

CHAPTER 2: Literature Review

2.1 Introduction of ionic liquid

2.1.1 History of ionic liquid

It is well known, that ionic liquid is a remarkable class of materials that clearly has been an explosion of interest among researchers. In reality, based on Science Direct search engine, entries in chemical abstract for the term of “ionic liquid”, there were 5,089 publications in 1996 and has grown to 14,676 publications in the year of 2012. This sudden and augmented interest is due to its great utility in chemical industries which it is potentially and actually used in electrochemical application [46–47], as a reaction solvent [48-50] and others.

In 1914, ethylammonium nitrate is the earliest reported room temperature ionic liquids [51]. The discovery of ethylammonium nitrate was synthesized using neutralization reaction between concentrated nitric acid and ethylamine. The water produced was removed by simple distillation giving out a pure nitrate salt that exists as a liquid at room temperature.

The discovery of the “red oil”, a separate liquid phase, observed in Friedel Crafts reactions in the mid-19th century could be the most primitive ionic liquid found. This “red oil” finding has evolved the development of molten salt. In 1963, U.S. Air Force academy has conducted a research resulted in a patent for a NaCl/AlCl₃ thermal battery, which triggered continuous study on ionic liquids all over the world.

2.1.2 Overview of ionic liquid

Fused organic salt, room temperature ionic liquid and neoteric solvent are few synonyms for ionic liquid that have been used in research world. In the early stage of ionic liquid era, ionic liquid is commonly mistaken with common inorganic salts such as sodium chloride, NaCl. However, as time evolved and more research have been focused on ionic liquids, the ionic liquid term was slowly defined as an ionic compounds or salts whose melting point is below 100°C, and has an inestimable vapour pressure thus making it a sustainable organic salts or a mixture of organic and inorganic salt. Owing to these advantages, ionic liquids can be used for separation studies [52-54], used as reaction media [55-58] for chemical reactions and as an electrolyte for batteries [59-62].

In one critical sense, the chemical functionality of ionic liquid is industrially and technologically important and enormous. Further, impressive features of ionic liquids can be tailored by substituting anions or cations or by designing task specific behaviour into the cations or anions. Consequently, task specific ionic liquids could contribute to the development of green chemistry such as replacing volatile organic solvents and preventing chemical wastage [63-65].

There are wide ranges of ionic liquid that have been used by researchers worldwide. Most researchers are most keen to imidazolium ionic liquids, specifically, 1-alkyl-3-imidazolium, pyridinium and phosphonium cations. On the other hands, halides, nitrates and tetrafluoroborates are the uttermost used anions. Figure 2.1 and 2.2 show the widely used structures of cations and anions in ionic liquids.

A fundamental knowledge of physical and chemical properties of ionic liquids is essentially important in order to optimize the use of ionic liquids. Distinctive physical and chemical properties of ionic liquid such as non-flammability, high-thermal stability, excellent dissolving capacity, wide liquidus range, wide electrochemical range and have low melting point motivates academic researcher and industries all around the world to focus on characterization and application of certain kinds of ionic liquids [1-3]. The non-volatility of ionic liquid compared to molecular organic solvent has regarded ionic liquid as environmental friendly candidate to substitute volatile organic solvents in pursuit of making the world a safer and sustainable place to live.

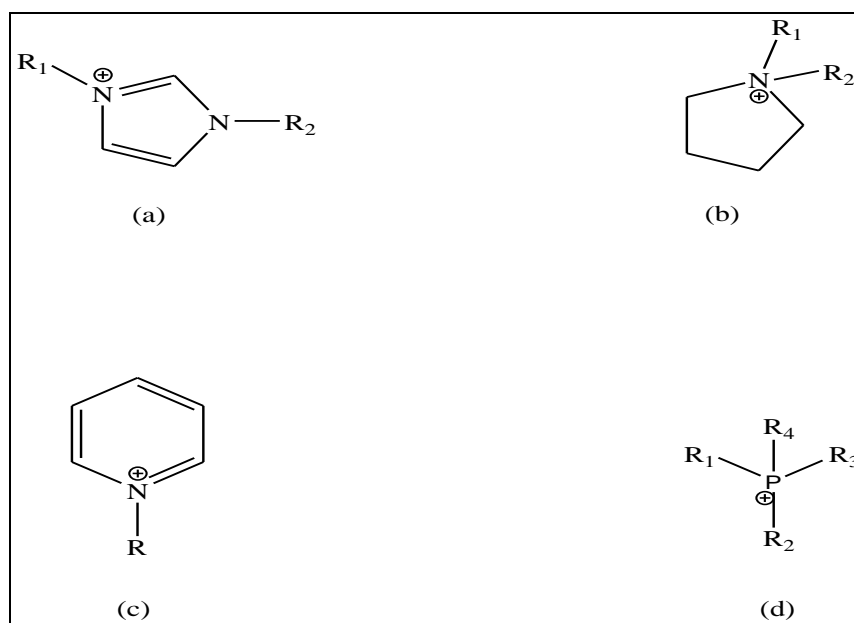


Figure 2.1. Most common cation used in ionic liquids, (a) imidazolium (b) pyrrolidinium (c) pyridinium (d) phosphonium.

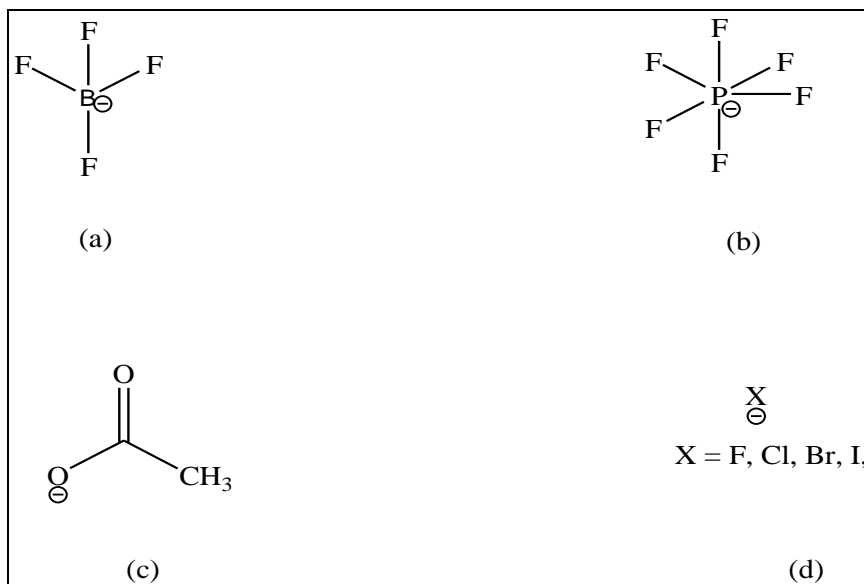


Figure 2.2. Most common anion used in ionic liquids, (a) tetrafluoroborate (b) hexafluorophosphate (c) acetate (d) halogens.

2.1.3 Protic ionic liquids

Two major types of ionic liquid; aprotic and protic; have been a focus in most ionic liquid studies. In aprotic system, a base gets ionized when the molecule accepts any group (except proton) to its basic site. Protic ionic liquid, on the other hand, is formed by proton transfer from Brönsted acid to a Brönsted base. Johansson *et al.* mentioned that there are distinguishing features between protic ionic liquids (PILs) and aprotic ionic liquids (AILs), as one of it, PILs have a proton available resulting in hydrogen bonding. This hydrogen bonding causing the PILs to have a non-negligible vapour pressure and some are distillable media where their boiling point occurs at a lower temperature than decomposition.

The most common cations used in protic ionic liquids are represented in Figure 2.3. The heterocyclic rings could contain substituents on any of the carbons in the ring as long as the nitrogen containing the positive charge and retains as proton. Figure 2.4 shows the anions commonly used in protic ionic liquids. Frequently, strong acid/strong base were considered in order to produce protic ionic liquid with greater proton transfer driving force. NMR changes in thermal properties in functions of stoichiometry, IR spectroscopy, ΔpK_a values and Walden plot are a few techniques that have been used to provide information about the ionicity of PILs.

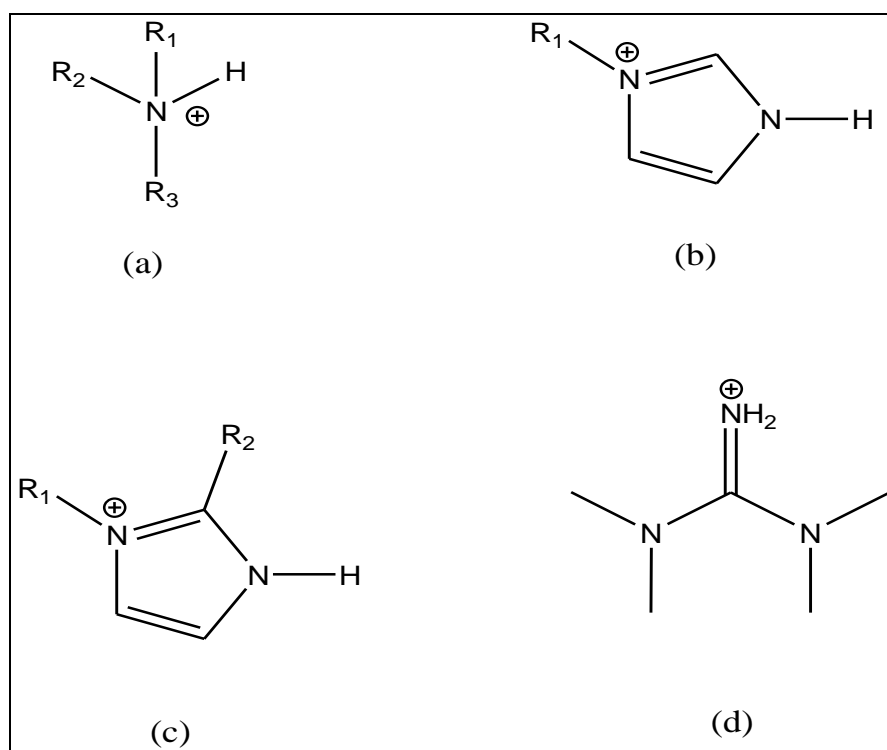


Figure 2.3. Most common cation used in protic ionic liquids, (a) ammonium (b) 1-alkylimidazolium (c) 1-alkyl-2-alkylimidazolium (d) 1,1,3,3-tetramethylguanidinium.

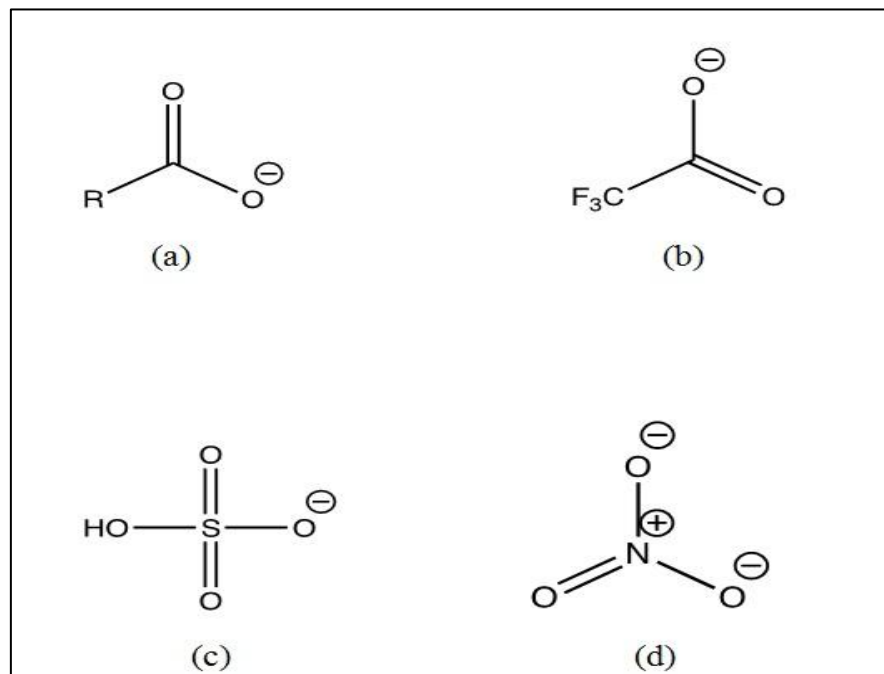


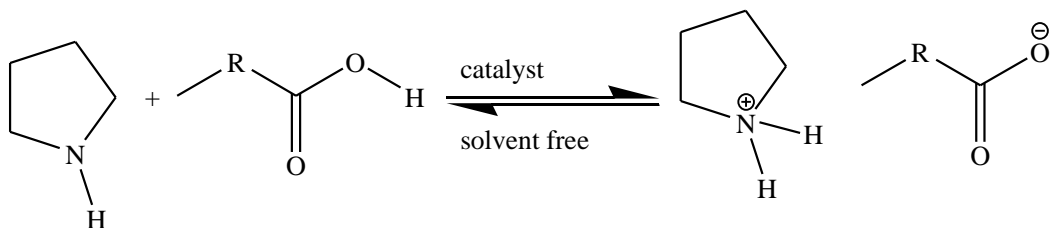
Figure 2.4. Most common anions used in protic ionic liquids, (a) carboxylates (b) trifluoroacetate (c) sulfate (d) nitrate.

Larger ΔpK_a values of acids and bases show an estimation of how complete the proton transfer is. Yoshizawa *et al.* [66] have projected that PILs with ΔpK_a more than 8 are ideally near to Walden plot. They also reported, many protic ionic liquids are actually used in the poorly ionized acid-base mixtures where it is very beneficial in solvent application. Apart from solvent application, in 2006, PILs were tried as lubricants for steel on aluminum applications. Qu *et al.* reported that PILs were able to change exposed metallic surfaces to form a boundary film in a very short time [67].

2.1.4 Synthesis of protic ionic liquids

Preparing protic ionic liquids is one simple task. By combining equimolar mixture of Brönsted acid and Brönsted base, highly pure protic ionic liquid can be directly produced. Walden rule stated, “poor” ionic liquids result from weak proton transfer and vice versa. Greaves *et al.* [68] synthesized protic ionic liquids where the cations are the primary amine and anions are organic or inorganic. They have studied the physicochemical properties of synthesized protic ionic liquids at the same amount of acid or base and at either excessive amount of acid or base.

Scheme 2.1 shows an example of neutralization reaction between pyridine and carboxylic acid to form a pyridinium based ionic liquid. The approximate pK_a range of a weak acid in water is -2 to 12. Large ΔpK_a , ($pK_a(\text{base}) - pK_a(\text{acid})$), value indicate stronger proton transition from an acid to the base took place [68]. Stoimenovski *et al.* [11] did a study on the ionicity effect to proton transfer effect in protic ionic liquids. In their study, n-heptylamine and N,N-dimethylbutylamine received a proton from acetic acid with ΔpK_a value 5.9 and 5.4 respectively. The result shows N-heptylamine produced highly ionised ionic liquid and immediately increased the hydrogen bonding ability to forms a protic ionic liquid. Contrary to the point above, N,N-dimethylbutylamine form a mixture with low degree of proton transfers.



Scheme 2.1. Preparation of pyridinium based ionic liquid.

2.3 Hydrogen bonding

Hydrogen bonding is an interaction when a hydrogen atom located in between a pair of other atoms and driving a high affinity for electrons, provided that this bond is weaker than an ionic or covalent bond but stronger than attractive forces between uncharged molecules, which is named as van der Waals forces.

Hydrogen bond can be classified into two types, firstly, intermolecular hydrogen bond where the bond is formed between two different molecules of the same or different substances such as water, H₂O molecule as the most famous example. Second type of hydrogen bond is intramolecular hydrogen bond where the bond is formed between the hydrogen atom and the highly electronegativity atom present in the same molecule such as hydrogen fluoride, HF and ammonia, NH₃.

Hydrogen bonding has always sought researchers attention. In 1993, Brady and Schmidt [69] mentioned in their finding that maltose were extensively hydrogen bonded to solvent molecules in aqueous solution, and these hydrogen bonds were found to have potential conformational consequences. Recently, Sedov and Solomonov [70] studied thermodynamics of hydrogen bonding between water and molecules of aliphatic alcohols in dilute aqueous solutions. They have mentioned in their finding huge negative values of the

Gibbs energies and increased in aqueous solubilities is due to strong interaction effects were observed when alcohol molecule binds to an associate of water.

2.4 Separation studies

Over the centuries, human have carried out solid or liquid extraction such as brewing of tea or the making of coffee. While solid or liquid extraction is applied in everyday use, liquid-liquid extraction is a very common method used in laboratory. This type of extraction is usually the initial step before the final purification of product. Liquid-liquid extraction or solvent partitioning in general is the most universal and an ancient method to separate compounds or chemicals based on the solubilities behaviour in two different immiscible or almost immiscible liquids. Yet, the process is easy and less tedious compared to other separation methods.

Extraction or separation process will always been a crucial area to be studied in research world. Liquid-liquid extraction (LLE) is one example of separation process type. The extraction is able to transfer wanted or unwanted component from one liquid to another, therefore, two phases consisting of immiscible and partially miscible liquids will be formed. Due to that, the process is very important in many industries such as food processing, pharmaceutical separation, oil purification and etc.

When choosing an extractant, two immiscible or almost immiscible solvents were selected. Some familiar solvent pairs are water-dichloromethane, water-hexane and water-ether. Most of the combinations involve water. This is because water is highly polar and immiscible with organic solvent. However, certain organic solvents like propanol, methanol

and isopropanol will not separate using liquid-liquid extraction method, since the solvents are too miscible with water. In liquid-liquid extraction, two phases will be formed which are water rich phase and organic rich phase. However, there are rare cases where both phases are organic or organic mixtures. The volatility, cost and toxicity of extractant are often used in separation process. Therefore, ionic liquid fits the criteria in order to proceed with this study.

2.4.1 Ionic liquids in separation studies

Liquid-liquid extraction using ionic liquid as an extractant has been very appealing to most separation studies. Recently, Wilfred *et al.* [71] reported the efficiency percentage of dibenzothiophene extraction from dodecane were 42 % - 66 % among eighteen types of ionic liquids that have been introduced. This study has revealed that ionic liquids have a strong facility interacting with organic molecules through many types of mechanism. Plus, these interactions can be attuned by changing the cations or anion of ionic liquids. These adjustments will produce a task-specific ionic liquid.

Alvarez-Guerra and Irabien [72] did a study on lactoferin extraction with hydrophobic imidazolium-based ionic liquids using conventional techniques to separate and purify the protein. Two types of different anion on ionic liquids have been used by them. Their study revealed that the task specific ionic liquids are able to separate lactoferin selectively, depending on the iron atom interaction of the protein.

Not to forget, protic ionic liquids were widely used in extraction or separation studies. Bai *et al.* [73] synthesized a range of protic ionic liquids with organic carboxylate anions and applied to extract asphaltenes from direct coal liquefaction residue (DCLR) at room temperature. The study proved that the structures of protic ionic liquids affected the extraction yield. However, they have also mentioned in their findings, protic ionic liquid is potential to extract asphaltenes from DCLR. On the same approach, Dai *et al.* [74] has introduced hydrophobic ionic liquid in solvent extraction of Sr^{2+} and Cs^+ . Their study revealed, excellent extractions were observed when selected protic ionic liquid were used. These excellent extractions could be attributed to the greater hydrophilicity of the cations of the protic ionic liquids.

From all the works that have been done, ionic liquids have been well explored in many fields. At present, the new applications by using ionic liquids in extraction of compounds have increased day by day.

2.4.2 Upper and lower critical solution temperature separation

Thermoresponsive solution separation is divided into two types which are upper critical solution temperature (UCST) and lower critical solution temperature (LCST). UCST is when a mixture is miscible at higher temperature and separated into two layers or more at lower temperature. Vice versa, lower critical solution temperature behaviour, that is, homogeneous upon heating and phase separation

occurs upon lowering down the temperature (Refer Figure 2.5 for schematic diagram).

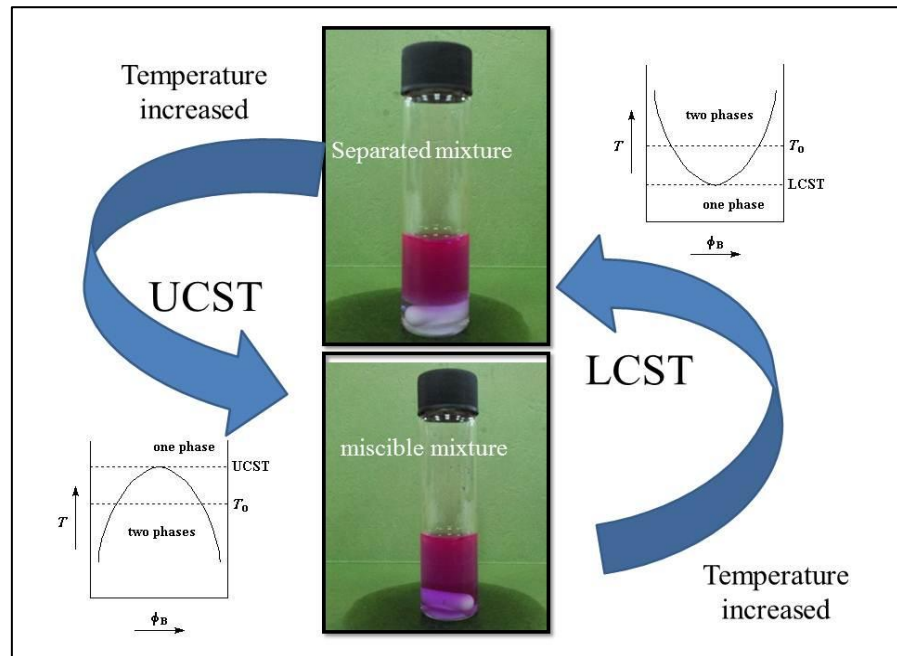


Figure 2.5. Schematic diagram of UCST and LCST phase behaviour in a mixture.

Because of the opposite behaviour, LCST and UCST transition has always been considered for having different theoretical foundations. In Flory-Huggins solution theory [75], due to the unfavourable entropy enthalpic interaction between solvent molecules and polymer molecules, a phase separation can only be occurred. On the other hand, when the positive enthalpy out balance the mixing entropy, the mixture will become homogeneous and miscible to each other.

These two behaviours are commonly studied in polymer research world [76 - 80], due to the existence of temperature-responsive polymers which can be

functionalized and applied in many industries such as bioseparation and liquid chromatography. Similarly, ionic liquid can be altered too to produce a task specific ionic liquid. According to Kohno and Ohno [81], moderate hydrophilic ionic liquid will undergo LCST-type phase transition. In their study, they have observed that aqueous mixture of moderate hydrophilic ionic liquid exhibits LCST behaviour which can be used in extraction of protein. Motivated by them, this particular study was conducted on aqueous isopropanol with an introduction of moderate hydrophobic ionic liquid into the aqueous organic mixture. As an addition, up until today there were no publications on similar study using ionic liquid.

2.5 Summary

The preceding literature review has acknowledged the hydrogen bonding, separation, extraction and phase equilibria of pure ionic liquids and other mixtures. However an important factor needs to be considered before advancing to further steps in achieving stated objectives.