Abstract

The chapter involves synthesis and characterization of amino acid (glycine, lysine and cysteine) ILs. Formation of IL is accomplished by the combination of phosphonium as cation and amino acid as the anion. The carboxylic acid and phosphonium group is the same in all the three amino acid ionic liquids. Hence, the functionality of AAIALs is determined by the side chain group of the amino acids. Moisture content and interaction (between the anion and cation) affects the physicochemical properties of the IL. Moisture content and environmental sensitivity is least in case of glycine IL followed by lysine and cysteine. Thermal and rheological properties support that highest interaction takes place between molecules of cysteine IL followed by lysine and glycine.
Chapter-3

Synthesis of AAILs and its Physico-chemical Properties

3.1 Introduction:

Generally the term “ionic liquids” stands for liquids composed of ions. These are usually molten salts or molten oxides [1]. It has been noted that the properties of molten salts as a solvent for chemical processes differ from those of aqueous and organic solvents. Some processes, such as, the electrochemical reduction of aluminium from alumina, can be conducted only in molten salts and are impossible in aqueous solutions. However, until recently the use of molten salts were considered to be confined to high-temperature applications. In the 1990s, an understanding that molten salts having melting point below 100 °C [2] created a new unique media for chemical reactions. This aspect became widespread and the term “room temperature ionic liquids” (RTILs) was assigned to them [3, 4]. However, electrochemists still prefer the term “room-temperature molten salts” or RTMS. At the present time the number of RTILs synthesized exceeds 500 and research in this area is expanding rapidly. There is virtually no limit in the number of salts with low melting points. Earle and Seddon [5] have estimated this number to be of the order of 1 billion.

3.2 IL functionalization:

The physico-chemical properties of ILs depend on the combination of the cation and anion. Thus, the preparation of “task-specific” or functionalized ILs is normally realized through the incorporation of functional groups on the cations, to date, mostly the imidazolium cation has been extensively exploited, although a few examples involving functionalized anions are also known.
3.2.1 Different cation based ionic liquid:

Different cations have been used for the synthesis of ILs, of which imidazolium salts have been the most popular and commonly used cation. There is increase in research papers using other cations such as ammonium, pyridinium and phosphonium salts. Specifically, phosphonium salts have shown a good improvement in thermal stability.

3.2.1.1 Imidazolium-based ionic liquids:

The imidazolium-based ionic liquids are the most commonly investigated group for synthesis in physical chemistry and for environmental studies. These were one of the first ILs to find application on an industrial scale [6]. Various types of anions have been used to make I-IL (Imidazolium Ionic Liquid) such as Chloride, -Bromide, -Iodide, -Tetracarbonylcobaltate, -Thiocyanate, -Dicyanamide, -Hydrogen sulphate, -Methylsulfate Octylsulfate etc with different alkyl chains [7-10] as shown in Figure 3.1.

![Figure 3.1: Chemical structure of I-IL](image)

3.2.1.2 Quinolinium-based ionic liquids:

Quinolinium ionic liquids are still studied even though their cytotoxicity potential (IPC-81) and molecular toxicity (inhibition of acetylcholinesterase) was observed to be extremely high, and this increased with the elongation of the substituted alkyl chain [11]

![Figure 3.2: The structure of the 1-alkylquinolinium cation.](image)
3.2.1.3 Pyridinium-based ionic liquids:

Ionic liquids containing a pyridinium head group constitute a rather important and well-studied group, as underlined recently by Madaan et al. in a review on their synthesis, highlighting the limitless pool of structural variations, properties and applications, especially as surfactants and antimicrobial agents [12]. The alkyl, alkoxy chain length and anion do affect the physico-chemical toxic properties of the pyridinium based IL. The toxicity of methylpyridine was slightly higher than [C₄mbpy]Br, suggesting that even though the alkyl chain is contributing to toxicity, the ionic liquid may have a greener character than its synthetic precursors [13].

![Figure 3.3: The structure of the pyridinium salts.](image)

3.2.1.4 Pyrrolidinium-, piperidinium- and morpholinium-based ionic liquids:

This group gives a cation in the form of alicyclic head groups. Some of the common structures used for the formation of such type of IL are shown in Figure 3.4. Due to the apparent low toxicity of ionic liquids with nitrogen-containing alicyclic cations there are no doubts that they will be in the heart of a more conscious design, and will certainly be harnessed more in the near future [14].

![Figure 3.4: Structures of common alicyclic cations used to form ionic liquids.](image)
3.2.1.5 Quaternary ammonium ionic liquids:

Quaternary ammonium ILs (Figure 3.5) are well known and widely used chemicals in numerous applications, as disinfectants, surfactants, antistatic agents, catalysts etc. [15] Their properties depend on the chain length and functional groups, and on the anion [16]. The selection of a benign cation, such as cholinium (cholinium chloride is known as choline, and is part of the vitamin B complex), combined with benign anions constituted a major breakthrough in the conscious design of ionic liquids [17, 18]

![Figure 3.5: Structure of quaternary ammonium cation.](image)

3.2.1.6 Quaternary phosphonium ionic liquids:

The physico-chemical and toxic properties of phosphonium ionic liquids (as shown in Figure 3.6), has seldom been investigated. Trihexyl(tetradecyl)phosphoniumbis{(trifluoromethyl)sulfonyl}amide combined with different anions, namely [PF₆]⁻ and [NTf₂]⁻ interestingly displayed high and low cytotoxic activities against a broad diversity of human cancer cell lines, respectively [19]. Because of this result, phosphonium IL has not been synthesized or studied extensively. It should finally be noted that apart from these characteristics, ILs are also known to serve as disinfectants, surfactants, antistatic and good reducing agents.

![Figure 3.6: Structure of quaternary phosphonium cation.](image)
3.2.2 Anion based ionic liquid:

Selection of anion is quite crucial as in most of the cases they are responsible for the toxic properties in ILs. As seen in case of fluorides, they tend to release HF when in contact with moisture.

3.2.2.1 Halide based ionic liquids:

The most prominent among these are PF$_6^-$ and BF$_4^-$ ions. They are probably the most common anions used in IL research. Though the expected variation in properties should be quite less if the cation salts are same for these anions. The actual differences can be dramatic: for example, [BMIM]PF$_6^-$ is immiscible with water, whereas [BMIM]BF$_4^-$ is water soluble [20]. Such variation that arise from different ion pairing, give rise to the description for ionic liquids as "designer solvents".

Despite their widespread use, IL featuring PF$_6^-$ and BF$_4^-$ has found to decompose when heated in the presence of water, giving off HF. This drawback has prompted to introduce alternate anions, even though many of these still contain fluorous materials. In these cases, fluorine of the anion is bonded to carbon, where the C-F bond being inert to hydrolysis. Thus, IL based upon CF$_3$SO$_3^-$, (CF$_3$SO$_3$)$_2$N$^-$ and related anions are being marketed [21].

3.2.2.2 Sulfonate based ionic liquids:

In response to environmental and health safety and also cost concerns, new ILs with non-fluorous anions have been introduced such as alkylsulfate anions. Alkylsulfate anions are likely to be reasonably non-toxic and biodegradable. One specific ionic liquid, ECOENG 500 (Peg-5 cocomonium methosulfate), is the first commercially available ionic liquid for which full toxicological data is available [22]. The docusate (dioctylsulfosuccinate) anion is known to exhibit low mammalian toxicity, and is widely used in food, drug and cosmetic applications [23]. In contrast to other ionic liquids, many incorporating decussate are highly lipophilic, some being fully miscible with hydrocarbons.
3.2.3 Amino Acid Ionic Liquids:

Amino acid is a peculiar ion that can be used both as an anion and cation in ILs. There are quite a few reports in which amino acids have been used as cations [24]. The preference for using amino acids in ILs is because of its biocompatible nature. Y. Kou *et al.* have reported a new class of ionic liquids directly derived from natural $\alpha$-aminoacids and their ester salts resulting in the synthesis of “fully green” ionic liquids, [AAE]$\text{NO}_3$ and [AAE]Sac [25]. Ohno *et.al* have used amino acids as the anion in their synthesis of ILs [26]. Hence, this clearly indicates the potential and versatile possibilities of designing different ILs using amino acids as one of its constituent ion.

3.3 Physico-chemical properties of pure ionic liquids:

Initial research on the properties of pure RTILs was aimed at developing and understanding the relationship between the nature and structure of the cation and anion, and its physico-chemical properties. The purity of an ionic liquid is a very important issue when measuring physical properties. The following physical properties are predominantly investigated when a new IL is synthesized.
3.3.1 Melting point:

For a substance to be considered as a RTIL, its melting point should be below 100 °C. The main factors that influence the melting point are the charge distribution on the ions, H-bonding ability, the symmetry of the ions and the van der Waals interactions [27, 28].

3.3.2 Viscosity:

Most of the RTILs are viscous liquids with two to three orders of magnitude greater than those of conventional organic solvents and more similar to those of oils. Their high viscosity is a major disadvantage since it negatively affects mass transfer and power requirements for mixing in heterogeneous liquid-liquid systems. Some representative viscosity values at 20 °C are: 430 mPa for [BMIM][PF₆] [29]. Apart from that, ILs are denser than water with values ranging between 1 and 1.6 g.cm⁻³. Similarly, the surface tensions of RTILs are lower than that for water (72.7 Nm⁻¹ at 20 °C) but higher than the values for n-alkane (16.0 Nm⁻¹ for pentane to 25.6 Nm⁻¹ for dodecane, all at 20 °C). As the alkyl chain length on the RTIL increases, the surface tension value decreases towards the values for the alkanes.

Various other physico-chemical properties are also studied to correlate the physical properties of IL such as NMR, FTIR, TGA etc. Here we have synthesized three AAILs using glycine, lysine and cysteine with a common cation : tetrabutylphosphonium. Presented below is our seminal work on the full characterisation of these AAILs and we report a variety of physico-chemical properties such as viscosity, conductivity, rheology and phase which were determined using characterisation techniques involving NMR, FTIR, TGA, Cryo-TEM and SAXS.

3.3.3 Polarity:

IL consisting of different combinations of anions and cations can produce solvents with different polarities. No ionic liquids have shown themselves to be “super-polar”; regardless of the method used to assess their polarities, ionic liquids come within the range of molecular solvents, especially, in the range of short to medium-chain alcohols [30]. It becomes more interesting when the solvent properties are broken down into their component parts. Ionic liquids can act as hydrogen bond acids and/or hydrogen bond bases, or as neither. Generally, the hydrogen bond basicity is determined by the anion and the hydrogen bond acidity is
determined by the cation. There is no obvious unique “ionic effect” to be seen in the available
data, but this may yet be found after further study and might explain the consistently high $\pi^*$
values (spectroscopic).

3.3.4 Colour:

From the literature one gets the impression that ionic liquids are all colourless and look
almost like water. However, most people who start ionic liquid synthesis will probably get a
highly coloured product at first. The chemical nature of the colour impurities in ionic liquids
is still not very clear, but it is probably a mixture of traces of compounds originating from the
starting materials, oxidation products and thermal degradation products of the starting
materials. Sensitivity to coloration during ionic liquid synthesis can vary significantly with
the type of cation and anion of the ionic liquid. Pyridinium salts, for instance, tend to form
coloured impurities more easily than imidazolium salts do [31]. From this it has become
obvious that freshly distilled starting materials and low temperature processing during the
synthesis and drying steps are key aspects for avoidance of colouration of the ionic liquid.

3.3.5 Water:

Presence of water has a significant effect on the physico-chemical properties of ILs. Special
drying procedures and completely inert handling is important as most of the ionic liquids are
quite hygroscopic. Even the apparently hydrophobic ionic liquid [BMIM][(CF$_3$SO$_2$)$_2$N]
saturates with about 1.4 mass% of water [32], a significant molar amount. For more
hydrophilic ionic liquids, water uptake from air can be much greater. Imidazolium halide
salts in particular are known to be extremely hygroscopic, one of the reasons why it is so
difficult to make completely proton-free chloroaluminate ionic liquids.

3.4 Synthesis of IL:

3.4.1 Metathesis reaction:

Many alkylammonium halides are commercially available or can also be prepared by simple
reaction using appropriate halogenoalkane and amine. Preparation of the pyridinium and
imidazolium halides can be achieved similarly. For volatile halogenoalkanes, the low boiling
points lead to preparations requiring either a sealed tube, such as in the synthesis of [EMIM]Cl (where [EMIM]$^+$ is the 1-ethyl-3-methylimidazolium cation). Hence, the use of salts with longer chain substituent’s, such as [BMIM]Cl (where [BMIM]$^+$ is 1-butyl-3-methylimidazolium cation), that can be prepared in conventional glassware by heating under reflux has become popular [33]. It was in 1992 the first of the new ionic liquids, [EMIM][BF$_4$], was prepared via metathesis of [EMIM]I with Ag[BF$_4$] in methanol [34]. This salt also has a melting point of 12 °C and may be prepared considerably more cheaply using [NH$_4$][BF$_4$] in acetone. The ease of preparation, together with its relative moisture stability and its immiscibility with a number of organic solvents is leading to its increasing use in biphasic catalysis. The preparation of [EMIM][PF$_6$] shortly followed; this time it was prepared by reaction of [EMIM]Cl with HPF$_6$. This salt has a melting point of 60 °C, which makes it slightly less attractive than the [BF$_4$]$^-$ salt, if room temperature working is desired. Since then, quite a few salts such as thiocyanate, nonafluorobutanesulfonate, bis((trifluoromethyl)sulfonyl)imide, tris((trifluoromethyl)sulfonyl) methide, trifluoroacetate and heptafluorobutanoate have all been synthesized by metathesis reaction [35]. These metathesis reactions are good candidates for those preparing new ionic liquids for the first time. However, they can leave the ionic liquids contaminated with a small amount of halide ions that may react with solute materials.

3.4.2 Neutralisation reaction:

Monoalkylammonium nitrate salts are best prepared by the neutralization of aqueous solutions of the amine with nitric acid [36]. The ionic liquids are isolated by the normal procedures i.e. removing excess water in vacuo. Similarly, reaction of tetraalkylammonium sulfonates have also been prepared by mixing equimolar amounts of sulfonic acid and tetraalkylammonium hydroxide. Again, excess water was removed in vacuo. To ensure the purity of the ILs, they were dissolved in either acetonitrile or tetrahydrofuran and treated with activated charcoal for at least 24 hr, and finally the organic solvent was removed in vacuo. The synthesis of AAILs mentioned in this chapter has been synthesized following neutralization reaction.
3.4.3 Purification of ionic liquids:

Ionic liquids that are based on the common cations and anions are expected to be colourless, with minimal absorbance at wavelengths greater than 300 nm. In practice, the salts often take on a yellow hue, particularly during the quaternization step. The amount of impurity causing this is found to be extremely small and being undetectable by $^1$H NMR or CHN microanalysis. In many applications the discoloration may not be of any importance. This is clearly not the case, however, when the solvents are required for photochemical or UV-vis spectroscopic investigations. To date, the precise origins of these impurities have not been determined, but it seems likely that they arise from unwanted side reactions involving oligomerization or polymerization of small amounts of free amine, or else from impurities in the haloalkanes [37].

3.4.4 Synthesis of Amino Acid IL:

The synthesis of different amino acids derived ionic liquids as shown in Figure 3.8 was adapted from previously reported procedure [26]. The procedure was modified as follows: Aqueous solution of TBPOH (26 ml of 40% solution-0.094M) was added to an excess amino acid (0.045mol) under constant stirring. The resultant reaction mixture was roto-evaporated and then centri-evaporated for 72 hr. The unreacted amino acids appeared as residues and only the supernatant ionic liquids were collected and stored in desiccators. In Figure 3.8, is a schematic representation of the synthesis sequences along with the as-synthesized IL.
3.5 Results and discussion:

ILs are also known as designer solvents as they can be tuned for fitting a desired reaction or obtaining a desired product. Here we used three different ILs by tuning their anion (amino acid), thus it is assumed that the final property of the IL will be affected by the change in the amino acid moiety. To confirm this, several characterization techniques were employed as described in following sections.

**Figure 3.8:** Synthetic procedure of AAILs.
3.5.1 Calculation of water content:

Presence of water has a significant effect on the physico-chemical properties of ILs. Special drying procedures and completely inert handling is important as most of the ionic liquids are quite hygroscopic. The water content was estimated using a Karl-Fischer colorimetric titrator. On average, for an evaporation time (using a centri-evaporator) for 72 hr, the water content for the AAILs are shown in the Table 3.1. It was found that cysteine IL had the highest moisture content (even after employing the same synthesis conditions for all the three AAILs). This is despite sulphur being less electronegative than nitrogen. To support our results we purported a concept i.e. cysteine has a small and a more polar side chain when compared to lysine. This helps to retain a larger extended hydrogen bonded network around each IL molecule. Whereas, with lysine there are small hydrophobic pockets because of the tetramethyl linkage in the side chain. This leads to fewer hydrogen bonded water molecules.

Table 3.1: Measured values of moisture content in different AAILs.

<table>
<thead>
<tr>
<th>IL</th>
<th>Moisture %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>1-2</td>
</tr>
<tr>
<td>Lysine</td>
<td>1.5 – 2.5</td>
</tr>
<tr>
<td>Cysteine</td>
<td>2.5 – 4</td>
</tr>
</tbody>
</table>

3.5.2 Viscosity of AAILs:

Viscosity of the three AAILs synthesized was also measured, as shown in Table 3.2. It is assumed that since the only difference between the three AAILs is the nature of the anion, the variation in viscosity can therefore be ascribed to the level of interaction between the ions, and also the nature and extent of hydrogen bonding that is present between the functional groups of the AAs. The explanation for the variation in viscosity is ascribed in a similar argument as above, in that the R group of cysteine (-CH$_2$SH) lends itself to force a stronger H- bond network than the R group of lysine (-CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH$_2$). This obviously will affect the viscosity.

Table 3.2: Measured values of viscosity in different AAILs.
### 3.5.2.1 Effect of water on the viscosity:

The viscosity of the individual ionic liquids clearly showed a steep decrease when the moisture content was increased, Figure 3.9. This is not an unexpected result and is purported to stem from dilution of the various strong ionic interactions present in AAIL. The decrease in viscosity is not linear but a pseudo exponential curve (fitting not performed). Similar trends were observed for all the three AAILs synthesized in this study.

![Figure 3.9: Change in viscosity with moisture content in glycine L.](image)

### 3.5.3 Conductance of AAILs:
Among the three as synthesized AAILs, cysteine IL showed highest conductance followed by lysine and glycine in pure and with 50% moisture content as shown in Table 3.3. The measurement is based on ionic conductance of ILs. Ionic conductance basically depends upon mass, charge, size and mobility of the ions. Glycine having the smallest intact size shows the highest conductance. Whereas, Cysteine ILs maintains the strong H-bonding network and hence, shows the lowest conductivity.

**Table 3.3:** Measured values of conductance in different AAILs.

<table>
<thead>
<tr>
<th>IL</th>
<th>Conductance (as synthesized IL)</th>
<th>Conductance (IL+50% moisture content)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>484µS</td>
<td>17304µS</td>
</tr>
<tr>
<td>Lysine</td>
<td>158µS</td>
<td>8295µS</td>
</tr>
<tr>
<td>Cysteine</td>
<td>69µS</td>
<td>4913µS</td>
</tr>
</tbody>
</table>

3.5.3.1 Effect of moisture on conductance of AAILs:

The conductance of glycine AAIL showed a steep increase with increase in the moisture content, Figure 3.10. This might be due to the increase in distance between the two ionic radii and also due to breaking of H-bonding between the cations and anions of AAILs. This decrease in physical interaction makes the AAILs more free flowing. However, the conductivity of pure water is lower than any of the AAIL + water mixture. Thus it clearly confirms that the increase in conductivity is due to ion charge migration.
Figure 3.10: Change in conductance with moisture content in glycine IL.

3.5.4 Structural properties:

3.5.4.1 NMR:

The structural characteristics of AAIL could be easily supported by $^1$H NMR data. Figure 3.11 shows the NMR spectra of (a) pure glycine (b) pure TBPOH and (c) after AAIL formation. NMR of pure glycine showed a main peak corresponding to C-H ($\delta$-3.3ppm). Similarly, TBPOH also displayed its fundamental peaks at ($\delta$-3.3ppm), C-H (CH$_3$ $\delta$-0.9ppm) C-H (CH$_2$ $\delta$-1.3ppm). Note that the consistent peak at 2.5 ppm is due to the internal standard of deuterated dimethyl sulfoxide (DMSO). After the formation of IL, all the peaks that belong to TBPOH and glycine get shifted towards lower chemical shift. This clearly indicates the formation of a strong adduct. The lower chemical shift is due to the shielding effect. As the OH group in TBPOH is replaced by amino acid and similarly the H proton in amino acid is replaced by TBP$^+$, this increase in size of the counterions does not much affect the electron density and hence, the protons are in a more shielded environment.
Figure 3.11: NMR of glycine, lysine and cysteine ILs along with their precursor molecules.

Similar feature is observed in the case of lysine and cysteine based IL also with comparatively large broadening and shifting towards lower chemical shift side.
3.5.4.2 FTIR:

FT-IR clearly supports the formation of IL. In case of AAILs, both N-H (1464 cm\(^{-1}\)) and C=O (1584 cm\(^{-1}\)) stretching frequency get shifted towards lower energy which supports the weakening or lengthening of C=O and N-H bond in comparison to pure glycine. In addition P-C stretching at 1224 cm\(^{-1}\) is also observed after the formation of IL. After addition of glycine in TBPOH it tends to opt a semifluid or gel type of nature. This gelation tendency in AAILs usually depicts a more enhanced type of molecular interaction which could either be in the form of hydrogen bonding with adduct formation, van der Waals or \(\pi-\pi\) stacking. Since IL does not have any double bond in its structure, the possibility of \(\pi-\pi\) stacking is overruled. Alkyl chain present in TBP\(^+\) cationic part leads to the van der-Waals interaction between molecules. As the strength of van der Waal force is very less and it would not be sufficient to give a gel tendency to the IL material. Thus, there must be both an adduct formation and hydrogen bonding interaction that plays a crucial role to impart the gel behavior. Oxygen of carbonyl group is a strong electronegative element and therefore has a tendency to bind with hydrogen of the alkyl chain and nitrogen through hydrogen bonding. Because of this hydrogen bonding, the strength of C=O and N-H reduces as shown in Figure 3.12. Similar feature is also observed in case of AAIL with comparatively larger shifting.

![FT-IR of glycine, TBPOH and their corresponding IL.](image)

**Figure 3.12:** FT-IR of glycine, TBPOH and their corresponding IL.
3.5.5 Thermal Properties:

Thermal property of ILs has been monitored by thermogravimetric analysis. Comparative TGA graphs of pure glycine, TBPOH and its corresponding IL are shown in Figure 3.13. Pure amino acid and TBPOH show one step and two step weight losses at 243 °C, and 97 °C, 223 °C respectively. Glycine shows a single peak of thermal degradation, however in case of TBPOH there is moisture removal followed by thermal degradation. Ionic liquid showed a drastic change in the thermal property. Glycine IL displays a three-step weight loss at 97 °C, 324 °C and 348 °C. Similar to that of IL lysine. This could be due to the presence of similar amino functional groups in both glycine and lysine ILs. Whereas, cysteine which consists of sulphur moiety shows a lower TGA peak at 155 °C. This is because less electronegative sulphur, though forms a strong hydrogen bonding but results in a formation of weak adduct when compared to the amino acids consisting of amino moiety.

Table 3.4: Comparative values of thermal degradation of AA, TBPOH and their corresponding ILs.

<table>
<thead>
<tr>
<th></th>
<th>Pure Amino Acid</th>
<th>TBPOH</th>
<th>IL</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL-Gly</td>
<td>243 °C</td>
<td>97 °C, 223 °C</td>
<td>97 °C, 324 °C, 348 °C</td>
</tr>
<tr>
<td>IL-Lys</td>
<td>210 °C</td>
<td>97 °C, 223 °C</td>
<td>97 °C, 325 °C, 332 °C</td>
</tr>
<tr>
<td>IL-Cys</td>
<td>225 °C</td>
<td>97 °C, 223 °C</td>
<td>97 °C, 155 °C, 326 °C</td>
</tr>
</tbody>
</table>

Figure 3.13: Derivative curve of thermal degradation of glycine, TBPOH and their corresponding IL
3.5.6 Rheological property:

Mechanical property of ILs was carried out by rheological measurement as shown in Figure 3.14 A and B. Figure 14A shows the change in viscosity with applied pressure in form of shear rate and it was observed that glycine based IL was affected more by applied pressure followed by lysine and cysteine due to its high viscosity and elastic nature. Degree of fluid behavior is estimated by difference in shear and loss modulus with change in shear frequency [38] as shown in Figure14B. As the gap between the modulus is more than 100 Pa.s, the sample falls under gel category, however, it is considered as semi-gel or fluid when the difference is less than 100 Pa.s. Thus it is concluded that cysteine IL has the highest gel tendency, however, glycine and lysine IL depicts a semi fluid behavior.
Figure 3.14: A) Change in viscosity with applied shear and B) variation of shear (upper) and loss modulus (lower) with frequency for gly (black), lys (blue) and cys (red) IL.

3.5.7 Morphological property:

Phase studies of the glycine IL was carried out using Cryo-TEM and SAXS as shown in Figure 3.15 A and B. In Figure 3.15A, the Cryo-TEM data does not show any agglomeration or extended phase structure. In addition, SAXS data, Figure 3.15B, also does not show strong reflections at lower q values to indicate formation of nanometer sized aggregates. As a result, this clearly indicates the absence of any secondary phase or agglomeration which is usually observed in case of amphiphilic ILs. It can therefore be purported that AAILs are homogeneous liquids without the presence of any phase separated aggregates.
Figure 3.15: A) Cryo-TEM and B) SAXS of glycine ILs.
3.5 Conclusion:

Here we synthesized AAILs from glycine, lysine and cysteine amino acids with phosphonium ion as the cation. In general, these chemical modifications influenced the properties such as viscosity, conductance and decomposition temperature. The trends observed in these properties were attributed to their structure, functionality and side chains of these ions. The side chain (R group) of the amino acids play an important role in determining and retaining a strong hydrogen bonded network and has a great impact on their physico-chemical properties. The moisture content was found to be below 4% of the total content in all the cases of AAILs synthesized.
3.7 References:


