



# Dielectric relaxation studies of binary mixture of diethylene glycol mono phenyl ether and methanol by Time Domain Reflectometry



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## ABSTRACT

The complex permittivity spectra of binary liquid mixtures of diethylene glycol mono phenyl ether (DEGMPE) with methanol (MeOH) were determined in a frequency range of 10 MHz to 25 GHz using Time Domain Reflectometry (TDR) at four different temperatures 283.15, 288.15, 293.15 and 298.15 K, through entire concentration range. The dielectric parameters viz. static permittivity ( $\epsilon'$ ), high frequency limit dielectric permittivity ( $\epsilon'_{\infty}$ ) and relaxation time ( $\tau$ ) have been obtained by CNLS fit method. From the experimental data, parameters such as excess static permittivity ( $\epsilon^E$ ), excess permittivity at optical frequency ( $\epsilon^E_{\infty}$ ), excess inverse relaxation time ( $1/\tau^E$ ), effective Kirkwood correlation factor ( $g^{\text{eff}}$ ), corrective Kirkwood correlation factor ( $g^f$ ) and some thermo-dynamical parameters have been calculated. Excess parameters were fitted to the Redlich–Kister type polynomial equation.

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## 1. Introduction

Observation of interactions between a material and electromagnetic waves provides information about the molecular dynamics of that material. Dielectric spectroscopy, which measures the complex permittivity of a material to time-dependent electric fields, is a suitable technique for investigating molecular dynamics. This measurement technique can cover a very wide frequency range and has been applied to many materials. The new experimental technique has also been applied to the study of the liquid state [1–3], and it has been proven to be a powerful tool for studying molecular dynamics in liquids. Among all liquids, hydrogen-bonded liquids, in particular, have attracted much attention because they exhibit several interesting features attributed to the presence of hydrogen bonds [3]. The dynamics accompanying the recombination of an intermolecular hydrogen bond should reflect the complex permittivity of such liquids in the THz region. The determination of the complex permittivity can aid the elucidation of the hydrogen bonding phenomenon in liquids [1].

Thus, the dielectric measurements have emerged as a tool for the engineers and the scientists to study the dielectric properties as a diagnostic index for material compounds in mixtures [4]. Polar–polar liquid mixtures have been subject to a number of dielectric studies [4–10], which provided important insight into H-bond dynamics.

Recently we studied relaxation of ethylene glycol mono phenyl ether with methanol [10], in a continuation to the previous work, it is aimed to carry out a systematic study on mixtures of diethylene glycol mono phenyl ether (DEGMPE) and methanol (MeOH) and to work out a relaxation model for describing the broadband complex permittivity spectra  $\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega)$  of DEGMPE–MeOH mixtures over the entire mixing range. In this paper, we have reported a detailed dielectric characterization of binary mixtures of DEGMPE and MeOH. The dynamical aspects of the DEGMPE–MeOH solutions have also been examined to gain some information on the expected interactions. Dielectric dispersion data for DEGMPE–MeOH solutions at various concentrations are presented at four different temperatures.

## 2. Materials and sample preparation

DEGMPE (extra pure), MeOH (AR grade) were obtained from HPLC Pvt. Ltd. (India) and were used without further purification. Binary mixtures of DEGMPE with MeOH were prepared at nine concentrations by volume. The concentration was then converted into the mole fraction of component 1, using following formula [10],

$$x_1 = \frac{\rho_1 \times v_1 / M_1}{\rho_1 \times v_1 / M_1 + \rho_2 \times v_2 / M_2} \quad (1)$$

where, M is molecular weight, v is volume and  $\rho$  is density. 1 represents MeOH and 2 represents DEGMPE. The mole fraction is accurate to 0.1%.

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### 3. Experimental methods

The dielectric spectra of DEGMPPE with MeOH mixture were obtained by Time Domain Reflectometry (TDR) technique. Block diagram of TDR experimental setup and measurement method was described in our earlier paper [11].

Fig. 1 shows complex permittivity spectra [ $\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$ ] for the entire molar concentration of MeOH in the frequency range of 10 MHz to 25 GHz at 298.15 K, where  $\varepsilon'(\omega)$  is real component known as dielectric constant and  $\varepsilon''(\omega)$  imaginary component known as dielectric loss.

### 4. Data analysis

To determine the dispersion parameters from the spectra, we have applied Cole–Davidson function [12]

$$\varepsilon^* = \varepsilon_{\infty 1} + \frac{\Delta\varepsilon}{[1 + (j\omega\tau)^\beta]} \quad (2)$$

as the dispersion models in CNLS fitting.  $\varepsilon_{\infty 1}$  is high frequency limit dielectric permittivity,  $\tau$  is the relaxation time,  $\Delta\varepsilon$  is dielectric relaxation strength, and  $\omega$  is the angular frequency, which reaches to Debye function when  $\beta$  equals to unity [12].

The choice of the relaxation model depends on the frequency range accessible by the experiment and on the quality of the data [13]. Since the complex permittivity spectra of DEGMPPE–MeOH mixtures is obtained in the frequency range 10 MHz–25 GHz single C–D/Debye model is used

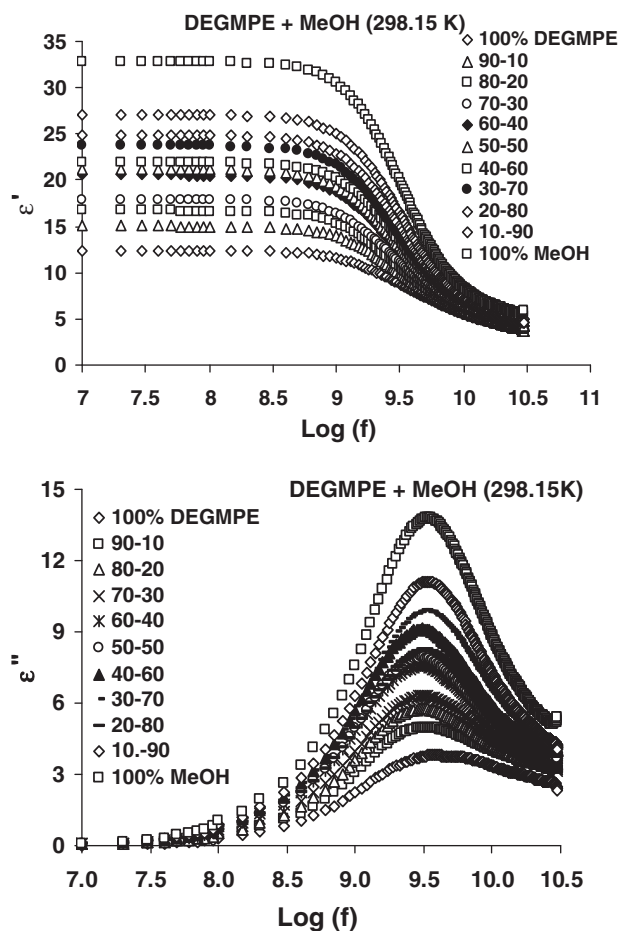


Fig. 1. Measured complex permittivity spectra for binary mixtures of DEGMPPE–MeOH at 298.15 K.

to fit the experimental data and the relaxation parameters are obtained for the main relaxation process.

Equations used to determine Kirkwood correlation factor ( $g$ ), effective Kirkwood correlation factor ( $g^{\text{eff}}$ ), corrective Kirkwood correlation factor ( $g^f$ ), Bruggmann's factor ( $f^B$ ) and excess parameters such as excess static permittivity ( $\varepsilon^E$ ), excess permittivity at optical frequency ( $\varepsilon_{\infty}^E$ ), excess inverse relaxation time ( $1/\tau$ )<sup>E</sup> were described in our previous paper [11].

The energy parameters for dielectric relaxation process ( $\Delta F_E$ ,  $\Delta H_E$  and  $\Delta S_E$ ) have been evaluated employing Eyring's equation [14]

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta F_E}{RT}\right) \quad (3)$$

$$\Delta F_E = \Delta H_E - T\Delta S_E \quad (4)$$

where  $h$  is plank's constant,  $k$  is Boltzmann constant,  $R$  is the gas constant,  $\Delta F_E$  is the molar free energy of activation,  $\Delta H_E$  is the molar free enthalpy of activation and  $\Delta S_E$  is the molar free entropy of activation for dielectric relaxation.

The variations of, excess static permittivity, excess permittivity at optical frequency ( $\varepsilon_{\infty}^E$ ) and excess inverse relaxation time with composition are expressed by Redlich–Kister [15] polynomial equation

$$Q = x_1 x_2 \sum_{r=0}^n a_r (x_2 - x_1)^r \quad (5)$$

where  $Q$  refers all excess parameters. The standard deviations,  $\sigma(Q)$  were defined as

$$\sigma(Q) = \left| \frac{\Phi_{\min}}{P-n} \right|^{0.5} \quad (6)$$

where,  $P$  and  $n$  are the experimental points and parameters respectively.  $\Phi_{\min}$  is the minimum value of the objective function  $\Phi$  defined as

$$\Phi = \sum_{k=1}^N (n_k)^2 \quad (7)$$

where  $n_k = Q_{\text{cal}} - Q$ ,  $Q$  is the experimental value and  $Q_{\text{cal}}$  is evaluated using Eq. (5).

### 5. Results and discussion

Complex plane plots of the measured complex permittivity data over the frequency range of 10 MHz to 25 GHz for binary mixtures of DEGMPPE–MeOH of different concentrations, at 298.15 K, are shown in Fig. 2. Addition of fractional part (10%) of DEGMPPE in MeOH results in domination of glycol ether (Fig. 2). For pure DEGMPPE and higher concentration of DEGMPPE, the Cole–Davidson function gives good fit to the experimental data points (Fig. 2). In previously studied ethylene glycol mono phenyl ether–methanol system, for pure and higher concentration of glycol ether, the Cole–Davidson function gives good fit and methanol rich region Debye function gives good fit whereas the intermediate region (40 and 50% concentrations of ethylene glycol mono phenyl ether) a dynamic transition region was observed [11].

The dispersion parameters for DEGMPPE, MeOH and their binary mixtures of different concentrations at different temperatures were obtained by CNLS fits of the spectra and are presented in Table 1. Dielectric relaxation data for DEGMPPE is not available in literature. Dielectric relaxation study of MeOH is well documented in literature [16–20]. Dielectric relaxation of pure MeOH was discussed in our recent publication [11]; however for completeness, the complex plane plot of MeOH at 298.15 K is reproduced in Fig. 2. The major dispersion part of the spectra of MeOH can reasonably be discussed with Debye model [11] but for the

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