PART - III

Spectroscopic Evaluation
CHAPTER V
SPECTROSCOPIC STUDY OF SOLUTIONS

5.1. NMR Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) studies the behaviour of certain atomic nuclei, namely those which have magnetic moments arising from their possessing 'spin', in the presence of applied magnetic fields. The applied field is responsible for the setting up of nuclear energy levels between which transitions may be caused to occur by absorption of suitable electromagnetic radiation; because the pattern of energy levels is a property both of the nuclei in a molecule and of their electronic environment and relationship to each other, the experiment is of enormous value to chemists both as a theoretical and a structural tool. It is fortunate that some of the most suitable nuclei for study are among the most important and widespread in Chemistry, e.g. $^1\text{H}$, $^{13}\text{C}$, $^{31}\text{P}$, $^{19}\text{F}$ and it is true to say that the development of NMR spectroscopy since the first successful experiments in 1945 has been of paramount importance to the chemist.

5.2. Quantum mechanical description

The particles, which make up an atomic nucleus, neutrons and protons, possess a property, which is described as spin angular momentum. Nuclear structure is complex since the sub-particles have orbital as well as spin motions which combine together in various ways to give a resultant spin angular momentum for the nucleus which may or may not be zero.

All nuclei with odd mass number possess 'spin', and the spin angular momentum vector is measured in units of $\hbar/2\pi = \hbar$ (where $\hbar$ =
Planck’s constant) and given the symbol I ħ. This is quantized, i.e., only certain values may occur, and it is necessary to define a quantum mechanical operator I corresponding to this property of spin. When I operates upon an eigen function (a nuclear spin wave-function) $\psi_N$ it generates eigen values $I$ according to the equation:

\[ I \psi_N = (I(I+1))^{1/2} \mu_N \psi_N \]  

(5.1)

$I$ is the nuclear spin quantum number, and for nuclei of odd mass number it is an odd integral multiple of $1/2$ i.e. $I = n/2$ where $n$ is an odd integer.

Nuclei having even mass number may have even nuclear charge, in which case $I = 0$, or odd nuclear charge, in which case $I$ is an integer (1, 2, 3, etc.).

If a nucleus has spin, it behaves as a spinning finite spatial distribution of charge, and a magnetic moment $\mu_N$ arises which is proportional to the magnitude of the spin, i.e.

\[ \mu_N = \gamma_N I \hbar \]  

(5.2)

Here $\gamma_N$ is a fundamental nuclear property known as the gyromagnetic ratio.

\[ \gamma_N = g_N\mu_N \]

Where, $g_N$ is the nuclear g factor and $\mu_N$ is the nuclear magneton.

Consider that an isolated nucleus of spin $1/2$ is placed in a steady magnetic field of induction $B_0$, two energy levels are produced, one corresponding to $m_z = + 1/2$, conventionally, spin $\alpha$, corresponding to a lowering of energy and the other to $m_z = -1/2$, conventionally, state $\beta$, corresponding to an increase in energy. In classical terms, the $\alpha$ state
corresponds to alignment of the nuclear moment parallel to the field, and state \( \beta \) corresponds to alignment anti parallel to the field.

The energy difference between the two levels is \( g_N \mu_N B_0 \), which corresponds to a frequency separation \( \nu \) given by the Planck relationship:

\[
\nu = g_N \mu_N B_0 / \hbar \quad (5.3)
\]

This is the so-called resonance condition.

\( N_\beta \) and \( N_\alpha \) are the numbers of nuclei in the \( \beta \) and \( \alpha \) states respectively. For magnetic induction realizable in laboratory, being fractionally more nuclei are in the lower level (\( \alpha \)) than in the upper (\( \beta \)), and the system of nuclei is magnetically polarized; The possibility, therefore, exists that nuclei may be transferred between the levels by an appropriate oscillating electromagnetic field of frequency \( \nu \), with net absorption of energy; this is the basis of the NMR experiment.

The resonance condition is defined by Equation (5.3), which suggests that the experimental observation of nuclear resonance absorption may be carried out either by fixing \( \nu \) and varying \( B_0 \) until resonance is observed, or by fixing \( B_0 \) and varying \( \nu \). In practice, both methods have found widespread application, and nowadays a third technique is of importance of which a pulse of radiation near to the frequency \( \nu \) is applied to the system of nuclei to excite the resonance very rapidly; the decay of magnetic polarization is observed as a function of time. Because different nuclei have different nuclear g-factors, the resonance condition (5.3) varies from nucleus to nucleus.
At resonance, the probability of the radiation of frequency ω inducing a transition in the sense α → β (absorption) is exactly equal to the probability of its inducing a transition in the sense β → α (emission). Because there are more nuclei in the lower energy state, a net absorption will occur. The excess population in the lower level will gradually diminish with time, while the population of the upper level will increase until they become equal and then there will be no net absorption and the signal, of a spectrometer designed to detect resonance, will disappear. This phenomenon is known as saturation, and if it were not for the fact that there exist means whereby the spin system exchanges energy with its surroundings and tends to restore the Boltzmann equilibrium, in opposition to the effects of net absorption of the applied radio frequency, the experiment would be of little practical value; these restoring processes are known as relaxation, and they effectively provide a continuous supply of excess nuclei in the lower level for excitation.

It is now necessary to bring into the classical picture one of the consequences of quantization, namely that the component of the nuclear magnetic moment vector along any given direction may only take up one of a discrete set of values. For a nucleus for which l = 1/2, this means that the magnetic moment can precess about the +z or −z axis with a unique angle θ [corresponding to the m_z = +1/2 (α) and m_z = -1/2 (β) states respectively] which depends upon the value of B_0 and the nature of the nucleus. In an assembly of identical nuclei of spin ½ all will precess with the same angle θ, and there will be slightly more precessing about +z than about −z since the Boltzmann distribution favours slightly the lower energy state. There is no way in which the nuclear moments distinguish the x and y directions, however, and so there is no phase coherence in the xy plane;

The net result is an overall magnetization M, of the nuclear sample, in the direction of the z-axis. At resonance the sample is able
to absorb energy from a secondary applied field which rotates at the Larmor frequency $\nu_L$ in the xy plane; conveniently, the magnetic vector of electromagnetic radiation of frequency $\nu_L$ supplies the energy. The effect is to change the net magnetization $M$, of the sample.

5.3 Chemical shift

(a) The Basis of shielding, Deshielding – Chemical Shift.

Electrons surrounding a nucleus, under the influence of a magnetic field circulates and in doing so they generate their own magnetic field. This is opposed to the applied field at the nucleus as shown for a proton of a C-H bond\(^87\). Because the induced field opposes the applied field, electrons are said to be diamagnetic and the effect on the nucleus is called diamagnetic shielding\(^88\).

Because the nucleus experiences a weaker magnetic field than that applied externally, it is said to be shielded. This type of shielding is termed diamagnetic shielding. The externally applied magnetic field $H_o$ is uniform over the entire molecule and therefore, it cannot make different protons nonequivalent. However, the magnetic field that is induced by the movement of electrons over the molecule is not uniform and this situation makes the protons to be nonequivalent. Thus each nucleus in a different environment in the molecule under study experiences a slight different local magnetic field due to the circulation of electrons in neighboring bonds and to through space effects. The hydrogen nuclei, near these magnetic fields induced by the molecule may be more highly shielded or deshielded and they experience an effective magnetic field that is either less or greater than that applied externally i.e., $H_o$ due to the induced field either opposing or reinforcing $H_o$. The shielded nuclei will need the application of stronger external magnetic field (to the sample of the compound under study) before the
spin of these hydrogen nuclei flip and appear as peaks on the spectrum as they absorb energy. Since the effective magnetic field at the shielded proton is always weaker than the external field, the applied field $H_0$ must be made stronger before resonance is observed. The reverse effect is deshielding. Thus, each nucleus (e.g., a proton) in a different environment requires a slightly different applied magnetic field $H_0$ for resonance and peaks occur in different regions of the spectrum.

Effects which cause shifts to lower fields (downfield) are called deshielding, while the opposite effect i.e., upfield shift is termed as shielding. These changes are termed as "chemical shifts" since these shifts result from the circulation of electrons in chemical bonds.

Thus in short, a high electron density shields the nucleus and causes resonance to occur at high field (low $\delta$ values) while a low electron density causes resonance to occur at low field (high $\delta$ values).

(b) The Measurement of Chemical Shift – Internal Standard.

The standard reference compound which is universally accepted and used for most $^1$HNMR spectra is tetra methyl silane, (CH$_3$)$_4$Si, commonly abbreviated TMS. It is chosen because it is a volatile liquid; b.p.26.5°C is inert to most reagents and is soluble in most organic liquids. A small amount is added to a sample and it gives an intense sharp signal even at low concentrations to the far right. All hydrogens in TMS are equivalent. Furthermore, silicon is electropositive relative to carbon and tends to donate electron density to the methyl groups, thereby increasing their shielding. The relatively high shielding of the protons in TMS causes is to resonate up field, well clear of most common organic protons encountered in organic compounds. Since its
boiling point is low, it can be easily removed from a sample of valuable organic compound to be recovered after spectral determination.

The chemical shift positions are frequently expressed in $\delta$ (delta) units, which are defined as differences, in ppm from the TMS signal. The $\delta$ unit is proportionality and is thus dimensionless. It is independent of field strength, thus the $\delta$ values for given protons would be correct (same) on a 60MHz spectrometer or on a 100- MHz spectrometer, etc. The chemical shifts are generally expressed in dimensionless units ($\delta$ scale) independent of the applied frequency.

In summary, the chemical shift of a proton is determined by its environment. Successful interpretation of $^1$HNMR spectra begins with the prediction of the chemical shift position for the different hydrogens in a given organic compound.

5.4 The experimental technique

The basic requirements of a spectrometer are simple:

1. A powerful magnet into which the sample is placed. A net magnetization is induced in the direction of the applied magnetic induction $B_0$.

2. A radiofrequency transmitter, which supplies the (Larmor) frequency appropriate for the particular field strength and nucleus under examination. The linearly oscillating r.f. field is applied perpendicularly to the direction of $B_0$ (in the $xy$ plane) and the magnetic vector of this field has a component rotating at the Larmor frequency, i.e. along the $x'$ axis in the rotating frame.

3. A radiofrequency receiver which is arranged to detect resonance by registering only the signals appearing in the $Y'$ direction of the rotating frame.
(4) A recorder, to provide a permanent record of the signals observed by the receiver.

(5) The probe, which is the electrical device at the center of the magnetic field into which the sample is placed in a suitable holder. The holder acts as a turbine, and air jets are arranged inside the probe to provide tangential forces, which spin the sample about the vertical axis. At resonance, absorption of r.f. energy causes the bridge to go out of balance and the resultant signal is displayed as the spectrum.

**Fourier transform (f.t.) spectrometer**

The basic spectrometer system consists of magnet, probe, radiofrequency oscillator, receiver, and a recorder. The heart of the system is the computer and its interface to the spectrometer system, which controls the timing of the system and the acquisition and manipulation of data. The experimental sequence is as follows.

(1) At a command from the computer, the pulsing unit allows high radio frequency power (close to the Larmor frequency for the nucleus under investigation) to pass to the transmitter coil. After a short interval of time (typically 10-100μs) the computer issues a command to shut down the radiofrequency source (i.e.,) an r.f. 'gate' or switch is opened and closed).

(2) The signal is observed by the observing receiver for an interval of time as instructed by the computer. This is the acquisition time and is typically about 1-5 s.

(3) After going through a low-pass filter, the analogue signal is converted to digital form (by an a.d.c) and stored in the computer.

(4) The pulsing unit is reactivated and the sequence repeated. The new signal is added to that already present in the computer.
(5) When a previously determined number of signals have been added coherently the computer applies a Fourier transform analysis to the stored (time domain) spectrum and produces the frequency domain spectrum in digital form.

(6) The digitized spectrum is converted to analogue form (d.a.c.) and output on a chart recorder is the usual way. A listing of line positions and intensities corresponding to the digitized spectrum is also printed out via the digital input / output device, typically a teletype.

All instructions for operating the system, e.g. pulse length in microseconds, acquisition time, spectral width, display parameters are input to the computer via the teletype, and during the whole process the computer controls everything via a master program which is permanently in residence in core. A magnetic tape or disc unit provides a convenient back up facility for the storage of programmes, spectra, or unprocessed data and considerably enhances the versatility of the system.

\(^{1}\)HNMR spectra of the samples chosen are taken from RSIC centre, I.I.T, Chennai using BRUKER ADVANCE 400 FTNMR. It consists of the magnet in ultra shield technology. The lock and shim are digitally controlled and can be operated via soft ware. The probes are the BBO probe with I H coupling, 2 H lock, standard region BB31P - 15N and Z gradient coil for GRASP II work. It has 2 channel amplifier system (20-420MHz each). The data processing unit consists of elegant, logical & compact pulse programming architecture.
5.5. Infrared Spectroscopy

Introduction

Infra red radiations refer broadly to that part of the electromagnetic spectrum between the visible and microwave regions, of greatest practical use to the organic chemist in the limited portion between 4000 and 400 cm\(^{-1}\). There has been some interest in the NEAR-IR (14,290 – 4000 cm\(^{-1}\)) and FAR-IR regions (700 -200 cm\(^{-1}\)).

Although IR spectrum is characteristic of the entire molecule, it is true that certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule. It is the persistence of these characteristic bands that permits the chemist to obtain useful structural information by simple inspection and reference to generalized charts of characteristic group frequencies.

IR spectra have been taken for the samples Tartaric acid and its salts with the help of Bruker IFS 66V FT – IR spectrometer (RSIC, I.I.T, Chennai)

Infrared analysis of solutions

Atoms are bound together in a certain geometric configuration by electronic clouds around the atomic nuclei in a molecule. When the centre of gravity of the electrons and nuclei in a molecule do not coincide, the molecule will possess a permanent dipole moment \(\mu = e d\) where \(e\) is the electronic charge and \(d\) is the distance between the charges. The greater the value of dipole moment, the greater is the polarity of the bond.

The charge distribution of a molecule such as ‘CO’ or ‘NO’ is not symmetric. One atom has a greater electron density than the other. When the distance between the centres fluctuates, an oscillating
electric field is established and the molecules undergo a net change in dipole moment. This change enables the molecule to interact with the electric field associated with the radiation. If the frequency of the radiation matches the natural vibrational frequency of the molecule, there occurs a net transfer of energy i.e. absorption of radiant energy by the molecule, which results in a change in amplitude of its vibration.

On the basis of simple harmonic motion potential energy of the vibrating molecule is

\[ E = \left( v + \frac{1}{2} \right) \left( \frac{h}{2\pi} \right)^2 \left( \frac{k}{\mu} \right)^{\frac{\hbar}{h}} \]  

(5.4)

Where, \( v \) is the vibrational quantum number which can take only positive integral values, \( k \) is the force constant of the bond, \( \mu \) is the reduced mass, and \( h \) is the Planck's constant. The vibrational frequency of the bond is expected to increase when the bond strength increases and also when the reduced mass of the system decreases.

Because the bonds are elastic, the atoms execute vibrational motions in which, its distances and internal angles change periodically. A molecule always has definite number of normal modes of vibration. Each mode has its fixed frequency. When many of them are superposed, the resulting motion is also a periodic normal mode.

**Modes of vibration**

Basic categories of molecular vibration are stretching and bending. An N atomic molecule has (N-1) bonds between its atoms, so (N-1) of the vibrations are bond stretching motions, the other (2N-5) for non linear or (2N-4) for linear molecules are bending motions. The stretching vibrations occur at higher frequencies whereas bending or deformation vibrations occur at lower frequencies. There is a possibility
for the same bond to perform stretching and bending vibration simultaneously in a molecule. Such a vibrating molecule can absorb IR radiation in the region $10,000 - 100 \text{ cm}^{-1}$ and can convert it into energy of molecular vibration.

Scientists\textsuperscript{94-96} usually examine certain region of the electromagnetic spectrum in a systematic way by using infrared techniques to confirm the presence or absence of certain group frequencies. In the electromagnetic spectrum, infrared radiation has wave numbers extending from roughly, $13,000 - 33 \text{ cm}^{-1}$ or wavelength from 0.75 to 300 μm. But majority of applications of infrared absorption is confined to the region from about 4000 to 667 cm\(^{-1}\).

5.6 Study of IR spectra of solutions

Amides

All amides show a carbonyl absorption band known as the amide I band. Its position depends on the degree of hydrogen bonding and, thus on the physical state of the compound.

Primary amides show two N – H stretching bands resulting from the symmetrical and asymmetrical N – H stretching. Secondary amides show only one N – H stretching band. As in the case of O – H stretching, the frequency of the N – H stretching is reduced by hydrogen bonding, through to a lesser degree. Overlapping occurs in the observed position of N – H and O- H stretching frequencies so that an unequal differentiation in structure is sometimes impossible.

Primary amides and secondary amides, display a band or bands in the region of 1650-1515 cm\(^{-1}\) due primarily to NH\(_2\), NH bending; the amide II band. This absorption involves coupling between NH bending and other fundamental vibrations and requires a trans geometry.
Out-of-plane NH wagging is responsible for a broad band of medium intensity in the 800-666 cm\(^{-1}\) region.

**Stretching vibrations**

In dilute solution in non polar solvents, primary amides show two moderately intense NH stretching frequencies corresponding to the asymmetrical and symmetrical NH stretching vibrations. These bands occur near 3520 and 3400 cm\(^{-1}\) respectively. In the spectra of solid samples, these bands are observed near 3350 and 3180 cm\(^{-1}\) because of hydrogen bonding\(^97\).

In IR spectra of secondary amides, which exist mainly in the trans conformation, the free NH stretching vibration observed in dilute solutions occurs near 3500-3400 cm\(^{-1}\). In more concentrated solutions and in solid samples, the free NH band is replaced by multiple bands in the 3330-3060 cm\(^{-1}\) region. Multiple bands are observed since the amide group can bond to produce dimers, with an s-cis conformation, and polymers with an s-trans conformation.

**C = O Stretching Vibrations (Amide I Band)**

The C=O absorption of amides occurs at lower frequencies than 'normal' carbonyl absorption due to the resonance effect. The position of absorption depends on the same environmental factors as the carbonyl absorption of other compounds.

Primary amides (except acetamide, whose C = O bond absorb at 1694 cm\(^{-1}\)) have a strong amide I band in the region of 1650 cm\(^{-1}\) when examined in the solid phase. When the amide is examined in dilute solution, the absorption is observed at a higher frequency, near 1690 cm\(^{-1}\). In more concentrated solutions, the C=O frequency is observed at some intermediate value, depending on the degree of hydrogen bonding.
**N - H Bending Vibrations (Amide II Band)**

All primary amides show a sharp absorption band in dilute solution, amide II band) resulting from NH₂ bending at a somewhat lower frequency than the C = O band. This band has an intensity of one-half to one third of the C = O absorption band. In mulls and pellets the band occurs near 1655 - 1620 cm⁻¹ and is usually under the envelope of the amide I band. In dilute solutions, the band appears at lower frequency, 1620 – 1590 cm⁻¹ and normally is separated from the amide I band. Multiple bands may appear in the spectra of concentrated solutions, arising from the free and associated states.

**5.7 Instrumentation**

The IR spectrometer used for taking the spectrum consists of

(i) source

(ii) monochromator

(iii) Detector

**i) Radiation Source**

The most important source of IR light for scanning the spectrum of an organic compound is Nernst glower which consists of a rod of the sintered mixture of the oxides of Zirconium, Yttrium and Erbium. The rod is electrically heated to 1500°C to produce IR radiation.

**ii) Monochromator**

The IR instruments used prisms or grating to diffract the light. For prism material, glass or quartz cannot be used since they absorb strongly through most of the IR region. Sodium chloride is commonly used as cell containers (or) for prism materials as these are transparent to most of the IR region. In the grating method, light falling
on the grating is diffracted at certain angles and so specific wavelength appear with constructive interference at specific angles of diffraction.

**Mode of operation**

Light from the source is split into two beams and one of the beams is passed through the sample under examination and it is called the sample beam and the other beam is called the reference beam. When the beam passes through the sample, it becomes less intense due to the absorption of certain frequency. Now, there will be a difference in the intensities of the two beams. Let $I_0$ be the intensity of the reference beam and $I$ be the intensity of the beam after interaction with the sample respectively.

The absorbance of the sample at a particular frequency can be calculated as,

$$A = \log \left( \frac{I_0}{I} \right)$$

Also the transmittance $T$ is given by,

$$T = \frac{I}{I_0} \quad \text{(or)} \quad A = \log \left( \frac{1}{T} \right)$$

Intensities of the bands can be recorded as a linear function $T$ against the corresponding wave number. The two beams are made to fall on a segmented mirror with the help of the other two mirrors. The chopper rotates at a definite speed and reflects the sample beam and the reference beam to a monochromator grating. As the grating rotates, it sends individual frequency to detector which converts IR energy into electrical energy.

**iii) Detectors**

Most instruments use thermopile detectors. In IR spectrometer the current will be proportional to the intensity of radiation falling on the thermopile. The IR energy which is converted into electrical energy is
amplified. Due to difference in intensities of the two beams, the A.C current starts flowing from detector to the amplifier. The amplifier is connected to a pen recorder which draws absorption bands on the chart.

5.8 Analysis of $^1$HNMR spectra

In the present study the $^1$HNMR spectra of Tartaric acid and Tartrate salts in Formamide solutions have been discussed.

Formamide:

The signal at 8.61, 8.57, 8.23, 8.20 (J = 7.75Hz) ppm are all assigned to CH of Formamide. These are observed as double doublets due to the splitting of the signal by the two different hydrogen atoms of the adjacent NH$_2$ groups. Two broad triplets (J = 7.2Hz) are observed at 6.23 to 5.82 ppm. The triplet splitting is due to the spin of the nitrogen atom. The hydrogen of adjacent CH group splits the triplets further into two signals. Hence double triplets are observed for the protons centered at 6.23 ppm and 5.82 ppm. These observations are due to the 2NH and 1 CH protons in Formamide CHCONH$_2$.

Generally in the $^1$HNMR spectrum of amides, the signal due to CH is excepted at 8 ppm and NH signal at 5-6 ppm. If there is an intramolecular bonding, these signals will experience a down field shift and also spin-spin interaction due to cis and trans coupling between the H of NH and CH groups.

In the spectrum of Formamide a double doublet is observed at 8.57 ppm (3Hz) and 8.21 ppm (5Hz). The presence of such doublets in a simple molecule like Formamide can be attributed to resonance in Formamide.

If the Formamide exists as a dimer, then again a similar double-doublet pattern will be observed for the CH signal. Considering the
intensity ratio of the peaks observed, it is 25%, 8% and 10%. Taking the ratio between least intense peak and the highly intense peak the ratio is found to be

<table>
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<th>Ratio</th>
<th>Intensity</th>
<th>Ratio</th>
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<tr>
<td>5.82</td>
<td>10/10</td>
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</table>

Considering the NH signals, two triplets are observed at 6.23 ppm and 5.82 ppm. The presence of these triplets indicates two non-equivalent H atoms on the nitrogen atom of Formamide (Dimer) structure.

The signal at 8.57 ppm (2H) corresponds to two hydrogen atoms. In the monomer, only one proton is present on the carbon and singlet is expected in the $^1$HNMR spectrum. Hence dimeric structure is
assigned to Formamide. Further the two triplets at 6.23 (1H), 5.81 (1H) for the NH signal also account for the dimeric structure\textsuperscript{97} of Formamide.

**Tartaric acid in Formamide**

A signal at 8.17 ppm is due to -COOH group of tartaric acid. At 8.03 and 7.99 ppm CH doublet is found. This gets merged with the solvent peak. At 7.33 and 7.09 ppm the OH signal is observed. Two close triplets at 5.88 ppm and 5.63 ppm are due to two NH protons. The signal at 4.94 – 4.85 ppm is assigned to OH of tartaric acid. At 1.98 ppm CH of tartrate is observed.

**Potassium bitartrate in Formamide**

A doublet at 8.18 ppm is due to CH proton. A pentet at 6.22-5.8 ppm is assigned to the two NH protons. At 3.5 ppm 6.9 ppm and 7.5 ppm the OH signal of tartrate is found. At 2.01 ppm CH of tartrate is observed.

**Disodium tartrate in Formamide**

In Disodium tartrate a signal at 8.23 ppm and 8.20 ppm are assigned to CH of Formamide solutions. At 8.3 ppm and 7.5 ppm broad signals are observed. These are due to the OH group of Formamide. The signal at 6.2 ppm and 5.8 ppm are assigned to two NH signals. At 4.5 ppm, OH of tartrate is observed. At 2.17 and 2 ppm two singlets are observed and these are assigned to CH of tartrate.

**Sodium potassium tartrate in Formamide**

A broad signal in the region 8.24-8.07 ppm is assigned to CH of Formamide merging with the solvent peak. At 7.52 – 7.27 ppm the OH of tartrate has merged with the solvent peak. Pentet in the region 5.82
is due to the NH protons. A broad signal at 4.42 – 3.76 is assigned to the OH of tartrate. The CH signal of tartrate is observed at 1.8 ppm.

**Sodium antimony tartrate in Formamide**

At 8.5 ppm a singlet is observed and at 8.25 ppm a doublet is found. A signal at 8.5 ppm is due to OH of tartrate. A doublet at 8.25 ppm is due to CH signal of Formamide. At 7.26 ppm the OH group has merged with the solvent peak. Two triplets at 6.19 and 5.91 ppm are assigned to NH protons of Formamide. At 2 ppm the CH signal of tartrate is observed.

**Copper tartrate in Formamide**

Singlets at 9.2 ppm and 7.2 ppm are due to the hydroxyl group in copper tartrate. The signal at 8.1 ppm due to the CH proton of Formamide has merged with the solvent signal. Two triplets centered at 6.18 and 5.78 ppm are assigned to the N-H protons. At 2.01 ppm CH proton of tartrate is observed.

**Calcium tartrate in Formamide**

Signal at 8.2 ppm has merged with the solvent peak. CH signals have merged at 2 ppm with the solvent peak. The signal at 7.26 ppm is due to the OH of tartrate. Two triplets at 6.22 and 5.68 ppm are due to NH protons. A signal at 2.01 ppm is due to CH proton of tartrate.

**Barium tartrate in Formamide**

A well-defined doublet at 8.18 and 8.15 ppm are assigned to CH proton of Formamide in the solution. At 7.5 ppm the OH signal of tartrate is found. Two triplets at 6.22 and 5.8 ppm are assigned to NH protons. At 4.2 ppm, OH signal is found. At 2.01 ppm the CH signal of tartrate is observed as a singlet.
# RESULTS OF STUDY OF $^1$HNMR SPECTRA

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<th>Name of the Sample</th>
<th>CH solvent signal</th>
<th>OH in solute</th>
<th>NH signals</th>
<th>CH solute signal</th>
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PL 1
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MODEL: GSX 400

***************
SAIF, IIT, MADRAS.
***************
OPERATOR:
5.9 IR spectral analysis

Tartaric acid in Formamide

In tartaric acid a broad absorption is observed in the region 3400-3100 cm\(^{-1}\). In this region, the stretching vibrations of OH, NH and CH bond in the solute and solvent are accounted. At 2881 cm\(^{-1}\) the absorption is due to C = N character of Formamide. Slightly broad and intense absorptions at 1683 and 1601 cm\(^{-1}\) are due to the Carbonyl group of tartaric acid and amide I and amide II of Formamide. The two absorptions at 1390 and 1306 cm\(^{-1}\) are assigned to the CH groups.

The absorptions at 1066 cm\(^{-1}\) is due to C-O group in solute and solvent. Number of absorptions 903-485 cm\(^{-1}\) is all due to bending vibrations.

Potassium bitartrate in Formamide

Two stretching vibrations at 3410 and 3333 cm\(^{-1}\) are due to the OH and NH vibrations of Formamide.

At 3185 cm\(^{-1}\) CH vibration is observed. At 2887 cm\(^{-1}\) C = N vibration is found. A very sharp absorption at 1689 cm\(^{-1}\) is due to the carbonyl group in solute and solvent. At 1612 cm\(^{-1}\) the amide II absorption is found. The two absorptions at 1391 and 1314 cm\(^{-1}\) are due to the C-H vibrations. At 1050 cm\(^{-1}\) C-O vibration is present. At 616 cm\(^{-1}\) the N-H bending vibration is found.

Disodium tartrate in Formamide

Stretching vibrations at 3410, 3331 and 3185 cm\(^{-1}\) are assigned to the OH group in tartrate, NH group in Formamide and CH group in Formamide and tartrate. Stretching frequency at 2885 cm\(^{-1}\) is due to partial double bond $\overset{\wedge}{C} = N$ in Formamide. Very sharp absorption
at 1687 cm\(^{-1}\) is due to carbonyl group in tartrate and amide I in Formamide. Small absorption at 1613 cm\(^{-1}\) is due to amide II absorption merging with carbonyl vibrations. Two absorptions at 1319 cm\(^{-1}\) and 1312 cm\(^{-1}\) are due to the CH group in the solute and solvent. The absorption at 1051 cm\(^{-1}\) is due to C - O present both in solute and solvent. A sharp absorption 615 cm\(^{-1}\) is due to N-H out of plane bending vibrations.

**Sodium potassium tartrate in Formamide**

For sodium potassium tartrate, the broad absorption in the region 3500-3100 cm\(^{-1}\) is accounted for O-H, N-H and C-H stretching vibrations. At 2884 cm\(^{-1}\) C = N stretching vibration is present. Broad stretching absorption at 1683 cm\(^{-1}\) and 1602 cm\(^{-1}\) is due to both Carbonyl group in Tartrate and amide I, amide II in Formamide.

Two absorptions at 1390 cm\(^{-1}\) and 1308 cm\(^{-1}\) are the characteristics of CH group. At 1050 cm\(^{-1}\) C - O vibration is observed. At 601 cm\(^{-1}\), the N-H out of plane bending vibration is observed.

**Sodium antimony tartrate in Formamide**

Very broad and intense absorption in the region 3500-3100 cm\(^{-1}\) are all due to O-H, N-H and C-H vibrations in solute and solvent. The very sharp absorption at 2886 cm\(^{-1}\) is assigned to C = N in Formamide. At 2770 cm\(^{-1}\), the absorption is very sharp. This is ascribed to partial NH\(^+\) absorption of Formamide.

Very broad absorption in the carbonyl region 1750 to 1500 cm\(^{-1}\) are due to C = O and NH of solute and solvent. Two well defined peaks at 1392 and 1312 cm\(^{-1}\) are due to CH group.
At 1051 cm\(^{-1}\) C-O stretching vibration is observed. Absorption at 776 cm\(^{-1}\) may be due to the antimony ion which is quite big. At 616 cm\(^{-1}\), the N-H out of plane bending vibration is observed.

Copper tartrate in Formamide

Sharp absorptions are found at 3413 cm\(^{-1}\), 3336 cm\(^{-1}\) and 3203 cm\(^{-1}\). They have merged together and observed as a slightly broad absorption. In this region O-H, N-H and C-H stretching vibrations can be accounted. At 2887 cm\(^{-1}\) C = N vibration is visible. At 1690 cm\(^{-1}\) a very sharp absorption is characterized as due to carbonyl group of tartrate. At 1618 cm\(^{-1}\) NH amide II band is observed. Two strong absorptions at 1391 cm\(^{-1}\) and 1314 cm\(^{-1}\) are due to CH group. At 1051 cm\(^{-1}\) C - O stretching vibration is found. Sharp absorption at 614 cm\(^{-1}\) is due to N-H bending vibration of Formamide.

Calcium tartrate in Formamide

In calcium tartrate, a broad and intense stretching absorption is found in the region 3500 - 3100 cm\(^{-1}\). In this region O-H, N-H and CH stretching vibrations have merged together. At 2885 cm\(^{-1}\) a sharp absorption is observed. This may be due to the C = N stretching vibration of Formamide.

At 2769 cm\(^{-1}\) another sharp absorption is observed. This may be due to partial ionic character of NH\(^+\) in Formamide. A broad and intense absorption at 1750 to 1600 cm\(^{-1}\) in the carbonyl region may be due to the C = O stretching vibration in the tartrate and amide I and amide II in the Formamide molecule.

Two identical stretching vibrations at 1387 and 1315 cm\(^{-1}\) are assigned to CH of tartrate and Formamide. At 1050 cm\(^{-1}\), a sharp absorption is attributed to the C - O vibrations in both the amide and
tartrate. Very broad and intense absorption at 628-620 cm\(^{-1}\) are assigned to the bending vibration.\(^8\)

**Barium tartrate in Formamide**

The stretching absorptions in the region 3500 – 3100 cm\(^{-1}\) is very broad and intense. In this region, the stretching vibrations of N-H, O-H and C-H have merged. The sharp absorptions at 2883 cm\(^{-1}\) and 2768 cm\(^{-1}\) are assigned to C = N and partial NH\(^+\) bonds. In the carbonyl region a broad absorption in 1750 – 1600 cm\(^{-1}\) are due to carbonyl group in the solute and solvent.

At 1390 and 1306 cm\(^{-1}\) two very sharp absorptions are observed. These are due to the C-H vibrations. At 1050 cm\(^{-1}\) C - O vibration is observed as a very sharp peak.

In the N-H bending region 588-603 cm\(^{-1}\) a number of bending vibrations have merged together. Compared to the calcium ion Barium ion is bigger and hence the bending vibrations are clearly observed in this region.

**5.10 Results and Discussion**

(a)\(^{1}\)HNMR Spectroscopy:

From the spectral studies of \(^{1}\)HNMR, by comparing the spectra of Tartaric acid, Potassium bitartrate, Disodium tartrate and Sodium potassium tartrate solutions in Formamide, NH protons exhibit an up field shift. This suggests the binding of cation to the carbonyl group of formamide. The up field shift is due to the cation entry into the dimeric cage.

Copper can form complex ions with formamide because it is a transient metal. Hence ion-solvent interaction is stronger and hence an
## RESULTS OF STUDY OF IR SPECTRA

<table>
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<th>Name of the Sample</th>
<th>OH, NH &amp; CH in cm$^{-1}$</th>
<th>C = N in cm$^{-1}$</th>
<th>C = O cm$^{-1}$</th>
<th>N-H amide I band cm$^{-1}$</th>
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</thead>
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upfield shift is observed. For ion-ion inter Calcium tartrate and Barium tartrate solution upfield shifts are similar since they both belong to the category of alkaline earth metals.

An upfield shift is observed for Sodium antimony tartrate and Barium tartrate solutions. This indicates that there is a decrease in diamagnetic anisotropy. The shift is greater for Sodium antimony tartrate and Barium tartrate solutions. As Antimony and Barium ions are quite big these cations cannot enter the dimeric structure however it can bind to the solvent from outside.

b) IR Spectroscopy:

On comparing the IR spectra of the solutions of Tartaric acid, Potassium bitartrate, Disodium tartrate, Sodium potassium tartrate solutions in Formamide with pure solvent, it is found that there is a decrease in the stretching vibration of NH group for all the systems. This indicates that NH stretching is easy in such solutions. Anion association to NH is highly increased. The vibration of carbonyl group has also undergone blue shift. This again indicates the binding of cation to carbonyl group. This carbonyl group exists as hydrogen bonded entity in dimeric cage of formamide. This dimer might have expanded well in its size in order to accommodate the solute such expansion of the cases may be another reason for this trend. This result supports the results of thermodynamic analysis. High values of \( \pi_i \), and the positive \( \Delta \pi_i \) values of the systems suggest that these salts supports the structure enhancement of the solvent.

For Sodium antimony tartrate solutions a red shift is observed. This red shift indicates strong binding of anion to the solvent N-H. However, in Sodium antimony tartrate this shift may be due to strong solute-solute interaction. This result along with thermo dynamical
analysis (negative value of $\Delta n_i$ and decrease in $n_i$) supports a weak ion-solvent interaction and strong solute-solvent interaction.

For the Copper tartrate, Calcium tartrate and Barium tartrate solutions in formamide, there is a stretching frequency. This is due to strong binding of the anion to NH. The increase in Carbonyl group stretching frequency also supports that there is a strong binding of cations. For Barium tartrate and Sodium antimony tartrate solutions even though there is an increase in stretching frequency, it is solvated from outside. From the results of thermodynamic analysis, there is a weak solute-solvent interaction and (negative values of $\Delta n_i$ and decreasing trend of $n_i$) strong solute-solvent interactions are weak in Sodium antimony tartrate and Barium tartrate solutions.

The various interactions studied from the acoustic, thermodynamic, thermochemical and spectroscopic analysis, the structures are picturized.
Sodium Potassium Tartrate - Formamide

Sodium Antimony Tartrate - Formamide
Copper Tartrate - Formamide

Calcium Tartrate - Formamide

Barium Tartrate - Formamide

Tartrates of alkaline earth cations - Formamide

Tartrates of Alkaline earth cations-formamide
Weak Interactions