarly, the excess inverse relaxation time $(1/\tau)^E$ can be derive as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_1 x_1 + (1/\tau)_2 x_2] \qquad (5)$$

where x represents mole fraction and suffices m,1,2 represents mixture, liquid 1(DE) and liquid 2 (DMF) respectively.

The excess inverse relaxation time represents the dynamic property of the liquid mixture. The inverse relaxation time analogy is lead from spectra line broadening in the resonant spectroscopy [22].

i) $(1/\tau)^E = 0$ indicates that there is no interaction between liquids and so as no field creates and there isn't any change in the dynamics of liquid 1 and 2.

ii) $(1/\tau)^E < 0$ indicates the liquid 1 and 2 interaction produces a field and this filed makes the effective dipoles to rotate slowly.

iii) $(1/\tau)^E > 0$ indicates the liquid 1 and 2 interaction produces

a field and that field cooperates the effective dipoles movements. So, dipoles rotate fast.

TABLE I
STATIC DIELECTRIC PARAMETERS OF DE-DMF SYSTEM

x_2	ε_0	ε_∞	τ
0.0	12.57(1)	3	9.75(3)
0.1	15.96(2)	2.9	13.26(3)
0.2	19.33(2)	2.75	13.63(4)
0.3	22.47(2)	2.7	14.61(3)
0.4	26.22(1)	2.65	15.07(2)
0.5	26.06(1)	2.5	14.99(2)
0.6	31.42(1)	2.48	14.47(1)
0.7	36.5(3)	2.45	14.43(2)
0.8	37.22(1)	2.25	13.51(0)
0.9	40.61(2)	2.15	12.47(1)
1.0	41.(4)	2	12.18(4)

x_2 represents the mole fraction of DMF in DE. Number in the bracket represents error in the corresponding value, e.g., 12.57 (1) means 12.57 ± 0.01.
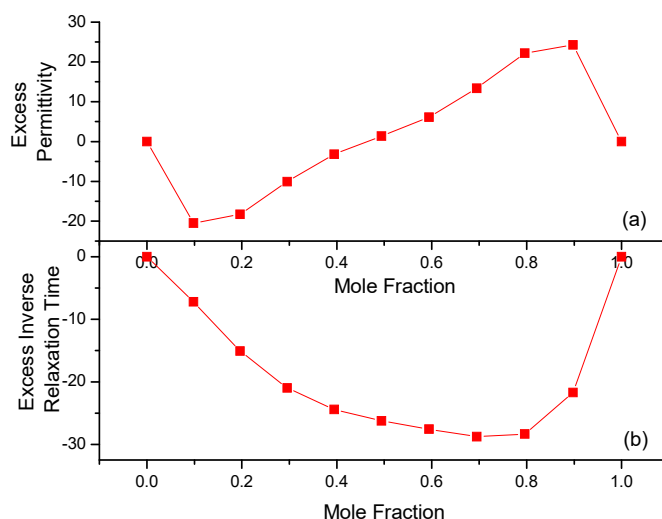

Fig. 2 (a) Excess permittivity (ε^E), (b) Excess inverse relaxation time $(1/\tau)^E$, versus mole fraction (x_2) of DMF in DE at different concentration

From Fig. 2 (b) it is noticed that the values of $(1/\tau)^E$ are negative for all concentrations, it indicate that the interaction between DE-DMF mixture reduces the dipole movement.

The experimental values of both the excess parameters were fitted to the Redlich Kister equation [23], [24].

$$A^E = (x_1 x_2) \sum_n B_n (x_1 - x_2)^n \qquad (6)$$

where A is either ε^E or $(1/\tau)^E$.

By using these B_n values, A^E value were calculated and with these values smooth curve is drawn as shown in Fig. 2.

C. Kirkwood Parameters

The Kirkwood correlation factor g [25] is used to get the information regarding the orientation of electric dipoles in polar liquids. The values of g^{eff} and g_f are shown in Fig. 3 for

the mixture of DE-DMF system. The dipole moments for DE and NMF are 1.24 g/cm^3 and 0.948 g/cm^3 [26] respectively.

From Fig. 3 (a) the values of g^{eff} for pure liquids are greater than unity, indicating a higher degree of coordinated chainlike structures. The values of g^{eff} increase with decrease in the concentration of DMF in DE. This pattern suggests a reorientation of neighboring molecules of the constituent polar binary liquids, forming a tendency towards antiparallel alignment of dipoles. Thus, the dipole - dipole interaction occurs in such a way that the effective dipole moment gets increases with the increase in the mole fraction of DMF in DE.

From Fig. 3 (b), it is clear that the values of g_f for the mixture of DE-DMF binary system greater than unity. This trend indicates that the strong molecular interaction between DMF and DE for all 11 concentrations.
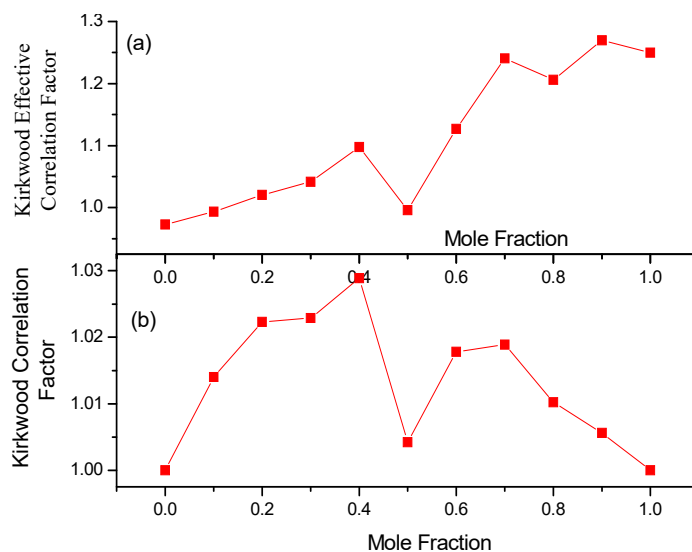
Fig. 3 (a) Kirkwood effective correlation factor (g^{eff}), (b) Kirkwood correlation factor (g_f) versus mole fraction ($\Phi2$) of DMF in DE at 10ºC temperatures

IV. Conclusion

Frequency dependent spectra for DMF-DE system is shown in the beginning. Continue with dielectric parameters, excess properties and Kirkwood parameters are also discussed. The maximum value for static dielectric constant observed for pure DMF liquid in DE-DMF system. The excess permittivity is positive in DMF rich region indicting the DMF work as a structure marker with increasing total effective dipole of the system.

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