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ABSTRACT

Dielectric relaxation measurements of Allyl Chloride (AC) with Ethanol mixture for different concentrations over the frequency range $10MH_Z$ to $20GH_Z$ at 308K and 318K have been carried out using Picoseconds Time Domain Reflectometry (TDR). Static permittivity (ϵ_0), dielectric constant at high frequency (ϵ_∞) and relaxation time (τ) were found through dielectric measurements. The Bruggeman factor (ϵ_0), Kirkwood correlation factor (ϵ_0), excess static permittivity (ϵ_0), and excess Inverse relaxation time (ϵ_0) were determined and discussed to yield information on the intermolecular interactions and the Dynamics of the mixture of the system.

KEYWORDS

Dielectric relaxation, intermolecular interactions, Bruggeman factor, Kirkwood Correlation factor.

INTRODUCTION

The Knowledge of frequency dependent dielectric properties of binary mixture is important both in fundamental studies of solvent structure determination and its dynamics as well as in the practical application of microwave heating process^{1,2}.At a fundamental level, the frequency-dependent dielectric behaviour of liquid mixture provides information on molecular process. The dielectric relaxation behaviour of mixture of polar molecules under varying conditions of compositions is very important as it helps in obtaining information about relaxation process in mixtures. Thus several investigations on the dielectric behaviour of solvent mixtures in which

dielectric relaxation spectra were used to examine molecular orientations hydrogen bonded networks and micro dynamics of these systems ³⁻⁹

Alcohols play an important role in many chemical reactions due to the ability undergo self-association with manifold structures and are in wide use in industry and science and reagents, solvents and fuels ¹⁰.Lone et al. 11 reported the dielectric parameters for methanol with ethanol mixtures at different concentrations. Sivagurunathan et al. 12 reported the dielectric parameters for acrylic esters with alcohol (primary alcohols) at different temperatures and concentration.

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This paper reports a systematic investigation of dielectric relaxation in binary mixture of Allyl Chloride with Ethanol at different temperatures and for different concentrations in the microwave region (10MHz to 20GHz) by using Time Domain Reflectometry (TDR).

MATERIALS AND METHODS

Chemicals

The chemical used in the present study is Allyl chloride, Ethanol of spectroscopic grade and used without further purification. The solutions were prepared at eleven different volume percentage of Allyl chloride 0% to 100% in steps of 10%.

Using these volume percents the mole fraction is calculated as ¹³⁻¹⁴

$$X_{1} = \frac{\left(\frac{V_{A}\rho_{A}}{M_{A}}\right)}{\left(\frac{V_{A}\rho_{A}}{M_{A}}\right) + \left(\frac{V_{B}\rho_{B}}{M_{B}}\right)}$$
(1)

Where M_A , V_A , ρ_A , M_B , V_B , ρ_B represents the molecular weight, volume percent and density of the liquid A and b respectively.

Apparatus

The complex permittivity spectra were studied using time domain reflectometry. The Hewlett-Packard HP 54750 sampling oscilloscope with HP 54754 a TDR plug- in module was used. A fast rising step voltage pulse of about 39 ps rise

time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance of 50 ohm. The transmission line system under test was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell, coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length.

All measurements were done under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, a time window of 5ns was used. The reflected pulse without sample R1 (t) and with sample Rx (t) were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through a 1.44 MB floppy diskette drive.

A temperature controller system with a water bath and thermostat has been used to maintain the constant temperature within the accuracy limit \pm 1° C. the sample cell was surrounded by a heat-insulating container through which the water of constant temperature using a temperature controller system was circulated. The temperature at the cell is checked using the electronic thermometer

DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over a frequency range 10 MHz to 20 GHz by using Fourier transform ^{15, 16} as

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$$\rho^*(\omega) = \left[\frac{c}{j\omega d}\right] \left[\frac{p(\omega)}{q(\omega)}\right] \tag{1}$$

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 effective pin length and $j=\sqrt{-1}$, $R_1(t)$ is reflected pulse without sample and $R_x(t)$ is reflected pulse with sample. The complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method ¹⁷. The static permittivity and relaxation time constant were obtained using the nonlinear least squares fit method ¹⁸.

The general form of the relaxation model is given by the Havriliak-Negami equation ¹⁹.

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{\left[1 + (j\omega\tau)^{(1-\alpha)}\right]^{\beta}} \tag{2}$$

Where ϵ_s is the static permittivity, ϵ_∞ is the permittivity at high frequency, τ is the relaxation time and α and β are empirical parameters for the distribution of relaxation times

Excess properties

Excess permittivity

For the detection of the cooperative domains in the mixture it is useful to compute the excess permittivity ϵ^E which may be further used to study dynamics of the mixture due to molecular interactions. The excess permittivity ϵ^E is defined as

$$\mathcal{E}^{E} = (\varepsilon_{0} - \varepsilon_{\infty})_{m} - \left[(\varepsilon_{0} - \varepsilon_{\infty})_{A} X_{A} + (\varepsilon_{0} - \varepsilon_{\infty})_{B} X_{B} \right]$$
(3)

Where X- mole fraction and suffices m, A, B represents mixture, liquid A and liquid B respectively. The excess permittivity provides qualitative information about (formation of monomers and multimers in the mixture as follows) structural aspects of the mixture.

If $\epsilon^E = 0$: indicates the liquid A and B do not interact at all.

If $\varepsilon^E < 0$: indicates the liquid A and B interaction in such a way that the total effective dipole gets reduced. This suggests that the liquid A and B may form multimers leading to less effective dipoles or in other words there is a tendency of dipole to align in antiparallel direction.

If $\epsilon^E > 0$: indicates the liquid A and B interaction in such a way that the total effective dipole moment increases. There is a tendency of dipole aligned in parallel direction

Excess inverse relaxation time

The information related to dynamics of the solute-solvent interaction might be obtained by excess properties related to the relaxation time in the mixture. The excess inverse relaxation time is defined as

$$\left(\frac{1}{\tau}\right)^{E} = \left(\frac{1}{\tau}\right)_{m} - \left[\left(\frac{1}{\tau}\right)_{A} X_{A} + \left(\frac{1}{\tau}\right)_{B} X_{B}\right] \tag{4}$$

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Where $(1/\tau)^E$ is the excess inverse relaxation time which represents the average broadening of dielectric spectra. The information regarding the dynamics of solute solvent interaction from this excess property is as follows:

 $(1/\tau)^{E} = 0$: Indicates there is no change in the dynamics of liquid A and B.

 $(1/\tau)^E$ < 0: Indicates liquid A and B interaction produces a field such that the effective dipole rotates slowly.

 $(1/\tau)^{E} > 0$: Indicates liquid A and B interaction produces a field such that the effective dipoles rotate rapidly, i.e., the field will co-operate in the rotation of the dipoles

Kirkwood correlation Factor

The structural information about the liquids from the dielectric relaxation parameters may be obtained using the Kirkwood correlation factor g_f^{20} this factor is also a parameter for obtaining

information regarding orientation of electric dipoles in polar liquids. The g_f for pure

liquid can be obtained from the following expression.

$$\frac{4\pi N \mu^2 \rho}{9 KTM} g = \frac{\left(\epsilon_0 - \epsilon_\infty\right) \left(2\epsilon_0 + \epsilon_\infty\right)}{\epsilon_0 \left(\epsilon_\infty + 2\right)^2}$$
 (5)

where ϵ_0 is static permittivity, ϵ_∞ is permittivity at high frequency, μ is dipole moment in gas phase, ρ is density at temperature T, M is molecular weight, K is Boltzman constant, N is Avogadro's number. A modified form of this equation has been used to study the orientation of electric dipoles in binary mixtures. For the mixtures of two polar liquids, say A and B, equation (6) is modified by assuming that g^{eff} has become the effective correlation factor in the mixture. The Kirkwood equation for the mixture can be expressed as follows $^{21-22}$

$$\frac{4\pi N}{9KT} \left(\frac{\mu_A^2 \rho_A}{M_A} X_A + \frac{\mu_B^2 \rho_B}{M_B} X_B \right) g^{eff} = \frac{\left(\varepsilon_{sm} - \varepsilon_{\infty m} \right) \left(2\varepsilon_{sm} + \varepsilon_{\infty m} \right)}{\varepsilon_{sm} \left(\varepsilon_{\infty m} + 2 \right)^2}$$
(6)

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture with X_A and X_B as volume fractions of liquids A and B, respectively, ϵ_0 is permittivity, ϵ_∞ is permittivity at high frequency, μ is dipole moment in gas phase, ρ is density at temperature T, M is molecular weight, K is Boltzman constant, N is Avogadro's number.



Bruggeman factor

The modified Bruggeman equation 23 is another parameter, which is used to study intermolecular interactions between two (components of) liquids A and B respectively. The Bruggeman factor f_B is given by

$$f_{B} = \left(\frac{\varepsilon_{0m} - \varepsilon_{0B}}{\varepsilon_{0A} - \varepsilon_{0B}}\right) \left(\frac{\varepsilon_{0A}}{\varepsilon_{0m}}\right)^{1/3} = 1 - V \tag{7}$$

According to equation (7) a linear relationship is expected between Bruggeman factor and volume fraction of Allyl chloride. Any deviation from this linear relation indicates existence of intermolecular interactions.

Table 1
Values of Dielectric constants & Relaxation Times at 308K, 318K

mole fraction	τ	τ	03	60
of ethanol	308 K	318 K	308 K	318 K
1	124.02	106.72	23.57	23.01
0.9266	120.42	104.45	22.32	21.52
0.8487	119.02	104.07	19.72	18.72
0.7659	116.07	102.57	17.06	16.06
0.6777	108.75	98.54	14.56	13.76
0.5837	100.32	94.86	12.52	11.82
0.4831	89.44	87.15	10.76	10.26
0.3753	82.14	73.19	9.67	9.07
0.2595	54.88	52.17	8.62	8.22
0.1348	29.22	26.57	8.32	7.84
0	9.57	9.22	7.8	7.56



RESULT AND DISSCUSSIONS

The determined values of static dielectric constant (ϵ_0) and relaxation time (τ) for solution of different concentrations of AC-Ethanol are listed in Table 1, 2. It has been observed that the dielectric constant (ϵ_0) increases as mole fraction of Ethanol increases. As Temperature increases values of dielectric constant decreases. The relaxation time, for the AC-Ethanol system increases with increase in concentration of Ethanol.

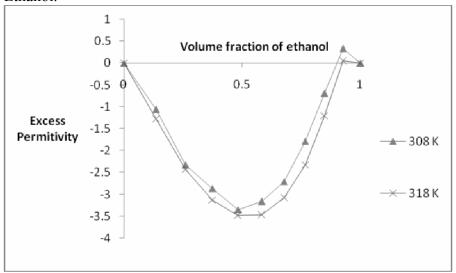


Fig 1. Excess Permittivity of Ethanol + AC at 308K &318K

In an ideal mixture of polar liquids, if the molecules are interacting, a nonlinear variation in dielectric constant and relaxation time with concentration is expected; fig 1, 2 shows the similar results . This confirms the existence of intermolecular interaction in the system. The dielectric relaxation time shows continuous decrease with increase in temperature. As concentration of ethanol decreases values of relaxation time also decreases.



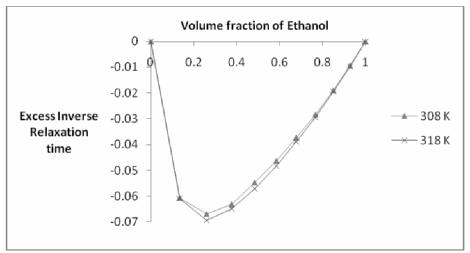


Fig 2. Excess Inverse RelaxationTime of Ethanol + AC at 308K &318K

The excess property related to relaxation time provides significant information regarding interaction between the polar-polar liquid mixtures. The excess relaxation (τ) of mixtures was calculated using eq. (4) and it's variation with mole fraction of AC in Ethanol at 308K, 318K is shown in fig 2. From the figure it is observed that $(1/t)^E$ is negative for entire range of concentration to all temperatures. The negative value of excess inverse relaxation time indicates the slower rotation of the dipoles of the system. Negative values of excess inverse relaxation time show ethanol molecule offers hindrance to the motion of AC molecule. According to Eq. (7) a linear relationship is expected between f_B and mole fraction.

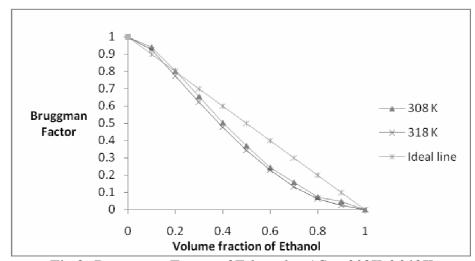


Fig 3. Bruggman Factor of Ethanol + AC at 308K &318K
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The estimated values of f_B are shown in fig.3, which shows the nonlinear relation between f_B and mole fraction of ethanol. The Bruggeman f_B shows a negative deviation to all temperatures from the ideal line. This indicates existence of intermolecular interaction in the mixture.

The Kirkwood correlation factor (g^{eff}) calculated using Eq. (6) is given in Fig 3 and The values of g^{eff} is greater than one shows strong hydrogen bonding between the given system.

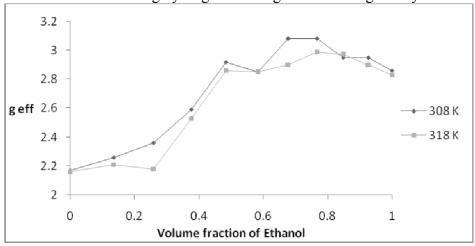


Fig 4. Kirkwood corelation factor for of Ethanol + AC at 308K &318K

CONCLUSION

Dielectric relaxation parameters and Kirkwood correlation factor have been measured for the Allyl Chloride with Ethanol mixture for various concentrations. The dielectric constant increases, with an increase in the percent of AC molecules .These data provide information about the interaction of the molecules in the system.

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