



Microwave dielectric spectra and molecular interaction in a binary mixture of ethanolamine with diethanolamine



A.V. Patil^{*}, V.P. Pawar

Department of Physics and Electronics, Maharashtra Udayagiri Mahavidyalaya, Udgir 413 517, India

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ABSTRACT

Microwave dielectric spectra for binary mixtures of ethanolamine with diethanolamine have been determined over the frequency range of 10 MHz to 20 GHz, at different temperatures, using a time domain spectroscopy (TDS) method at 11 concentrations. The values of the dielectric loss (ϵ'') have been plotted against the dielectric constant (ϵ') in the complex plane. The static dielectric constant (ϵ_0), dielectric constant at high frequency (ϵ_∞), and relaxation time (τ) have been determined using the Debye model, a single relaxation process. The dielectric behavior indicates a change of phase from a semi-solid to a liquid state. The effects of molecular size and number of –OH group molecules on H-bond molecular interactions from Kirkwood correlation factors are presented.

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1. Introduction

The aim of dielectric spectroscopy is to understand intermolecular interactions in a molecular system and the structural changes in liquids due to changes in hydrogen bonding [1–5]. The relative changes in dielectric parameters are important to predict structural changes in liquid. Studies of the dielectric behavior of polar mixtures at different concentrations and temperatures have led to valuable information regarding hydrogen bonding and solute–solvent interaction [6–11].

Ethanolamine (ETA) and diethanolamine (DEA) are highly polar liquids. Examination of the effect of the –OH and –NH₂ group of dielectric properties may provide new information concerning the nature of dielectric polarization and relaxation, since the hydrogen-bonding force of OH–H bonding is generally accepted to be stronger than that of NH–N bonding. Alkanolamine (ETA and DEA) molecules have the combined physical and chemical characteristics of both the alcohols and amines, and hence it is interesting to study the H-bond interaction of an alkanolamine mixture over the entire concentration range by dielectric constant measurements at different temperatures.

The present work is a study of the dielectric behavior and molecular interactions between pure ETA and DEA as well as their mixtures at 11 different concentrations from dielectric properties. Complex permittivities of this system were found over the frequency range of 10 MHz to 20 GHz at various temperatures (278, 283, 288, 293, 298, 301 and 303 K), by employing TDS measurements. Measurements in this frequency range are interesting because the dielectric dispersion of these molecules occurs in the same frequency range. Further the frequency dependent complex permittivity measurements using TDS are more

reliable because a single measurement covers a wide frequency range in a very short time.

2. Experimental section

ETA (AR grade, Qualigens Fine Chemicals Pvt. Ltd., Mumbai, India) and DEA (Spectroscopy, Merck Specialties, Pvt. Ltd., Mumbai, India) were used without further purification. The solutions were prepared at 11 different volume percentages of DEA from 0% to 100%. Using these volume percentages the mole fraction is calculated as

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

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

The complex permittivity spectra were studied using the time domain spectroscopy [12–14] method. A Hewlett Packard HP 54750 sampling oscilloscope with an HP 54754A TDR plug in module was used. A fast rising step voltage pulse with about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system with a characteristic impedance of 50 Ω . The transmission line system under test was placed at the end of a coaxial line in a standard military application (SMA) coaxial connector with a 3.5 mm outer diameter and a 1.35 mm effective pin length. All measurements were carried out under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by a sampling oscilloscope. In the experiment, a time window of 5 ns was used. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ was digitized in 1024 points in the oscilloscope memory and transferred to a PC through a 1.44 MB floppy diskette drive.

^{*} Corresponding author. Tel.: +91 9405619621.

E-mail address: avpattil333@rediffmail.com (A.V. Patil).

The temperature controller system had a water bath and a thermostatically maintained temperature within ± 1 °C. The sample cell was surrounded by a heat insulating container through which water with a constant temperature was circulated. The temperature at the cell was measured with an electronic thermometer.

3. Data analysis

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz using Fourier transformation [15,16] as

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

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

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method [12].

The experimental values of $\varepsilon^*(\omega)$ were fitted with the Debye equation [17].

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

with ε_0 , ε_∞ and τ as the adjustable parameters. A nonlinear least-squares fit method [18] was used to determine the values of dielectric parameters.

Fig. 1 shows the frequency dependence dielectric permittivity (ε') and dielectric loss (ε'') for different concentrations of DEA in ETA at 278 K. The dielectric constant is high in the lower frequency region and decreases with an increase in frequency as shown in Fig. 1(a). The

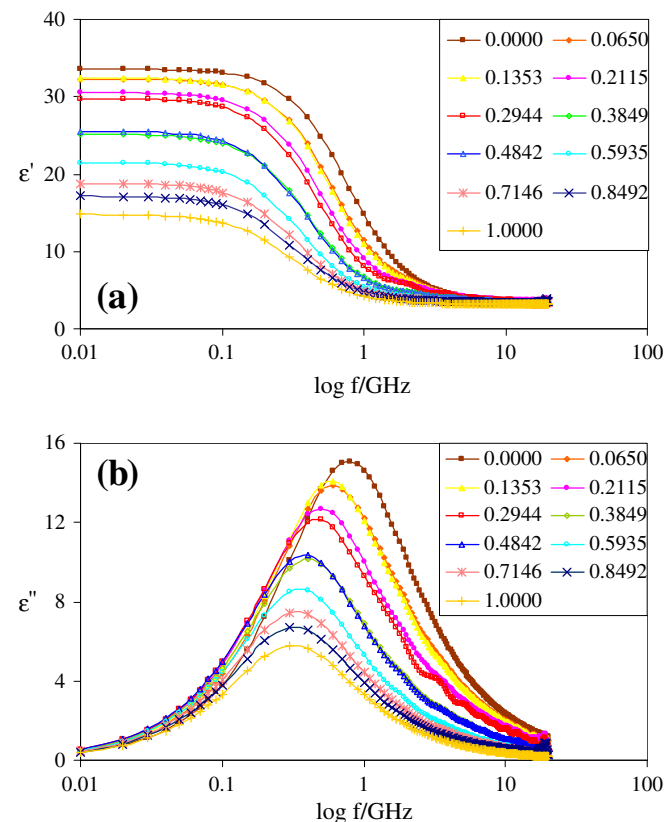


Fig. 1. Frequency dependence (a) dielectric permittivity (ε'), and (b) dielectric loss (ε'') for various concentrations of DEA in ETA at $T = 278$ K.

dielectric loss was studied as a function of frequency for different concentrations at 278 K as shown in Fig. 1(b). The low dielectric loss at high frequencies for the given sample indicates the very high purity of the mixture. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field. Only one relaxation peak is observed for the ETA, DEA and ETA–DEA mixtures. Further, it seems that in the mixture of these liquids, the individual principal relaxation processes of the components coalesce, and hence the mixture exhibits a single relaxation time. The dielectric loss peaks for these molecules and their mixtures are found in the frequency range of 0.4 to 0.8 GHz. The peak of these curves shifted towards lower frequencies when the concentration of DEA increases in ETA.

The complex plane plot for the ETA, DEA and ETA–DEA mixture at 278 K is shown in Fig. 2. The dielectric model for the fitting dielectric parameters suitable for the present system is the Debye model. Therefore the complex permittivity spectra have been fitted in the Debye model along with ε_0 , ε_∞ , and τ .

4. Result and discussion

The values of the dielectric constant and density of pure polar liquids in Table 1 are in good agreement with their literature values [19–22]. The values of the static dielectric constant randomly increase with an increase in the temperatures up to the melting points of ETA and DEA in the system, and then these values smoothly decrease with an increase in temperatures. This behavior of static dielectric constants of ETA and DEA indicates the change of phase from a semi-solid to a liquid state. The values of relaxation time decrease with the increase of temperature, and suddenly drop down at the melting point of ETA and DEA. This rapid decrease in relaxation time also indicates the change in phase from a semi-solid to a liquid state.

In the ETA–DEA system the static dielectric constant decreases with an increase in the concentrations of DEA for all temperatures. The values of relaxation time increase with the increase in concentration of DEA in the system for all temperatures. The variation of the static dielectric constant (ε_0), dielectric constant at high frequency (ε_∞), and relaxation time (τ) with mole fraction of DEA at different concentrations and temperatures are tabulated in Table 2. It is observed that, with the addition of DEA, changes in static permittivity and relaxation time for various concentrations at different temperatures are as follows:

- (i) In the ETA rich region, the values of the static dielectric constant increase with the increase in temperature from 278 to 283 K, and decrease with the increase in temperature from 288 to 303 K. Similarly, in the DEA rich region, these values increase with increasing temperatures from 278 to 301 K and decreases at 303 K.

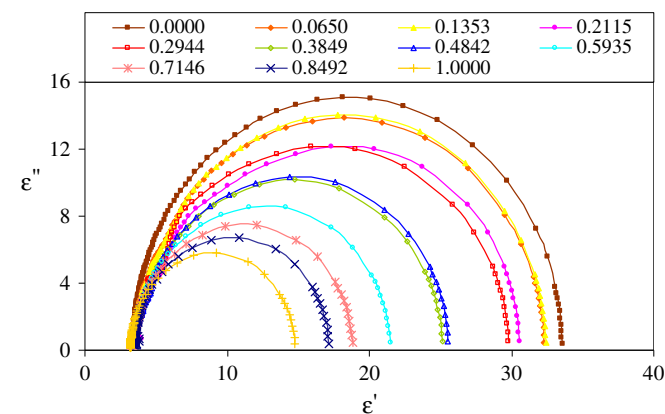


Fig. 2. Complex plane plot of dielectric loss (ε'') vs. dielectric constant (ε') for various concentrations of DEA in ETA and $T = 278$ K.

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