別紙様式５(Attached Form 5)

学位論文要旨 Abstract of Thesis

所属専攻 Field: **CHEMISTRY** 専攻(Field)
氏　名 Name: HAQUE, MD AMINUL (ハク　エムディー　アミヌル)

Title of Thesis

Electrodialytic Universal Synthesis Method for Highly Pure and Mixed Ionic Liquids

高純度なイオン液体合成のための電気透析によるユニバーサルな合成法

Abstract（within 1600 words）

Abstract

Ionic liquids (ILs) have undoubtedly become an important area of study in modern chemistry. ILs are described as salts that are composed exclusively of ions and have low melting points of up to 100 °C or less. Low melting point salts were usually less studied materials because their potential impressive application was not anticipated by the scientists. Now researchers have made a series of salts that are liquid even at room temperature, with invaluable utilities. Most ILs use organic cations and inorganic and/or organic anions to produce ILs. Asymmetry, bulkiness, and size discrepancies of combined cations lead to ILs with lower melting points. These molten salts have many useful properties in laboratories and industries at low temperatures. Although ILs were first described more than a century ago, their importance was not recognized until the 1980s of the last century. However, in the late 1980s, researchers became fully aware of the stunning physicochemical properties of ILs. Many research groups from multidisciplinary areas of study started to synthesize and apply ILs in various sciences and technologies. Today, the synthesis and application of ILs have established themselves as a state-of-the-art technology that has brought about visible changes in almost all areas of synthetic and applied materials chemistry and related technologies.

What has made ionic liquids so important is their distinctive physicochemical properties. They have a wide range of solvents, electrolytes, and many other functional properties that traditional aqueous and organic solvents do not possess. For example, if a process needs to operate at temperatures above 100 □C, this is impossible under ambient conditions using aqueous media. ILs with a high liquid range and high boiling point is perfect for this type of operation. This unconventional liquid has exceptionally low volatility, moderate to high viscosity, broad electrochemical and thermal stability, finely tunable

hydrophilicity and hydrophobicity, exceptional solubilization capabilities for a large variety of materials, and broad heat transfer and storage properties, electrolyte and solvent properties, proton donor and acceptor capacity, etc. These liquids are now popularly referred to as green solvents and designer materials. Because of these innovative properties, ionic liquids have attracted considerable attention in a variety of industries such as bulk chemicals, pharmaceuticals, nanomaterials, and nuclear and energy applications in recent years. These versatile designer materials have been adopted for lubrication, membranes, heat transfer, and temperature control, as well as electrochemical energy applications such as fuel cells, batteries, and capacitors. As these advanced materials open up more and more new and important applications, there are also efforts to develop methods to fabricate a broader range of ILs. However, despite the high demand, only a few methods have been described to date, and, more importantly, efficient but general methods for IL synthesis are lacking. Furthermore, the purity of ILs is a key factor for many demanding applications. Several synthesis methods and purification techniques have been reported, however, the reported methods are occasionally very expensive, not environmentally friendly, and sometimes very complex purification steps are required. That is why scientists are looking for simple and effective alternatives. Therefore, it would be very advantageous to develop an inexpensive, environmentally benign method to produce a wide variety of pure ILs. Electrodialysis (ED) is a well-designed process that has been adopted industrially for more than 50 years to produce drinking water from brackish water sources. Recently, it has found a multitude of new, interesting applications in the chemical process industry, in the food and pharmaceutical industries, as well as in wastewater treatment and in the manufacture of high-quality pure products and drinking water. As already mentioned, ionic liquids are essentially consisting of cations and anions. On the other hand, electrodialysis transports ions across charged membranes under an applied electromotive potential. Therefore, it is very likely that electrodialysis can bring cations and anions together using a specially designed ED device. Our laboratory also reported an ion transfer device (ITD), a modified ED device, for several important electrodialysis-based analytiacal applications to date after its introduction in 2012. We have applied ITD to the analysis ranging from blood samples to radioactive materials.

The first part of the dissertation presents work demonstrates a general electrodialysis method for the formation of 9 high-purity ILs. Three quite popular cations, namely the 1-butyl-3-methylimidazolium, 2-hydroxyethylammonium, and 1-butyl-1-methylpyridinium cations, and five widely used anions, the nitrate, formate, acetate, and tetrafluoroborate anions, were utilized for the generation of 9 ILs. No new ILs were tried, but very popular and commercially available ILs were synthesized to assess the viability of our newly developed method. Before synthesizing the ILs, the effect of various parameters on the synthesis was evaluated. The entire synthesis used water only as reaction medium and electricity as the clean energy source, demonstrating the environmental friendliness of our process. The most widely used method to generate ILs is ion metathesis. The major disadvantage of ion metathesis is that it produces an equivalent amount of by-products. The most common challenge of this method is to remove the by-products to obtain high-purity ILs. Silver halide salts are sometimes used to precipitate and filterring off the halide impurities from the reaction media, ultimately increasing production costs. Other methods are not widely used and suffer from other limitations; One is the lack of versatility in using reactants. Unlike traditional processes, the membrane-based ED technology can prevent the formation of by-products within the product stream. Thus, this process offers the advantages of avoiding the use of hazardous organic solvents and eliminating lengthy and costly purification procedures. The IL was obtained with our current method with a purity of more than 99%. Halogenated and non-halogenated cation sources were tested for IL syntheses, and the inexpensive halogenated source produced purer ILs, demonstrating the cost-effectiveness of the current method.

Mixing appropriate ILs has also been found to change the properties of ILs to a very useful level, and mixed ILs (MILs) have many potential applications. MILs were used like pure ILs in almost all cases where ILs have been adopted. Our present technique also demonstrates a simple generation of different mixed ILs based on a simple adjustment of the applied current.

Hexafluorophosphate ions have been incorporated into many traditional and advanced materials. In particular, they have been used in many electrolyte materials that have been extensively used in numerous electrochemical devices. Usually, hexafluorophosphates are produced by the metathesis reactions with alkali metal hexafluorophosphate salt solutions. Hexafluorophosphoric acid solutions are also used in many syntheses. However, hexafluorophosphoric acids are not found in high purity since they are supplied as several percent solutions of hexafluorophosphoric acids in water and are known to hydrolyze in an aqueous solution. Thus, for a practical application of synthesizing high purity hexafluorophosphate-based materials, high purity hexafluorophosphoric acids are required, which are very difficult to obtain from suppliers. In the second part of the present work, a simple approach for the synthesis of high-purity hexafluorophosphoric acid for the synthesis of ionic liquids using the generated hexafluorophosphoric acid has been demonstrated.