Chapter IV

Section (A): Physical Properties of Acetonitrile, Ethanol and Their Binary Mixture Using Frequency Domain Reflectometry Technique

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4.1 (A) Introduction

Alcohols play an important role in many chemical reactions due to their ability to undergo self-associations with manifold internal structures and are in wide use in industry and as reagents, solvents and fuels [69, 70].

Hydrogen bonds constitute a very interesting class of intermolecular interactions which are extreme importance in many fields of chemistry and molecular biology. In hydrogen bonded complexes a redistribution of electron density can takes place because of three types of interactions namely, electrostatic, polarization and change transfer interaction. Alcohols are excellent proton donors.

Studies of Physiochemical Properties of binary mixtures are of considerable importance in the basic understanding of the nature of the interactions between unlike molecules [71]. Refractive index and density measurements are expected to get rid of some light on both solvent-solvent and solute-solvent interactions [72]. Density, viscosity and refractive index data for the sodium D line of pure components as well binary mixture at different temperatures are important in chemical industries.

The excess properties of binary liquid mixtures are essential for understanding the interactions between molecules of a mixture [73] acetonitrile (CH$_3$CN) a non-hydrogen bonded liquid. Ethanol (CH$_3$CH$_2$OH) is a 2-carbon alcohol and a non-aqueous protic solvent [74]. It is used as an antiseptic and a fuel. It is found in paints, tinctures, markers, mouthwashes, perfumes and deodorants. Thus, because of its large applications, it is hoped that the study of dielectric behavior of acetonitrile, ethanol and their binary mixtures provides useful information about formation of complex in the mixture. In the present chapter, Section (A) we have presented the values of dissipation factor ($D$), dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) obtained experimentally by using surber’s technique at 10.75GHz microwave frequency and at different temperatures (0º, 10º, 20º, 30º and 40ºC). These values are used to calculate loss tangent ($\tan\delta$), molar polarization ($P_{12}$), a. c. conductivity ($\delta_p$), Excess dielectric constant ($\Delta\varepsilon'$), Excess dielectric loss ($\Delta\varepsilon''$), Excess loss tangent ($\Delta\tan\delta$).

The values of viscosity refractive index ($n_D$), density ($d$) viscosity ($\eta$), activation energy ($E_a$) for viscous flow are also calculated. These values of $n_D$, $\eta$, $E_a$ are used to calculated the excess square of refractive index ($\Delta n^2$), apparent excess value of viscosity ($\delta_p$) and Excess activation energy ($\Delta E_a$) at different temperatures and at fixed 10.75 GHz microwave frequency. These parameters have been explained
in terms of molecular interaction between the unlike molecules of acetonitrile, ethanol and their binary mixtures.

4.2 Experimental Details

Acetonitrile (A R grade) purity (Gc) $\leq 10$ Identity IR supplied by Merk KGaA, Darmstadt, Germany and Ethanol, molecular weight 46.07, density 0.789 g/ml at 25°C (4+) supplied by sigma-Aldrich were used without further purification.

The binary mixtures were prepared by mixing acetonitrile + ethanol in proper proportion in volume and then these mixtures were mixed well and kept for six hours in a well stopper bottle to ensure good thermal equilibrium.

Viscosity of pure acetonitrile, pure ethanol and their mixtures were measured at different temperatures 0º, 10º, 20º, 30º and 40ºC by using viscometer brook field engineering laboratories, INC, USA. The density of pure acetonitrile, pure ethanol and their binary mixtures were measured at various temperatures 0º, 10º, 20º, 30º and 40ºC by using DMA 35 portable vibrating density meter, antan paar, Austria(Europe) and with the help of the parts of enhanced ULA adapter ULA-49 EAY water jacket, sample chamber, tube end cap URA-34, ULA-31 EP, ULA-31 EYZ clamping collar URA-OZE of brook field. Engineering laboratories, USA and low temp circulating water both, Nivtech Instruments and engineers, Thane India. Density meter can measure the density of liquid mixtures in the range 0 to 3g/cm$^3$ for temperature range 0º to 40ºC. The refractive index of pure acetonitrile, pure ethanol and their binary mixtures were measured at several temperatures 0º, 10º, 20º, 30º and 40ºC by using Abbe’s refractometer (with glass scale) Mittal enterprises, New Delhi, India with the help of sodium D line.

The x-band microwave bench was used to measure wavelength in dielectric ($\lambda_d$) and voltage standing wave ratio (VSWR) using short circuit plunger. To hold the liquid sample in the closed dielectric cell. A thin mica window is introduced between the cell and rest of microwave bench VSWR and attenuation were neglected. The experimental setup is as shown in figure (3.1) of chapter (III).

Low temperature water circulating bath (ethylene glycol 40%+ distilled water 60%) was used for maintaining required constant temperature of pure acetonitrile, pure ethanol and their binary mixtures for measurement of viscosity, density and refractive index and plunger reading of x-band microwave bench.
Output power is measured by pm-437 power meter, India, rectangular wave
guide working $T_{E10}$ mode 10dB, vidynt yantra udyog, India. The dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) were measured by using surber technique. The details of the experimental procedure are given in article (3.2) of chapter (III).

4.3 Results and Discussion

In recent years, there has been considerable advancement in the theoretical and experimental investigation about the dielectric properties of binary liquid mixtures. Liquid mixtures exhibit various phenomenon, those cannot be found in pure liquid. The most interesting of these are possibly the new types of phase equilibrium, which arise from the extra degrees of varying the proportions of the components. A limited number of studies have been reported for mixtures.

The values of dissipation factor ($D$), dielectric constant ($\varepsilon'$) dielectric loss ($\varepsilon''$) loss tangent (tan$\delta$), molar polarization ($P_{12}$), a. c. conductivity ($\delta_p$) and activation energy ($E_a$) of binary liquid mixtures at different temperatures $0^\circ$, $10^\circ$, $20^\circ$, $30^\circ$ and $40^\circ$C with increasing mole fraction of acetonitrile in the binary mixture (acetonirile + ethanol) are presented in tables [(4.1), (4.2), (4.3), (4.4) and (4.5)] respectively. The values densities, viscosity and refractive index of binary mixture at various temperatures $0^\circ$, $10^\circ$, $20^\circ$, $30^\circ$ and $40^\circ$C with increasing mole fraction of acetonitrile in the binary mixture (acetonitrile + ethanol) are listed in tables (4.6, 4.7, 4.8, 4.9, 4.10) respectively.

4.3.1 Dielectric constant ($\varepsilon'$)

![Dielectric constant vs Mole fraction of acetonitrile](image)
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It is observed that at a given temperature the dielectric constant varies as a function on concentration for binary liquid mixtures. Chandrashekhar [75], has reported as that $\varepsilon'$ decrease with increasing temperature due to combination of the decrease in density and increase in kinetic of the dipoles in the applied electric field [76]. The temperature increases the dielectric constant decreases, our results support this new point. In our present work, it is observed that temperature increases from the dielectric constant and density of pure acetonitrile, pure ethanol and their binary liquid mixtures decreases. Dielectric constant changes because acetonitrile is an aprotic solvent [23]. The values of dielectric constant are all positive values indicating strong interaction between acetonitrile and ethanol molecules. This result obtained for all temp. 0º, 10º, 20º, 30º and 40ºC respectively.

The variation of the dielectric constant ($\varepsilon'$) versus mole fraction ($X_A$) of actonitrile in the binary mixtures at different temperatures 0º, 10º, 20º, 30º and 40ºC and at 10.75 GHz frequency is represented in figure (4.1).

$$CH_3 - CH_2 - O - H \quad \cdots \cdots \quad N \equiv C - CH_3$$

Hydrogen bonding interaction

H-bonding was formed between the H of alcoholic group of ethanol and nitrogen of acetonitrile at different temperature 0º, 10º, 20º, 30º and 40ºC respectively.

In figure (4.1) deviation from linearity, indicates the complex formation in the mixture as suggested by P. Job [30]. The deviation is maximum at about 0.5 mole fraction of acetonitrile in the binary mixture. Hence, there is formation of 1:1 complex in the binary mixtures for temperatures 0º, 10º, 20º, 30º and 40ºC respectively. The curves of figure (4.1) suggest that there is occurrence of intermolecular interaction between acetonitrile and ethanol molecules. Similar behavior obtained kawale et al. [31].

4.3.2 Loss tangent (tan$\delta$)

It is seen from figure (4.2), that the microwave energy absorption in the binary mixture of acetonitrile, and ethanol liquids. A maxima in tan$\delta$ curve occurring at 0.21701 mole fraction of acetonitrile in the acetonitrile + ethanol mixtures at 0º, 10º, 20º, 30º and 40ºC temperatures respectively.
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Dielectric behaviour of some binary liquid mixtures at microwave frequencies

**FIGURE 4.2** Variation of loss tangent (tanδ) versus mole fraction of acetonitrile in the mixture of (acetonitrile and ethanol) at different temperatures

The non linear behavior is expected for alcohols, since both acetonitrile and ethanol are polar liquids and in the mixture of acetonitrile + ethanol liquids a complex may be formed due to H-bond association. Similar result have been obtained by [19,81,32]. It is observed that temperature increases the loss tangent (tanδ) get increases.

This result regarding the formation of complex supported figure (4.2) the complex is formed by our earlier conclusion made from ε’ versus mole fraction plot figure (4.1).

**4.3.3 Molar Polarization (P_{12})**

The solvent – solvent interaction between types of polar protic- solvent is due to hydrogen bonding formation as a result of amphi protic H-bond acceptor- donor (HBA-D) these solvent-solvent interaction property is depends mostly on various physical properties of solvent such as dielectric constant (ε’), dipole moment, molar polarization, donor number[24].

The values of molar polarization (P_{12}) at different temperatures are plotted against the mole fraction of acetonitrile (X_A) shown in figure (4.3).

In present investigation as concentration of acetonitrile in the binary system increases molar polarization get increases. It is due to formation of kamlet taft hydrogen bonding between acetonitrile and ethanol binary system.
Dielectric behaviour of some binary liquid mixtures at microwave frequencies

FIGURE 4.3 Variation of molar polarization versus mole fraction of acetonitrile in the mixture of (acetonitrile and ethanol) at different temperatures

Figure (4.1) and figure (4.3) shows that as dielectric constant ($\varepsilon'$) increases molar polarization also increases it indicates that the solvent – solvent interaction is increases this is due to the formation of hydrogen bonding and this occurred due to the increasing the concentration of more polar solvent.

In our present investigation of acetonitrile + ethanol mixture the amount of complex present is responsible for the nature of polarization wave. Thus this result regarding the formation of complex supported by our earlier conclusion made for the $\varepsilon'$ versus mole fraction of acetonitrile plot. Deviation is maximum at $X_A = 0.322208$, mole fraction of acetonitrile in the binary liquid mixture of acetonitrile + ethanol at different temperatures 0º, 10º, 20º, 30ºand 40ºC respectively.

The value of molar polarization ($P_{12}$) are all positive values for 0º, 10º, 20º, 30º and 40ºC temperatures, indicating strong interaction between acetonitrile + ethanol binary mixtures. Similar nature of graph is obtained [31, 32, 74].

4.3.4 A.c. conductivity ($\delta_p$)

a.c. conductivity of binary mixture is obtained by the formula

$$\delta_p = \omega \varepsilon_o \varepsilon'' = 2\pi f \varepsilon_o \varepsilon''$$

where $\omega = 2\pi f$

$\varepsilon_o = 8.854187816 \times 10^{-12}$ C$^2$/Jm, $\varepsilon''$ = dielectric loss of binary liquid mixtures

$f = 10.75$GHz
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The values of a. c. conductivity is shown in tables (4.1, 4.2, 4.3, 4.4,4.5) at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively.

![Variation of a.c.conductivity (σ_p) versus mole fraction of acetonitrile in the mixture of (acetonitrile and ethanol) at different temperatures](image)

**FIGURE 4.4** Variation of a.c.conductivity (σ_p) versus mole fraction of acetonitrile in the mixture of (acetonitrile and ethanol) at different temperatures

Variation of a. c. conductivity versus mole fraction are shown in figure (4.4) at different temperatures 0º, 10º, 20º, 30º and 40ºC.

In our present work It is found that a. c. conductivity depends upon dielectric loss (ε''). Dielectric loss increases as a. c. conductivity increases and dielectric loss decreases a. c. conductivity decreases. a.c. conductivity is proportional to dielectric loss. Hence, a. c. conductivity is depends upon the dielectric loss [33].

### 4.3.5 Dielectric loss

The variations of dielectric loss (ε'') versus mole fraction of acetoneitrile (X_A) in the binary mixture at different temperature are shown in figure (4.5).

It is observed that  
1) The dielectric loss values increases attaining maxima and again it decreases. Dielectric loss increases may be due to rotational or translational motion of the molecules (increases) occur [78].
2) The dielectric loss got decreased as temperatures of the binary mixtures increases.

Dielectric loss increases with increasing temperature due to the fact that viscosity decreases by increasing temperature [79]. When a dielectric material is
placed in an alternating field, a part of energy is wasted which is known as dielectric loss. This is because of the fact that the reversing nature of the field causes the direction of the dipole to reverse. The dielectric loss depends on the frequency and the mechanism by which the polarization is produced in the material. An ideal dielectric does not absorb electrical energy however, in a real dielectric; there is always a loss of some electrical energy [80].

![Dielectric loss vs mole fraction of acetonitrile](image)

**FIGURE 4.5** Variation of dielectric loss ($\varepsilon''$) versus mole fraction of acetonitrile in the mixture of (acetonitrile and ethanol) at different temperatures

### 4.3.6 Refractive index

Refractive index and excess square of refractive index of the mixtures are used to explain the nature of solvent-solvent interactions.

The values of refractive index of binary mixtures against mole fraction of acetonitrile in the binary mixtures are depicted in tables (4.6, 4.7, 4.8, 4.9, and 4.10) at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively and graph is shown in figure (4.6).

In general, refraction increases with molecular weight for symmetric and non-symmetric molecules. Density and refractive index depends on molecular weight and nature of liquids. In our present work it is observed from figure (4.6) that the values of the refractive indices decreases as increasing mole fraction in the binary mixtures at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively and decreases with increasing temperatures for all mixtures [82]. The deviation may be used for
interpreting the structure interactions in the liquid and liquid mixtures [35]. Similar trend of the values of reference indices is obtained [25, 51].

**FIGURE 4.6** Variation of refractive index \( (n_D) \) versus mole fraction of acetonitrile in the mixture of (acetone and ethanol) at different temperature

### Effect of temperature on refractive index

Refractive Indices of binary mixtures are found to decreases as the temperature increases. This is indicating that the solvent–solvent interaction processes decrease as the temperature increases. Similar decreasing trend of refractive Indices is obtained [53]. Similar nature of graph is obtained [54, 83].

### 4.3.7 Viscosity \( (\eta) \)

The values of viscosities of pure acetonitrile, pure ethanol and their binary mixtures at different temperatures 0º, 10º, 20º, 30º and 40ºC have been given in tables (4.6, 4.7, 4.8, 4.9, 4.10).

In figure (4.7) the graph shows the viscosities got decreased with increasing mole fraction of acetonitrile in the binary mixtures at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively. It is also found that viscosities of pure acetonitrile, pure ethanol and their binary mixture decreases as their temperature increases. As temperature increases, the average speed of the molecules in the binary liquid mixtures increases and the amount of time they spend in contact with their nearest molecules decreases. Therefore, as temperature increases, the average intermolecular forces decreases.
Kenneth Hickey et.al [36] reported similar decreasing result. Pratic Ngoy T shibangh et.al [26] reported ionic liquid viscosity is ordinarily influenced by other interactions such as hydrogen bonding and the symmetry of the ions. Weak types of dipole induced dipole of interactions are not sufficient to produce bulky or less movable entities in system and hence decreased trend of viscosity is observed in the binary mixtures [53, 87]. The values of viscosities are all positive values indicating strong interactions between acetonitrile and ethanol molecules. The viscosity behavior of the binary mixture is mainly due to the changes in the liquid associated structure of alcohol i.e. ethanol [88]. This behavior is characteristics of systems in which at least one of the components exhibits hydrogen bonding [89].

**4.3.8 Density (d)**

The measured values of densities of pure acetonitrile, pure ethanol and their binary mixtures are given in tables (4.6, 4.7, 4.8, 4.9, 4.10) at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively. Figure (4.8) shows the variation of densities verses of mole fraction of acetonitrile in the binary mixtures at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively. It is observed that densities of binary liquid mixtures decrease as mole fraction of acetonitrile in the mixture increases. at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively. It is also observed that the densities of acetonitrile, ethanol and their binary mixtures decrease as their
temperature increases [51]. This is indicating that the solvent–solvent interaction processes decrease as the temperature increase [25, 26, 84, 85, 86].

**FIGURE 4.8** Variation of density (d) versus mole fraction of acetonitrile in the mixture of (acetonitrile and ethanol) at different temperatures

4.3.9 Activation energy ($E_a$)

**FIGURE 4.9** Variation of activation of energy ($E_a$) versus mole fraction of acetonitrile in the mixture of (acetonitrile and ethanol) at different temperatures

It is seen that, activation energy from fig.4.9 get decreases as the mole fraction of acetonitrile in the binary mixture increases. And also get increases as the temperatures of corresponding binary mixture increases 0º to 40ºC respectively.
4.4 Excess parameters

The emergent technology of the today’s world demands the stringent requirement of a process that should be environmentally safe and less expensive. Hence, environmentally viable chemical products and processes are required for the green industry. A large number of efforts have been undertaken since from last few decades to study on binary dielectric parameters of binary mixture. Importance has been given for the study of dielectric behavior, excess properties and thermodynamic behavior of polar-polar and polar-non polar liquid mixtures [103]. However still yet, no linear behavior has been observed in the binary mixtures even the molar concentration of the liquid mixtures varies linearly the deviation from linearity of these parameters which are helpful to understand the nature of bonding between the two liquids [45, 104, 105].

Information of frequency dependent dielectric properties of binary liquid mixtures is important both in basic studies of determination of solvent structure and its dynamics as well as the practical applications. At a fundamental level the frequency dependent dielectric nature of liquid mixtures provides information on molecular interactions and mechanical of molecular process.

Acetonitrile is a non-hydrogen bonded system. Acetounitrile is as a solvent. As an excellent polar aprotic solvent, with a large dipole moment and dielectric constant 36. And allows precise conductometry and potentiometry measurements; yet it is more inert then hydroxylc solvent in that it solvents the majority of the cations and particularly anions much more weakly. It is used in the production of insulin and antibiotic and as a new material in the production naturally occurring pesticides. Ethanol is a 2-carbon alcohol (CH₃CH₂OH). Ethanol is used in the manufacture of alcoholic beverages, as an industrial solvent, in the manufacture of drugs flavorings extracts, and perfumes’ as an antiseptic, as a low freezing and mobile liquid in thermometers and spirit level. Ch V.V. Ramana et.al [23] have studied and explained at a given temperature the dielectric constant varies as a function of concentration for all the binary liquid mixtures and variation of excess dielectric constant with acetonitrile in all binary mixtures shows that they are positive and comparatively less in magnitude. Chandrashekhar [75] has reported as that the temperature increases, the dielectric constant get decreases our results support the view point.
This chapter describes the excess properties and molecular behavior of acetonitrile, ethanol and their binary liquid mixtures. In the present Section (B) we have used the values of dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), obtained experimentally by employing surber’s technique of Section (A) of this chapter. The values of $\varepsilon'$ and $\varepsilon''$ have been calculated by measuring reflection coefficient from air dielectric boundary of binary liquid mixture at 10.75 GHz microwave frequency at different temperatures $0^\circ$, $10^\circ$, $20^\circ$, $30^\circ$, $40^\circ$C and $50^\circ$C.

Using these experimental values of $\varepsilon'$ & $\varepsilon''$ at different temperatures the value of excess dielectric constant ($\Delta\varepsilon$), excess dielectric loss ($\Delta\varepsilon''$) and excess molar polarization ($\Delta P_{12}$) are calculated at different temperatures $0^\circ$, $10^\circ$, $20^\circ$, $30^\circ$, $40^\circ$C and $50^\circ$C. The values of square of refractive indices, viscosities and activation energies for viscous flow are also estimated and used for computation work of excess square of refractive indices $\Delta (n_D)^2$, Excess apparent viscosities ($\delta \eta$) and excess activation energies ($\Delta E_a$).

### 4.4.1 Experimental Details

Acetonitrile (AR grade), supplied by Merck K gardarn stadt. Germany and Ethanol (AR grade) molecular weight 46.07, density 0.789 g/ml at $25^\circ$C supplied by sigma Aldrich were used without further purification. Acetonitrile and Ethanol were mixed according to their proportions by volume and kept for six hours in a well stopper bottle to make sure good thermal equilibrium. The experimental techniques for the measurements of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) were the same as explained in article (3.2) of chapter III. All measurements were carried out at several temperatures $0^\circ$, $10^\circ$, $20^\circ$, $30^\circ$ and $40^\circ$C in a dielectric cell. Low temperature (ethylene glycol 40% + distilled water 60%) circulating bath was used for maintaining required constant temperature of pure actonitrile, pure ethanol and their binary liquid mixtures in a dielectric cell.

The excess values were calculated by using the relation of the form

$$\Delta Y = Y_m - (X_A Y_1 + X_B Y_2)$$

Where $\Delta Y$ any excess parameter and $Y$ refers to the above mentioned quantities the subscripts $m$, 1 and 2 are used in the equation represented. For mixtures component 1 and 2, $X_A$ and $X_B$ are the mole fractions of the two components in the liquid mixtures.
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The values of excess dielectric constant ($\Delta \varepsilon'$), excess dielectric loss ($\Delta \varepsilon''$), excess molar polarization ($\Delta P_{12}$), excess square of refractive index ($\Delta E_a$), Apparent excess value of Viscosity ($\delta \eta$), excess loss tangent ($\Delta \tan \delta$) with increasing mole fraction ($X_A$) of acetonitrile for binary liquid mixture (acetonitrile + ethanol) are listed in tables (4.11),(4.12),(4.13),(4.14),(4.15) at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively.

4.4.2 Excess Dielectric constant ($\Delta \varepsilon'$)

Figure (4.10) shows variation of excess dielectric constant ($\Delta \varepsilon'$) versus mole fraction of acetonitrile in the binary mixtures (acetonitrile + ethanol).

Excess properties of binary liquid mixtures are the measure of deviation from ideal nature of the mixture and found to be highly sensitive towards molecular interactions in the liquid mixtures. For the ideal mixture, the excess parameter is zero, but real mixtures have finite values the excess can be negative or positive depending on the complex formation [90]. The excess dielectric constant $\Delta \varepsilon'$ is such parameter that indicates the strength and intermolecular interactions in binary liquid mixtures.

**FIGURE 4.10** Variation of excess dielectric constant ($\Delta \varepsilon'$) versus mole fraction of acetonitrile in the mixture of (acetonitrile and ethanol) at different temperatures

The excess dielectric constant data provide the following information in relation to the molecular information.

(i) $\Delta \varepsilon' = 0$ indicates that mixtures constituents do not interact and hence have ideal mixing behavior.
(ii) $\Delta\varepsilon' < 0$ indicates the mixtures constituents interact so as to reduce the total number of effective dipoles that contributed to the mixture dielectric polarization;

(iii) $\Delta\varepsilon' > 0$ indicates that the constituents of a mixture interact in such a way that there is an increase in number of effective dipoles contributed in the mixture dielectric polarization.

(iv) The magnitude of $\Delta\varepsilon'$ values is the evidence of the strength of unlike molecular H-bond interactions i.e. higher $\Delta\varepsilon'$ values represent the stronger H-bond unlike molecules connectivity between unlike molecules and vice versa.

(v) The molar concentration corresponding to pronounced maximum $\Delta\varepsilon'$ values represents the stoichiometric ratio of a stable adduct in the mixture.

The observation of excess dielectric constant with acetonitrile in binary mixtures at all temperatures 0º, 10º, 20º, 30º and 40ºC indicates they are positive as well as negative.

At the concentration for which $\Delta\varepsilon'$ is positive indicates that the molecules of the mixture from multimers structure through hydrogen bonding in such a way that the effective dipole moments are increased where as the concentration of $\Delta\varepsilon'$ is negative indicates that molecules of the mixtures from multimers structure through hydrogen bonding in such a way that the effective dipole moment gets reduced.

The multi peaks of excess dielectric constant $(\Delta\varepsilon')$ are observed in the binary mixture at 0º, 10º, 20º, 30º and 40ºC temperatures respectively.

### 4.4.3 Excess dielectric loss

The figure (4.11) shows the excess dielectric loss $(\Delta\varepsilon'')$ shows positive deviation over the entire range of mole fraction of acetonitrile at different temperatures 0º, 10º, 20º, 30º and 40ºC except $X_A= 0.81607$ mole fraction of acetonitrile in the binary mixtures at temperature 40ºC. We observed similar nature of graph for all temperature 0º to 40ºC. Initially excess dielectric loss increases up to $X_A=0.32208$ mole fraction of acetonitrile in the binary mixture after this it decreases at $X_A=0.425114$ after then it reaches maximum at $X_A=0.52589$ mole fraction of acetonitrile in the binary mixture after that mole fraction excess dielectric loss decreases. Hence, complex is at greatest concentration at $X_A=0.52589$ formation of
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1:1 complex in the binary indicating the liquid mixtures at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively.

Here we have accepted that the excess loss is regarded due to molecular motions which are governed by the complex forces of the molecular. Hence, the excess loss is regarded as a parameter which reflects the entropy change in the binary system. Similar nature of graph is obtained [91, 92].

![Graph showing variation of excess dielectric loss (Δε") versus mole fraction of acetonitrile](image)

FIGURE 4.11 Variation of excess dielectric loss (Δε") versus mole fraction of acetonitrile in the mixture of (actonitrile and ethanol) at various temperatures

4.4.4 Excess molar polarization

The values of excess molar polarization (ΔP_{12}) with mole fraction of acetonitrile in the binary mixtures at different temperatures 0º, 10º, 20º, 30º and 40ºC respectively are presented in tables (4.1), (4.2), (4.3), (4.4), (4.5) and graphically represented in figure (4.12). The trend of variation of excess molar polarization is almost positive for all the studied mole fraction of acetonitrile in (actonitrile and ethanol) binary liquid mixture at different temperatures 0º, 10º, 20º, 30º and 40ºC shown in figure (4.12).

The maximum values of excess molar polarization are observed at X_A = 0.52589 mole fractions of acetonitrile in the binary mixtures (actonitrile and ethanol) at various temperatures 0º, 10º, 20º, 30º and 40ºC respectively. This is most probably due to the fact that the parallel alignment of molecular dipoles is the main factor in the aggregated large region where the long range electrostatic interaction take part in the polarization [93].
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The molar polarization substance that allows electron polarizability of molecules in various states of association (gases, liquid, and solid) to be determined it is necessary for computing the dipole moment of the complex from the experimental data. Larger value in the system may be due to the effect of hydrogen bonding in a mixed solvent [47]. Excess molar polarization is the only relation that can be used to recognizes the short range interaction between the dissimilar molecules and similar molecules in the mixtures taking molecular properties of the polar as well as non-polar liquids in the mixture into consideration [94]. The excess values may be due to the specific forces between molecules, such as the physical intermolecular forces.

![Graph showing variation of excess molar polarization (\(\Delta P_{12}\)) versus mole fraction of acetonitrile in the mixture of (acetolnitrile and ethanol) at different temperatures.](image)

**FIGURE 4.12** Variation of excess molar polarization (\(\Delta P_{12}\)) versus mole fraction of acetonitrile in the mixture of (acetolnitrile and ethanol) at different temperatures

This phenomenon is probable for molecular liquids, in which the formation of a lattice or other form of order is apparently associated with an increase in the deviation from the closest packing of the molecules and hence with some volume expansion [92]. Similar nature of graph is obtained [37, 45, 46, 49, 92, 93].

**4.4.5 Excess square of refractive Index (\(\Delta n_0\))^2**

The values of excess square of refractive index of binary liquid mixtures at different temperatures 0º, 10º, 20º, 30º and 40ºC are depicted in tables (4.11, 4.12, 4.13, 4.14, 4.15) and are graphically represented in figure (4.13).
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FIGURE 4.13 Variation of excess square of refractive index ($\Delta n^2_D$) versus mole fraction of acetonitrile in the mixture of (acetonitrile+ethanol) at various temperatures

It is obtained that the values of $\Delta n^2_D$ are positive as well as negative $\Delta n^2_D$ are positive indicating the strong interaction between acetonitrile +ethanol molecules.

$\Delta n^2_D$ are negative indicating weak interaction between the binary liquid mixtures acetonitrile + ethanol molecules. maxima is occurred at $X_A= 0.52589$, $X_A = 0.425114$ mole fraction of acetonitrile in the binary mixture at 0ºC and 30ºC frequency temperature respectively. The curve of $\Delta n^2_D$ suggest of a 1:1 complex in the binary mixture.

4.4.6 Excess activation energy ($\Delta E_a$)

FIGURE 4.14 Variation of excess activation energy ($\Delta E_a$) for acetonitrile and ethyl alcohol system at various temperatures
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The calculated values of excess activation energy ($\Delta E_a$) of binary liquid mixtures at different temperatures 0º, 10º, 20º, 30º and 40ºC are presented in tables (4.11, 4.12, 4.13, 4.14, 4.15) and are graphically represented in figure (4.14).

The values of excess activation energy are found to be negative of over the range of entire concentration of acetonitrile. Indicating that the dispersion forces are dominant in the binary liquid mixtures. It has been reported that the dispersion forces are dominant in the binary liquid mixture where the component molecules have various molecular size. There is weak interaction between the acetonitrile and ethanol molecules Same behavior is obtained [91, 95].

4.4.7 Apparent Excess Value of Viscosity ($\delta \eta$)

Figure (4.15) shows the variation of $\delta \eta$ with mole fraction of acetonitrile in the binary mixture (acetonitrile + ethanol) at different temperatures 0º, 10º, 20º, 30º, 40ºC. The deviations viscosity is influenced by (1) the difference is size and shape of the component molecules and the loss of dipolar association to a decrease in viscosity. (2) specific interactions between unlike molecules such as H-bond formation and change transfer complexes can cause for the increase in viscosity in mixtures rather than in pure component. The former effect produces negative in excess viscosity as well as latter effect produces positive in excess viscosity. Positive value of excess viscosity are indicating of strong interactions whereas negative values indicate weaker interactions.

The negative deviations in viscosity support the core factor of breaking of the self associated alcohols and weak interactions between unlike molecules [106, 107] increases systematically with an increased temperatures of the binary liquid mixtures.

The magnitude and sign of the excess viscosity depend on the fluid composition. It is seen from figure (4.15) that the deviation in viscosity $\delta \eta$ are negative for the whole composition range and at different temperatures 0º, 10º, 20º, 30º, 40ºC. The negative $\delta \eta$ values are generally observed for the systems where dispersion or weak dipole-dipole forces are primarily responsible for the interaction between the component molecules [53, 54, 97, 99, 100]. The negative deviation in excess viscosity values may also be observed due to the difference in molecular size of the component molecules as in the present binary mixture [91]. The excess viscosity becomes less negative and tend towards zero as the temperatures of the mixtures increases i.e. With rise in temperature the system approach towards ideal
behavior [54] is characteristics of system in which at least one of the components exhibits hydrogen bonding (Migul Katz et al [53]).

![Graph showing variation of apparent excess value of viscosity (δη) for acetonitrile and ethyl alcohol system at various temperatures.](image)

**FIGURE 4.15** Variation of apparent excess value of viscosity (δη) for acetonitrile and ethyl alcohol system at various temperatures.

There is intermolecular interaction among the atoms and molecules of the binary mixtures leading to possible hydrogen bond formation between the dissimilar molecules confirming H-bonding formation between acetonitrile and the ethanol mixtures. Figure (4.15) shows for acetonitrile + ethanol system a minimum value of δη at X_A = 0.52589, X_A = 0.322208, X_A = 0.52589, X_A = 0.425114 and X_A = 0.322208 mole fraction of acetonitrile in the binary mixture at different temperatures 0º, 10º, 20º, 30º, 40ºC respectively shows the possibility of hydrogen bonding between acetonitrile + ethanol binary mixture. Same behavior is obtained [50, 53, 91, 101, 102].

Excess values were calculated by using the relation.

\[ \Delta Y = Y_m - (X_A Y_1 + X_B Y_2) \]  

(3.8 of chapter III)

Where \( \Delta Y \) any excess parameter and \( Y \) refers to the above mentioned quantities the subscripts m, 1 and 2 used in the given equation are respectively for the mixture component 1 and 2. \( X_A \) and \( X_B \) are the mole fractions of the two components in the liquid mixtures. It is preferred to define the above equation (3.8) as the apparent excess value of viscosity \( \delta_\eta \) instead of excess viscosity (\( \Delta \eta \)) Shantilal Oswal et al. [49, 96, 97]. It does not represent true excess function as per the definitions excess functions. [98]. the values of \( \delta_\eta \) are small and negative for the binary mixtures.
The binary mixture (acetonitrile + ethanol) shows significant negative excess viscosity probably due to changes in the liquid associated structure of ethanol [20].

The strength of the specific forces is not the factor influencing the viscosity deviation in the liquid mixture. This suggests that combinations of an interactive and non-interactive force are responsible in negative and positive interactions. Ezekiel D. Dikio et. al [55].

4.4.8 Excess Loss tangent (Δtanδ)

![Graph of Excess Loss tangent (Δtanδ) vs Mole fraction of acetonitrile](image)

**FIGURE 4.16** Variation of excess loss tangent (Δtanδ) versus mole fraction of acetonitrile in the mixture of (acetonitrile and ethanol) at different temperatures

The values of excess loss tangent with mole fraction of acetonitrile in the binary mixture (acetonitrile + ethanol) are presented in tables (4.11, 4.12, 4.13, 4.14) and (4.15) at different temperatures 0°, 10°, 20°, 30° and 40°C respectively and graphically represented in figure (4.16).

The values of Δtanδ are positive for 0°, 10°, 20° and 30°C and positive as well as negative for 40°C. Similar nature of graph is obtained [92].
Chapter IV - Section (A): Physical Properties of Acetonitrile, Ethanol and Their Binary Mixture Using Frequency Domain Reflectometry Technique

Table 4.1 Mole fraction of solute ($X_A$), dissipation factor ($D$), dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), loss tangent (tan $\delta$), molar polarization ($P_{12}$), a.c. conductivity ($\sigma_p$) and activation energy ($E_a$) of binary liquid mixtures of acetonitrile and ethanol at 0°C

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Table 4.2 Mole fraction of solute ($X_A$), dissipation factor ($D$), dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), loss tangent (tan $\delta$), molar polarization ($P_{12}$), a.c. conductivity ($\sigma_p$) and activation energy ($E_a$) of binary liquid mixtures of acetonitrile and ethanol at 10°C

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<th>$P_{12}$</th>
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Chapter IV - Section (A): Physical Properties of Acetonitrile, Ethanol and Their Binary Mixture Using Frequency Domain Reflectometry Technique

Table 4.3 Mole fraction of solute ($X_A$), dissipation factor ($D$), dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), loss tangent (tan $\delta$), molar polarization ($P_{12}$), a.c. conductivity ($\sigma_p$) and activation energy ($E_a$) of binary liquid mixtures of acetonitrile and ethanol at 20°C

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Table 4.4 Mole fraction of solute ($X_A$), dissipation factor ($D$), dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), loss tangent (tan $\delta$), molar polarization ($P_{12}$), a.c. conductivity ($\sigma_p$) and activation energy ($E_a$) of binary liquid mixtures of acetonitrile and ethanol at 30°C

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### Table 4.5 Mole fraction of solute ($X_A$), dissipation factor ($D$), dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), loss tangent (tan $\delta$), molar polarization ($P_{12}$), a.c. conductivity ($\sigma_p$) and activation energy ($E_a$) of binary liquid mixtures of acetonitrile and ethanol at 40°C

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</tr>
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<td>5.739011</td>
</tr>
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<td>4.073851</td>
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<td>5.713616</td>
</tr>
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<td>9</td>
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</tr>
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<td>5.610478</td>
</tr>
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<td>5.534651</td>
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### Table 4.6 Mole fraction of solute ($X_A$), mole factor of solvent ($X_B$), density ($d$), viscosity ($\eta$), refractive index ($n_D$), of binary liquid mixture of acetonitrile and ethanol at 0°C

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>$X_A$</th>
<th>$X_B$</th>
<th>$d$ (gm/cm³)</th>
<th>$\eta$ (cP)</th>
<th>$n_D$</th>
</tr>
</thead>
<tbody>
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<td>1</td>
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<td>2.63</td>
<td>1.37</td>
</tr>
<tr>
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<td>0.109723</td>
<td>0.890277</td>
<td>0.8194</td>
<td>2.05</td>
<td>1.369</td>
</tr>
<tr>
<td>3</td>
<td>0.217101</td>
<td>0.782899</td>
<td>0.8192</td>
<td>1.87</td>
<td>1.368</td>
</tr>
<tr>
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<td>0.677792</td>
<td>0.8189</td>
<td>1.7</td>
<td>1.367</td>
</tr>
<tr>
<td>5</td>
<td>0.425114</td>
<td>0.574886</td>
<td>0.8151</td>
<td>1.5</td>
<td>1.366</td>
</tr>
<tr>
<td>6</td>
<td>0.52589</td>
<td>0.47411</td>
<td>0.8141</td>
<td>1.15</td>
<td>1.365</td>
</tr>
<tr>
<td>7</td>
<td>0.6246</td>
<td>0.3754</td>
<td>0.8122</td>
<td>1.1</td>
<td>1.362</td>
</tr>
<tr>
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<td>0.278694</td>
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</tr>
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<td>0.18393</td>
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<td>0.98</td>
<td>1.358</td>
</tr>
<tr>
<td>10</td>
<td>0.90895</td>
<td>0.09105</td>
<td>0.8053</td>
<td>0.95</td>
<td>1.356</td>
</tr>
<tr>
<td>11</td>
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<td>0.8051</td>
<td>0.89</td>
<td>1.355</td>
</tr>
</tbody>
</table>
Chapter IV - Section (A): Physical Properties of Acetonitrile, Ethanol and Their Binary Mixture Using Frequency Domain Reflectometry Technique

Table 4.7 Mole fraction of solute (X_A), mole factor of solvent (X_B), density (d), viscosity (η), refractive index (n_D), of binary liquid mixture of acetonitrile and ethanol at 10°C

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>X_A</th>
<th>X_B</th>
<th>d</th>
<th>η</th>
<th>n_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1</td>
<td>0.8141</td>
<td>1.95</td>
<td>1.367</td>
</tr>
<tr>
<td>2</td>
<td>0.109723</td>
<td>0.890277</td>
<td>0.812</td>
<td>1.53</td>
<td>1.365</td>
</tr>
<tr>
<td>3</td>
<td>0.217101</td>
<td>0.782899</td>
<td>0.81</td>
<td>1.51</td>
<td>1.364</td>
</tr>
<tr>
<td>4</td>
<td>0.322208</td>
<td>0.677792</td>
<td>0.7994</td>
<td>1.21</td>
<td>1.363</td>
</tr>
<tr>
<td>5</td>
<td>0.425114</td>
<td>0.574886</td>
<td>0.7985</td>
<td>1.12</td>
<td>1.361</td>
</tr>
<tr>
<td>6</td>
<td>0.52589</td>
<td>0.47411</td>
<td>0.7976</td>
<td>1.08</td>
<td>1.359</td>
</tr>
<tr>
<td>7</td>
<td>0.6246</td>
<td>0.3754</td>
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</tr>
<tr>
<td>8</td>
<td>0.721306</td>
<td>0.278694</td>
<td>0.7968</td>
<td>0.89</td>
<td>1.355</td>
</tr>
<tr>
<td>9</td>
<td>0.81607</td>
<td>0.18393</td>
<td>0.7949</td>
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</tr>
<tr>
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<td>0.90895</td>
<td>0.09105</td>
<td>0.7941</td>
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<td>1.353</td>
</tr>
<tr>
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<td>0.79</td>
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</tr>
</tbody>
</table>

Table 4.8 Mole fraction of solute (X_A), mole factor of solvent (X_B), density (d), viscosity (η), refractive index (n_D), of binary liquid mixture of acetonitrile and ethanol at 20°C

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>X_A</th>
<th>X_B</th>
<th>d</th>
<th>η</th>
<th>n_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0.7909</td>
<td>1.5</td>
<td>1.361</td>
</tr>
<tr>
<td>2</td>
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<td>0.890277</td>
<td>0.7912</td>
<td>1.3</td>
<td>1.36</td>
</tr>
<tr>
<td>3</td>
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<td>0.782899</td>
<td>0.7899</td>
<td>1.15</td>
<td>1.359</td>
</tr>
<tr>
<td>4</td>
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<td>0.677792</td>
<td>0.7893</td>
<td>1.05</td>
<td>1.357</td>
</tr>
<tr>
<td>5</td>
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<td>0.574886</td>
<td>0.7889</td>
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<td>1.356</td>
</tr>
<tr>
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<td>0.47411</td>
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<td>1.354</td>
</tr>
<tr>
<td>7</td>
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<td>0.3754</td>
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<td>0.85</td>
<td>1.353</td>
</tr>
<tr>
<td>8</td>
<td>0.721306</td>
<td>0.278694</td>
<td>0.7848</td>
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<td>1.349</td>
</tr>
<tr>
<td>9</td>
<td>0.81607</td>
<td>0.18393</td>
<td>0.7842</td>
<td>0.81</td>
<td>1.348</td>
</tr>
<tr>
<td>10</td>
<td>0.90895</td>
<td>0.09105</td>
<td>0.7835</td>
<td>0.79</td>
<td>1.346</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0</td>
<td>0.7827</td>
<td>0.75</td>
<td>1.345</td>
</tr>
</tbody>
</table>
**Chapter IV- Section (A): Physical Properties of Acetonitrile, Ethanol and Their Binary Mixture Using Frequency Domain Reflectometry Technique**

**Table 4.9** Mole fraction of solute ($X_A$), mole factor of solvent ($X_B$), density ($d$), viscosity ($\eta$), refractive index ($n_D$), of binary liquid mixture of acetonitrile and ethanol at 30ºC

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>$X_A$</th>
<th>$X_B$</th>
<th>$d$ gm/cm³</th>
<th>$\eta$ cP</th>
<th>$n_D$</th>
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</thead>
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</tr>
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<td>1.357</td>
</tr>
<tr>
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<td>0.677792</td>
<td>0.7851</td>
<td>0.98</td>
<td>1.354</td>
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<tr>
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<td>1.353</td>
</tr>
<tr>
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<td>0.47411</td>
<td>0.7825</td>
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</tr>
<tr>
<td>7</td>
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<td>0.3754</td>
<td>0.779</td>
<td>0.81</td>
<td>1.347</td>
</tr>
<tr>
<td>8</td>
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<td>0.278694</td>
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</tr>
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<td>0.18393</td>
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<td>0.09105</td>
<td>0.7721</td>
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<td>0.74</td>
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**Table 4.10** Mole fraction of solute ($X_A$), mole factor of solvent ($X_B$), density ($d$), viscosity ($\eta$), refractive index ($n_D$), of binary liquid mixture of acetonitrile and ethanol at 40ºC

<table>
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<th>$d$ gm/cm³</th>
<th>$\eta$ cP</th>
<th>$n_D$</th>
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</tr>
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</tr>
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<td>0.7684</td>
<td>0.8</td>
<td>1.353</td>
</tr>
<tr>
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<td>0.574886</td>
<td>0.7669</td>
<td>0.78</td>
<td>1.349</td>
</tr>
<tr>
<td>6</td>
<td>0.52589</td>
<td>0.47411</td>
<td>0.7655</td>
<td>0.76</td>
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</tr>
<tr>
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</tr>
<tr>
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Table 4.11 Mole fraction of solute (Xₐ), excess molar polarization (ΔP₁₂), excess dielectric constant (Δε'), excess dielectric loss (Δε''), apparent excess value of viscosity (δₙ), excess square of refractive index Δ(n₀)², excess activation energy (ΔEₐ) and excess loss tangent (Δtanδ) of binary mixture of acetonitrile and ethanol at 0°C

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Xₐ</th>
<th>ΔP₁₂</th>
<th>Δε'</th>
<th>Δε''</th>
<th>δₙ</th>
<th>Δ(n₀)²</th>
<th>ΔEₐ</th>
<th>Δtanδ</th>
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</tr>
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<td>0</td>
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<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.12 Mole fraction of solute (Xₐ), excess molar polarization (ΔP₁₂), excess dielectric constant (Δε'), excess dielectric loss (Δε''), apparent excess value of viscosity (δₙ), excess square of refractive index Δ(n₀)², excess activation energy (ΔEₐ) and excess loss tangent (Δtanδ) of binary mixture of acetonitrile and ethanol at 10°C

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Xₐ</th>
<th>ΔP₁₂</th>
<th>Δε'</th>
<th>Δε''</th>
<th>δₙ</th>
<th>Δ(n₀)²</th>
<th>ΔEₐ</th>
<th>Δtanδ</th>
</tr>
</thead>
<tbody>
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<td>-0.105099</td>
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</tr>
<tr>
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Dielectric behaviour of some binary liquid mixtures at microwave frequencies
### Chapter IV- Section (A): Physical Properties of Acetonitrile, Ethanol and Their Binary Mixture Using Frequency Domain Reflectometry Technique

#### Table 4.13 Mole fraction of solute ($X_A$), excess molar polarization ($\Delta P_{12}$), excess dielectric constant ($\Delta \varepsilon'$), excess dielectric loss ($\Delta \varepsilon''$), apparent excess value of viscosity ($\delta_\eta$), excess square of refractive index $\Delta(n_D)^2$, excess activation energy ($\Delta E_a$) and excess loss tangent ($\Delta \tan\delta$) of binary mixture of acetonitrile and ethanol at 20°C

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<th>$\Delta(n_D)^2$</th>
<th>$\Delta E_a$</th>
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#### Table 4.14 Mole fraction of solute ($X_A$), excess molar polarization ($\Delta P_{12}$), excess dielectric constant ($\Delta \varepsilon'$), excess dielectric loss ($\Delta \varepsilon''$), apparent excess value of viscosity ($\delta_\eta$), excess square of refractive index $\Delta(n_D)^2$, excess activation energy ($\Delta E_a$) and excess loss tangent ($\Delta \tan\delta$) of binary mixture of acetonitrile and ethanol at 30°C

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### Table 4.15 Mole fraction of solute ($X_A$), excess molar polarization ($\Delta P_{12}$), excess dielectric constant ($\Delta \varepsilon'$), excess dielectric loss ($\Delta \varepsilon''$), apparent excess value of viscosity ($\delta_\eta$), excess square of refractive index $\Delta(n_D)^2$, excess activation energy ($\Delta E_a$) and excess loss tangent ($\Delta \tan\delta$) of binary mixture of acetonitrile and ethanol at 40°C

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Section (B) Dielectric Relaxation and Thermodynamic Parameters of Acetonitrile, Ethanol and Their Binary Mixtures In Benzene

4.5 (B) Introduction
4.6 Experimental Measurements
4.7 Determination of Thermodynamic Parameters
4.8 Results and Discussion
4.5 (B) Introduction

Investigations of dielectric properties of materials or molecules provide information about the structure of the molecules. This information is required in many areas of science and technology. Many researchers have attempted to obtain information about inter and intra molecular interactions in the binary mixture as well as ternary mixture of molecular systems of industrial, biological and pharmaceutical importance [108, 109].

Dielectric relaxation of liquid mixtures at the microwave frequency range is investigated to characterize different types of molecular interactions such as solute-solute, solute-solvent as well as self-association in the solution. This is because of the capacity of microwaves to detect the weaker molecular interactions [110, 111, and 112]. Raman Kumar et.al [67] has studied Dielectric relaxation studies of binary mixtures of tetrahydrofuran and N. methylacetamide in benzene solutions using microwave absorption data. Mehrotra N.K. et.al [113] have studied dielectric investigation of relaxation in same heterocyclic compounds. Dielectric relaxation studies of binary mixtures of chlorobenzene and ethyl alcohol in Benzene solution from microwave absorption data have been studied by Sharma Vimal et.al [114]. They observed a linear dependence of the relaxation time on the increase of the mole fraction of temperature in the binary mixtures (ethanol + Chlorobenzene) at all temperature. The frequency and temperatures dependent dielectric behaviour of liquid mixtures provides information on molecular interactions and mechanisms of molecular process.

Acetonitrile is a dipolar solvent. The acetonitrile liquid is a non hydrogen bonded system. It has been used as a solvent in molecular dynamics investigations of molecular processes in solutions [115, 116]. It is used as a solvent in biochemistry electrochemistry, and also in pharmaceutical and technological industries [117, 118]. Ethanol is a volatile solvent. Ethanol is a non aqueous protic solvent [119,120]. Ethanol is a 2 carbon alcohol with molecular formula CH$_3$ CH$_2$OH It is used in thermometers as a solvent and as a fuel. Ethanol is used in herbal medicines products and tinctures the use of ethanol is necessary for extraction of Some Constituents that are important for efficacy [2]. This motivated the authors to perform experimental study concerned with dielectric relaxation Process in binary mixtures diluted in benzene at different temperatures using 10.75 GHz microwave frequency.
In the present chapter IV we have reported the dielectric constant ($\varepsilon'$), and dielectric loss ($\varepsilon''$) for acetonitrile + ethanol binary mixture diluted in benzene at different molar concentration and different temperatures at 283ºK, 293ºK, 303ºK, 313ºK, 323ºK at 10.75GHz microwave frequency. Dielectric data was used for determination of relaxation time ($\tau$). The energy parameters free energy of activation, enthalpy, and entropy for viscous flow process has been computed for acetonitrile ethanol binary mixture diluted in benzene. Using energy parameters, we have been explained solute-solute, solute- solvent interactions in the mixture system.

4.6 Experimental measurements

Ethanol, Molecular weight 46.07, density 0.789g/ml at 25ºC, supplied by Sigma-Aldrich. Acetonitrile (AR Grade) supplied by Merck K GaA, Darn Stadt Germany and benzene (AR) C6H6. M.W 78.11 g/mol density 0.88 g/cm3, ventch Tm reagent grade Sigma Aldrich chem. Pvt. Ltd. Bangalore, India. Were used without further purification. The procedure for preparation of solution (acetonitrile + ethanol ) diluted in benzene was used similar explained in chapter III Section (B).

The same experimental setup shown in figure (3.1) of chapter III of X-band microwave bench used to measure the $\lambda_d$ in the dielectric medium. Microwave absorption of experimental techniques of Heston [16] and Equations (1) and (2) of chapter III Section (B) were used to calculate $\varepsilon'$ and $\varepsilon''$ at different temperatures 10º, 20º, 30º, and 40ºC at 10.75GHz microwave frequency.

The viscosity of benzene was measured at different temperatures 10º, 20º, 30º, 40º and 50ºC by using viscometer brook field DV-II + Pro.model LV DV-II +P Brook, USA. The calculated values of $\varepsilon'$ and $\varepsilon''$ are listed in tables (4.16 to 4.20) several temperatures at several temperatures 10º, 20º, 30º, 40º and 50ºC respectively. The measured values of viscosity of benzene are presented in table (3A of chapter III section (B)). The use of dilute solution helps to minimize the effect of molecular interactions, internal field, viscosity and other factors [1, 2].

4.7 Determination of thermodynamic parameters

The dielectric relaxation time ($\tau$) was determined by Gopal Krishna method [12] of equation ($\tau$) of chapter III. The values of dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and relaxation time ($\tau$) are presented in tables (4.16 to 4.20) at different temperatures 10º, 20º, 30º, 40º and 50ºC respectively.
The energy parameters free energy ($\Delta F_\tau$), enthalpy ($\Delta H_\tau$) and entropy ($\Delta S_\tau$) for the dielectric relaxation process and the corresponding parameters $\Delta F_\eta$, $\Delta H_\eta$ and $\Delta S_\eta$ for the viscous flow have been calculated by using eyring’s relaxations [11] for rate process.

4.8 Results & Discussion

Dielectric constant ($\varepsilon'$) is the measure of efficiency of transfer of electric force dielectric loss ($\varepsilon''$) is the measure of dissipation of energy in the medium. The calculated values of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) and relaxation time ($\tau$) for pure acetonitrile pure ethanol and their binary mixtures for different temperatures are depicted in tables (4.16 to 4.20) at 10°, 20°, 30°, 40° and 50°C temperatures. It is seen from table (4.16 to 4.20), the values of dielectric constant ($\varepsilon'$) increases with increase the mole fraction of acetonitrile in the mixture of (acetonitrile+ ethanol) in benzene.

The figure (4.17 to 4.21) shows that dielectric constant is in increasing trend with increasing mole fraction of acetonitrile in the mixture of (acetonitrile+ ethanol) in benzene.

**FIGURE 4.17** Variation of the dielectric constant ($\varepsilon'$) with the weight fraction of (w) of the solute at 0 mole fraction of acetonitrile in (acetonitrile+ethanol) binary mixture in benzene at 20°C
Chapter IV- Section (B): Dielectric Relaxation and Thermodynamic Parameters of Acetonitrile, Ethanol and Their Binary Mixtures In Benzene

Dielectric behaviour of some binary liquid mixtures at microwave frequencies

![Graph](image-url)

**FIGURE 4.18** Variation of dielectric constant ($\varepsilon'$) with the weight fraction of the solute at mole 0.176471 fraction of acetonitrile in (acetonitrile + ethanol) binary mixture in benzene at 20°C

![Graph](image-url)

**FIGURE 4.19** Variation of dielectric constant ($\varepsilon'$) with the weight fraction of the solute at mole 0.333333 fraction of acetonitrile in (acetonitrile + ethanol) binary mixture in benzene at 20°C
Chapter IV - Section (B): Dielectric Relaxation and Thermodynamic Parameters of Acetonitrile, Ethanol and Their Binary Mixtures In Benzene

**FIGURE 4.20** Variation of dielectric constant ($\varepsilon'$) with the weight fraction of the solute at 0.666667 mole fraction of acetonitrile in (acetonitrile + ethanol) binary mixture in benzene at 20°C

**FIGURE 4.21** Variation of dielectric constant ($\varepsilon'$) with the weight fraction of the solute at 1 mole fraction of acetonitrile in (acetonitrile + ethanol) binary mixture in benzene at 20°C
The relaxation time gives the time taken by electron in a condition to the equilibrium condition after the applied electric field is turned off.

The relaxation time depends on the size as well as shape of the rotating molecular entities in the solution; this technique determines the average value of the relaxation time for the molecular. The linear change of the relaxation time from its value corresponding to one component to the value which corresponds to the pure other component with varying mole fraction in the whole concentration range may be taken s the absence of any solute - solute association in the mixture [12].

On the other hand the non-linear variation of the relaxation time with the mole fraction is interpreted as a possible solute –solute intermolecular association in the binary mixture [122].

The values of relaxation time ($\tau$) vary non-linearly with the increase in the binary mixtures (acetonitrile+ ethanol) at all temperatures. (10º, 20º, 30º and 40ºC) as shown in figure (4.22). The relaxation time ($\tau$) of pure compounds and their binary mixture decreases with increase in temperatures. This may be due to fact that increases in temperature causes the rate of loss of energy due to large number of collisions and hence the molecules reorient with faster rate while field changes its direction similar result have been obtained [123].

The average relaxation time ($\tau$) decreases gradually with the increases of mole fraction of solute in all the binary mixtures, this may possible due to increases in the molar volume. The dielectric absorption or relaxation time by its molecule is not solely contributed by their rotation as single unit, but also contains contribution from the intra molecular rotation of mixtures.

It is concluded that in the mixtures, the intra molecular rotations are dominant as compared to the intermolecular rotation the average relaxation time decreases with increasing mole fractions may be attributed to decreasing the effective radius of the rotating unit. The relaxation time is frequency dependent phenomenon [124].

The relaxation times ($\tau$) for the mixture (acetonitrile + ethanol) in benzene at different temperatures do not lie be the values for the individual components, so in the mixture, it is concluded that although the polar molecules retain their own characteristic dielectric behavior the relaxation times largely on the change in the molecular environment and other related factors. Hence apparent necessarily lie between those of the individual constituents [125]. It is increasing to note that the
relaxation times $(\tau)$ of (acetonitrile + ethanol) in benzene decreases non linearly with increases in mole fraction of acetonitrile in the binary system and falls towards the value of pure acetonitrile in the benzene solution. The behavior of the curves indicates solute-solute type of molecular association between acetonitrile and ethanol binary mixture.

**FIGURE 4.22** Relaxation time $(\tau)$ versus mole fraction of acetonitrile in (acetonitrile+ ethanol) mixture in benzene solution at different temperatures

The value of relaxation time $(\tau)$ is found to be maximum at 0.0 mole fraction of pure ethanol where as lower value for 1.0 mole fraction of acetonitrile in the binary mixture at all temperatures from 10° to 40°C.

The relaxation time $(\tau)$ suddenly decreases from 0.0 mole fraction of acetonitrile to 0.176470588 mole fraction of acetonitrile then slightly increases at 0.333333 mole fraction of acetonitrile then again decreases. Thus, solute-solute type of molecular association is predicted in the whole concentration range in the binary mixture.

The values of relaxation time are observed to decrease systematically with increase in temperature from 10° to 50°C for the pure components as well as for the binary mixtures (acetonitrile + ethanol) diluted in benzene this may be possible because of the increase in the molar volume, in increase in size of the dipole with increase in the temperature and the rate of loss of energy due to the large number of
collisions and hence the molecules reorient with faster rate while field changes its directions.

Molecular association arising because of the interaction of negative fractional charge at the site of nitrogen atom in the acetonitrile molecule and active positive hydrogen atom of ethanol.

Figure (4.23) shows the molecular association between ethanol and acetonitrile arising from the H-bonding between the hydrogen atom of ethanol and nitrogen atom of the acetonitrile molecule.

H-bonding was formed between the H of alcoholic group of ethanol and nitrogen of acetonitrile at different temperature 10º, 20º, 30º, 40º and 50ºC respectively.

\[\text{FIGURE- 4.23 Solute- solute interaction of (acetonitrile and ethanol) in benzene.}\]

Using equations 3.15, 3.16, 3.17, 3.18 of chapter III section (B) the energy parameters \(\Delta F, \Delta H, \Delta S\) of the dielectric relaxation process in the binary mixture of (acetonitrile + ethanol) in benzen have been calculated. These energy parameters have been compared with the viscosity parameters for the flow of benzene solution as shown in table (4.21).

The enthalpy of activation depends on the ambient environment of the molecules. The enthalpy of activation \(\Delta H_r\) of the dielectric relaxation process is found to be dissimilar from the enthalpy of activation \(\Delta H_\eta\) of viscous flow process. This variation shows that the dielectric relaxation process comprises different types of bonding and a breaking of the bond to different extents. It is also evident that, for individual components and their binary mixtures, the molar enthalpy of activation \(\Delta H_r\) values are greater than the corresponding \(\Delta F\) values resulting the positive entropy \(\Delta S_r\) of activation. The ratio of enthalpies of activation for relaxation and viscous flow processes \(\Delta H_r / \Delta H_\eta\) for 0%, 30%, 50%, 80% and 100% of acetonitrile in (acetonitrile + ethanol) binary mixtures is more than 0.6. According to Krishnaji and Mansingh classification [182]. Polar liquids for which \(\Delta H_r / \Delta H_\eta\) ratio is less than 0.45 should show a solid rotator phase but those for which it is greater than 0.55 do not show solid rotator phase for all mixtures and pure compounds. The values of
enthusiasm of activation for dielectric relaxation and viscous flow suggest that there is non-existence of the solid rotator phase.

It is also suggested that for non-aggregated polar liquids, the free energy of activation for rotation and for viscous flow would be $\Delta F_r < 0.5 \Delta F_\eta$. in the current study, $\Delta F_r$ is less than $\Delta F_\eta$. The rotator phase molecules are usually nearly spherical in form and can reorient without demanding translation displacement for dielectric relaxation.

The positive values of $\Delta S_r$ for activated process indicate that activated state is disordered in comparison to normal state as dipoles are more non-aligned in the activated state [109]. It is also found that enthalpy of activation ($\Delta H_r$) of the dielectric relaxation process is greater than enthalpy of activation ($\Delta H_\eta$) of viscous flow process.

Entropy of the system is a measure of disordered or randomness of the system Branin F.H. et.al [66]. Ordered system has low entropy, a disordered system has high entropy. suggest that the negative values of the entropy of activation indicates that a comparatively smaller number of configurations is possible in an activated state, which is more ordered in comparison to the normal state. This again indicates that presence of co-operative orientation of the molecules by the steric forces or by strong-dipole-dipole interactions with the dipole being better aligned in an activated state. However, positive value of the activation entropy indicates that the activated state is more disordered.

In the present work, it is found that the change in entropy ($\Delta S_r$) of the dielectric process is positive indicating that the environment of the system is non-co- operative.

It is also observed that the change in entropy ($\Delta S_\eta$) for viscous flow process is negative showing that the environment of the system is co-operative and activated state is more ordered in comparison to the normal state. This indicates that the presence of a co-operative orientation of the molecules by the steric forces or by strong dipole-dipole interactions with the dipole binary better aligned in an activated state. Similar positive values of ($\Delta S_r$) and negative values of ($\Delta S_\eta$) are obtained [68].
Table 4.16 Dielectric constant, dielectric loss, relaxation time of different mole fraction ($X_{\text{Acetonitrile}}$) of acetonitrile in (acetonitrile+Ethanol) binary mixture in benzene at 10°C

<table>
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<th>MoleFraction ($X_{\text{Acetonitrile}}$) of acetonitrile in (Acetonitrile + Ethanol) binary mixture in benzene</th>
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Table 4.17 Dielectric constant, dielectric loss, relaxation time of different mole fraction \( (X_{\text{Acetonitrile}}) \) of acetonitrile in (acetonitrile+Ethanol) binary mixture in benzene at 20°C

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<th>( \varepsilon'' )</th>
<th>( \tau ) sec</th>
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### Table 4.18 Dielectric constant, dielectric loss, relaxation time of different mole fraction ($X_{\text{Acetonitrile}}$) of acetonitrile in (acetonitrile+Ethanol) binary mixture in benzene at 30°C

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Dielectric behaviour of some binary liquid mixtures at microwave frequencies

Table 4.19 Dielectric constant, dielectric loss, relaxation time of different mole fraction ($X_{Acetonitrile}$) of acetonitrile in (acetonitrile+Ethanol) binary mixture in benzene at 40°C

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### Table 4.20

Dielectric constant, dielectric loss, relaxation time of different mole fraction (X_{Acetonitrile}) of acetonitrile in (acetonitrile+Ethanol) binary mixture in benzene at 50°C

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<th>ε'</th>
<th>ε''</th>
<th>τ</th>
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### Table 4.21

Free energies of activation ($\Delta F_r$, $\Delta F_\eta$ in kcal mole\(^{-1}\)), enthalpies of activation ($\Delta H_r$, $\Delta H_\eta$ in kcal mole\(^{-1}\)) and entropies of activation ($\Delta S_r$, $\Delta S_\eta$ in cal mole\(^{-1}\)°K) for acetonitrile, ethanol and their binary mixture in benzene at different temperature.

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<tr>
<th>Percentage</th>
<th>T °K</th>
<th>$\Delta F_r$ kcal/mol°K</th>
<th>$\Delta H_r$ kcal/mol°K</th>
<th>$\Delta F_\eta$ Kcal/mole</th>
<th>$\Delta H_\eta$ Kcal/mole</th>
<th>$\Delta S_r$ cal/mol°K</th>
<th>$\Delta S_\eta$ cal/mol°K</th>
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