Dielectric dispersion and thermodynamical effect of aqueous morpholine by using picosecond TDR

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The dielectric permittivity parameters, excess characteristic properties, conductivity and thermodynamic properties of binary mixtures morpholine + water have been measured as a function of frequency for various mole fractions. Dielectric dispersion and molecular interactions of morpholine binary mixture depend on concentration and temperature. The results obtained have been used to interpret the nature of solute-solvent interactions. The relaxation process attained in the solution constituents have been related to probable molecular complex formation and its associated behaviours have been discussed. The concentrations have relaxation in a selective frequency region with symmetrical distribution in relaxation times. Additional measurements on aqueous mixtures of morpholine reveal a considerable tendency towards hetero-association. Confirmations of orientated dipole ordering by Kirkwood correlation factors of the mixtures have been assessed. The enthalpy ($\Delta H$), entropy ($\Delta S$) and Gibbs free energy ($\Delta G$) have been calculated for various concentrations and temperature. Thermodynamic parameters depend on concentrations and their relative relaxation processes have been discussed. The interaction and relative dipole ordering are discussed in term of correlation ($g_{eff}$) and excess properties ($\varepsilon_E$) and ($1/\tau_E$).

Keywords: Dielectric parameters, Relaxation time, Kirkwood correlation, Excess properties, Thermodynamic properties, Time domain reflectometry

1 Introduction

Molecular interaction and association formation in liquid state is confessed by broadband dielectric spectroscopy. The hetero-association and self-association with spring polar mixtures with and without N-substituent occur, respectively. Polar liquids consist of orientation polarization and electrical conductivity induced by ionic conductivity 1-2. The interaction of particles depending on their mole fraction, chemical composition, dielectric properties of component exhibit depressiveness in liquids 3,4. The knowledge of physical as well as chemical properties of materials is gained from the description of complex dielectric permittivity (CDP) spectrum 5,6 and the quality of the material 7,8. The temperature divergence of the spectrum and comprehensive description of measurement by varying temperature has been studied 9,12. The complex value of dielectric on materials associated with the effect of molecular polarization as real part and the loss of energy to force the polarization and conduction as imaginary part.

The study provides lot of information on the molecular interaction, physical property of the medium and specific interaction between molecules of the component liquids leading to the formation of complexes through hydrogen bonding 13. In this regard, morpholine finds wider application of various fields. In pharmaceutical industry there is need to improve enzymatic hydrolysis, anticancer drug delivery. In industries this is used as pH moderator, chemical emulsifier and solvents 14. This creates interest to study dielectric relaxation of aqueous morpholine system.

The heterocyclic compound morpholine can behave as proton acceptor through the oxygen as well as nitrogen lone pair electrons. The strong hydrogen bonding sites capable of interact with other proton donating compounds/molecules. Morpholine can exist in chair and boat form either equatorial or axial structural formation. Due to these structural arrangements it generates self association if there is no N-substituent else forms hetero association with other protic solvents. The hydroxyl group exists in solvent and nitrogen in solute offer strong polarity in the present study. However number of methyl groups which is naturally hydrophobic plays an important
role and favours interaction with non-polar solvents. The fractional force exists in mixture within the relaxation time is influence by many other factors.

2 Experimental Method

The solutions are prepared in air tight container to prevent contamination by moisture. Analytical grade morpholine purchased from Sigma Aldrich Company with 99% purity is used without further purification. HPLC water having conductivity 1 μ Siemens used for preparation of mixture. Solution prepared in room temperature 303 K and in normal pressure before 5 min of measurement.

TDR setup consists of DSA8200 Tektronix digital serial analyzer with 80E08 sampling module. This module gives precise oscilloscope measurement in the selectable band width of 10 MHz to 30 GHz. The module is connected with semi-rigid copper coaxial cable E286M17 supplied by Huber Suhner Electronics Pvt., Ltd. of 50 Ω impedance through which 200 mv rising step pulse with 18ps incident pulse and 20 ps reflected pulse time and 200 kHz repetition rate passed. The inner diameter and outer diameter of the conductor is 2.2 mm, and 0.51 mm, respectively, and the diameter of the dielectric is 1.66 mm. All measurements were carried out in open load conditions. Sampling oscilloscope analyze the changes in step pulse after reflection from the end of the line. Reflected pulse without sample \( R_1(t) \) and with sample \( R_x(t) \) were recorded in the time window of 2 ns and digitized in 2000 points. A refrigerator system with temperature sensor of accuracy ±0.5 °C is used to reach temperature less than room temperature. Error of the instrument reduced by calibrated with polar and non-polar liquids for many time.

3 Data Analysis

The reflection coefficient spectra \( \rho^*(\omega) \) was obtained by the expression:

\[
\rho^*(\omega) = c p(\omega) / j\omega dq(\omega)
\]

where \( p(\omega) \) and \( q(\omega) \) are Fourier transforms of \( p(t) \) and \( q(t) \), respectively. The generalized expression of Havriliak and Negami equation18,19 is as below:

\[
\varepsilon^*(\omega) = \varepsilon_c + (\varepsilon_0 - \varepsilon_c) / [1 + (j\omega\tau)^\alpha]^\beta
\]

The complex permittivity spectra was obtained by the fitting parameters \( \varepsilon_0, \varepsilon_c, \tau, \alpha \) and \( \beta \). The complex spectra of Cole-Debye model and the fits were performed only in the limited temperature interval where the fits are reliable. At high temperature the relaxation frequencies approach the soft mode, which is above the investigated frequency range.

At low temperature (below 275 K) the dielectric loss (\( \varepsilon'' \)) is independent of frequency. The dielectric spectrum is much diffused and a very wide distribution of relaxation time has been observed. Frequency independence of \( \varepsilon'' \) does not allow estimating the relaxation time using conventional accustomed relaxation models or empirical equations. Therefore the low temperature dielectric spectra analyzed for morpholine binary mixtures limited to 288 K. The rapid increase in the mean relaxation time \( \tau \) with the temperature decrease (figure) shows a substantial sluggish down of the relaxation processes. The concurrent increases in the distribution parameter \( \alpha \sim 0.9 \) shows that the dielectric spectrum becomes tremendously diffused. In the same way distribution of the relaxation times becomes exceptionally stretched. The loss factor \( \tan\delta < 1 \) indicates that the dielectric dispersion occurs in the selective frequency range.

4 Results and Discussion

4.1 Distribution properties

The temperature dependent real (\( \varepsilon' \)) and imaginary (\( \varepsilon'' \)) parts of the complex dielectric permittivity \( \varepsilon^*(\omega) \) at different frequencies for morpholine + water show a typical relaxation behaviour from low frequencies to extended frequency range. The dispersal begins in the kilohertz region, but at higher temperatures the dispersion occurs in the higher frequency identical as in most of in order at 0.172 mf.
The ‘N’ contains one lone pair electrons and ‘O’ has two lone pair of electrons in morpholine molecule. Hence there is a strong potential interaction on hetero-association in binary aqueous mixture. These charges influence the change in the dielectric parameters. There is composition dependent interactions by salvation force between short ranges which are identified. Hydrogen bonding formation between morpholine and water is conformed and evident. On the other hand this is invariant with hydroxyl produces the some sort of long range order effects.

Morpholine contains resonating paired electrons which are freely interacting with hydroxyl group and increase in relaxation time that favours increasing chain length\(^{22}\). Increasing the concentration of morpholine, it becomes more ring structured with side chains and depleted the linear molecules that create the existing particle-particle interactions or friction and it plays a vital role in relaxation characteristics. All binary system values trends clearly signify that both inter and intra molecular interaction is present in our system of study.

A nonlinear nature is found on static permittivity on increasing the concentration with aqueous mixture. This indicates the dipolar interaction between these two compounds. Mehrotra et al.\(^{23}\) mentioned that change in dipole modifies the packing density. Addition of solute implying transition of spherical molecular aggregates (clusters) to more correlate elongated on increasing the concentration of the solution. This influence alters the static dielectric constant and dielectric permittivity. The static permittivity of this binary solution are less than pure water, the value reaches the lowest for 0.172 mole fractions of increase in concentration and temperature.

The formation of aggregation reduces the energy loss on higher concentrations. Increase in static permittivity and decrement in energy loss in the mixture is an indication of unlike molecular interactions\(^{24}\). The values of \(\varepsilon'\) and \(\varepsilon''\) move towards higher frequency with increasing concentration and temperature. Increase of effective dipole moment between unlike molecule causes non-linear increment in static permittivity with concentration. There is hetero association complex exists in our system. The relaxation time is found to vary with frequency, concentration and temperature this shows typical relaxation dispersion in a wide frequency range.

Morpholine molecule contains \(\pi\) electrons in its ring structure, these are main possibility of interaction with water molecules containing hydroxyl group. Such intra molecular interaction reduces the value beyond particular concentration level. This reflects on our system both dielectric and relaxation time. Morpholine contains own free electrons, it creates delocalization effect and it is associated with resonating dipoles that lead its resonance formation. The delocalization electrons in solute and hydroxyl in aqueous can mutually make induced dipoles. The molecular interaction between hydroxyl group and resonance electrons of morpholine makes a dipole-dipole or induced dipole-dipole nature. Morpholine resonating electrons manifest dispersive nature that indirectly supports the formation (or) existence of more space between the molecules. This effect reduces the dielectric static value as shown in Fig. 2. More number of hydroxyl is fully saturated by more morpholine molecules, the creation an inducement of dipoles are present in the system. It is represented as the interactions are increasing in order as chain length increases. The probabilities of dipole-dipole or induced dipole are represented by their contribution is less compared with dipole-dipole type. For a given binary concentration the value of dielectric relaxation and excess parameter are higher than the expected values\(^{25-29}\). This behavior reflects the dominating nature of hydroxyl group than alkyl group. In addition to temperature, concentration, the structural arrangement of polar group, their area of contact, the relative movement between the components is also make considerable variation in dielectric and

![Fig. 2 — Plot between dielectric constant versud mole fraction for various temperature.](image-url)
relaxation parameters. The variations of relaxation time of morpholine water mixture with concentration and temperature shown in Fig. 3. The stretching in relaxation time with varying mole fraction and temperature are found to be linear. At 0.172 mf the stretching is restricted and narrowed almost to attain a common value and further advances normally.

4.2 Thermodynamic properties
The dielectric relaxation is a rate process across a path over a thermal potential barrier of the system is a measure of maximum reversible work in a specified temperature and pressure and is a quantum of heat exchanged with its surroundings within the medium24.

Thermal parameters $\Delta H$ enthalpy and entropy $\Delta S$ of morpholine water mixture were calculated from Eyring equation:

$$\tau = \left(\frac{h}{kT}\right) \exp \left(\frac{\Delta H}{RT}\right) \exp \left(-\frac{\Delta S}{R}\right) \quad \ldots (3)$$

Gibb’s free energy determined from the calculated enthalpy and entropy which confirms the direction of reaction:

$$\Delta G = \Delta H - T\Delta S \quad \ldots (4)$$

Thermal parameters enthalpy ($\Delta H$) is negative, entropy ($\Delta S$) is positive and Gibb’s free energy $\Delta G$ of binary mixture is negative which favors both endothermic and exothermic reactions. The randomness occurs for reversible work as $\Delta S$ positive. Further at 0.172 mf both thermal parameters nearer to zero indicating there is no exchange of heat with surroundings shown in Fig. 4.

$\Delta G$ shows a function of solution composition at different temperature (Fig. 5). At 0.172 to 0.3 mf dispersion of energy with concentration maximized as the activation of reversible work increases with temperature. This is in relative to Fig. 4 this is due to intermolecular dependency between ortho- nitrogen and hydroxyl presence in the mixture. The changes in relaxation raises linearly till 0.172 mf beyond that is longer in time for lower temperature which accolades by thermodynamic property.

4.3 Excess properties
The excess permittivity values indicate existence of molecular interaction. The interaction and relative molecular movement are determined by the parameters dielectric and excess properties. The

Fig. 3 — Plot between relaxation time versus mole fraction for various temperatures.

Fig. 4 — Plot between enthalpy ($\Delta H$), entropy ($\Delta S$) for various concentrations.

Fig. 5 — Plot between Gibb’s free energy ($\Delta G$) versus mole fraction for various temperatures.
magnitude of excess values increases with decrease in concentration is shown in Fig. 6. It may be concluded that the strength of the interaction increases with decrease of morpholine concentration. The higher excess permittivity value at lower concentration signifies the polymeric structure. Morpholine rich region the values of excess dielectric indicate the strong dipole formation in the mixture, confirming active dielectric dispersion and relaxation process. There is a slight variation in dielectric and excess parameters clearly convey that the interaction types are dispersive in nature.

\[ \varepsilon^E_0 = (\varepsilon_0)_M - \left[ (\varepsilon_0)_W X_W + (\varepsilon_0)_A (1-X_W) \right] \quad \ldots (5) \]

where \( M \) is mixture, \( W \) is water and \( A \) is solute.

The different molecular association bond necessary to broke for dielectric relaxation process to be produced. This has been envisaged in consideration of Kirkwood correlation factor \( g^{\text{eff}} \) is higher than unity\(^{30,31}\). This indicates the dipolar correlation between the molecules and its surroundings. This represents that there is a strong interaction and strength at minimum morpholine region further on increase in morpholine richness \( g^{\text{eff}} \) decreases as shown in Fig. 7. Hence it confirms in all concentration the electric dipoles have parallel ordered orientation.

The excess inverse relaxation of the solution is determined by using following expression:

\[ \left( 1/\tau \right)^E = \left( 1/\tau \right)_M - \left[ \left( 1/\tau \right)_A X_A + \left( 1/\tau \right)_B X_B \right] \quad \ldots (6) \]

where \( M \)-mixture, \( A \)-solute, \( B \)-water and \( X_A, X_B \)- mole fraction of solute and water. Solute-solvent interaction produces an effective field with which the dipoles rotates quicker comparative to pure morpholine. Thus the inverse excess relaxation time\(^{32,33}\) decreases as shown in Fig. 8.

5 Conclusions
The morpholine mixture may be attribute strong polar nature between the components involved. The macroscopic factors density and viscosity influence the smart changes in relaxation time. The Debye fitting indicates the mixture has intra molecular interactions between morpholine being a strong polar and high denser with hydroxyl group. There is an increase in molecular interaction and association that higher members cause less flexible for movement. The interaction and relative molecular movement is determined by the parameters like dielectric and
excess properties and their dependency with frequency and temperature. The changes in relaxation raises linearly to a specific concentration beyond that longer the relaxation time for lower temperature, this reflects the thermodynamic property. The dipolar correlation between the molecules and its surroundings are conformed to a strong interaction and strength at minimum morpholine region further on increase in morpholine richness $g_{eff}$ decreases. This confirms for all concentration the electric dipoles have parallel ordered orientation.

References
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