3.1 Introduction

In the present chapter, the materials used, methods of preparation of ionic liquids and polymer gel electrolytes and the techniques employed to characterise the ionic liquids and polymer gel electrolytes have been discussed. The following ionic liquids have been studied in the present work:

- 2,3-dimethyl-1-hexylimidazolium bis(trifluoromethanesulphonyl)imide (DMHxImTFSI)
- 2,3-dimethyl-1-hexylimidazolium triflate (DMHxImTf)

Different polymer gel electrolytes containing ionic liquids studied in the present thesis are:

- PC-DMHxImTFSI-PMMA
- PC-DMHxImTFSI-PVdF-HFP
- DMHxImTFSI-PMMA
- PC-DMHxImTFSI-PEO
- DMHxImTFSI-PEO
- PC-DMHxImTf-PMMA
- DMHxImTf-PMMA
- PC-DMHxImTf-PEO
- DMHxImTf-PEO

3.2 Method of Preparation

3.2.1 Preparation of Ionic Liquids

The starting materials used to synthesize ionic liquids are 1,2-dimethylimidazole, 1-bromohexane, lithium trifluoromethanesulphonate or lithium triflate (LiCF$_3$SO$_3$), lithium trifluoromethanesulphonimide (LiN(CF$_3$SO$_2$)$_2$), acetonitrile, dichloromethane, ethyl acetate, deionised double distilled water. The important properties of the materials used for the preparation of ionic liquids are shown in Table 3.1
Table 3.1 Some important properties of materials used for the preparation of ionic liquids

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical Formula</th>
<th>Molecular mass (g mol$^{-1}$)</th>
<th>Melting Point ($^\circ$C)</th>
<th>Boiling Point ($^\circ$C)</th>
<th>Density (g cm$^{-3}$) (at 20$^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dimethyl- imidazole</td>
<td>C$_5$H$_8$N$_2$</td>
<td>96.13</td>
<td>35-38</td>
<td>204</td>
<td>1.02</td>
</tr>
<tr>
<td>1-bromohexane</td>
<td>C$<em>6$H$</em>{13}$Br</td>
<td>108.97</td>
<td>-118</td>
<td>37-39</td>
<td>1.46</td>
</tr>
<tr>
<td>Lithium (trifluoromethanesulphonimide)</td>
<td>LiN(CF$_3$SO$_2$)$_2$</td>
<td>287.08</td>
<td>~ 238</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Lithium triflate</td>
<td>LiCF$_3$SO$_3$</td>
<td>156.0</td>
<td>&gt;300</td>
<td>----</td>
<td>---</td>
</tr>
</tbody>
</table>

Ionic liquids used in the present work have been synthesized by the metathesis reaction [Bonhote et al. (1996); Sakaeb and Matsumoto (2003); Nishida et al. (2003); Singh and Sekhon (2005)]. The detail procedure for the preparation of ionic liquids is given below:

3.2.1 (a) Preparation of 2,3-dimethyl-1-hexylimidazolium bromide (DMHxImBr)

To prepare ionic liquids by metathesis reaction, first the equimolar amounts of 1,2-dimethylimidazole and 1-bromohexane were taken in a round bottom flask equipped with reflux condenser. The mixture was continuously stirred and maintained at 120 $^\circ$C for 40 minutes. A yellow viscous solution of 2,3-dimethyl-1-hexylimidazolium bromide (DMHxImBr) was obtained and cooled for 20 minutes. The scheme of the reaction is shown below:

\[
\begin{align*}
\text{DMHxImBr prepared above, was then used for anion exchange reaction with lithium salts of desired anion to prepare ionic liquids.}
\end{align*}
\]
3.2.1 (b) Preparation of 2,3-dimethyl-1-hexylimidazolium bis(trifluoromethanesulphonylimide) (DMHxImTFSI)

DMHxImTFSI was prepared by the anion exchange reaction of DMHxImBr with lithium trifluoromethanesulphonimide (LiN(CF₃SO₂)₂). (LiN(CF₃SO₂)₂) was dissolved in deionised double distilled water and was slowly added to DMHxImBr along with continuous stirring. To extract out ionic liquid 2,3-dimethyl-1-hexylimidazolium trifluoromethanesulfonylimide (DMHxImTFSI), this mixture was taken in separatory funnel and dichloromethane and deionised double distilled water was added and mixture was shaken vigorously. The organic layer containing ionic liquid gets separated from aqueous layer containing LiBr. Organic layer was again washed with deionised double distilled water to remove LiBr completely. Dichloromethane and residual water were removed from ionic liquid by vacuum evaporation using rotavapor at 100-120 °C. The scheme of the reaction is shown below:

\[
\begin{align*}
\text{H}_3\text{C} \quad \text{N} \quad \text{C}_6\text{H}_{13} \quad + \text{LiN(CF}_3\text{SO}_2\text{)}_2 + \text{H}_2\text{O} & \quad \text{stir, 10 min} \quad \text{H}_3\text{C} \quad \text{N} \quad \text{C}_6\text{H}_{13} \quad + \text{LiBr} \\
\text{CH}_3 & \quad \text{Br}^{-}
\end{align*}
\]

3.2.1 (c) Preparation of 2,3-dimethyl-1-hexylimidazolium triflate (DMHxImTf)

DMHxImTf was prepared by the anion exchange reaction of lithium trifluoromethanesulphonate or lithium triflate (LiCF₃SO₃) in deionised double distilled water. The aqueous solution was slowly added to 2,3-dimethyl-1-hexylimidazolium bromide (DMHxImBr) and then this mixture was stirred for 20 minutes. The mixture of DMHxImTf and LiBr in water was added in 150 ml of dichloromethane in seperatory funnel and then 200 ml deionised double distilled water was added and shaken vigorously. The lower organic layer containing ionic liquid separated from the aqueous layer containing LiBr. Then again organic layer was washed two three times with deionised double distilled water to remove the LiBr completely from the ionic liquid. DMHxImTf was obtained by evaporating the DCM under reduced pressure. The scheme of the reaction is:

\[
\begin{align*}
\text{H}_3\text{C} \quad \text{N} \quad \text{C}_6\text{H}_{13} \quad + \text{LiCF}_3\text{SO}_3 & \quad \text{stir, 10 min} \quad \text{H}_3\text{C} \quad \text{N} \quad \text{C}_6\text{H}_{13} \quad + \text{LiBr} \\
\text{CH}_3 & \quad \text{Br}^{-}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} \quad \text{N} \quad \text{C}_6\text{H}_{13} \quad + \text{LiCF}_3\text{SO}_3 + \text{H}_2\text{O} & \quad \text{in double distilled H}_2\text{O} \quad \text{stir, 10 min} \quad \text{H}_3\text{C} \quad \text{N} \quad \text{C}_6\text{H}_{13} \quad + \text{LiBr} \\
\text{CF}_3\text{SO}_3 & \quad \text{Br}^{-}
\end{align*}
\]
3.2.2 Preparation of polymer gel electrolytes containing ionic liquids

The materials used for the preparation of polymer gel electrolytes containing ionic liquids are: Poly(ethylene oxide) (PEO, mol. wt. 5x10^6, Aldrich), poly(methylmethacrylate) (PMMA, mol. wt. 120,000, Aldrich); polyvinylidenefluoride-co-hexafluoropropylene (PVdF-HFP, Fluka), propylene carbonate (PC, Merck), 2,3-dimethyl-1-hexylimidazolium bis(trifluoromethanesulphonyl)imide (DMHxImTFSI) and 2,3-dimethyl-1-hexylimidazolium triflate (DMHxImTf).

In the present work, the following polymer gel electrolytes have been prepared:

**Solvent free polymer gel electrolytes**
- DMHxImTFSI-PMMA
- DMHxImTFSI-PEO
- DMHxImTf-PMMA
- DMHxImTf-PEO

**Polymer gel electrolytes containing solvent**
- PC-DMHxImTFSI-PMMA
- PC-DMHxImTFSI-PEO
- PC-DMHxImTf-PMMA
- PC-DMHxImTf-PEO

Solvent free polymer gel electrolytes have been prepared by the immobilization of ionic liquid with the addition of suitable polymer in different concentrations. Polymer gel electrolytes containing solvent have been prepared by firstly solvating the ionic liquid in an organic solvent propylene carbonate (PC) followed by the immobilization of this liquid electrolyte using a polymer matrix. Viscous and homogeneous gel electrolytes so obtained have been used for different experimental measurements.

3.3 Characterization techniques

Ionic liquids and polymer gel electrolytes containing different ionic liquids have been characterised by using the following techniques:
- \(^1\text{H} \& \(^{13}\text{C}\) Nuclear Magnetic Resonance (NMR) Spectroscopy
- Complex Impedance Spectroscopy
- Viscosity Measurement
- Fourier Transform Infrared (FTIR) Spectroscopy
- Differential Scanning Calorimetry/Thermogravimetric Analysis (DSC/TGA)
3.3.1 $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy

NMR is a powerful technique used in the determination of molecular structure of unknown organic compounds [Martin et al (1980), Sanders and Hunter (1987)]. The $^1$H and $^{13}$C spectra of a compound provide information on:

- the number of different types of hydrogen and carbon atoms present in the molecule and their relative positions
- the electronic environment of hydrogen and carbon atoms
- the number of neighboring hydrogen and carbon atoms

**Basics of NMR spectroscopy**

NMR spectroscopy is a technique that involves the magnetic spin energy of atomic nuclei. For elements that have non-zero nuclear spin, such as $^1$H, $^7$Li, $^{13}$C etc. an applied magnetic field will influence the energy of nuclei. The atomic nucleus behaves as a tiny spinning magnet, as it possesses both the electric charge and the mechanical spin. Therefore, it can align itself in the direction of an external magnetic field or opposite to it, as well as it can precess around the axis of an applied magnetic field with a frequency ‘ν’ called precessional frequency.

The precessional frequency is proportional to the external magnetic field $B_o$

$$\nu \propto B_o$$

$$\nu = \gamma B_o / 2\pi$$

or

$$2\pi \nu = \gamma B_o$$

where $\gamma$ is the magnetogyric ratio, the ratio between the nuclear magnetic moment ‘$\mu$’ and the nuclear angular momentum $I$.

$$\gamma = \mu / I$$

In the absence of magnetic field, nuclear spins are randomly oriented. However, when a sample is placed in a magnetic field, nucleus with spin +1/2 align with applied field (in the lower energy $\alpha$-spin state) and nucleus with −1/2 align against the applied field (in the higher energy $\beta$-spin state).

When sample is subjected to radio frequency radiations, nuclei in $\alpha$–spin can be raised to $\beta$–state and when nuclei return to their original state, they emit signal whose frequency depends on the difference in energy ($\Delta E$) between $\alpha$ and $\beta$ spin states (Fig.3.1).
The NMR spectrometer detects these signals and displays them as a plot of frequency of the absorption peak versus peak intensity as shown in Fig. 3.2.

![Diagram of NMR phenomenon]

**Figure 3.1** Energy description of the NMR phenomenon

![Graph of frequency versus intensity for NMR spectroscopy]

**Figure 3.2** Frequency versus intensity curve for NMR spectroscopy

The interaction energy between the nuclear magnetic moment and the external magnetic field is given by:

\[ E = h \gamma H m_I \]

where, \( \gamma \) is gyromagnetic ratio of nucleus, \( H \) is external magnetic field, \( m_I \) is magnetic quantum number having \((2I+1)\) possible values, where \( I \) is the nuclear spin quantum number of the nucleus.

The precise resonant frequency of the energy transition is dependent on the effective magnetic field at the nucleus. This field is affected by electron shielding which is in turn dependent on the chemical environment. As a result, information about the
chemical environment of nucleus can be derived from its resonant frequency. NMR signal has been obtained for resonance and frequency of the signal is known as chemical shift. It is customary to adopt tetramethylsilane (TMS) peak as reference and designated zero on the δ scale (where δ(ppm) is a unit of chemical shift). This is because the precise resonant frequency shift of each nucleus depends on the magnetic field used. The chemical shift of NMR spectra is represented as δ_{ppm} and calculated from frequency as follows:

\[ \delta_{ppm} = 10^6 \times \frac{(\nu - \nu_{TMS})}{\nu_{TMS}} \]

where ν is frequency observed for chemical shift for some specific proton, ν_{TMS} is frequency value for TMS signal as shown in Fig. 3.3. The chemical shift using this equation is not dependent on the magnetic field and it is convenient to express it in ppm.

In the present work, \(^1\)H and \(^{13}\)C NMR of the ionic liquids were recorded at room temperature using JEOL AL-300MHz NMR spectrometer at 300MHz and 75MHz respectively in CDCl₃ with tetramethylsilane (TMS) as internal standard. Chemical shifts were expressed as δ(ppm) down field from TMS. The spacing between the lines of a doublet, triplet or quartet is called the coupling constant (J) and is measured in Hertz. The abbreviations used to explain the multiplicity are: s-singlet, d-doublet, t-triplet, dd-doublet of doublet, m-multiplet, J-coupling constant.

### 3.3.2 Complex impedance spectroscopy

The complex impedance spectroscopy is extensively used to measure the conductivity of the ionic materials [Bauerle (1969); Badwal (1988)]. Polymer electrolytes have both the resistance and capacitance and hence impedance can be measured using ac impedance spectroscopy.

The electronic conductivity is generally measured by the dc measurement technique. However the conductivity of the superionic solids, in which conduction is due to the movement of ions cannot be measured by using dc measurement technique. Because, when we apply direct current between two electrodes (specimen is between the electrodes), after some time all the cations accumulate on the electrode having negative charge and anions accumulates on the electrodes having positive charge. Due to this polarization of the specimen takes place which inhibits the further movement of
ions in the specimen and we can not measure the true bulk conductivity of the superionic materials by dc measurement technique.

**Basics of impedance spectroscopy**

When a sinusoidal potential is applied across the sample whose impedance is to be measured, a current flows through it. Suppose a potential (or voltage) $V(t) = V_0 \sin \omega t$ is applied to a cell, which results in flow of current, $I(t) = I_0 \sin (\omega t + \theta)$, where $\theta$ is phase difference between voltage and current and, $V_0$ and $I_0$ are the amplitude of voltage and current respectively then impedance can be determined as

$$Z = \frac{V(t)}{I(t)} = |Z| e^{i\theta} = Z' + jZ''$$

where $Z'$ and $Z''$ are real and imaginary parts of $Z$.

Impedance $Z$ and admittance $Y$ are related as

$$Y(\omega) = \frac{1}{Z(\omega)} = G(\omega) + jB(\omega)$$

where $G$ is conductance, $B$ is susceptance and $\omega$ corresponds to the frequency of measurement. Impedance ($Z$) of a cell is represented as shown in Fig. 3.3.

![Figure 3.3](image)

**Figure 3.3** Representation of the impedance ($Z$) of a cell.

Two rectangular co-ordinate values are

$$R_e(Z) = Z' = |Z| \cos \theta$$

$$I_m(Z) = Z'' = |Z| \sin \theta$$

with phase angle $\theta = \tan^{-1} \left( \frac{Z''}{Z'} \right)$ and $|Z| = [(Z')^2 + (Z'')^2]^{1/2}$.

Real and imaginary parts of the impedance/admittance in the complex plane give the frequency dispersion curves.

Impedance spectroscopy is characterized by the measurement and analysis of impedance related functions $Z$, $Y$, $\varepsilon$, etc, and plotting these functions in the complex plane [Cole and Cole (1941); Macdonald (1953); Gabrielli (1998)]. The electrochemical
behavior of the electrode and electrolyte materials is measured by electrical measurements by using cell with two identical electrodes in rectangular or circular shapes. The complex impedance response from the electrodes and electrolyte is derived by forming the relation between a sinusoidal alternating signal $V$ and time dependent current response from the sample and electrodes. To relate the current flowing to the applied potential, two parameters are required. One is the opposition to the flow of charge, which is the ratio of the voltage and current maxima, $Z_{\text{max}}=\frac{V_{\text{max}}}{I_{\text{max}}}$ and other parameter is $\theta$, phase angle between voltage and current. The combination of these parameters represents the impedance, $Z$, of the cell.

\[ V(t)=V_0 \sin \omega t \]
\[ I(t)=I_0 \sin (\omega t+\theta) \]

where $\theta =$phase angle between voltage and current.

There are three basic impedance components viz. (i) anode/electrolyte interface, (ii) cathode/electrolyte interface and (iii) bulk electrolyte. Impedance response of the bulk electrolyte can be represented by simple resistor, however electrode/electrolyte interface requires a more complicated arrangement of components. For resistor, impedance is simply equal to $R$ as it is considered independent of frequency. Capacitive impedance is dependent on frequency ($\omega$), $1/\omega C$ and would be a spike on a complex plot. Admittance ($Y$) of resistor and capacitor are the reciprocal of the impedance ($Z$) relationships when the resistor and capacitor are in parallel.

The relationship of total admittance ($Y$) and total impedance ($Z$) in terms of $R$, $\omega$ and $C$ is given below:

\[ Y=\frac{1}{Z} \]
\[ Y=\frac{1}{R+j\omega C} \]

\[ Z = R \left[ \frac{1}{1+(\omega CR)^2} \right] - jR \left[ \frac{\omega RC}{1+(\omega CR)^2} \right] \]

In a complex impedance plot, the above equation represents a semicircle. The response of any cell to an a.c. signal can be represented by an equivalent circuit consisting of components such as resistors and capacitors, which individually represent charge migration and polarization occurring in the cell. Complex admittance and impedance plots and equivalent circuits of some simple circuit arrangements are shown in Fig. 3.4 and Fig. 3.5 respectively.
Figure 3.4: Admittance plots of some simple circuits [Chandra (1981); Singh (2007)]

Figure 3.5: Impedance plots of some simple circuits [Chandra (1981); Singh (2007)]
From these plots the resistance value can be obtained and hence conductivity of the samples [Chandra (1981); Paul (2001)] can be calculated by

\[
\sigma = \frac{G l}{A} = \frac{l}{R A}
\]

where G is the conductance [Atkins (1998)] and is determined from admittance plots, R is the resistance which is determined from the impedance plots, l is the distance between the electrodes and A is the area of cross section of each electrode.

The behaviour of admittance plots is affected by the electrodes used in the ac impedance measurements. The non-blocking/reversible and blocking electrodes can be used for the measurement of ac conductivity of the materials.

(i) cell with blocking electrodes
(ii) cell with non blocking electrodes

In the high frequency range, samples with non-blocking and reversible electrodes has a geometrical capacitance \(C_g\) in parallel with the bulk resistance \(R_b\). No polarization takes place at the electrode-electrolyte interface because of non-blocking and reversible electrodes. Hence at low frequencies, no dispersion in frequency will be there in complex impedance/admittance plots. The intercept of plots on real axis gives the bulk resistance/conductance. Some typical plots and equivalent circuits are shown in Fig. 3.6.

**Figure 3.6** Equivalent circuit of sample with blocking electrodes (a) impedance plot (b) and admittance plot (c) [[Chandra (1981); Singh (2007)]]
In case of samples having blocking electrodes, the impedance/admittance plots show a additional low frequency dispersion region and this is due to an additional double layer capacitance ($C_{dl}$) is in series with the $C_g - R_b$ combination. Polarization of the electrode-electrolyte interface, which is due to the double layer capacitor, dominates at low frequencies and the effect of $C_g$ becomes negligible. This is the case where the perfectly smooth and flat electrode-electrolyte interface is considered, but in practice it is not possible to have perfectly smooth and flat interfaces, due to which the impedance/admittance plots gets modified in the low frequency region. The intercept of low frequency and the high frequency dispersion curve on the real axis gives the bulk resistance/conductance of the sample. The impedance/admittance plot along with their equivalent circuit is shown in Fig. 3.7.

\[ \omega R_b C_g = 1 \]

Figure 3.7 Equivalent circuit of sample with blocking electrodes (a) impedance plot (b) and admittance plot (c)

In the present work, HP 4284A precision LCR meter (frequency range 20 Hz – 1 MHz) and computer interfaced Hioki 3532 – 50 LCR HiTester (frequency range 42 Hz – 5 MHz) have been used to measure the conductivity of electrolytes. The conductivity of polymer gel electrolytes has been measured by using a cell having platinum electrodes.
3.3.3 Viscosity measurements

Viscosity is a measure of internal friction of a fluid, which becomes apparent when a layer of fluid is made to move relative to another layer. Greater the friction, higher is the amount of force required to cause the movement. Viscosity is highly dependent on environmental conditions such as temperature and pressure. The change in the viscosity of electrolyte affects its transport properties. Also other parameter such as conductivity is a dependent parameter on the viscosity of the electrolytes. The viscosity ($\eta$) is related to the conductivity ($\sigma$) by the relation

$$\eta = \frac{q}{6\pi r \sigma}$$

where $q$ is charge on the ions and $r$ is the radius of the carrier ions. The increase in viscosity results in the decrease of conductivity and vice versa.

Generally, capillary method is used to determine the viscosity of liquid samples. But, in the case of ionic liquids and polymer gels, this method is not suitable due to their high viscosity. Viscometer used for the measurement of viscosity of ionic liquids and polymer gel electrolytes is rotating cylinder (or spindle) viscometer.

**Basics of viscosity measurement**

The basic principle of rotating cylinder (or spindle) viscometer is to measure the torque required to rotate a cylinder in a given sample. A motor through a calibrated spring drives the spindle and deflection of the spring is measured to quantify the amount of resistance to flow. The resulting resistance or torque is the measurement of the flow of viscosity. Greater the resistance of the product to be determined, higher is the viscosity. Based on the speed and characteristics of the spindle, the torque is calculated. And the direct reading of the viscosity is recorded in centipoise (cP) or millipascal-second (mPa s) in cgs system. The viscometers are equipped with different types of spindles and speeds which provide a wide range of measurement of viscosity values. Presently, viscosity of the liquid and polymer gel electrolytes has been measured by Fungi Lab rotating viscometer (Visco Basic L). A stainless steel spindle of suitable size is immersed in the sample which rotates and viscosity value is directly displayed alongside the temperature of the sample. The temperature is maintained by using a Julabo water circular (F-12EC) which can control temperature with an accuracy of ± 0.1 °C. The measuring range of viscosity is 20-20,000,000 mPa s. Minimum size of the sample required for the viscosity measurement is about 5-10 ml.
3.3.4 Fourier transform infrared (FTIR) spectroscopy

Infrared spectroscopy is an analytical technique that is used for the identification of specific functional groups. When infrared light is passed through a sample, some of the frequencies are absorbed whereas other frequencies are transmitted through sample without absorption. IR spectra are plots of intensity of absorption or transmittance as a function of frequency or wavenumber. The position of absorption bands can be specified in units of frequency, $\nu$ ($s^{-1}$, or Hz), or wavelength, $\lambda$ (micrometers, $\mu m$), or wavenumber, (reciprocal centimeters $cm^{-1}$) although the widely used one is the wavenumber units ($cm^{-1}$). For example, the stretching vibration of C-H bond appears at 3000 $cm^{-1}$.

The infrared region of the electromagnetic spectrum may be divided into three sections:

(i) near infrared (overtone region) ($4,000 \sim 14,000 \, cm^{-1}$)

(ii) mid infrared (vibration-rotation) ($400 \sim 4,000 \, cm^{-1}$)

(iii) far infrared (rotation region) ($4 \sim 400 \, cm^{-1}$).

However, it is the mid infrared region ($400 \sim 4,000 \, cm^{-1}$) that is generally used for infrared spectroscopy as organic molecules rarely undergo absorption of radiation in the near and far infrared regions. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to absorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule.

The atoms constituting a molecule are not rigidly held in fixed positions, instead, they are in constant state of vibration, each bond having its characteristic stretching and bending frequency, and being capable of absorbing light of that frequency. Molecules with assembly of atoms possess many vibrational frequencies. For a nonlinear molecule the number of vibrational modes is $(3n-6)$, where $n$ is the number of atoms in the molecule. Each of the different vibration modes may give rise to a different absorption band.
The different modes of vibration are (Fig 3.8):

(a) stretching vibration
(b) bending vibration

Figure 3.8: Schematic representation of stretching and bending vibrations [Sharma 2007]
3.3.4 (a) Stretching vibration:

In this vibration, the distance between two atoms increases or decreases but the atoms remain in the same bond axis. There is a continuous change in the interatomic distance along the axis of the bond between two atoms. Stretching vibrations can further be categorized as: symmetrical vibrations and asymmetrical vibrations.

In symmetrical vibrations, the movement of the atoms with respect to the central atom in a molecule is in same direction i.e. all the bonds to the central atom are either stretched or compressed simultaneously. In asymmetrical vibrations, one atom approaches towards the central atom, while the other moves away from it i.e. one bond is being stretched and the other is being compressed.

3.3.4 (b) Bending vibration:

Bending vibration involves a change in the angle between the two bonds. In this vibration, the position of the atom changes relative to the original bond axis. These vibrations are also referred to as deformations. Bending vibrations can further be classified as:

(i) **Scissoring**: This is an in plane bending vibration, in which the two atoms move towards each other.

(ii) **Rocking**: This is an in plane bending vibration in which the two atoms move in the same direction.

(iii) **Wagging**: This is an out of plane bending vibration in which the two atoms move simultaneously either above or below the plane with respect to the central atom.

(iv) **Twisting**: This is an out of plane bending vibration in which one atom moves above the plane while the other moves down the plane with respect to the central atom.

Stretching absorption of the bond appear at higher frequencies as compared to bending absorptions of the same bond as higher energy is required to stretch a bond than to bend it.

Infrared radiation can be analyzed by means of a scanning Michelson interferometer. The spectrometer records infrared spectra by first collecting an interferogram of a sample signal with an interferometer, which measures all of infrared frequencies simultaneously [Silverstein (1997); Pavia et al. (2001)]. When infrared light
of same frequency is incident on the molecule, energy is absorbed and it gets excited. When the molecule reverts from the excited state to the original ground state, the absorbed energy is released. For a particular vibration to result in the absorption of infra-red energy, that vibration must cause a change in the dipole moment of the molecule. The infrared signal after interaction with the sample gives unique characteristic of the sample. The beam finally arrives at the detector and is measured by the detector. The detected interferogram is interpreted with a mathematical technique called Fourier Transformation. Computer performs the Fourier transformation calculation and an infrared spectrum is obtained, which plots absorbance (or transmittance) versus wavenumber.

In the present work, FTIR spectroscopy has been used to study different polymer electrolytes by using computer interfaced Shimadzu 8400S FTIR spectrometer in 400-4000 cm\(^{-1}\) wavenumber range.

3.3.5 Thermal Analysis

3.3.5 (a) Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) records the temperature and the heat flow associated with the transitions in materials as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. A DSC thermogram can provide information on:

- Glass transition
- Melting and boiling point
- Crystallisation temperature
- Thermal stability
- Heats of fusion and reactions

**Basics of DSC**

In the DSC method, the sample and the reference are maintained at the same temperature and the heat flow required to keep the equality in temperature is measured. Generally, the temperature program for a DSC analysis is designed such that the
temperature of sample holder increases linearly as a function of time. The reference sample should have a well defined heat capacity over the range of temperatures to be scanned. The basic principle is that, when the sample undergoes a physical transformation such as phase transition, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Therefore, DSC plots are obtained as the differential rate of heating against temperature in the units of W/s, cal/s or J/s. The area under a DSC peak is directly proportional to the heat absorbed (endothermic process) or evolved (exothermic process) by the thermal event and the integration of these peak areas yields the heat of reaction.

In an endothermic process, heat is absorbed and therefore heat flow to the sample is higher than that of reference, hence the enthalpy change is positive. In exothermic process, the enthalpy change is negative. So as the temperature of the sample is increased, the supply of thermal energy may induce physical and chemical processes in the sample, for example melting or decomposition. The reference is an inert material such as alumina or just an empty aluminum pan.

3.3.5 (b) Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a measure of the thermally induced weight loss of a material as a function of temperature. In conventional thermogravimetry, the mass of a sample, m, is continuously recorded as a function of temperature T, or time, t, as:

\[ m = f \left( T \ or \ t \right) \]

If the derivative of the mass change with respect to time, \( \frac{dm}{dt} \), is recorded as a function of time (t) or temperature (T), it is the derivative thermogravimetry:

\[ \frac{dm}{dt} = f \left( T \ or \ t \right) \]

In the TGA curve mass or percent mass is plotted against temperature or time. An alternative method of presenting the results is to take the first derivative of TGA curve with respect to temperature or time. The curve is known as Differential Thermogravimetric curve (DTG) and it shows the rate at which the change in mass occurs. The change in the mass takes place when the sample looses material or reacts with the surrounding atmosphere which produces steps in the TGA curve or peaks in the DTG curve. Generally the steps in the TGA curve are caused by the following:
- Evaporation of volatile constituents, drying, desorption and adsorption of gases, moisture, loss of water of crystallization etc.
- Oxidative decomposition of organic substances in air or oxygen
- Thermal decomposition in an inert atmosphere with the formation of gaseous products.
- Uptake or loss of water in a humidity controlled experiment

In the present work, the thermal stability of polymer electrolytes was studied by simultaneous DSC/TGA measurements by using Perkin Elmer (Pyris Diamond) system. The thermal studies of polymer electrolytes were carried out under nitrogen atmosphere over the 25 °C to 550 °C temperature range at 10 °C/minute heating rate.

3.3.6 $^1$H and $^{19}$F solid state NMR spectroscopy

Nuclear Magnetic Resonance (NMR) is a spectroscopic technique, which covers a very large range of application areas, due to the multitude of different NMR techniques which are available today. Roughly three principal NMR domains can be distinguished, namely liquid state NMR spectroscopy, spatially resolved NMR techniques and solid state NMR spectroscopy. While the main application of liquid state NMR spectroscopy refers to the area of chemical and biochemical analysis of liquid or soluble compounds, spatially resolved NMR techniques are primarily employed for medical and technical applications. Solid state NMR spectroscopy is devoted to the chemical analysis of insoluble compounds, to the study of electronic structures in conducting systems, and mainly to the characterization and investigation of structural and dynamic properties of solid systems.

The NMR phenomenon is possible because in addition to charge and mass, many nuclei possess spin, or angular momentum. Since the spinning charge generates a magnetic field, there is a magnetic moment associated with this angular momentum. According to the principles of quantum mechanics, maximum experimentally observable component of angular momentum of a nucleus possessing a spin is a half-integral or integral multiple of $\hbar/2\pi$, where $\hbar$ is Planck’s constant. In the absence of any external magnetic field, nuclei are spinning randomly in their atomic or molecular environment, but when placed in a strong external field ($B_0$) they behave like small magnets and orient themselves with respect to the magnetic field. Each individual
nucleus spins around its axis and axis of nuclear magnetic moment so generated precesses about the force line of applied magnetic field. The frequency of precision \( \nu_0 \) is known as Larmor frequency of nucleus. When an external magnetic field is applied, an energy transfer is possible between lower energy level to a higher energy level. The energy transfer takes place at a wavelength that corresponds to a radio frequency (rf) and when the spin returns to its base levels, energy is emitted at same frequency. When the frequency of radio frequency field becomes equal to Larmor frequency, then rf field and spinning nuclei can exchange energy. The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum [Brown and Emsley (2003)].

In the experiment, a solid specimen (crystalline or amorphous, aligned or randomly oriented) is placed in a strong magnetic field and irradiated with intense radio frequency pulse over a frequency range required to excite a specific atomic nucleus from ground state to higher state. This is known as nuclear magnetic resonance (NMR). When a nucleus is isolated, a very sharp resonance line (narrow band) is observed. However, actually splitting or broadening of the line occurs because the resonating nucleus undergoes various interactions with its surroundings. For solid samples, the molecules can not move so fast, so the broad lines are observed because of the interaction with magnetic dipoles of other magnetic nuclei at fixed lattice points. NMR methods have been developed for determining dynamic properties like jump frequency, diffusion coefficient and conductivity. A plot of frequencies of absorption peak versus peak intensities constitute an NMR spectrum. Various terms, for example, Zeeman interaction, dipolar interaction, chemical shift, quadrupolar interaction (non-zero for nuclei with \( I>1/2 \)), electron coupled nuclear interaction, interaction with applied radio frequency radiation describe the nucleus in the solid when placed in magnetic field. Out of above terms, only Zeeman term is responsible for the NMR absorption and rest of the terms control the shape and width of line. In real systems, i.e. when the nuclei can no longer be considered isolated, other interactions like nuclear dipole-dipole, electric quadrupole and nuclear-electron are superimposed on the Zeeman effect and modify the linewidth, alter the shape and shift the position of absorption line.

### 3.3.6 (a) Linewidth

The linewidth of NMR signal is defined as the full width at half maxima (FWHM). It is determined from the NMR spectra at different temperatures. With the
increase in temperature, thermal motion of atoms raised which decreases the time intervals between magnetic dipole interactions. Therefore, local field fluctuations arise the rapid motion of nuclear spin, which cause narrowing of width of resonance band called motional narrowing or line narrowing [Fedin (1970); Ibbett (1993), Sharma (2007)]. Decrease in linewidth depends upon second moment ($M_2$) of dipole-dipole interaction of solid as given below:

$$\omega - \omega_0 \propto M_2^{1/2}$$

The necessary condition for line narrowing is the much larger value of time as compared to fluctuation time. Line narrowing occurs due to the average local field fluctuations, which arises due to rapid motion of nuclear spin or fast changes of nuclear environment.

The finite NMR signal width observed in the NMR spectra is due to the fact that spin states have a finite lifetime and there are many other processes which varies relative energies of spin levels. The finite lifetime of spin states are associated with spin - lattice relaxation time ($T_1$), which actually measures how fast the spin system reaches thermal equilibrium with its surroundings, or in other words, we can say that it is related to the change of nuclear magnetization that is parallel to external magnetic field. Local magnetic fields fluctuating at Larmor frequency are responsible for this process. Spin - spin relaxation time ($T_2$), which is the measure of how fast a nuclear magnetization perpendicular to magnetic field ($M_{\perp}$), will decay due to interactions between spinning nuclei, is the responsible factor for processes involving variation in the energies of spin levels. The decay in nuclear magnetization is generally written as

$$M_{\perp}(t) \propto \exp(-t / T_2)$$

From this equation, it is observed that this decay is exponential in nature. As this decay arises from fluctuating local magnetic fields at nuclear sites, so it is clear that the fast changes in nuclear spin or in nuclear environment average out the local field fluctuation and reduce the linewidth. This effect is known as motional narrowing or line narrowing. The observation of NMR linewidth is useful to determine the diffusion coefficient.

At lower temperatures, every constituent atom is fixed at each lattice point and no motion is observed, we observe a broad spectrum which is due to rigid lattice linewidth but at high temperatures we observe residual linewidth, which comes into
picture due to those interactions, which are not affected by the atomic measurements. Therefore, line narrowing gives information about the nature of mobile ions.

3.3.6 (b) Jump frequency

Probability for ion to jump from one site to other in a given direction in unit time is known as jump frequency ($\nu$). It depends upon the potential barrier seen by ions. This is an important ion transport parameter to understand the conduction mechanism of a superionic conductor. The angular jump frequency was calculated [Bolembenberg (1948); Gutowsky and G. E. Pake (1950); Abragam (1961); Sekhon et al. (2003)] at different temperatures by using the relation:

$$\nu_c (\text{angular frequency}) = \frac{\alpha \Gamma \Delta \omega}{\tan \left( \frac{\pi}{2} \left( \frac{\Delta \omega^2 - B^2}{A^2 - B^2} \right) \right)}$$

where $\alpha = 1$, $\Gamma = 2.52 \times 10^4 \text{ sec}^{-1} \text{ G}^{-1}$ for $^{19}\text{F}$ and $2.67 \times 10^4 \text{ sec}^{-1} \text{ G}^{-1}$ for $^1\text{H}$. $\Delta \omega$ is the linewidth at temperature $T$, $B$ is the fully narrowed linewidth and $A$ is the unnarrowed linewidth and the units of $\nu_c$, $\Delta \omega$, $A$ and $B$ are of angular frequency.

3.3.6 (c) Diffusion coefficient

The motion of ions/particles from higher concentration to lower concentration side is known as diffusion, which is directly related to the concentration gradient as:

$$J = - D (\Delta C)$$

$$\Rightarrow D = - J/\Delta C$$

where $J$ is the number of atoms of diffusing species (i.e. particles/ions) passing through unit volume in unit time, $C$ is the concentration of atoms of the diffusive species at the plane and $D$ is diffusion coefficient. Hence diffusion coefficient is defined as the ratio of number of atoms of diffusive species to concentration gradient of atoms of diffusive species. In the present work, diffusion coefficient was calculated from NMR data by using Einstein relation:

$$D = \frac{1}{6} L^2 \nu_c$$

where $\nu_c$ is the jump frequency and $L$ is the bond length. In the present case, $L$ is the H-H or F-F bond length in ionic liquids DMHxImTFSI and DMHxImTf, which has been calculated by molecular modeling using Gauss View software.
3.3.6 (d) Conductivity ($\sigma_{\text{NMR}}$):

The electrical conductivity ($\sigma_{\text{NMR}}$) was also evaluated from NMR data by using the relation:

$$\sigma_{\text{NMR}} = \frac{nDq^2}{kT}$$

where $n$ is concentration of mobile ions, $q$ is charge on the mobile species, $D$ is diffusion coefficient, $k$ is the Boltzmann constant and $T$ is temperature.

In the present work, $^1\text{H}$ & $^{19}\text{F}$ NMR studies were carried out by using a pulsed spectrometer at 6.4 T with a corresponding Larmor frequency 255.1 and 271.1 MHz respectively. The spectrum was obtained by a single pulse sequence followed by a Fourier transformation. Typical dead time of spectrometer was 4 $\mu$s. These studies were carried out to get the information about the nature of mobile species.