Int J Pharm Bio Sci 2013 Apr; 4(2): (P) 761 - 769

Research Article **Polymer sciences**

International Journal of Pharma and Bio Sciences **ISSN 0975-6299**

DIELECTRIC RELAXATION STUDY OF MIXTURES OF METHANOL AND DIMETHYLAMINOETHANOL USING TIME DOMAIN REFLECTOMETRY

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ABSTRACT

Dielectric relaxation measurements on Methanol – Dimethylaminoethanol solvent mixtures have been carried out across the entire concentration range using Time Domain Reflectometry technique at 15, 25, 35 and 45^{0}C over the frequency range from 10 MHz to 20 GHz. The mixtures exhibit a principle dispersion of the Davidson-Cole relaxation type at microwave frequencies. The Bilinear calibration method is used to obtain complex permittivity $\varepsilon^*(\omega)$ from complex reflection coefficient $\rho^*(\omega)$ over the frequency range 10 MHz to 10 GHz. The excess permittivity (ε^E), excess inverse relaxation time $(1/\tau)^E$, Kirkwood correlation factor (g^{eff}) and thermodynamic parameters are also calculated to study the Solute-Solvent interaction.

KEYWORDS: Dielectric Constant, Relaxation time, Excess parameter, Kirkwood correlation factor, Time Domain Reflectometry

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INTRODUCTION

Microwave energy has been applied directly in many fields especially in scientific research such as communication, microwave-assisted chemistry and in food industry [1,2]. The successful application of microwaves is directly associated with the dielectric properties of the materials. An accurate measurement and working knowledge of these properties are key factors in better understanding the interaction of microwaves with the materials. Dielectric relaxation spectroscopy, for instance, is a powerful tool for examining the underlying physics of solvent systems and for exploring the molecular dynamics of liquids, which is characterized by inter- and intra-molecular structures that vary rapidly with time. The knowledge of frequency dependent dielectric properties of solvent systems is important both in fundamental studies of solvent structure and dynamics and in practical application of microwave heating processes[1]. At a fundamental level, the frequency dependent dielectric behavior of solvent mixtures provides information on molecular interactions and mechanism of molecular processes. The dielectric relaxation behavior of mixtures of polar molecules under varying conditions of compositions is very important as it helps in obtaining information about relaxation processes in mixtures. To compare the influence of the different polar groups in the relaxation mechanism, we have considered it interesting to perform an analogous treatment such as that carried out for binary mixture of primary alcohols – alcohol [3], amine – diamine [4]. For this reason dielectric dispersion study in methanol (ME) with dimethylaminoethanol (DMAE) mixtures over the frequency range of 10 MHz to 20 GHz have been carried out using pico-second Time Domain Reflectometry. The binary system of ME-DMAE selected to understand the effect of amino, hydroxyl and methyl side-group of the dielectric parameters, where the significance is based upon the tetrahedric nature of the – NH_2 group.

MATERIALS AND METHODS

(i) Chemicals

The chemicals used in the present work were dimethylaminoethanol and methanol were of spectroscopic grade and were obtained from ACROS ORGANICS, New Jersey, USA, and Qualigens Fine Chemicals Ottokem, Mumbai, respectively commercially with 99% purity and used without further purification. The solutions were prepared at different volume percentage of ME in IPA in the step of 10% at room temperature. The concentrations were prepared for 5ml solution at room temperature assuming ideal mixing behavior, within 0.02% error limit.

(ii) TDR set-up and data acquisition

The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug in module has been used. After observing TDR response for the sample under study, the time window was kept to 5 ns. By observing TDR response for the sample under study, the SMA sample cell with 1.35mm effective pin length has been used**.** The sample cell holds the liquid under consideration. The physical dimensions of the cell are very important, so one must be careful while designing the sample cell. The impedance of the cell should be matched with coaxial transmission line to which cell is connected. If there is impedance mismatch then unwanted reflections may disturb the wave thereby causing some errors in the measurements. The proper design of cell includes the inner conductor and outer conductor diameters. The length of the inner conductor is called as 'pin length' of the cell and is a very important factor in analysis. The sample length must be enough to avoid unwanted reflections. In total reflection method, the sample length must be long enough to produce an adequate difference signal but short enough to keep less complication of resonance effects at frequencies above the range of interest. The characteristicimpedance of a coaxial line is given by

$$Z = \frac{138}{\sqrt{\varepsilon}} .2 \, Log_{10}\left[\frac{b}{a}\right] \qquad (1)$$

This impedance of our transmission line is frequently 50 Ω. Here 'a' is the diameter of inner conductor and 'b' is the inner diameter of outer conductor. The ε is the relative permittivity of the dielectric between the conductors. Using Teflon and air, and taking appropriate 'a', 'b' a cell can be designed to have a matching impedance of Z = 50 Ω (for air ε = 1 and for Teflon, ε = 2.2). The sample cell consists of standard military applications (SMA) coaxial connector with matching impedance with 3.5 mm inner diameter of outer conductor. The inner conductor of SMA connector itself is considered as 'inner conductor' and hex-nut is treated as an outer conductor. Since these SMA connectors have already been designed for precise 50 Ω impedance, a special design, when used with high frequency, is not required. The physical length of inner conductor can be changed. When a cell is filled with sample above the physical length of inner conductor the fringing effect takes place [5,6]. Due to the fringing field the effective pin length [7] will not be equal to physical pin length. The effective electrical pin length will be more than the physical pin length. The accurate determination of effective pin length 'd' is very important for the accurate evaluation of dielectric parameters. It is found that for SMA type cell, effective pin length[7] is greater than an actual physical length by 0.1 - 0.2 mm.To reduce noise, the time dependent response curve was averaged for 64 times and then stored in TDR oscilloscope memory with 1024 points per waveform. First, the response waveform for the empty cell is acquired and stored in memory and then secondly, the response waveform for sample is acquired and stored in other memory. The empty cell waveform is used as the reference waveform. Both the response waveforms are the reflected waveforms from the sample cell with open termination transmission line. The data acquisition is carried out for 11 concentrations at 15, 25, 35 and 45°C. The temperature of the sample was maintained at a desired value, within the accuracy limit of ± 1°C, by circulating constant temperature water through heat insulating jacket surrounding the sample cell. At each time the response waveforms without sample and with sample were recorded. The time dependent response waveform without sample is referred as $R_1(t)$ and with sample referred as $R_x(t)$.

(iii) Data analysis

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 10 GHz using Fourier transformation as [8,9] where $p(\omega)$ and $q(\omega)$ are Fourier transformations of $(R_1(t) - R_x(t))$ and $(R_1(t) + R_x(t))$, respectively, c

$$\rho^*(\omega) = \left(\frac{c}{j\omega d}\right)\left[\frac{p(\omega)}{q(\omega)}\right] \qquad (2)$$

is the velocity of light, ω is angular frequency, d is effective pin length and j = √-1. The complex permittivity spectra $\varepsilon^*(\omega)$ [10] were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method [11]. The complex permittivity spectra measured using TDR are fitted by the non-linear least square fit method to the Havriliak Negami expression [12] to obtain various dielectric parameters. The accuracy in the measurement of dielectric dispersion ε′ and dielectric loss ε″ values obtained from this technique is within ±5%.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{\left[1 + (i\,\omega\tau)^{(1-\alpha)}\right]^{\rho}} \qquad (3)$$

where $\varepsilon^*(\omega)$ is the complex permittivity at an angular frequency ω, ε_∞ is the permittivity at high frequency, ε_0 is the static permittivity, τ is the relaxation time of the system, α is the shape parameter representing symmetrical distribution of relaxation time and β is the shape parameter of an asymmetric relaxation curve. Equation (3) includes Cole-Cole (β = 1) [13], Davidson-Cole (α = 0) [14] and Debye (α = 0, β = 1) [15] relaxation models. The dielectric model for fitting dielectric parameters suitable for present system is a Debye dispersion model.

RESULTS AND DISCUSSION

Frequency dependence curves for the dielectric dispersion (ε') and absorption (ε″) of ME-DMAE with varying volume fraction of ME at 25°C are depicted in figure 1a and 1b, respectively. In the case of ME-DMAE mixtures, there is a considerable possibility of modifications in these homomolecular clusters, due to molecular interactions between the ME and DMAE molecules. Apart from the complexities in the ME-DMAE mixtures, the observed dielectric dispersion behavior is a simple Debye-type for all the concentrations studied, and this is also the case for the individual molecules.Both the ε′ (Figure 1a) and ε″ (Figure 1b) increase with the increasing volume percentage of ME in the binary mixture ME-DMAE at the low frequency end and decrease at the high-frequency end. The frequency at which the loss factor is a maximum, $f_{max}(\tau = 1/2\pi f_{max})$, shifts to higher values with an increase in the volume percentage of ME in the mixture, corresponding to their individual relaxation times, because the individual molecular values are sufficiently different (i.e. 54 ps and 104 ps) to allow their resolution in practice. However, in a mixture of two associated liquids it seems that the individual principle relaxation processes of the components coalesce, and hence the mixture exhibit a single relaxation time. Earlier, Kumar et. al.,[16] had observed Debye-type behavior in amines (aliphatic/ aromatic)–alcohol mixtures, despite the large differences in the values of individual molecule relaxation times. The values of the dielectric parameters ε_0 and τ obtained from the equation (3) for DMAE, ME and DMAE-ME with the volume fraction of ME at four different temperatures are presented in Figure 2a and 2b, respectively. From figure 2a, it can be observed that the dielectric constant (ε_0) increases with increase in volume percentage of ME in DMAE. Same type of change in ε_0 values has been observed at four temperatures under study. From Figure 2b.It can be seen that by increasing the concentration of ME in DMAE, the relaxation time values decrease towards the corresponding value of ME. With increase in temperature, both static dielectric constant values and relaxation time values decrease was maintaining the same type of change with the corresponding change in the concentration

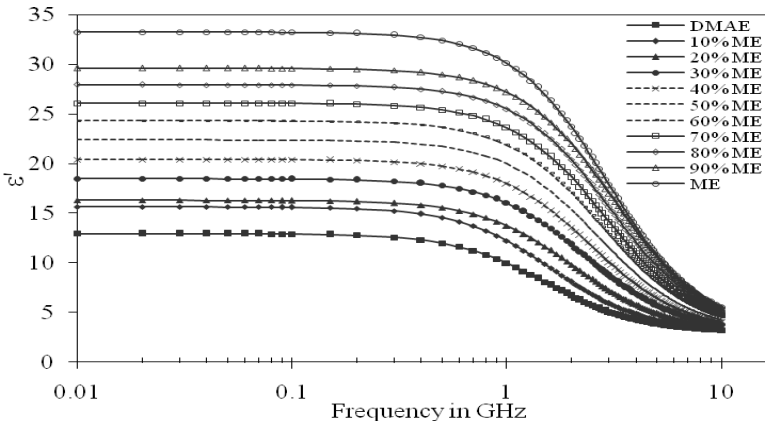

Figure 1a
Frequency dependent of dielectric permittivity (dispersion) ε' curves for Methanol, Dimethylaminoethanol and their mixtures at 25°C

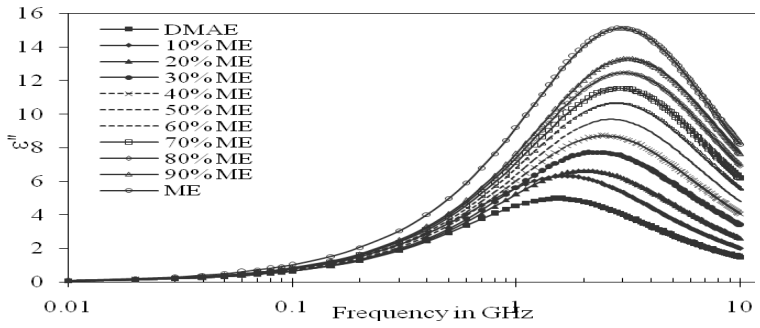

Figure 1b
Frequency dependent of dielectric loss (absorption) ε" curves for Methanol, Dimethylaminoethanol and their mixtures at 25°C

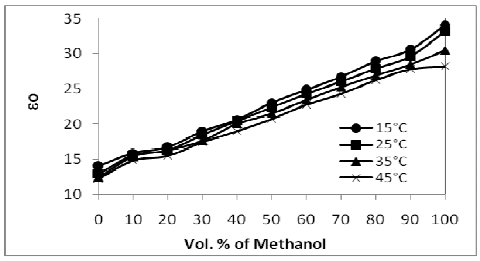

Figure 2a
Variation of ε_o with volume percentage of ME in DMAE at various temperatures.

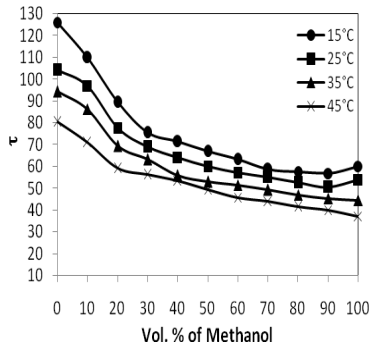

Figure 2b
Variation of τ with volume percentage of ME in DMAE at various temperatures.

The excess parameters [17,18] related to ε_0 and τ provide valuable information regarding interaction between the (solute–solvent) polar–polar liquid mixtures. These properties are also useful for the detection of the cooperative domain in the mixture and may give evidence for the formation of multimers in the mixture due to intermolecular interaction. The excess permittivity is defined as

$$\varepsilon^E = (\varepsilon_{om} - [(\varepsilon_o)_A X_A + (\varepsilon_o)_B X_B)] \qquad (4)$$

where X is the mole fraction and suffixes m, A, B represent mixture, liquid A and liquid B respectively. The excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A + (1/\tau)_B X_B] \qquad (5)$$

which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) from the resonant spectroscopy [19].

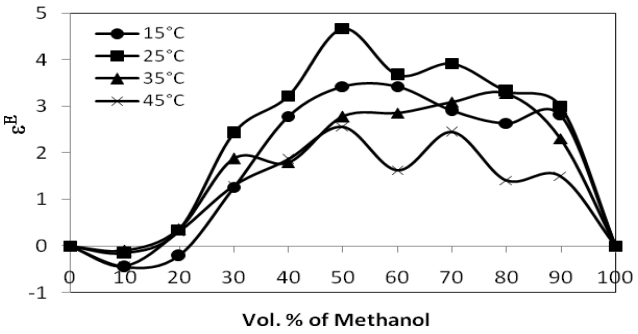

Figure 3a.
Variation of excess permittivity with mole faction of ME in IPA at various temperatures

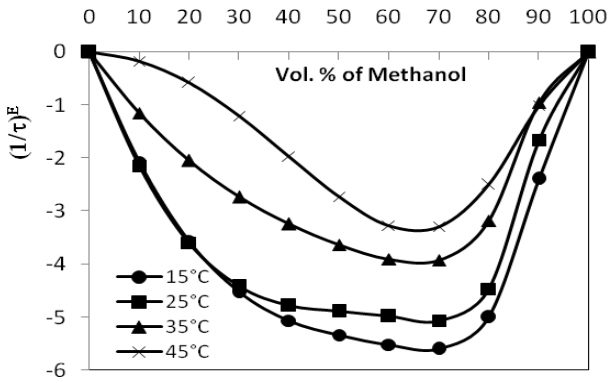

Figure 3b
Variation of excess inverse relaxation time with mole Faction of ME in IPA at various temperatures

The obtained excess permittivity (ε^E) and excess inverse relaxation $(1/\tau)^E$ data for the binary mixture of ME-DMAE are presented in figure 3a and 3b, respectively. The observed ε^E is found to be positive (except around 10% volume percentage of ME) for all concentrations and temperatures. The positive values of ε^E indicate that the total number of dipoles increase in the ME-DMAE mixture which is due to the parallel alignment of the dipoles of the interacting ME and DMAE molecules. From figure 3b, it is found that the $(1/\tau)^E$ values of ME-DMAE binary mixtures are negative over the entire concentration range.

The negative values of $(1/\tau)^E$, indicates the formation of linear structures, probably dimeric and these rotate slowly under the influence of an external varying field.The different molecules are connected by hydrogen bonds, it will be necessary to break these bonds for the dielectric relaxation to be produced. This question has been envisaged by considering the Kirkwood correlation factor g,[20] which itself expresses the existing dipolar correlation between the molecule and its surroundings.The g for pure liquid can be obtained by the expression

$$\frac{4\pi N\mu^2\rho}{9KTM}g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \qquad (6)$$

where μ is the dipole moment, ρ is the density of liquid at temperature T, M is the molecular weight, K is the Boltzmann constant, and N is the Avogadro's number. The effective averaged angular Kirkwood correlation factor (g^{eff}) [21] of the mixed solvents were determined by the following volume fraction-weighted mixture law

$$\frac{4\pi N}{9KT}\left(\frac{\mu_A^2\rho_A}{M_A}\phi_A+\frac{\mu_B^2\rho_B}{M_B}\phi_B\right)g^{eff}=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \qquad (7)$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, and Φ_A , Φ_B are volume fraction of liquid A and liquid B, respectively. Variation of g^{eff} with change in concentration of ME in DMAE is shown in figure 4. The g^{eff} values increase with increase in volume fraction of ME in DMAE mixture. The g values of ME are greater than unity at all temperatures, indicating parallel orientation of molecular dipoles, suggesting the formation of self-aggregates probably due to the formation of intermolecular hydrogen bonds (O–H--O). It is observed that, the g^{eff} values increase with increase in percentage of ME in DMAE. The concentration-dependent non-linear behavior of the investigated mixed solvents confirms the change in dipolar ordering of ME molecules due to their H-bond molecular interactions with DMAE molecules.

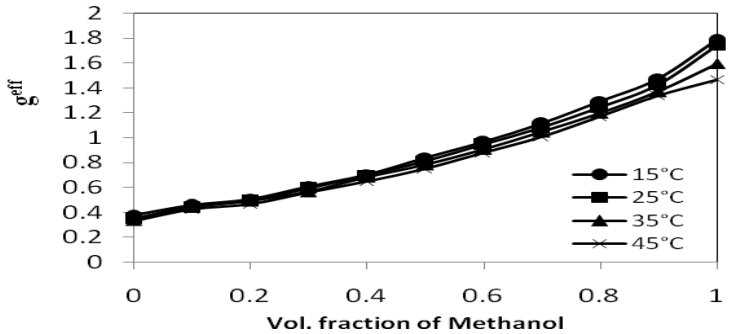

Figure 4.
Variation of g^{eff} with volume percentage of ME in IPA at various temperature.

Since the Arrhenius plots of log τ vs 1/T displayed a good linearity for all the studied liquid mixtures, the kinetic parameters that characterize the molecular mobility in those systems were evaluated using the Eyring formula [22, 23].

$$\tau=\frac{h}{kT}e^{[(\Delta F/RT]} \qquad (8)$$

$$\tau=\frac{h}{kT}e^{[(\Delta H-T\Delta S)/RT]} \qquad (9)$$

where ΔF is the free energy of activation, ΔH is the molar enthalpy of activation and ΔS is the molar entropy of activation of the dipole reorientation process. ΔH is obtained from the slope of ln (τT) versus 1/T. It follows from this equation that, if ΔH and ΔS are independent of the temperature, the plot of ln (τ T) versus 1/T is linear. The order of magnitude of ΔH and ΔS can give some clue to the molecular energy and order of molecules in the relaxation

process. The dielectric relaxation can be treated as a rate process involving a path over a potential barrier [19,23] figure 5 show the free energy of activation (ΔF) of the ME-DMAE mixtures as a function of solution composition at different temperatures. Over the temperature range of 15°C - 45°C, ΔF gradually decreases with increase in mole fraction of DMAE. It is observed that the ΔF values of DMAE are higher than those of ME over the temperature range of 15°C - 45°C. This difference is attributed to the formation of hydrogen bonded networks for ME and DMAE that tend to increase the effective size of a rotating dipole and the dielectric frictional force between the rotating dipole and its neighboring molecules.

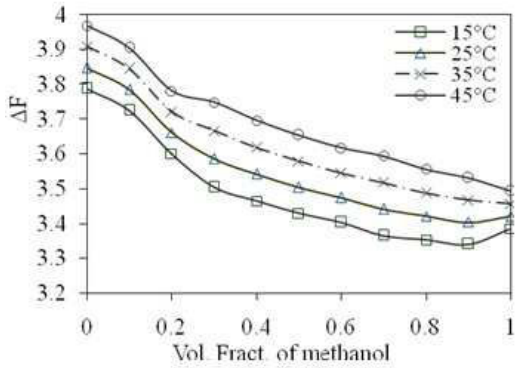

Figure 5
Variation of free energy of activation (ΔF) for the dipolar relaxation for dimethylaminoethanol -methanol binary mixture.

The plot of the change in enthalpy of activation (ΔH) and the change in entropy of activation (ΔS) with variation in volume fraction of ME in ME-DMAE mixtures is shown in figure 6. From this figure it is clear that the ΔH, has got low value at around 0.7 volume fraction of ME, which indicates that less energy is required to achieve group dipole reorientation in this region. It is also found that ΔS values are negative for all compositions in the mixture and same type of nature is observed for ΔS as that of the ΔH. The ΔS for pure DMAE (-0.0254 KJ/mol) is smaller than that of the ΔS value (-0.0150 KJ/mol) for ME. It is also observed that the ΔS values are smaller at around 0.3 volume fraction of ME in ME-DMAE, which indicates that there is a highly ordered group dipole reorientation in this region.

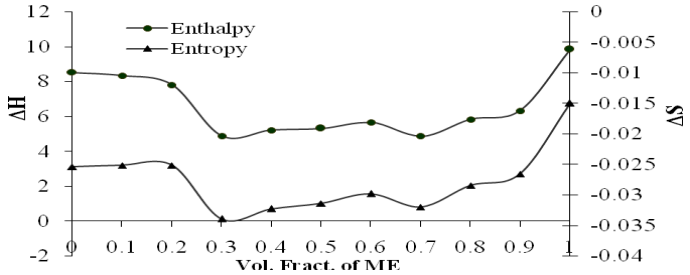

Figure 6.
Variation of enthalpy of activation and entropy of Activation for ME–DMAE binary mixture

CONCLUSION

The dielectric relaxation of binary mixture of methanol in dimethylaminoethanol has been studied using the TDR technique in the frequency range 10 MHz to 20 GHz over the entire concentration at 15, 25, 35 and 45°C. The ε_0 increases where τ decrease with

increase in volume fraction of ME in DMAE. The excess permittivity is found to be positive. The excess inverse relaxation time values are negative for all concentration and temperature indicates the formation of linear structures, probably dimeric and these rotate slowly under the influence of an external varying field. Free energy of activation values decrease with increase in DMAE composition, which suggests that there is more hindrance to the rotation of the DP and DMAE molecule clusters in ME-DMAE in comparison with the rotation of their homogeneous clusters. The systems studied show Arrhenius behaviour.

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