

Structural Properties Of Polar Liquids Using Microwave Technique

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Abstract

The complex permittivity spectra of polar liquids in binary mixture has been carried out at the temperature 20C in the frequency range of 10 MHz to 30 GHz using time domain reflectometry at 11 different concentrations. The dielectric properties of solute-solvent mixture in the microwave frequency give information about the formation of monomers and multimers, structural changes, kinematics and dynamics. The least square fit method is used to obtain dielectric properties viz static dielectric constant (ϵ_0), permittivity at high frequency (ϵ_∞) and relaxation time (τ) of binary mixture in the polar liquids. The nature and strength of molecular interactions in liquids have been established as the cause for the behavioural change in chemical compounds.

Keywords: Time Domain Reflectometry, Static Permittivity, Relaxation Time, Excess Parameters.

1. Introduction

The study of dielectric properties gives the information regarding solute-solvent interaction in the binary mixture and also monomers and multimers [1-3], we report the dielectric properties at 20°C temperature for 11 different concentrations. 1,2-dichloroethane (DCE) is a non polar associative liquid and n,n-dimethylformamide (DMF) is a highly polar non associative liquid. One with chloro group and the other with C=O group. It is very interesting to observe the interaction of polar with non polar liquid for 11 different concentrations. The main objective of this paper is to hold brief information of dielectric properties in DCE- DMF system at 20°C using time domain reflectometry at microwave frequency.

The phenomena of dielectric relaxation of binary mixture of like and unlike molecules at microwave frequency has been carried out by many workers [4-8]. DCE and DMF have high polarity and strong solvating

power, which makes them very effective in the industrial and technological applications. The DCE and DMF linkage (-CH₂-CL) and (-NCH₂-C=O) respectively, are an important functional group in field of chemistry, biochemistry, pharmaceutical and material science. The main objective of this paper is to report dielectric properties for DCE and DMF mixture.

2. Experimental

2.1 Material

DCE and DMF (AR grade, Qualigens fine chemical Pvt. Ltd., Bombay, India) were used without further purification. The solutions were prepared at 11 different volume percentage of DCE from 0% to 100%. Using volume percent mole fraction is calculated as

$$x_1 = (v_1\rho_1/m_1)/[(v_1\rho_1/m_1)+(v_2\rho_2/m_2)] \quad (1)$$

where m_i , v_i and ρ_i represents the molecular weight, volume percent and density of the i^{th} ($i=1,2$) liquids respectively.

Table 1: Comparison of static dielectric practical values with literature values [9-11].

Liquids	Properties of liquids		Static permittivity (ϵ_0)	
	Mol.Weight (g/mol)	Density (g/cm ³)	This work	Literature
DCE	98.959	1.2454	10.23	10.42
DMF	73.094	0.9445	38.37	38.25

2.2 Apparatus

The dielectric spectra were obtained by the time domain reflectometry (TDR) technique [12-16]. Tektronix model number DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 has been used for the TDR. A repetitive fast rising voltage pulse with 18ps incident rise time was fed through coaxial line system of impedance 50 ohm. All measurements are carried out in open load condition. Sampling oscilloscope monitors changes in step pulse after reflection from the end of line. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in time window of 5ns and digitized in 2000 points. The nature of reflected pulse with and without sample for DCE and DMF are observed.

3. Data Analysis

The time dependent data were carried out to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range of 10 MHz to 30 GHz using Fourier transformation [15-16]

$$\rho^*(\omega) = (c/j\omega d) [\rho(\omega)/q(\omega)] \quad (2)$$

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 the angular frequency, d is the effective pin length and $j=\sqrt{-1}$.

The effective permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method [17].

The experimental values of ϵ^* are obtained by Debye equation [18]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau} \quad (3)$$

where ϵ_0 , ϵ_∞ and τ are fitting parameters. A nonlinear least square fit method [19] was used to determine the values of dielectric parameters.

4. Results and Discussions

By fitting experimental data in the Debye equation static dielectric constant (ϵ_0) and relaxation time (τ) obtained are listed in table1. The values of static dielectric constant decreases with increase in temperature as expected. However the relaxation time increases and then decreases.

Table2: Static dielectric constant and relaxation time for 11 different concentration of DMF-DCE system

x_2	ϵ_0	ϵ_∞	τ
0 (DCE)	10.23 (0)	2.48	8.84(1)
10	14.00(0)	2.95	12.88(2)
20	17.3(1)	3.07	13.81(1)
30	20.24(0)	3.16	13.89(1)
40	23.48(0)	3	14.06(1)
50	24.19(0)	3.24	14.85(0)
60	28.94(0)	3.51	13.97(0)
70	32.97(0)	3.64	13.89(0)
80	34.07(1)	4.86	13.68(0)
90	37.04(1)	5.61	12.77(1)
100 (DMF)	38.37(1)	4.36	11.77(1)

where x_2 represents the volume fraction of DMF in DCE. Number in the bracket represents error in the corresponding value, e.g., 17.3 (1) means 17.3 ± 0.01 .

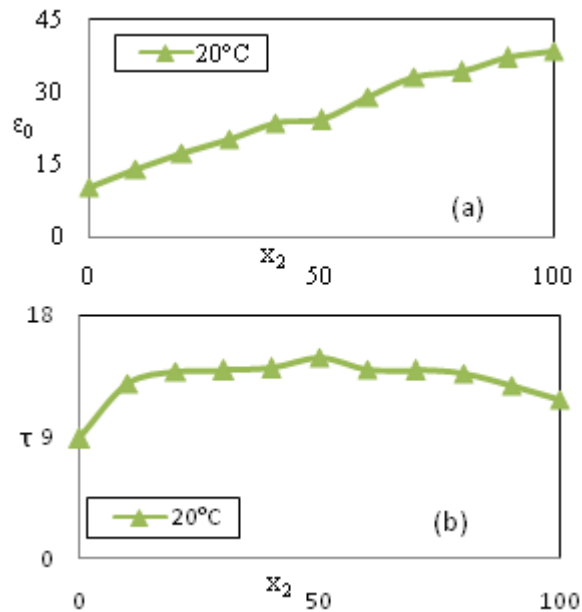


Figure 1.(a) Static dielectric constant (ϵ_0), (b) relaxation time (τ), versus volume fraction (x_2) of DMF in DCE for 11 different concentrations at 20°C.

The information related to liquid 1 and 2 may be obtained by excess properties [20]. ϵ^E is defined as

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_1 x_1 + (\epsilon_0 - \epsilon_\infty)_2 x_2] \quad (3)$$

where x represents mole fraction and suffices $m, 1, 2$ represents mixture, liquid 1(DCE) and liquid 2 (DMF) respectively. The excess permittivity may provide qualitative information multimers formation in the mixture as shown below

- i) $\epsilon^E = 0$ indicates the liquid 1 (DCE) and 2 (DMF) doesn't interact at all.
- ii) $\epsilon^E < 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipoles get reduced. The liquid 1 and 2 may form multimers leading to the less effective dipoles.
- iii) $\epsilon^E > 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipoles moment increases. There is a tendency to form multimers, dipole aligned in parallel direction.
- Similarly, the excess inverse relaxation time defined as

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

where $(1/\tau)^E$ is excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectra line broadening in the resonant spectroscopy [21].

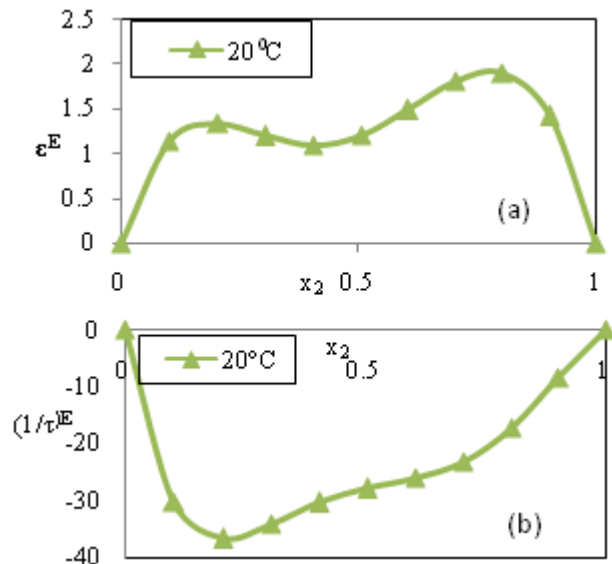


Figure 2. (a) Excess permittivity (ϵ^E), (b) Excess inverse relaxation time $(1/\tau)^E$, versus mole fraction (x_2) of DMF in DCE for 11 different concentrations at 20°C.

The variation of ϵ^E and $(1/\tau)^E$ with mole fraction DMF at 20°C temperature are shown in fig2.

The experimental values of both the excess parameters were fitted to the Redlich Kister equation [22, 23].

$$A^E = (x_1 x_2) \sum_n B_n (x_1 - x_2)^n \quad (5)$$

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).

Conclusion:

Dielectric properties have been reported for DCE-DMF system mixtures for various concentrations at 20°C temperature. This data provides the information about molecular interaction and structural changes. The values of static dielectric constant increase, due to increase in the concentration of DMF in DCE. The relaxation time of DMF is found to be much higher to that of DCE. The value of relaxation time in the solution increases exponentially with an increase in concentration of NMF. The excess properties indicate the structural changes in the system. It is due to intermolecular interaction of the chloro group with C=O bonded liquids.

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