Dielectric dispersion, relaxation and molecular interaction of pyrazine binary mixtures

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Abstract
The dielectric depressiveness, absorption and orientation behavior is investigated in relation to solution properties of pyrazine with water, methanol and ethanol for varying temperature and mole fraction. This behavior is discussed in terms of inter molecular bonding. Orientation effects and their dielectric properties are indicated by surface dipole potential charges by displacement of oriented solvent. The charge dependence of polar solvents with organic molecular orientation can be qualitatively evolved and can be calculated in terms of its own dielectric properties, relaxation time, and correlation factor and thermodynamical behavior of solvent mixtures. The macroscopic and optical spectroscopic properties of pyrazine + water and pyrazine + alcohol mixtures are also studied.

1. Introduction

Pyrazine is a heterocyclic aromatic organic compound with equal numbers of carbon and hydrogen with nitrogen half of it. It is a symmetrical molecule with point group D₂h and less basic than pyridine, pyridazine and pyrimidine. The structural importance has been described with nitrogen containing in a cyclic structure is reported and concerned with wide range of biological applications [1]. Pyridine and its functional derivative (Pyrazine) are an important class of compound and that exists in several natural flavours, complex organic compounds and is responsible for aroma in food stuffs [2, 3] cooked meat, cheese, coffee, tea etc [4]. Recent years various interesting works in pyrazine and their derivatives in medicinal chemistry of their biological signifance they are Analgesic, Anti-allergic, Anti-bacterial, Anti-inflammatory, Anti-viral, Anti-cancer, HIV, Anti-hypertensive, Cardiovascular controlling [5–13].

Hydrogen bonding is interesting molecular interaction in organic compound especially in aqueous medium. Occurring of H-bond between molecules has been well defined by Arunan et al [14, 15]. The interaction between the lone pair of electrons through-space overlaps the atomic orbital and the inconceivable present state concentrates on inter-nitrogen coupling that could be large enough to prevent symmetry lowering on formation. Based on various spectroscopic and molecular orbital calculations ensures the interaction is a ‘through bond interaction’ and precede a much longer coupling as expected. Through bond coupling is a magnitude of the distortive forces which compete with the through bond interaction to determine molecular geometry. The present work focuses the interaction between pyrazine + water mixture on various mole fractions and temperature. The presence of water leads to formation of hydrogen bonds between the lone pair exists in N-atoms and a water-hydrogen atom interacts in the various molecular states and the lone pair ion depelled and eliminating the additional hydrogen bonds that stabilizes the structural formation. The hydrogen bonding interactions and their effects on molecular spectral studies was established by Brealey and Kash et al.
Primary alcohol has been selected as a representative of strong proton donors introduced to binary to ensure the formation of typical molecular bonding.

2. Experimental method

2.1. Material and sample preparation

Pyrazine of purity 99% purchased from sigma Aldrich and HPLC water, methanol, ethanol were used as a solvent without further purification. Binary solution of Pyrazine with 20%, 40%, 50%, 60%, 80%, 60%, 50%, 40% 20% of Water/methanol/ethanol in mole fraction were prepared very carefully in a uniform homogenous method. By weighing appropriate amounts of the constituents the mixture kept in a tightly packed suitable flask to avoid the uptake of moisture from the air. The solution is maintained at room temperature for about 10 to 15 min before conduct of experiment.

2.2. Dielectric measurement and data analysis

Ostwald viscometer is a function of both dynamic viscosity and density used to determine the relationship between dynamic viscosity and density is called the kinematic viscosity and is defined as the ratio of dynamic viscosity and density. The accuracy of measurement is in the order of $10^{-3}$ gm, at 0.1 MPa. Viscosity and density of each mole fraction of mixture have been evaluated and reported in table 1.

The frequency dependent dielectric parameters were measured in the frequency width $10^9–10^{12}$ Hz. The measurement techniques are discussed in detail in our earlier works [17–21]. The reported values of $\varepsilon^*$ are fit with values $\alpha = 0, \beta = 1$ obtained by Debye fit using following Havirliak-Negami equation [22–24]

$$\rho^*(\omega) = \frac{\text{cp}(\omega)}{j\omega \text{dq}(\omega)}$$

Where p(\omega) and q (\omega) are Fourier Transform of p(t) and q (t) obtained using summation and Samulon method.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + (j\omega\tau)^{-\alpha}]^\beta}$$

A nonlinear least-square fit method was used to determine the values of the dielectric parameters and relaxation time ($\tau$) were obtained from equation (2).

The conductivity of the sample is computed using the expression

$$\sigma = \frac{C\varepsilon R_0(t) - R_x(t)}{d (R_0(t) + R_x(t))}$$

Were $R_0(t)$ and $R_x(t)$ values of reflected pulses at time $t = \infty$ without and with samples respectively and $\varepsilon$ is the permittivity of free space.

3. Results and outcome

3.1. Dielectric permittivity and relaxation time

The complex permittivity spectra $\varepsilon^*(\omega)$ is shown in figures 1(a) to (c). Dielectric properties of aqueous pyrazine are studied by Kaatze [25]. Figure 2 shows the variation in static permittivity with temperature for various mole fractions of pyrazine—binary mixture. Paradiazine in polar medium (water), has temperature disturbs the alignment of dipoles in an outer field is well pronounced one and the dielectric constant decreases with temperature and with increasing mole fraction due to dipolar molecules rotating or reorientation of ions. The value of $\varepsilon_\infty$ (permittivity at high frequency) was taken to be 4 for all solution studied, since for the frequency range considered here, $\varepsilon^*$ is not sensitive with respect to $\varepsilon_\infty$. The intermolecular bonding in the system
contributes structural changes which in turn alter the dielectric properties. Intermolecular bonding as H-bond in aqueous pyrazine studied by Caminati et al [26] estimated water molecules bound above the ring and also in the plane of the ring. The mechanism of interaction involved in formation of dimers and particularly the self associative hydrogen bond pairs [27, 28] with alcohol (−OH) group dominates it to be a polar. The electrostatic potential between negative oxygen and nitrogen is well balanced with positive carbon and hydrogen. The interaction with shifting of ions of the symmetrical hetero cyclic molecule of pyrazine is compatible to flow of charges and movement of charges in oscillating electric field. The thermal effects are associated with dissipation of energy as dielectric loss in the medium that influence significant changes in their dielectric properties. The addition of polar protic solvent which acts as a hydrogen-bonded donor and the bound water molecules makes random orientation about the hydrogen bonded axis explained by Oster and Kirkwood [29]. The measured static dielectric constant nearly matches with the literature values.

The effect of heat on orientation polarization occurs due to dipolar natures of water molecules go through variation in dielectric constant with temperature. It is not so that the temperature is lowered the dielectric constant increases. Since it is a protic polar medium the temperature disturbs the formation and alignment of dipoles in an outer field. The dielectric constant decreases with temperature, also in methanol and ethanol solvents. The dipole moments of the various pyrazine mixtures are in the direction expected from general solvent effects, the slightly lower dielectric constant is attributable to varying inductive effects associated with the size and number of alkyl groups attached to the nitrogen atom. There is no evidence of any unfavorable effect from these alcohol groups that would influence the molecular association between N···H–O hydrogen bonding.

The present 3D molecular structure was determined to be a planar. Our experimental establishment of complex system arrives at an understanding of intermolecular interaction and its governing association process that can be regarded at prototype for salvation of heterocyclic aromatic rings containing more than one nitrogen.

The dielectric constant is strongly dependent on the structure. The electron shifting within molecules and orientation polarizability causes dielectric polarization in pyrazine with organic molecules. The effect of electronic shifting within molecules has rather weak temperature dependence than the orientation polarization. In the presence of lower order alcohol is a passive active medium with higher static permittivity in the applied electric field. The potential energy of orientations aligned with the field is lowered and orientations aligned against the field are raised. Therefore over a time excess molecule will align with the field and less energy is required to switch to orientations aligned with the field and more energy required to switch to orientations aligned against the field. The molecular energy need to be more than the any energy barrier within the system for a change in orientation rather with lower energy cannot change its orientation. The orientation mode becomes ‘frozen out’ leading to drop in the dielectric constant. The dielectric constant increases with fall in temperature above their literature value of pure solvents (Water, Methanol and Ethanol) with pyrazine as shown in figure 2 at various mole fractions and temperature. The energy of the lowest mole fraction has maximum dielectric permittivity but restrains with molecular size of the solvent methanol and ethanol respectively. In figures 2(b) and (c), pyrazine with methanol and ethanol mixture at 0.26 and 0.75 respectively the lone pair of the electron as an acceptor in N···H–O hydrogen bond is loosely bound shifts of due to its stretched length and bulk property.

Figure 1. The complex permittivity spectra of (a) Pyrazine + Ethanol, (b) Pyrazine + Methanol, (c) Pyrazine + Water binary mixtures for various temperature.
has influence with the temperature mentioned.

Figure 2. A plot between static permittivity versus temperature for various mole fraction of binary mixture of (a) pyrazine-water (b) pyrazine-methanol and (c) pyrazine-ethanol.
The used microwave frequency is close to the relaxation frequency of the orientational polarisation mechanism and most of the energy is absorbed by water later dissipated as heat. The relaxation time more closes with the orientation polarization with applied frequency. The relaxation time of pico seconds obviously interpret that the resonance occurs from MHz to GHz as function of frequency. In the binary mixture the hydrophobic hydration effect plays a vital role to contribute the dielectric parameters and relaxation time changes. This hydrophobic hydration provides two significant relaxation times (i) hydration water (or) bound water relaxation time (ii) pure water (or) free water relaxation time. It discussed widely and accepted that hydrophobic hydration effects reflects a clathrate-like structure (or) shells like (or) cages like structure of the water surrounded the solute molecules. This structure makes retardation of the solute molecule and reduces the reorientational motions of the solvent molecules, at the same time it increased permittivity of complex solution.

The relaxation times reported on tables2–4, get extended for Water, Methanol and Ethanol as their frequency of relaxation depends on structure. There are several discontinuities in the dielectric constant along with relaxation time with respect to temperature and mole fraction changes are shown in figure 3. The existences of heterogeneous interactions of polar solvents owing to the variations in relaxation time value are minimum in lower mole fractions of solutions. Relative increases from the molecular size of the protic solvents increases the relaxation times value. In figure 3(b) for concentration 0.12 mf at 298 K, the static permittivity restrain with molecular size of the solvent that reflects the adverse effect of relaxation time. The composition of the constituents of the molecular mixture alters the interaction between the molecules. The relaxation value inversely depends on temperature. The viscosity increases to a certain mole fraction due to formation of clathrate structure and formation of group molecular rotation increases the time period of relaxation. The viscosity and density increases from mole fractions due to formation of hydrogen bonds between the molecules at 303 K are shown in table 1. The linear dependency of density on temperature is generally accepted and

3-D model molecular structure of (a) pyrazine + water mixture, (b) pyrazine + methanol,(c) pyrazine + ethanol

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Table 2. Static dielectric constant($\varepsilon_0$), relaxation time($\tau$), Kirkwood (g) and effective Kirkwood correlation factor ($geff$), Activation energy($\Delta F$), Dielectric strength ($\Delta \varepsilon$), Conductivity ($\sigma$) of Pyrazine and Water mixture at various temperature and mole fraction. $\varepsilon_\infty = 4.0$.

| Temp. K | Mole fraction | \(\varepsilon_0\) | \(\tau_{ps}\) | g | $geff$ | $\varepsilon$ | $\Delta F$ kJ mol\(^{-1}\) | $\Delta \varepsilon$ | $\sigma$ mS/m |
|---------|---------------|-----------------|-----------|---|------|--------|-----------------|----------------|----------|
| 303     | 0.06          | 83.16           | 8.61      | 1.000 | 3.067  | 65.57  | 20.25           | 28.08          | 19.43    |
|         | 0.13          | 82.05           | 8.67      | 1.004 | 3.081  | 49.67  | 22.38           | 27.2           | 12.43    |
|         | 0.19          | 81.71           | 8.73      | 1.009 | 3.097  | 41.94  | 21.7            | 27.09          | 10.32    |
|         | 0.26          | 81.54           | 8.83      | 1.017 | 3.119  | 34.37  | 21.69           | 25.9           | 10.09    |
|         | 0.48          | 81.37           | 8.90      | 1.034 | 3.172  | 19.41  | 22.7            | 25.34          | 14.18    |
| 298     | 0.06          | 83.83           | 8.58      | 1.000 | 3.041  | 65.88  | 21.35           | 25.79          | 23.13    |
|         | 0.13          | 83.22           | 8.98      | 1.011 | 3.074  | 50.12  | 22.84           | 25.53          | 12.45    |
|         | 0.19          | 82.87           | 9.09      | 1.016 | 3.090  | 42.20  | 22.93           | 22.1           | 2.53     |
|         | 0.26          | 82.05           | 9.23      | 1.015 | 3.087  | 33.81  | 21.71           | 25.42          | 8.83     |
|         | 0.48          | 81.83           | 9.45      | 1.032 | 3.14   | 18.44  | 23.37           | 23.34          | 13.87    |
| 293     | 0.06          | 85.03           | 9.17      | 1.000 | 3.034  | 66.72  | 22.8            | 21.44          | 15.16    |
|         | 0.13          | 84.23           | 9.38      | 1.006 | 3.060  | 50.41  | 24.35           | 21.69          | 8.29     |
|         | 0.19          | 83.38           | 9.41      | 1.016 | 3.053  | 41.8   | 23.85           | 20.22          | 0.84     |
|         | 0.26          | 83.32           | 9.53      | 1.016 | 3.080  | 33.98  | 24.18           | 20.89          | 9.17     |
|         | 0.48          | 82.70           | 9.70      | 1.028 | 3.11   | 17.85  | 23.99           | 21.2           | 5.23     |
| 288     | 0.06          | 86.76           | 9.67      | 1.000 | 3.043  | 68.08  | 22.93           | 16.29          | 11.46    |
|         | 0.13          | 85.68           | 9.74      | 1.005 | 3.060  | 51.11  | 25.72           | 16.72          | 5.10     |
|         | 0.19          | 85.36           | 9.92      | 1.001 | 3.001  | 42.85  | 24.61           | 15.29          | 3.36     |
|         | 0.26          | 84.89           | 10.08     | 1.015 | 3.088  | 34.44  | 24.03           | 15.16          | 2.56     |
|         | 0.48          | 83.71           | 10.15     | 1.020 | 3.103  | 17.37  | 24.65           | 15.76          | 5.10     |
expected that both density and viscosity of all concentrations of the mixture decrease is evident from the reduction in static dielectric permittivity with raise in temperature.

The studies on pyrazine form an azeotrope with water (60% pyrazine-40% water at an higher temperature(b.p), 760 mm of Hg amd $n_0^2 = 1.451$. Once this composition has been achieved, the liquid and vapour have same composition, and no further separation occurs. Our study has been limited to experimental observations between 288 K–303 K[31]. Trace of existence of microscopic inhomogeneities occurs in mid concentration.

| Temp. K | Mole fraction | $\varepsilon_0$ | $\tau_{ps}$ | $g$ | $g^{eff}$ | $\varepsilon^e$ | $\Delta F$ kJ mol$^{-1}$ | $\Delta\varepsilon$ |
|---------|---------------|-----------------|--------------|-----|----------|-----------------|-------------------------|----------------|
| 303     | 0.12          | 30.31           | 45.27        | 1.000 | 2.972    | 22.63           | 1.15                    | 22.53          |
|         | 0.26          | 31.19           | 43.92        | 1.049 | 3.117    | 15.98           | 3.59                    | 21.55          |
|         | 0.34          | 29.06           | 43.83        | 0.983 | 2.924    | 11.85           | 2.94                    | 20.56          |
|         | 0.44          | 28.17           | 43.49        | 0.961 | 2.858    | 8.08            | 1.38                    | 23.1           |
|         | 0.68          | 27.16           | 42.9         | 0.943 | 2.804    | 1.3             | 1.41                    | 20.3           |
| 298     | 0.12          | 33.66           | 53.49        | 1.000 | 3.26     | 24.8            | 1.64                    | 24.76          |
|         | 0.26          | 32.72           | 50.09        | 0.989 | 3.22     | 17.8            | 4.3                     | 22.09          |
|         | 0.34          | 30.08           | 46.83        | 0.915 | 2.980    | 12.13           | 4.2                     | 20.25          |
|         | 0.44          | 30.17           | 46.18        | 0.926 | 3.018    | 9.19            | 0.29                    | 23.06          |
|         | 0.68          | 27.32           | 45            | 0.852 | 2.775    | 2.28            | 1.08                    | 22.11          |
| 293     | 0.12          | 34.77           | 52.72        | 1.000 | 3.331    | 25.84           | 2.2                     | 24.78          |
|         | 0.26          | 32.11           | 50.86        | 0.938 | 3.106    | 17.03           | 2.14                    | 23.02          |
|         | 0.34          | 31.78           | 50.57        | 0.937 | 3.101    | 13.65           | 4.49                    | 21.17          |
|         | 0.44          | 31.06           | 50            | 0.923 | 3.058    | 9.87            | 0.87                    | 23.21          |
|         | 0.68          | 29.08           | 47.64        | 0.879 | 2.911    | 1.76            | 0.12                    | 22.64          |
| 288     | 0.12          | 37.41           | 56.1         | 1.000 | 3.22     | 28.37           | 2.97                    | 25.63          |
|         | 0.26          | 35.03           | 54.29        | 1.037 | 3.34     | 19.75           | 2.4                     | 24.57          |
|         | 0.34          | 33.94           | 53.56        | 1.004 | 3.234    | 15.54           | 3.77                    | 23.05          |
|         | 0.44          | 33.65           | 52.72        | 1.023 | 3.293    | 12.13           | 2.81                    | 22.75          |
|         | 0.68          | 32.79           | 52.01        | 1.006 | 3.239    | 5.03            | 2.15                    | 23.4           |
range for methanol and ethanol mixtures. The influence of viscosity has a reverse shift values between 0.13–0.19 and 0.19–0.26 for methanol and ethanol respectively.

Concentration of solute solvent interactions and its frequency dispersion depends on activation energy ($\Delta F$). The surface dipole potential charge and molecular association also depends on concentration. The energy of activation required for dielectric relaxation, the process of viscous flow involves greater persuade with neighbouring molecules. The acquired energy for the chemical processes advances due to its activation energy $\Delta F = \varepsilon_0 - \varepsilon_\infty$. The activation energy $\Delta F$ is the difference between the reactants and the transition state, where

Figure 3. A plot between relaxation time versus temperature for various mole fraction of binary mixture of (a) pyrazine-water (b) pyrazine-methanol and (c) pyrazine-ethanol.
the activated complex is formed needs, no additional energy to proceed the reaction. The energy substantially increases with decrease in temperature.

The internal electric field before electrical breakdown which depends on the molecular structure of the material is the dielectric strength ($\Delta \varepsilon$). Within a dielectric material this can be subjected without breaking down or discharging substantially decreases with concentration and temperature. The values of dielectric strength $\Delta \varepsilon = \varepsilon_0 - \varepsilon'$ confirm the polarisation nature of the material. The calculated values of activation energy ($\Delta F$) and dielectric strength ($\Delta \varepsilon$) are reported in tables 2–4. The electrical conductivity $\sigma$ for pyrazine-water mixture its evident that formation complexes may be observed from the characteristic behaviour of the conductivity within the concentration range by equation (3).

### 3.2. Thermodynamic properties

The thermodynamic parameter of pyrazine water mixture calculated from the obtained dielectric relaxation time by using Eyring equation

$$\tau = \left( \frac{h}{kT} \right) \exp \left( \frac{\Delta H}{RT} \right) \exp \left( -\frac{\Delta S}{R} \right)$$  \tag{4}

where $\Delta S$-entropy, $\Delta H$- enthalpy and $\Delta G$–Gibbs free energy.

$$\Delta G = \Delta H - T\Delta S$$  \tag{5}

Gibbs free energy $\Delta G$ predicted that the reaction is spontaneous at increasing temperature and exothermicity is relatively unimportant of all mixture constituents. The Gibb’s energy of dissociation signifies negative of all concentrations. The pragmatic value signifies the structure breaking effect on the solvent molecules and with the increase of salvation contribution. Gibb’s energy is connected with salvation of solute ion in solvent and movement of ion and molecules, especially the core contribution of proton ion molecules [34].

Spontaneity of the direction of reaction is solute to solvent in which the reaction will take place without outside interference. This thermodynamic potential expresses the exchange of heat and work with its surroundings not with matter and is minimized at chemical equilibrium as reaction coordinates vanishes. With available energy the amount of mechanical works to electrons shifting of ions within the molecules and favors orientational polarizability. The enthalpy of formation $\Delta H$ is the due factor for intermolecular interaction confirms endothermic reactions. $\Delta S$ is positive which increases the disorder at random and is discontinuous with mole fractions of the pyrazine with water, methanol and ethanol. The thermodynamic values are reported in tables 5–7.

### 3.3. Correlation and excess property

The excess permittivity ($\varepsilon''$), Kirkwood correlation factor ($g$) effective Kirkwood correlation factor($g_{\text{eff}}$), ionic conductivity ($\sigma$) and activation energy ($\Delta F$) values of binary system are shown in tables 2–4 for
Pyrazine + water, Pyrazine + methanol, Pyrazine + ethanol respectively. The mode of orientation of dipoles is indicated Kirkwood correlation factor (g\text{eff}) is defined by

\[ g = 1 + z \cos \gamma \]  

(6)

where \( z \) and \( \gamma \) are the average number and the angle between the dipole moments of the neighboring molecule respectively. Kirkwood correlation factor \( g \) of pyrazine + water and pyrazine + alcohol is greater than unity indicates there is molecular interaction between solute-solvent molecules. The molecular ordering in liquids can be determined by Kirkwood-Frohlich expression given below

\[ \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} = \text{geff} \frac{4\pi N/\rho}{9KT} \]

(7)

Where \( \varepsilon_0, \varepsilon_\infty, g, \mu, M \) and \( \rho \) are usual meanings.

The effective Kirkwood correlation factor gives information if \( \text{geff} \) is greater than unity 1, there are tending towards parallel alignment of dipoles, less than unity antiparallel alignment is preferential and equal to unity is absence of orientational ordering.

In the present case, since \( \text{geff} > 1 \) indicates parallel alignment of dipoles. The effective Kirkwood correlation factor \( \text{geff} \) increases with increase in mole fractions. This suggests that increase in molecular size will not hinder the effect of the decrease in their intermolecular association. The orientation ordering is parallel alignment of dipole observed in this system. The \( \text{geff} \) calculated values of the mixtures are reported in tables 2–4. In all mole fractions the calculated values of \( \text{geff} > 1 \) confirm parallel orientation of electric dipoles. \( \text{geff} \) value increases with increase in solvent mole fractions smoothly indicating the formation of cage-type structure [32].

\[ \varepsilon_0^E = (\varepsilon_0)M - [(\varepsilon_0)W X_W + (\varepsilon_0)M (1 - X_W)] \]

(9)

The increase in \( \varepsilon_0^E \) values reveals that there is increased in contribution of effective dipoles provides the information as \( \varepsilon_0^E = 0 \) indicating the mixture constituents do not interact, \( \varepsilon_0^E < 0 \) the mixture constituents interact by reducing the total number of effective dipoles contributed in the mixture values and \( \varepsilon_0^E > 0 \) the constituents of a mixture interacts with increased number of effective dipoles contributed in the mixture.

The attained values \( \varepsilon_0^E \) are positive over the whole mole fraction range of the present work confirming the formation of the strongest heterogeneous species [33, 34]. The increases in net parallel dipolar alignment due to the formation of heterogeneous molecular complexes between the pyrazine + water and pyrazine + alcohol is linear through entire mole fraction and alter the polarization.

### 3.4. FTIR analysis

The presence of co-ordinate water in complex solution conformed by the appearance of broadband around 3400 cm\(^{-1}\) (\(\nu\text{O–H}\)) in the FTIR spectrum. A strong peak appears at 3696 cm\(^{-1}\) confirms O–H stretching. The in-plane and out-plane bending O–H vibrations are obtained at 1395–1440 and 960–875 cm\(^{-1}\) respectively. These planes bending absorption values increases because of strong hydrogen bonding through carboxyl group. A specific at 1418 cm\(^{-1}\) signifies C=N stretching of the aromatic ring. 1033 and 1031 cm\(^{-1}\) appears both mixtures (Pyrazine + water, Pyrazine + alcohol) significantly show C–N stretching tertiary carbon atom. The strong peaks appear around 1650 and 1333 cm\(^{-1}\) caused by asymmetric and symmetric stretching vibration of carboxyl group. The separation between asymmetric and symmetric is used to diagnose the coordination modes.

A common signature peaks for pyrazine, water and alcohol mixtures noted at 1129, 1152 and 1149, 1274 cm\(^{-1}\) corresponds to C–O stretching. The augments of the peak values confirms the clear information on existence of hydrogen bonding in all cases and reorientation of molecular position. The each spectrum consists
of various mole fractions in molar ratios of the mixtures and they are combined together shown in figure 4. The frequency assignment and their investigations are mentioned in table 8.

### Table 8. FTIR Frequency assignments of pyrazine in complex solution and alcohol mixture.

| FTIR Frequency Assignments | Assignments |
|-----------------------------|-------------|
| 687                         | N–H deformation |
| 784, 796                    | C–H deformation |
| 797                         | O–H out of plane bending vibration |
| 1031                        | C–N stretching tertiary carbon atom |
| 1073                        | C–N stretching |
| 1149, 1274                  | C–O stretching |
| 1333                        | Strong Peaks at \( \nu_{\text{sym}} (\text{COO}^-) \) |
| 1415                        | O–H in plane bending vibration, –C=N stretching |
| 1418                        | N–H bending vibrations in medium |
| 1650                        | Strong Peaks at \( \nu_{\text{asym}} (\text{COO}^-) \) |
| 2902                        | C–H weak bond |
| 2928                        | CH\(_2\) group vibration |
| 3370                        | O–H stretching intermolecular bond |
| 3400                        | Broad band \( \nu_{\text{v3,23}} \) |
| 3696                        | O–H stretching vibration |

4. Conclusion

There is inter molecular bonding between the pyrazine and water molecules depend on the relative strength of the hydrogen bond existing among them. The parallel dipolar ordering is facto of the existence of homogeneous H-bonded structures of pyrazine + water. The molecular interaction in pyrazine + alcohol mixtures is due to aggregation of the composition. The mixture constituents and is mainly influenced by the nature of solvent. Water and alcohol forms complexes with pyrazine as superficial structure and there is a well pronounced inter molecular interaction between them. Much like a closure, the interaction alters the structure and the formation of aggregates. The molecule of water and alcohols extensively changes the polarity of the solvent. The hydration indexed the stability of complexes. Influence of temperature favours the rate of the reaction as increased. The dielectric permittivity and the relaxation times demonstrate the gradual increase with mole fractions of pyrazine mixture. The increase in the internal viscosity leads to extended relaxation time with dipolar orientation.
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