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SYNTHESIS AND APPLICATIONS OF IMIDAZOLIUM-BASED IONIC LIQUIDS
AND THEIR POLYMER DERIVATIVES

by

WOON SU OH

A DISSERTATION

Presented to the Faculty of the Graduate School of the
MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY
In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

in

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ABSTRACT

Imidazolium-based ionic liquids have been increasingly used as green solvents to replace the volatile and relatively toxic organic solvents, in homogeneous and heterogeneous catalysis, materials science, nano materials, lithium ion batteries, and separation technology. Section 1 describes the modulating effect of the imidazolium based room temperature ionic liquids (RTILs) on the critical micelle concentrations (CMC) of surfactants. CMC of sodium dodecyl sulfate (SDS), an anionic surfactant, has been investigated in aqueous solutions of a variety of room temperature ionic liquids (RTILs). CMC values decrease with increasing alkyl chain-length and with fluorinated side chains on the imidazole moiety. In section 2, applications of ionic liquids and their polymer derivatives immobilized with Lewis acid catalysts, as heterogeneous catalysts, for various organic transformations is described. For example, the water-tolerant Lewis acid, gadolinium triflate ($\text{Gd}(\text{OTf})_3$), immobilized in RTILs and their polymeric derivatives are convenient recyclable and green catalysts for acetylation of a variety of alcohols, phenols, amines, and Michael additions of amines and thiols to α , β -unsaturated esters and acrylonitrile. Section 3 outlines synthesis of polynorbornene based imidazolium ionic liquids. Through Grubbs' catalyst mediated ring opening metathesis polymerization (ROMP), we were able to obtain oligomers of the polynorbornene-imidazolium salts, which are potentially useful as gel-polymer electrolytes in lithium ion batteries, and in the preparation of Ag nanowires and carbon nanotubes.

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1. STRUCTURAL EFFECTS OF IONIC LIQUIDS ON THE CRITICAL MICELLE CONCENTRATIONS (CMC) OF SURFACTANTS^{1,2}

1.1 INTRODUCTION

Ionic liquids are the organic salts, composed entirely of ions and they exist in the liquid state at temperatures lower than 100 °C.³⁻⁵ Due to their unique properties such as low volatility, non-flammability, liquid-phase stability at high temperature, high ability in solvating organic, inorganic or polymeric materials, and high ionic conductivity, ionic liquids have attracted attention and increasingly numerous applications as industrial scale catalysts and as green solvents in recent years. Ionic liquids are mainly organic cations, associated with inorganic anions, and form crystalline structures with low lattice energies, allowing these salts to be in the liquid state at or near room temperature. One of the interesting applications of ionic liquids is to replace conventional organic molecular in solvents, including chemical, catalytic and biological reactions,⁶⁻⁹ inorganic synthesis,¹⁰⁻¹³ separation and purification of gases,^{14, 15} and contaminant removal from aqueous streams.¹⁶ There are some industrial processes that already use ionic liquids due to their economical advantages and reaction yields,^{17, 18} such as the BASIL (Biphasic Acid Scavenging utilizing Ionic Liquids) process,^{8,9,19} by BASF technologies.

Historically, the following four main steps must be mentioned. The field of ionic liquids began in 1914 with their observation by Paul Walden, who reported the physical properties of ethylammonium nitrate [C₂H₅NH₃][NO₃] (m.p. 12-14 °C) (see Figure 1.1), which was formed by the neutralization of ethylamine with concentrated nitric acid.²⁰

The second major studies of room temperature molten salts were made in the 1940's by a group led by Frank Hurley and Tom Weir at Rice University.

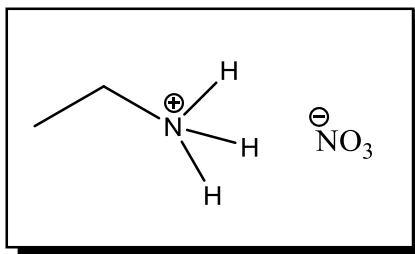


Figure 1.1 Chemical structure of ethylammonium nitrate $[\text{C}_2\text{H}_5\text{NH}_3]^+ [\text{NO}_3]^-$.

When they mixed and gently warmed powdered pyridinium halides with aluminum chloride, a clear, colorless liquid was obtained in Figure 1.2.²¹

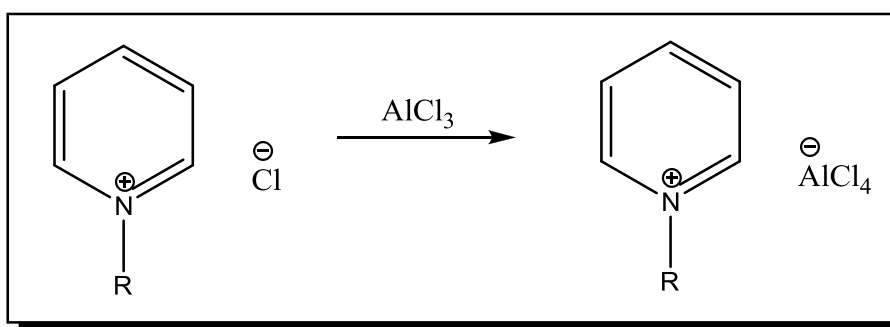


Figure 1.2 Chemical structure of N-alkyl-pyridinium tetrachloroaluminate.

The third step was the introduction of alkylimidazolium salts in the early 1980s by Wilkes and Hussey.²² It was the discovery of 1-ethyl-3-methylimidazolium-based chloroaluminate ionic liquids in 1982 that accelerated activities in the area of room temperature ionic liquids (RTILs). The exciting property of halogenoaluminate ionic liquids is their ability for acid-base chemistry, which can be varied by controlling the molar ratio of the two components.²³ A major drawback of all chloroaluminate(III) ionic liquids was their moisture sensitivity. This is a major disadvantage for industrial

application. Almost that time, in the 1980s, the term “ionic liquid” became more popular to describe organic salts that melt below ~ 100 °C and have an appreciable liquid range. The number of papers published on ionic liquids has grown exponentially (see Figure 1.3).

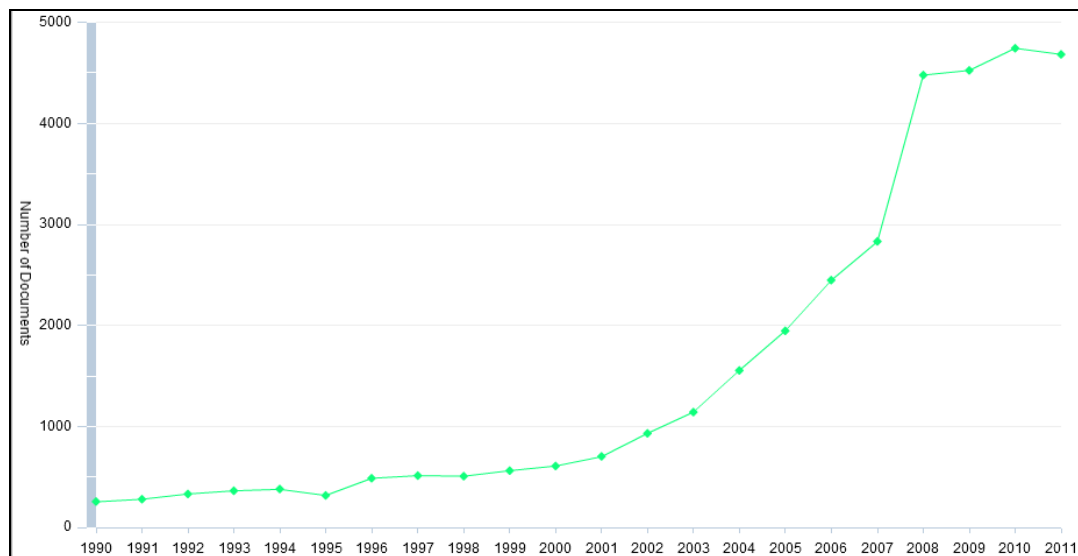


Figure 1.3 The rise in publications concerning ionic liquids as a function of time, as determined using Scopus (from 1990 to 2011).

More recently, “Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids” was reported by Wikes and Zaworotko in 1992.¹³ These ionic liquids have received extensive attention not only because of their water stability, but also because of water immiscibility.

1.1.1 Structures of Room Temperature Ionic Liquids [RTILs]. Common ionic liquids contain imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, and sulfonium cations. They are generally abbreviated as [C_nC_mIM], [C_nPy], and [C_nC_mPyr] for alkyimidazolium, pyridinium, and pyrrolidinium cations, respectively,

where Im stands for imidazolium, Py for pyridinium, and Pyr for pyrrolidinium. The number of carbons in the N-alkyl chains is expressed by n , and m . The examples of numbering ionic liquids and most common ionic liquids are shown in Figure 1.4 and Figure 1.5, relatively.

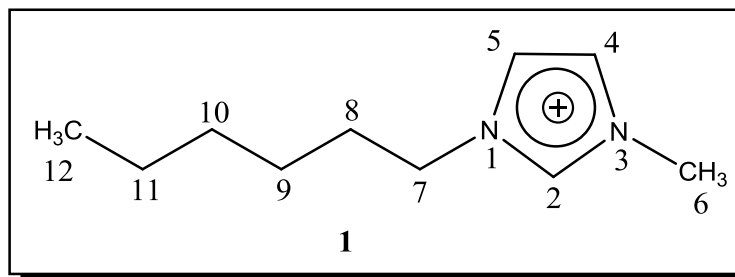


Figure 1.4 Numbering scheme on the 1-hexyl-3-methylimidazolium cation, $[\text{C}_6\text{C}_1\text{Im}]^+$, showing the three ring protons H_2 , H_4 , and H_5 .

A wide range of ionic liquids has been developed incorporating many different anions, including chloride $[\text{Cl}]^-$, hexafluorophosphate $[\text{PF}_6]^-$, tetrafluoroborate $[\text{BF}_4]^-$, trifluoromethanesulfonate $[\text{CF}_3\text{SO}_3]^-$ anion abbreviated as $[\text{TfO}]^-$, bis[(trifluoromethyl)sulfonyl]amide $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ anion abbreviated as $[\text{Tf}_2\text{N}]^-$, tris[(trifluoromethylsulfonyl)methanide] $[\text{C}(\text{SO}_2\text{CF}_3)_3]^-$ $[\text{Tf}_3\text{C}]^-$ (Tf is a short-hand notation for triflate), and so on. The more recent research has mainly focused on room temperature ionic liquids composed of asymmetric N,N'-dialkylimidazolium cations associated with a variety of anions.

Most common ionic liquids are prepared through the combination of an organic heterocyclic cation, such as N,N'-dialkylimidazolium, and an inorganic/organic anion, such as chloride or methanesulfonate.

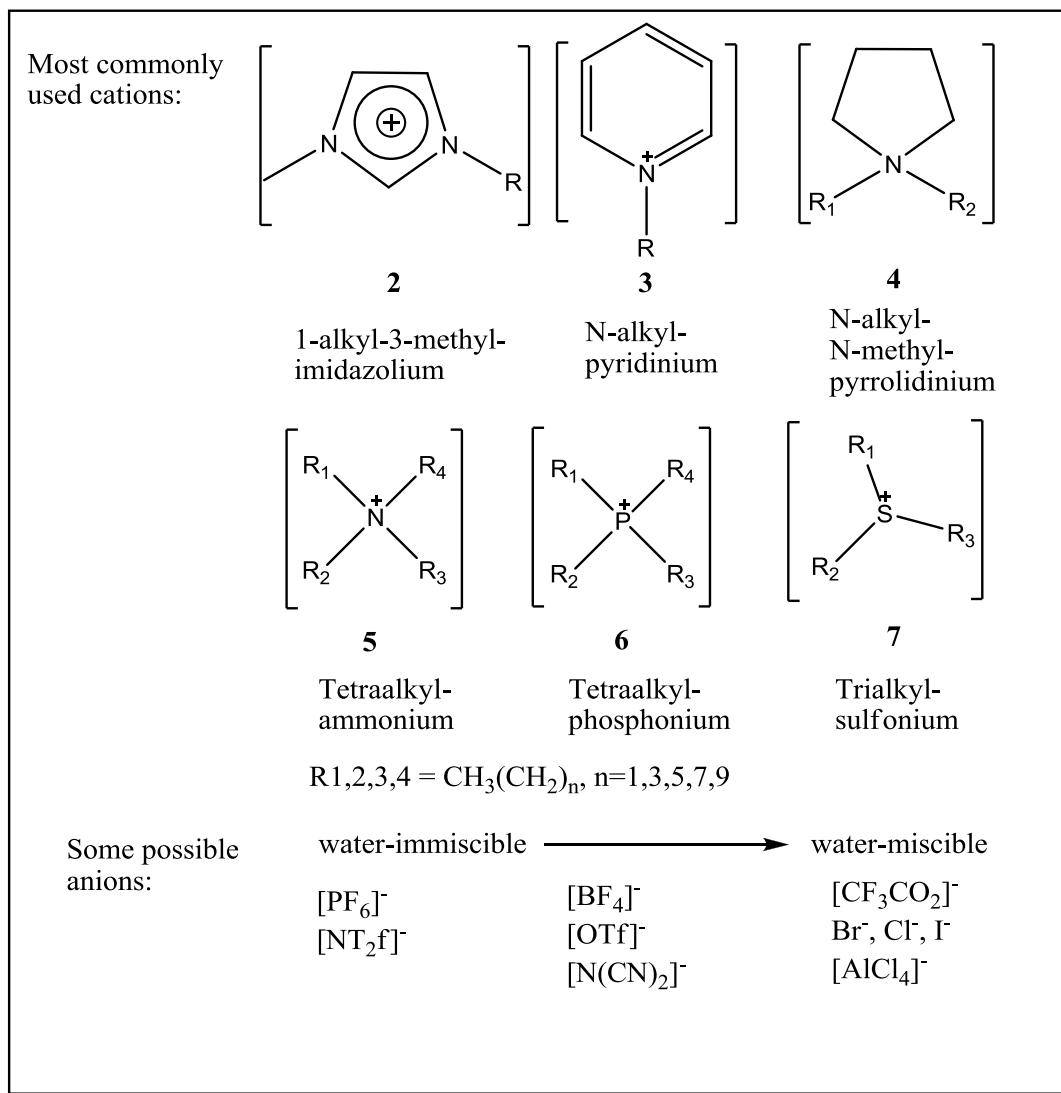


Figure 1.5 Some commonly used ionic liquid systems.²⁴

1.1.2 Synthesis Method of Room Temperature Ionic Liquids [RTILs]. The basic method for the preparation of ionic liquids is reaction of alkyl halide with imidazole (see Figure 1.6). After a metathesis of a halide salt desired room temperature ionic liquids are readily obtained.

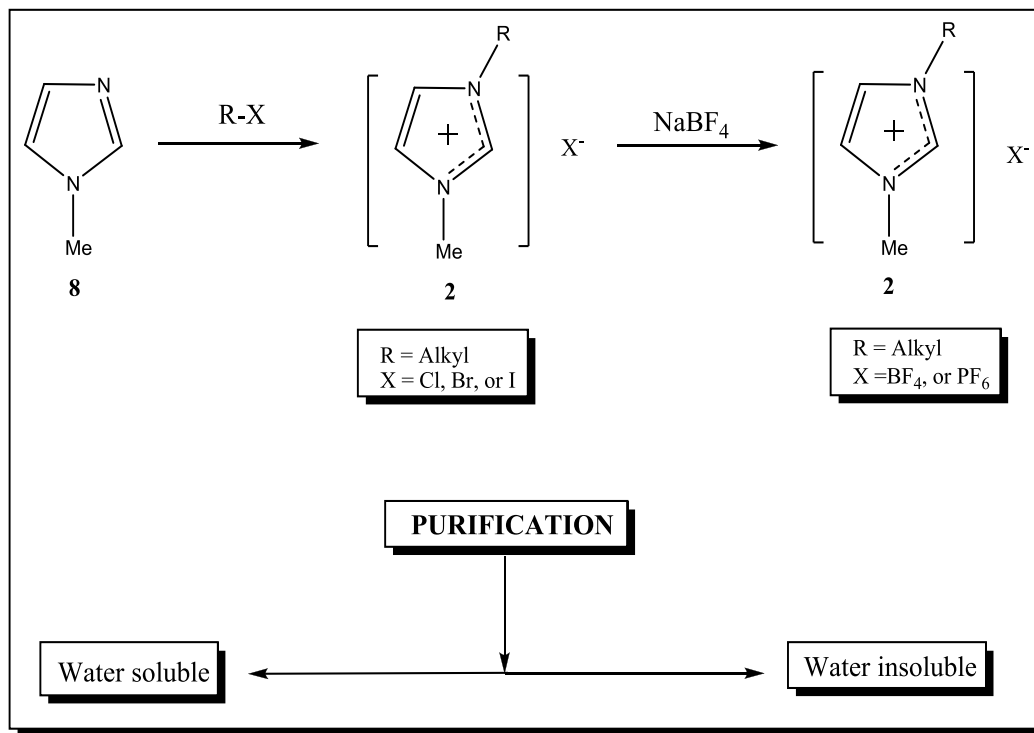


Figure 1.6 Typical preparation routes for ionic liquids.

1.1.3 Physical and Chemical Properties of Room Temperature Ionic Liquids

[RTILs]. The physical/chemical properties of ionic liquids depend on the nature and size of both their cation and anion constituents (see Table 1.1). Their applications in academia and industries are rapidly increasing due to their unique properties. The effect of the cation/anion structure on their densities was discussed for more than 300 ionic liquids in a recent publication.²⁵⁻²⁸ Density depends strongly on the size of the ring in the cation, on the length of the alkyl chain in the cation, and on the interaction forces between the cation and the anion. The densities of ionic liquids based on 1,3-dialkylimidazolium cations increase for typical anions in the order: $[\text{Cl}]^- < [\text{BF}_4]^- < [\text{C}_2\text{SO}_4]^- < [\text{PF}_6]^- < [\text{Tf}_2\text{N}]^-$.²⁹⁻³⁴

Solubility of imidazolium-based ionic liquids in water is dependent on the substituents on the imidazole, and on the nature of the counteranions. For example, tetrafluoroborate salts are relatively more water soluble than those of the hexafluorophosphate salts. The reason for this behavior is that relatively stronger hydrogen bonds can form between water and the tetrafluoroborate.³⁵

The viscosity of ionic liquids is determined by van der Waals forces and hydrogen bonded structures. In case of [BMIM]⁺[X]⁻, the viscosities for typical anions decrease in the order: [I]⁻ > [PF₆]⁻ > [BF₄]⁻ > [TfO]⁻ > [CF₃CO₂]⁻ > [Tf₂N]⁻.^{28, 36-38} For a series of 1-alkyl-3-methylimidazolium cations, increasing the alkyl chain length from butyl to octyl increased the hydrophobicity and the viscosity of the ionic liquids, whereas densities and surface tension values decrease.³⁹

In general, lower alkyl chains containing ionic liquids are expected to give relatively more hydrophilic compounds, while increase in the chain length should give relatively hydrophobic compounds.

1.1.4 Application of Room Temperature Ionic Liquids. In most successful example of an industrial process using ionic liquid technology is the BASILTM (Biphasic Acid Scavenging utilizing Ionic Liquids) process in the BASF.^{8, 41, 42} The BASILTM process (Figure 1.7) is used for the production of the generic photoinitiator precursor alkoxyphenylphosphines.

Table 1.1 Physical properties of various ionic liquids.⁴⁰

RTILs		mp (°C)	Density (g/cm ³)	Viscosity (cP, 25 °C)
[EMIM] ⁺ [BF ₄] ⁻	9	15	1.24	37.7
[BMIM] ⁺ [BF ₄] ⁻	10	-71	1.21	118.3
[HxMIM] ⁺ [BF ₄] ⁻	11	-82	1.15	234
[EMIM] ⁺ [CF ₃ SO ₃] ⁻	12	-9	1.39	45 (20 °C)
[BMIM] ⁺ [CF ₃ SO ₃] ⁻	13	13-17	1.29	99 (20 °C)
[HxMIM] ⁺ [CF ₃ SO ₃] ⁻	14	18-23	-	-
[EMIM] ⁺ [PF ₆] ⁻	15	60	-	-
[BMIM] ⁺ [PF ₆] ⁻	16	6.5	1.37	272.1
[HxMIM] ⁺ [PF ₆] ⁻	17	-73.5	1.30	497
[EMIM] ⁺ [CF ₃ CO ₂] ⁻	18	-14	1.29	35
[BMIM] ⁺ [(CF ₃ SO ₂) ₂ N] ⁻	19	-3	1.52	34

EMIM: 1-ethyl-3-methylimidazolium, **BMIM:** 1-butyl-3-methylimidazolium,
HxMIM: 1-hexyl-3-methylimidazolium.

In the original process, triethylamine was used to scavenge the acid that was formed in the course of the reaction, but this made the reaction mixture difficult to handle as the waste by-product, triethylammonium chloride formed a dense insoluble paste. Replacing triethylamine with 1-methylimidazole results in the formation of 1-methylimidazolium chloride, an ionic liquid, which separates out of the reaction mixture as a discrete phase. The 1-methylimidazole is recycled after nucleation.⁴³

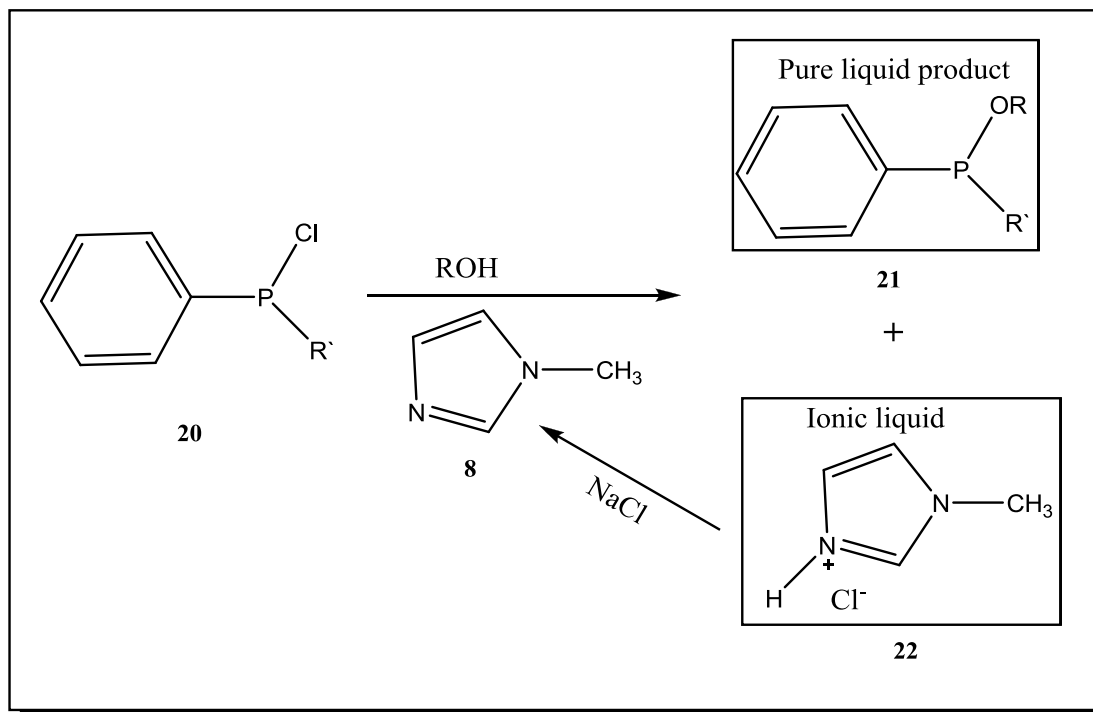


Figure 1.7 The BASIL™ process.⁴³

1.1.5 Application of Room Temperature Ionic Liquids to Silver Nanowires.

The imidazolium ionic liquids associated with specific anions are known to self-organize in a way that is adaptable to the fabrication of metal nanostructures.⁴⁴⁻⁵⁰ Recently, the demand for a transparent electrode in such fields as flat panel displays, touch panels, solar cells, etc. has been increasing. Silver nanowire and transparent conductive film are shown in Figure 1.8. The material for the transparent electrode is currently being mainly used includes a metal oxide such as indium tin oxide (ITO) for vacuum deposition. However, indium tin oxide (ITO) has a number of drawbacks and is unlikely to be the material of choice in future optoelectronic devices. The difficulties with ITO revolve around the rising cost of indium, the brittleness of ITO, concerns about toxicity and carcinogenicity⁵¹, and the high temperature processing used in its production. It has been

known for the past few years that flexibility and low temperature processing can be achieved by deposition of nanostructured thin films from the liquids phase. While polymer,⁵² and graphene⁵³⁻⁵⁸ films have been studied, the most common material used to date has been metal nanowire and carbon nanotubes.⁵⁹⁻⁷¹

There have been proposed methods of forming a transparent conductive film having high electrical conductivity and optical transparency by manufacturing a metal such as silver in the form of a nanostructure, dispersing the metal nanostructure in a solution and then applying the resulting dispersion solution on a plastic film.⁷³

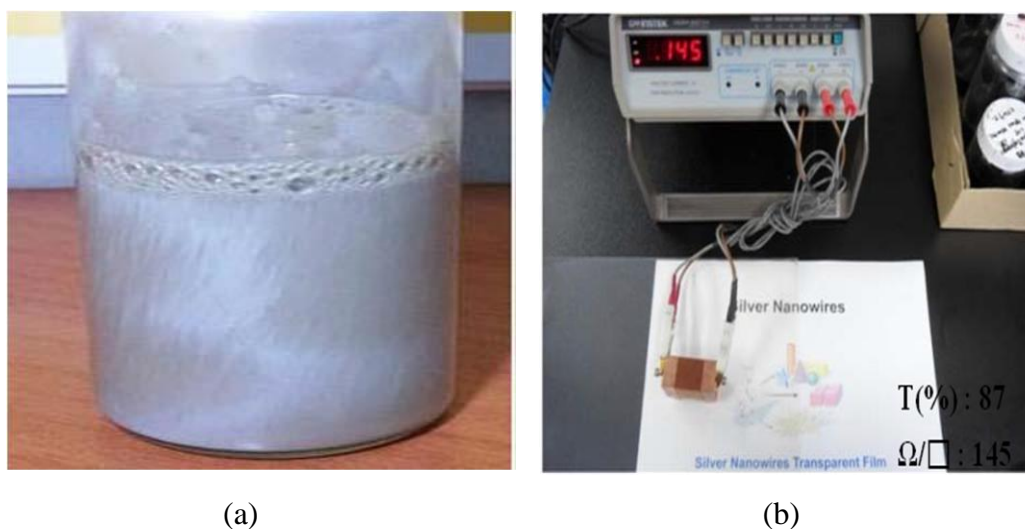


Figure 1.8 Silver nanowire and transparent conductive film. (a) Dispersion of silver nanowire in water prepared by “Polyol method through reduction of silver nitrite using ethylene glycol as reducing agent and polyvinylpyrrolidone [PVP] as a capping agents ; (b) Transparent conductive film using the dispersion of the above silver nanowire. Conductivity: Conductivity: $145 \Omega/\text{cm}^2$, Transparency: 87%.⁷² The electrical conductivity can be increased by replacing PVP with ionic liquids.

In general, metal nano wire is prepared from a metal salt precursor using a polyol method such as ethyleneglycol as a reducing agent in the presence of polyvinylpyrrolidone. This technique is advantageous because the metal nanostructure is

comparatively easily prepared using a solution through the reaction, called “polyol reduction”.⁷⁴ However, according to Kim T.Y. and co-workers,⁵⁰ a common problem of the standard polyol process is the inability to effectively reproduce uniform silver nanowires, as a result a mixture of nanostructures of several shapes, such as wires, particles, cubes, and tetrahedrons (Figure 1.9) due to the concentration, addition sequence, and rate of addition of the capping and reducing agent.

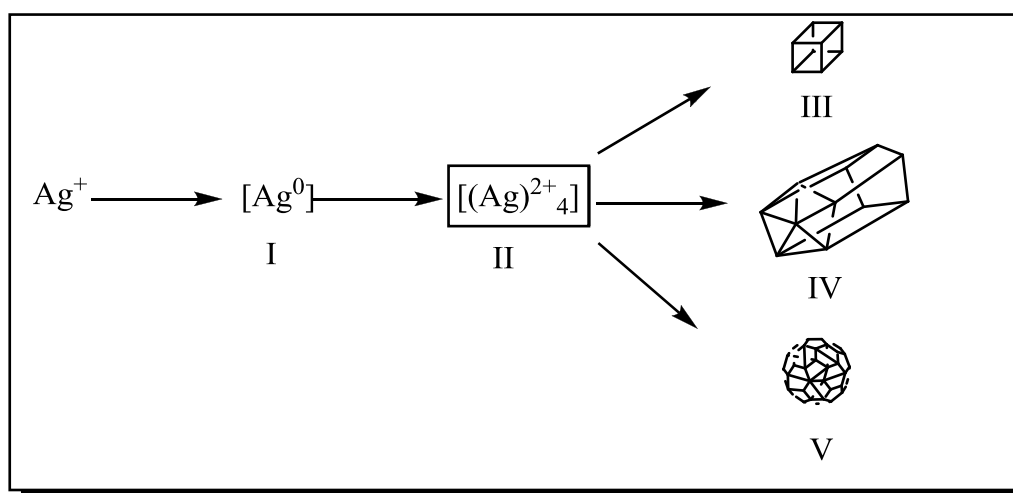


Figure 1.9 Schematic diagram illustrating the reduction of silver ions. (I) by ethylene glycol, (II) the formation of silver clusters, (III) the nucleation of seeds and the growth of seeds into nanocubes, (IV) nanorods or nanowires, and (V) nanospheres.⁷⁵

Kim T.Y. and co-workers demonstrated that the simple reduction of a silver precursor in the presence of ionic liquids and ionic liquids can act as a capping agent to kinetically control the growth rates of different crystalline faces. They determined the role of the ionic liquids on the wire-formation process by doing comparative experiments. The use of chloride or bromide as an anion for ionic liquids (i.e. BMIM-Cl⁻ or Br⁻, 1-butyl-3-methylimidazolium) results well-defined nanoparticles with cubic and octahedral shape,

respectively, while BMIM-MeSO₄ afforded silver nanowires in a highly reproducible manner. The SEM image of silver nanowires is shown in Figure 1.10. These results indicate that the morphology of silver nanostructures is strongly dependent on the anion in the ionic liquids. This anion effect could arise from the different abilities of the anions to coordinate with the silver metal, leading to different nucleation mechanisms.

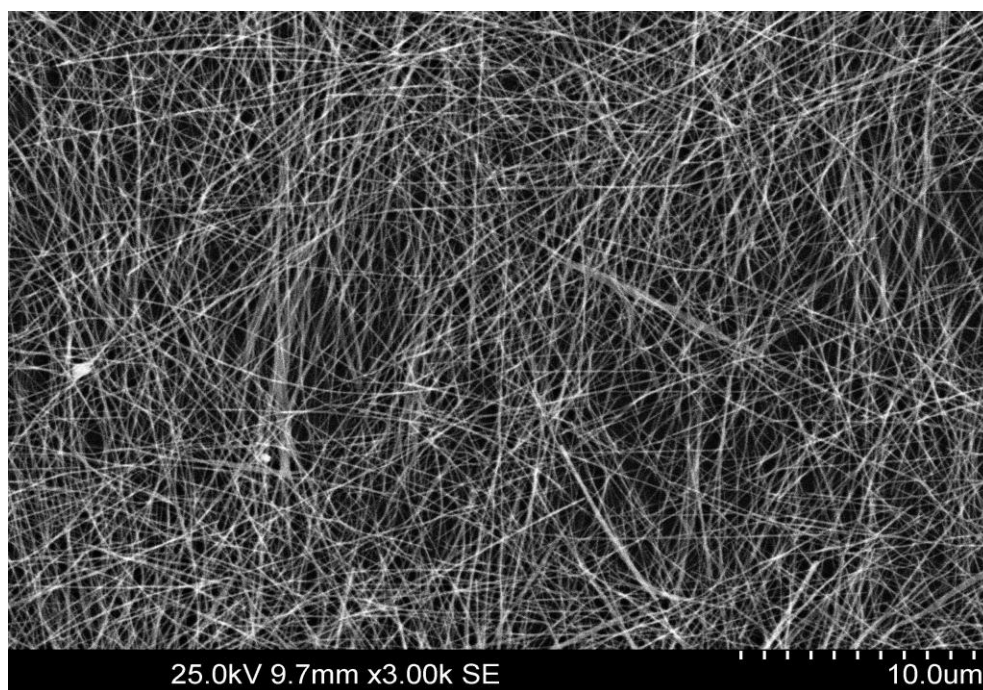


Figure 1.10 SEM image of silver nanowires.⁷²

1.1.6 Application of Room Temperature Ionic Liquids to Carbon Nanotubes [CNTs]. Carbon nanotubes [CNTs] were observed for the first time by Sumio Iijima in 1991.⁷⁶ CNTs have a unique set of properties that position them for a wide scope of possible applications in suspensions and polymer based solutions, melts and composites.⁷⁷⁻⁷⁹ Their outstanding characteristics include high mechanical properties, excellent thermal and electric conductivities, and low percolation thresholds (loading

weight at which a sharp drop in resistivity occurs).⁸⁰ However, due to their high aspect ratios and strong van der Waals interaction, as-synthesized CNTs form bundled structures.⁸¹ The mechanism of the de-bundling of CNTs is believed due to the “unzipping” mechanism proposed by Smalley and co-workers,⁸² which is triggered by sonication, followed by the wrapping of CNTs by dispersants. Surfactant micelles, π -aromatic compounds and synthetic polymers can act as dispersants for CNTs. The most convenient and frequently-used dispersant for CNTs in aqueous media is surfactants including sodium dodecyl sulfate (SDS),⁸³⁻⁸⁵ Sodium dodecylbenzene sulfonate (SDBS),^{82, 86-89} Brij,^{82, 90} Tween,^{82, 90} and Triton X (see Figure 1.11).^{82, 89-91}

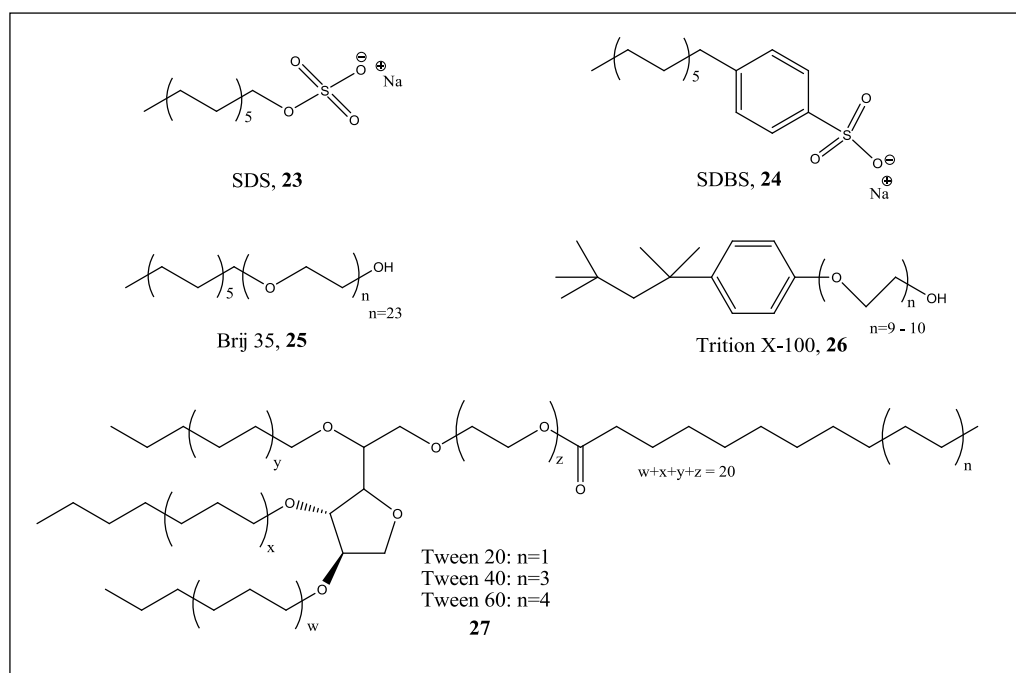


Figure 1.11 Chemical structures of surfactants for CNTs solubilization.⁹²⁻⁹⁴

The mechanism of the individual dispersion is the encapsulation of CNTs in the hydrophobic interiors of the micelles, which results in the formation of a stable dispersion.

Among the conventional surfactants, SDBS is one of most powerful solubilizers for CNTs, even in the concentration of 20mg/mL of CNTs in an SDBS micelle, no aggregation of the CNTs forms for more than 3 months.⁸⁹

Figure 1.12 depicts a schematic illustration of a plausible mechanism of flocculation of CNTs via surfactant molecules. At high concentrations, the surfactant molecules form micelles in solution. The size of these micelles keeps on increasing with increasing surfactant concentration due to interaction between groups of the same polarity.

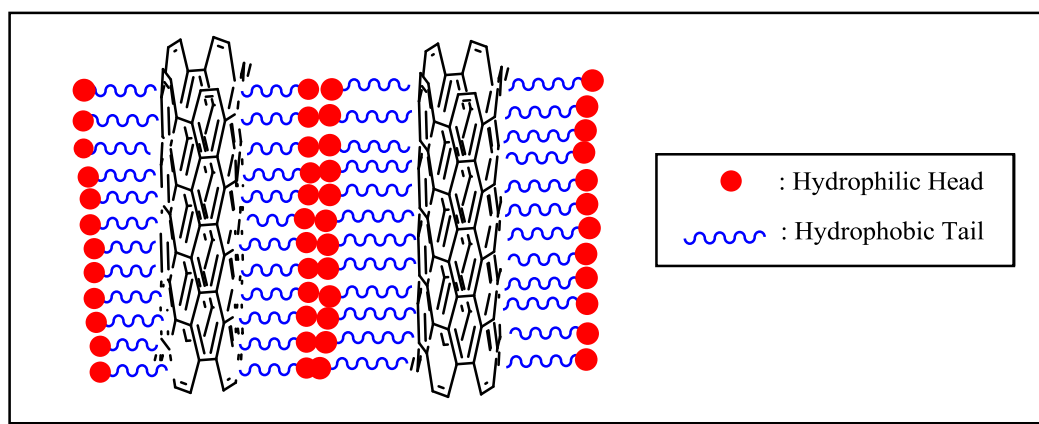


Figure 1.12 Mechanism of flocculation of CNTs via surfactant molecules (SDS).⁹⁵

M. F. Islam and co-workers⁸⁹ reported also the solubilizing capabilities of the various surfactants for CNTs. They believe that the CNTs are stabilized by hemimicelles instead of encapsulated CNTs. The superior dispersing capability of SDBS compared to that of SDS (dispersing capability ≤ 0.1 mg/ml) or Triton X100 (≤ 0.5 mg/ml) can be explained in terms of graphite-surfactant interactions, alkyl chain length, headgroup size,

and charge, particularly to those molecules that lie along the surface, parallel to the tube central axis (hemimicellar adsorption of surfactant molecules on a CNTs).⁹⁶

As shown in Figure 1.13, alkyl chain groups of a surfactant molecule adsorb flat along the length of the CNTs instead of the diameter. SDBS and Triton X-100 disperse the CNTs better than SDS because of their benzene rings, and SDBS disperse better than Triton X-100 because of its head-group and slightly longer alkyl chain.

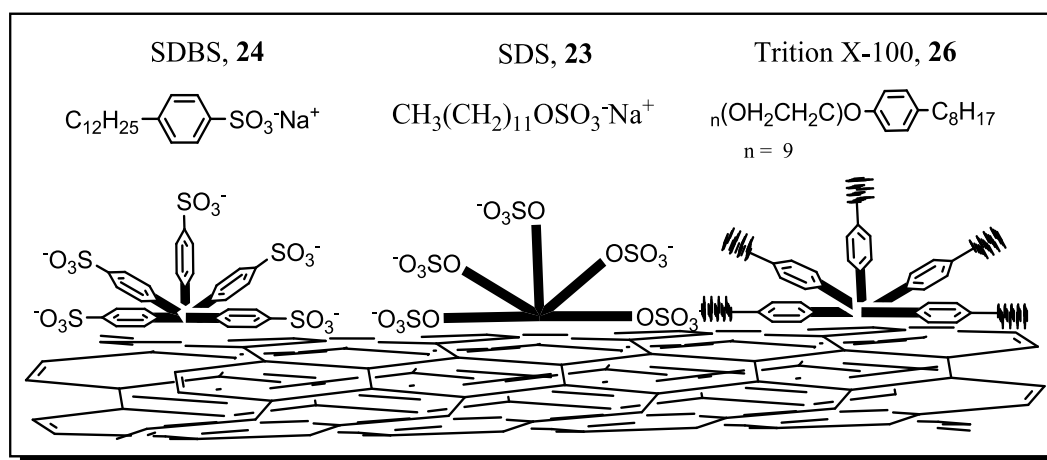


Figure 1.13 Schematic representation of how surfactants may adsorb onto the CNTs surface.⁸⁹

In 2008, J.Y. Wang and co-workers reported that they used an ionic liquid [BMIM-Cl/ BF_4 , 1-butyl-3-methylimidazolium chloride/ tetrafluoroborate] to disperse CNTs more efficiently than do surfactant and polymers.⁹⁷⁻⁹⁹ As shown in Figure 1.14, CNTs with ionic liquids, OMIM-Cl, was well dispersed in water (b). However, CNTs suspension without ionic liquids was re-aggregated (a).

By varying anions of ionic liquids, CNTs can be also dispersed in various binary solutions such as water and methylene chloride.

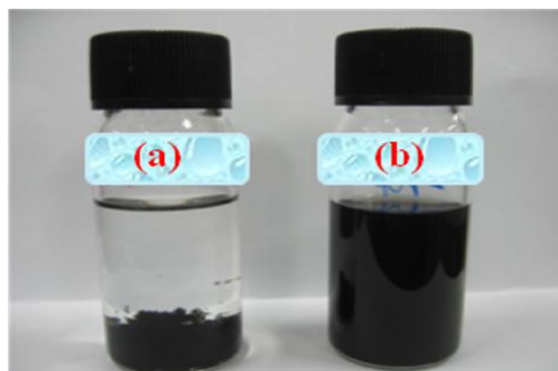


Figure 1.14 Dispersion of carbon nanotubes (CNTs). (a) in water in the absence and (b) presence of ionic liquids.⁷²

As shown in Figure 1.15, CNTs were dispersed in water with OMIM-Cl (b), and in methylene chloride (CH_2Cl_2) with OMIM- BF_4 (c). This indicates that the solubility of modified CNTs can be altered by anion exchange with the relatively hydrophilic or hydrophobic anions coupled with cationic imidazolium rings.

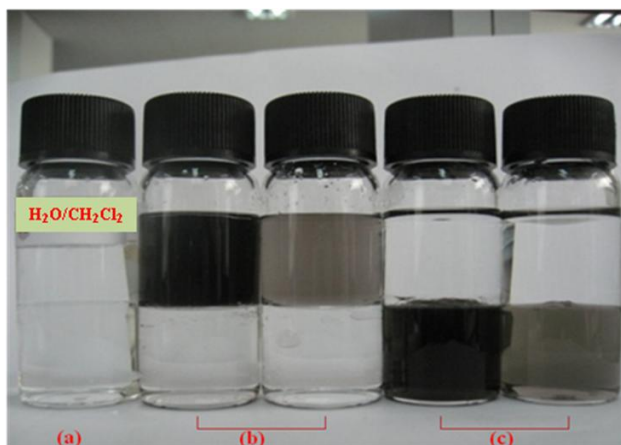


Figure 1.15 Dispersion of carbon nanotubes (CNTs) with ionic liquids. (a) a two-phase mixture of H_2O and CH_2Cl_2 , (b) CNTs dispersion solution with OMIM-Cl [0.05wt% (left) and 0.01wt% (right) of CNTs], (c) CNTs dispersion solution with OMIM- BF_4 [0.05wt% (left) and 0.01wt% (right) of CNTs].⁷²

This represents a simple and convenient way to alter the solubility of CNTs by simply switching salt solutions. The concentration of CNTs was 0.05, and 0.01 wt%, respectively, and the concentration of [OMIM-Cl] and [OMIM-BF₄] was 0.1wt% each. SEM image of carbon nanotubes [CNTs] dispersion solution is shown in Figure 1.16.

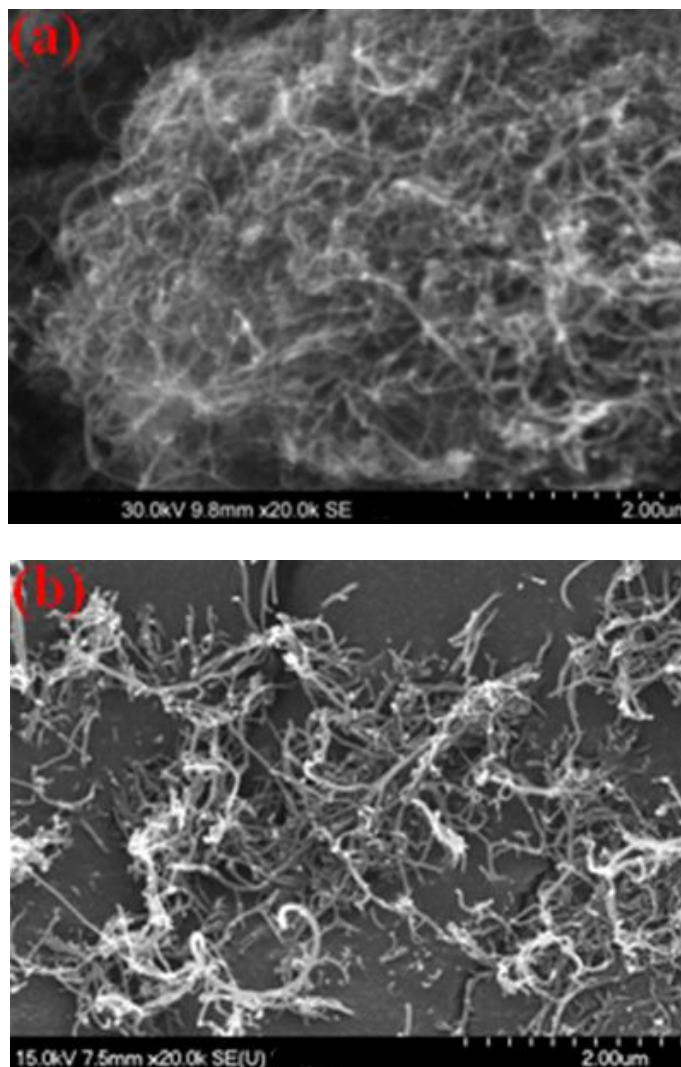


Figure 1.16 SEM image of carbon nanotubes [CNTs] dispersion solution.⁷²

1.1.7 Critical Micelle Concentration [CMC]. There has been recent interest in the formation of micelles in RTILs.^{100, 101} Micelles are nanosized structures formed by

surfactant molecules. The characteristic concentration of surfactants above the development of micelles brings about sudden variation in certain physico-chemical properties of the solution (e.g., surface tension, and UV-vis absorbance).^{102, 103} This critical concentration is referred to as the critical micelle concentration (CMC). Below this concentration range surfactant exist as monomers in the solution and above this range they form micelles. The CMC is the simplest defined and very useful value that describes the colloid and surface behavior of a surfactant solute.¹⁰⁴⁻¹⁰⁶ CMC has a major impact in a variety of applications. Modulation of the CMC of surfactants can be achieved by varying the nature of the surfactant, the net charge of the surfactant, or the nature of the polar head groups and gigenions. For example, dimeric (gemini) surfactants show very low CMC values and have strong efficacy in decreasing surface tension.¹⁰⁷

1.1.7.1 Surfactants. Surface-active agents, surfactants, due to the presence of distinct hydrophobic and hydrophilic regions form micelles readily. Depending on the chemical structure of their polar head groups, surfactants may be either ionic or neutral compounds. Sodium dodecyl sulfate [SDS] is an example of an anionic surfactant (see Figure 1.17).



Figure 1.17 Chemical structure of sodium dodecyl sulfate [SDS].

Surfactant-based processes are found to be very important in pollution control, conventional groundwater pump-and-treat (P&T) processes, and wastewater purification.¹⁰⁸ Surfactants are used in a broad range of processes and products such as pharmaceuticals, inks, varnishes, wetting agents, and impregnating solutions for fabrics.

Fluorinated surfactants have relatively low CMC values as compared to those of the non-fluorinated analogues. They have been used in a variety of applications, such as buffer additives in capillary electrophoresis and in preparation of biosensors.¹⁰⁹ They have also been used for oxygen transport (blood substitutes), and as emulsifiers in liquid CO₂ solvent.^{110, 111} It is well recognized that perfluorinated surfactants have lower CMC values and higher degree of hydrophobicity as compared to their hydrocarbon analogs. Thus it would be interesting to study the effect of fluorinated analogs of the imidazolium-based quaternary salts on the CMC values of the surfactants.

1.1.7.2 Micelle formation in ionic liquids. Armstrong and co-workers and Fletcher and co-workers have recently demonstrated an impressive solvation ability of ionic liquids towards a variety of surfactants. They determined surfactant CMC values by surface tension measurements. It has been shown that dissolution of surfactants in ionic liquids lowers their surface tension due to the solvatophobic interactions of the ionic liquids with the hydrocarbon portion of the surfactants.^{100, 101}

There are many different methods which have been applied to the determination of CMC values of surfactants. Changes in a variety of physicochemical properties are usually followed to determine the CMC values. Techniques such as NMR, surface tension, light scattering, UV-Vis and FTIR are commonly used to determine CMC and bulk thermodynamic properties such as aggregation number and micelle formation

constants.¹¹²⁻¹¹⁴ The UV-Vis spectroscopy technique is a convenient technique for determination of the CMC of the SDS solutions containing imidazolium based quaternary salts, and provides more accurate measurements which is able to determine small changes or differences in the CMC values.^{92-94, 115}

The CMC studies of SDS in the presence of a variety of RTILs as additives was reported by using imidazolium-based RTILs with varying side chains to modulate the CMC of SDS. It has been found that the UV-vis spectroscopy technique, using the dye-indicator 8-anilino-1-naphthalenesulfonic acid is ideally suited for determination of the CMC of the RTIL-SDS solutions. (see Figure 1.18).

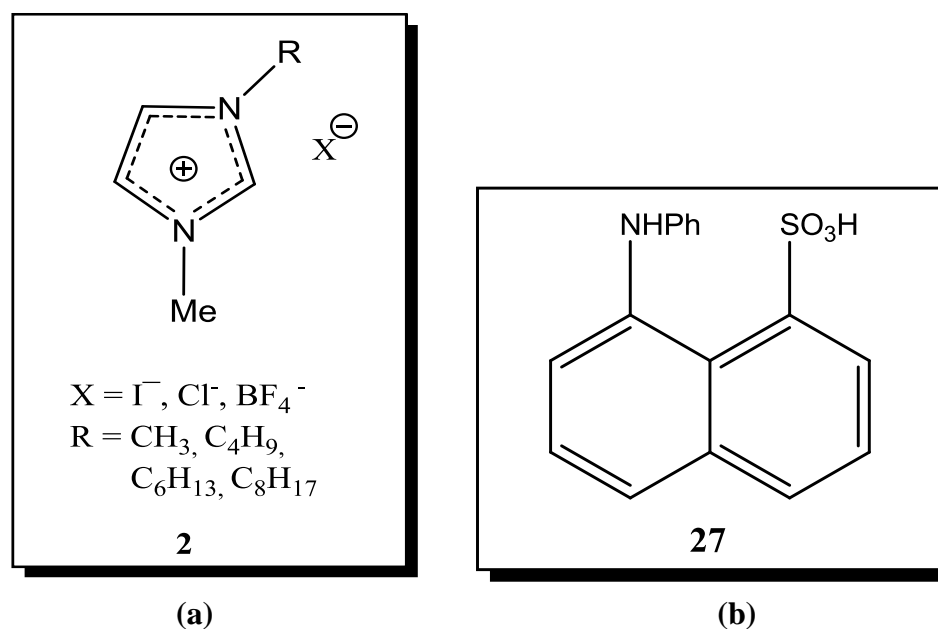


Figure 1.18 Chemical structure of imidazolium based room temperature ionic liquids (a), and 8-anilino-1-naphthalenesulfonic acid (b).

1.2 EXPERIMENTAL

1.2.1 Ionic Liquids as Modulators of the Critical Micelle Concentration of Sodium Dodecyl Sulfate [SDS]. Solvents were dried using appropriate drying agents, and purified by distillation under nitrogen. 1-Methylimidazole, Iodomethane, 1-Chlorobutane, 1-Chlorohexane, and 1-Chlorooctane, SDS (reagent grade, 98% pure), and 8-anilino-1-naphthalenesulfonic acid (used as chromoform) were obtained from Aldrich and used as received. Stock solutions of SDS (0.9 M or 0.5 M) and chromoform (1 mM) were prepared using distilled water. All RTILs were dried under reduced pressure prior to CMC determination.

The UV-vis spectrophotometric measurements were performed on a Beckman DU 640B spectrophotometer using 1 cm² quartz cuvettes. Data was collected using DU 600/7000 Data Capture/Network Software program. ¹H NMR spectra were obtained at 400 MHz using a Varian INOVA 400 MHz NMR spectrometer and are referenced to internal tetramethylsilane (TMS).

1.2.1.1 Synthesis of room temperature ionic liquids [RTILs]. 1-alkyl-3-methylimidazolium chloride can be synthesized by reacting 1-methylimidazole with 1-alkyl chloride. After exchanging anion by reacting sodium tetrafluoroborate, 1-alkyl-3-methylimidazolium tetrafluoroborate can be synthesized (see Figure 1.19).

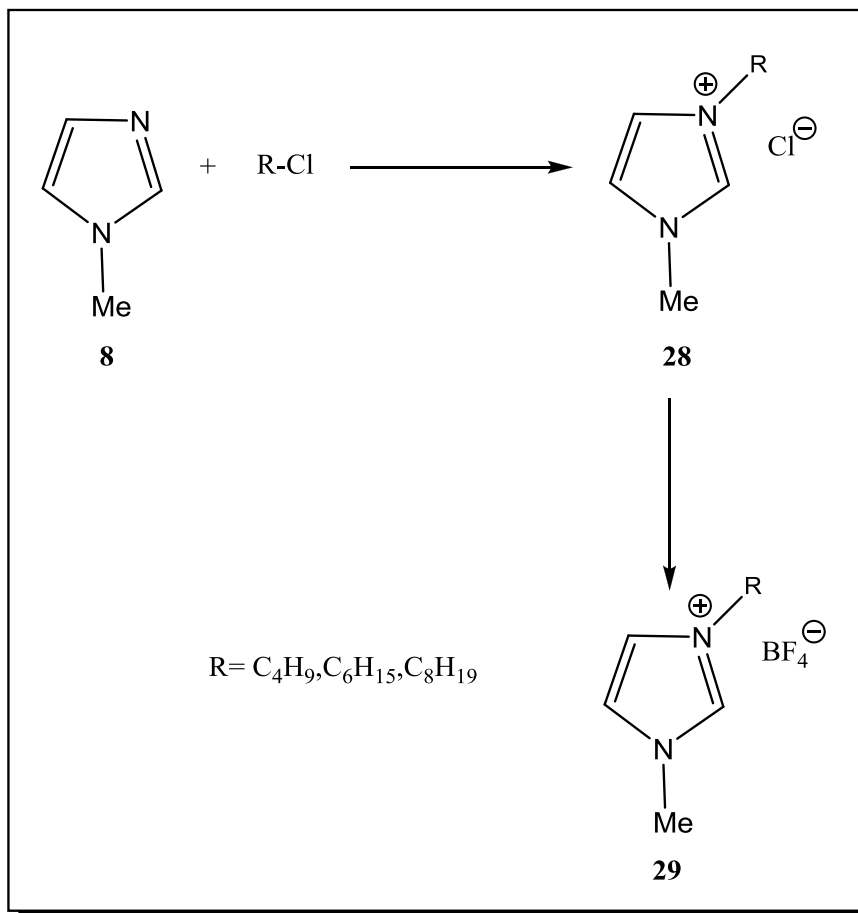


Figure 1.19 General synthesis of imidazolium-based room temperature ionic liquids.

1.2.1.2. 1,3-Dimethylimidazolium iodide [Me₂IM-I]. Compound **30** was obtained as light-yellow solid by the reaction of iodomethane (5g, 0.06 mol) with methylimidazole (8.7 g, 0.06 mol) at 0 °C for 1 h (11.86 g, 87 %) (116 ¹H NMR (400 MHz, CDCl₃): δ 9.54 (s, 1 H, C₂-H), 7.81 (d, J = 1.6 Hz, 2 H, C₄-H, C₅-H), 4.08 (s, 6 H, N₁,N₃-CH₃).

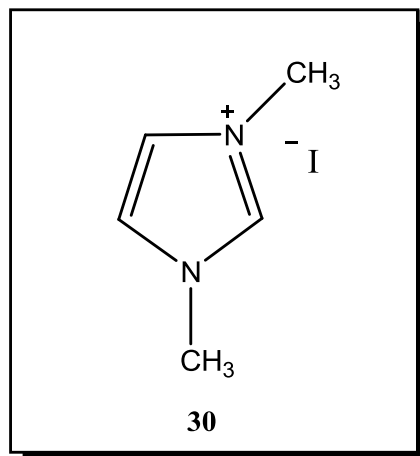


Figure 1.20 Chemical structure of 1,3- dimethylimidazolium iodide.

1.2.1.3 1-Butyl-3-methylimidazolium chloride [BMIM-Cl]. A solution of 1-methylimidazole (8.21 g, 0.20 mol) and 1-chlorobutane (18.51 g, 0.10 mol) was refluxed under nitrogen for 24 h. The unreacted starting materials were removed by extraction with diethyl ether to give compound **31** (15.72 g, 90 %), as a low-melting solid (see Figure 1.21). 117 ^1H NMR (400 MHz, CDCl_3): δ 10.60 (s, 1 H, $\text{C}_2\text{-H}$), 7.79 (t, $J = 1.6$ Hz, 1 H, $\text{C}_4\text{-H}$), 7.62 (t, $J = 1.6$ Hz, 1 H, $\text{C}_5\text{-H}$), 4.35 (t, $J = 7.2$ Hz, 2 H, butyl $\text{C}_1\text{-H}$), 4.14 (s, 3 H, N-methyl), 1.91 (m, 2 H, butyl $\text{C}_2\text{-H}$), 1.38 (m, 2 H, butyl $\text{C}_3\text{-H}$), 0.96 (t, $J = 7.6$ Hz, butyl- CH_3).

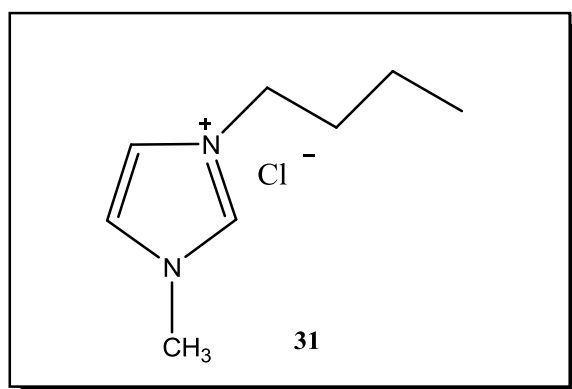


Figure 1.21 Chemical structure of 1-butyl-3-methylimidazolium chloride.

1.2.1.4 1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM-BF₄].

Compound **31** (5 g, 0.029 mol) was stirred with a saturated aqueous solution of sodium tetrafluoroborate (3.14 g, 0.029 mol) for 12 h at room temperature. At the end of the reaction an oily layer was formed, which was extracted with dichloromethane (2 x 10 mL), washed with water (3 x 10 mL), dried (MgSO₄), and the solvent removed under reduced pressure to give compound **10** (4.95 g, 92 %) (see Figure 1.22).¹¹⁷ ¹H NMR (400 MHz, CDCl₃): δ 9.48 (s, 1 H, C₂-H), 7.58 (t, J = 1.6 Hz, 1 H, C₄-H), 7.52 (t, J = 1.6 Hz, 1 H, C₅-H), 4.35 (t, J = 7.2 Hz, 2 H, butyl C₁-H), 4.14 (s, 3 H, N-methyl), 1.91 (m, 2 H, butyl C₂-H), 1.38 (m, 2 H, butyl C₃-H), 0.96 (t, J = 7.6 Hz, butyl-CH₃).

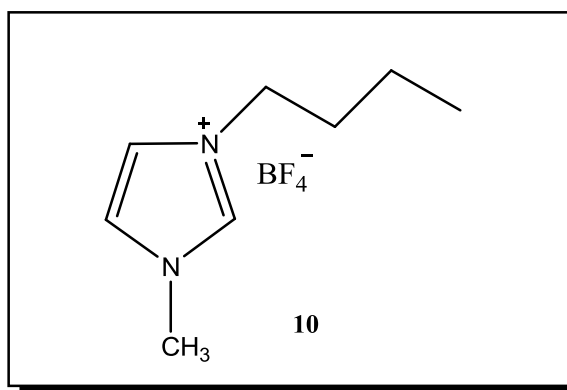


Figure 1.22 Chemical structure of 1-butyl-3-methylimidazolium tetrafluoroborate.

1.2.1.5 1-Hexyl-3-methylimidazolium chloride [HxMIM-Cl]. Using a procedure similar to that for compound **31**, 1-methylimidazole (5g, 0.06mol) was reacted with 1-chlorohexane (7.35 g, 0.06 mol) at 135 °C for 24 h. to give compound **32** as a viscous liquid (11.07 g, 90%) (see Figure 1.23).¹¹⁷ ¹H NMR (400 MHz, CDCl₃): δ 10.49 (s, 1 H, C₂-H), 7.83 (t, J = 2 Hz, 1 H, C₄-H), 7.61 (t, J = 2 Hz, 1 H, C₅-H), 4.34 (t, J = 7.6

Hz, 2 H, hexyl C₁-H), 4.14 (s, 3 H, N-methyl), 1.93 (m, 2 H, hexyl C₂-H), 1.32 (m, 6 H, hexyl-C₃,C₄,C₅-H), 0.88 (t, J = 7.6 Hz, hexyl-CH₃).

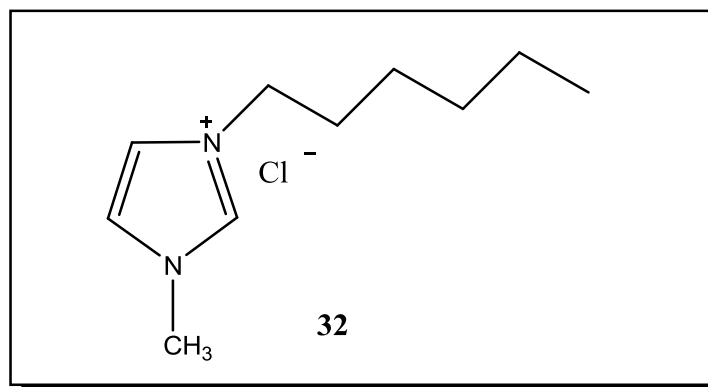


Figure 1.23 Chemical structure of 1-hexyl-3-methylimidazolium chloride.

1.2.1.6 1-Hexyl-3-methylimidazolium tetrafluoroborate [HxMIM-BF₄].

Compound **32** (3 g, 0.015 mol) was stirred with a saturated aqueous solution of sodium tetrafluoroborate (1.65 g, 0.015 mol) for 12 h at room temperature. At the end of the reaction an oily layer was formed, which was extracted with dichloromethane (2 x 10 mL), washed with water (3 x 10 mL), dried (MgSO₄), and the solvent removed under reduced pressure to give compound **11** (3.47 g, 92 %) (see Figure 1.24).¹¹⁷ ¹H NMR (400 MHz, CDCl₃): δ 8.75 (s, 1 H, C₂-H), 7.41 (t, J = 2 Hz, 1 H, C₄-H), 7.31 (t, J = 2 Hz, 1 H, C₅-H), 4.34 (t, J = 7.6 Hz, 2 H, hexyl C₁-H), 4.14 (s, 3 H, N-methyl), 1.93 (m, 2 H, hexyl C₂-H), 1.32 (m, 6 H, hexyl-C₃,C₄,C₅-H), 0.88 (t, J = 7.6 Hz, hexyl-CH₃).

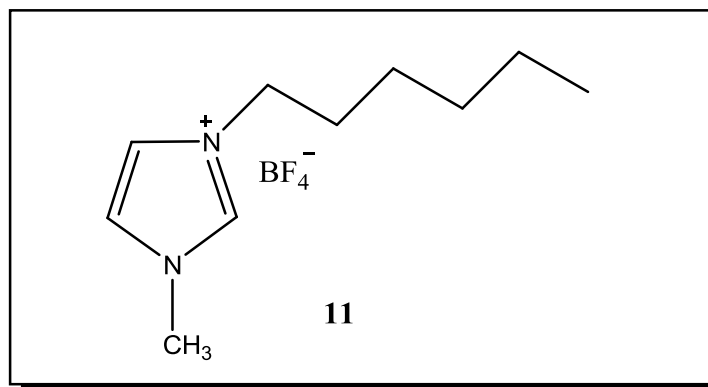


Figure 1.24 Chemical structure of 1-hexyl-3-methylimidazolium tetrafluoroborate.

1.2.1.7 1-Octyl-3-methylimidazolium chloride [OMIM-Cl]. Using a procedure similar to that for compound **31**, reaction of 1-methylimidazole (5 g, 0.06 mol) with 1-chlorooctane (8.92 g, 0.06 mol) at 185 °C for 24 h gave compound **33** as a viscous liquid (12.9 g, 92 %) (see Figure 1.25).¹¹⁷ ¹H NMR (400 MHz, CDCl₃): δ 10.61 (s, 1 H, C₂-H), 7.71 (t, J = 2 Hz, 1 H, C₄-H), 7.49 (t, J = 2 Hz, 1 H, H₅), 4.32 (t, J = 7.2 Hz, 2 H, octyl-C₁-H), 4.14 (s, 3 H, N-methyl], 1.91 (m, 2 H, octyl-C₂-H), 1.28 (m, 10 H, octyl-C₃,C₄,C₅,C₆,C₇-H), 0.87 (t, J = 6.8 Hz, 3 H, octyl-CH₃).

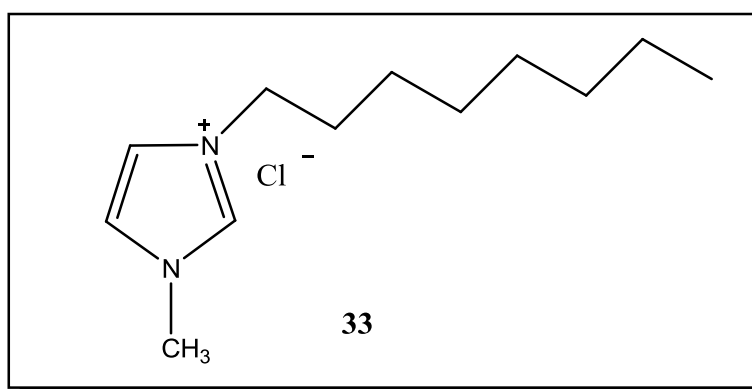


Figure 1.25 Chemical structure of 1-octyl-3-methylimidazolium chloride.

1.2.1.8 1-Octyl-3-methylimidazolium tetrafluoroborate [OMIM-BF₄].

Compound **33** (3 g, 0.013 mol) was stirred with a saturated aqueous solution of sodium tetrafluoroborate (1.43 g, 0.013 mol) for 12 h at room temperature. At the end of the reaction an oily layer was formed, which was extracted with dichloromethane (2 x 10 mL), washed with water (3 x 10 mL), dried (MgSO₄), and the solvent removed under reduced pressure to give compound **34** (3.31 g, 90 %) (see Figure 1.26).¹¹⁸ ¹H NMR (400 MHz, CDCl₃): δ 8.75 (s, 1 H, C₂-H), 7.42 (t, J = 1.6 Hz, 1 H, C₄-H), 7.36 (t, J=1.6 Hz, 1 H, C₅-H), 4.17 (t, J = 7.2 Hz, 2 H, octyl-C₁-H], 3.94 (s, 3 H, N-methyl), 1.87 (m, 2 H, octyl-C₂-H), 1.28 (m, 10 H, octyl-C₃,C₄,C₅,C₆,C₇-H), 0.86 (t, J = 6.8 Hz, 3 H, octyl-CH₃).

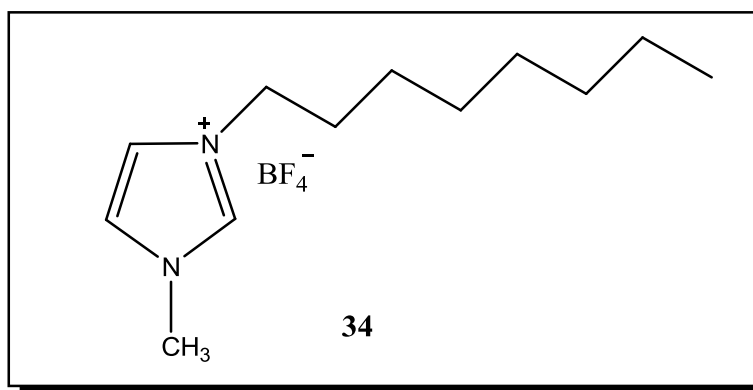


Figure 1.26 Chemical structure of 1-octyl-3-methylimidazolium tetrafluoroborate.

1.2.2 General Method for the Determination of CMC by UV-vis Spectroscopy.

The CMC determinations were done at 20 °C. A 50 μL aliquot of 8-anilino-1-naphthalenesulfonic acid from the 1 mM stock solution was added to a quartz cuvette containing 3 mL of 30 mM aqueous solution of ionic liquid. The UV-vis spectrum was recorded. Incremental amounts (10 μL or 100 μL) of the stock solutions of the SDS were added using a micro syringe to the contents in the cuvette and a series of spectra were

recorded. Thorough mixing of the components was insured after each incremental addition of the surfactant stock solution. The absorption spectra in the range of 200 nm to 500 nm were recorded after allowing the solution to reach steady state (about 5 min). The spectra showed two λ_{max} at 270 nm and 360 nm. The absorbance of both of these absorptions increased with increasing SDS concentration. The CMC was obtained from the combined spectra by monitoring the absorbance values at 360 nm for different concentrations of SDS. The inflection point of the absorbance versus [SDS] plot was taken as the CMC of the SDS in the corresponding RTIL solution.¹¹⁹⁻¹²¹ Typically, about 40 spectra were accumulated for each CMC determination.

1.2.3 Synthesis and CMC Studies of 1-Methyl-3-(Pentafluorophenyl)-

Imidazolium Quaternary Salts. The reactions were carried out under nitrogen atmosphere. Acetone (HPLC grade), 1-methylimidazole, benzyl chloride, SDS (reagent grade, 98% pure), and 8-anilino-1-naphthalenesulfonic acid (used as the chromoform) were obtained from Aldrich and used as received. 2,3,4,5,6-pentafluorobenzyl chloride, (97%), was obtained from Lancaster. Stock solutions of SDS (0.5 M, 0.25 M or 0.005 M) and the chromoform (1 mM) were prepared using distilled water. The quaternary salts were dried under reduced pressure prior to CMC determinations.

The UV-Vis spectrophotometric measurements were performed on a Beckman DU 640B spectrophotometer using 1 cm² quartz cuvettes. Data were collected using DU 600/7000 Data Capture/Network Software program. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA-2 instrument under air atmosphere. The heating rate of the sample was 10 °C min⁻¹. ¹H, ¹³C and ¹⁹F NMR spectra were obtained using a Varian INOVA spectrometer at 400 MHz, 100 MHz and 376 MHz, respectively, and

were reported as parts per million (ppm) using internal TMS ($\delta^1\text{H} = 0$, $\delta^{13}\text{C} = 0$) and CFCl_3 ($\delta^{19}\text{F} = 0$).

1.2.3.1 Synthesis of fluorinated room temperature ionic liquids. Fluorinated ionic liquids can be synthesized as shown in Figure 1.27.

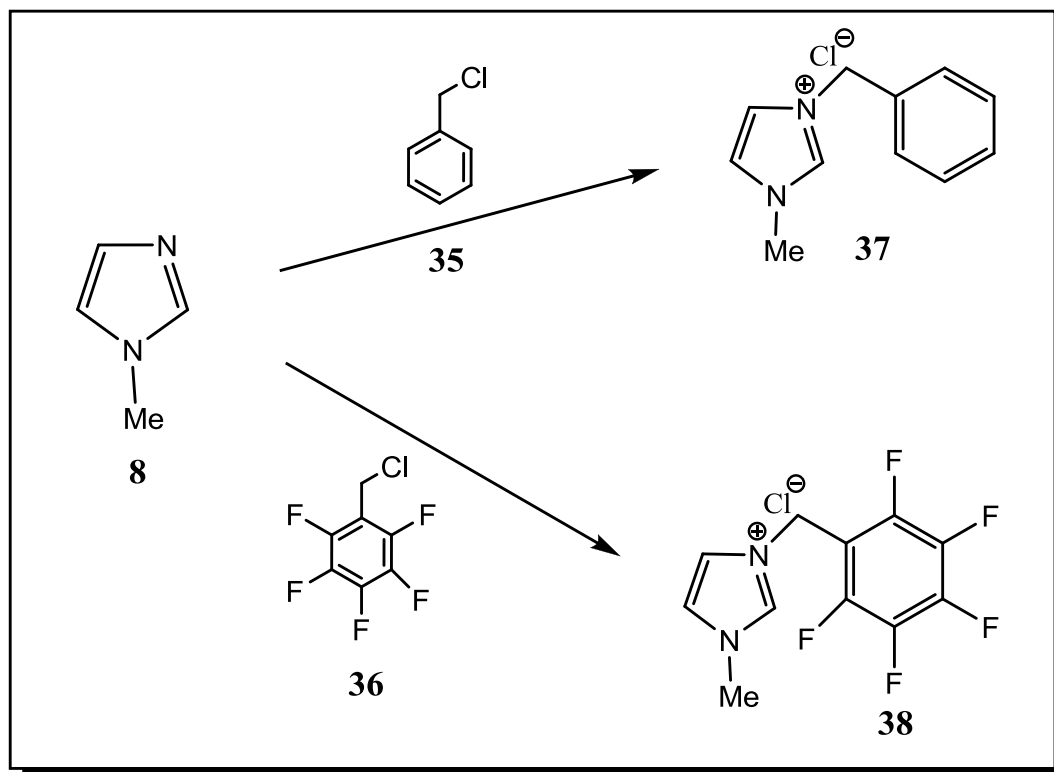


Figure 1.27 General synthesis of imidazolium-based fluorinated room temperature ionic liquids.¹²²

1.2.3.2 1-Benzyl-3-methylimidazolium chloride.¹²² A neat solution of 1-methylimidazole (2 g, 0.024 mol) in benzyl chloride (3.08 g, 0.024 mol) was stirred at room temperature for 3 h. The reaction was monitored by TLC using CH_3OH in CH_2Cl_2 (20 : 80 v/v) as the eluent. After completion of the reaction, residual starting materials were removed by extraction with diethyl ether. Compound **37** was obtained as a colorless

viscous liquid after purification by column chromatography (silica gel) using a solution of CH₃OH in CH₂Cl₂ (60 : 40 v/v) as the eluent (4.60 g, 92 %) (see Figure 1.28). ¹H NMR (400 MHz, CDCl₃): δ 10.50 (s, 1 H, C₂-H), 7.68 and 7.50 (apparent triplets, J = 2 Hz, 1 H each; C₄- and C₅-H), 7.49 (d, J = 2.8 Hz, 2 H, *o,o'*-Ph-H), 7.35 (m, 3 H, *m,m'*, *p*-Ph-H), 5.59 (s, 2 H, benzylic-H), 4.05 (s, 3 H, N-CH₃); ¹³C NMR δ 137.5 (C₂), 133.1 (*i*-Ph), 129.2 (*o, o'*-Ph), 129.1 (*m, m'*-Ph), 128.7 (*p*-Ph), 123.6 and 121.7 (C₄ and C₅), 52.9 (N-CH₂), 36.3 (N-CH₃).

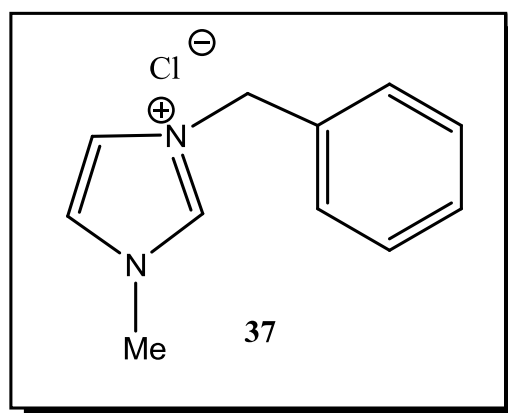


Figure 1.28 Chemical structure of 1-benzyl-3-methylimidazolium chloride.

1.2.3.3 1-Methyl-3-(pentafluorophenyl)imidazolium chloride. A neat solution of 1-methylimidazole (1.14 g, 0.014 mol) in 2,3,4,5,6-pentafluorobenzyl chloride (3.0 g, 0.014 mol) was stirred at room temperature for 3 h. The reaction was monitored by TLC using CH₃OH in CH₂Cl₂ (70 : 30 v/v) as the eluent. After completion of the reaction, residual starting materials were removed by extraction with diethyl ether. Compound **38** was obtained as a light yellow solid after purification by column chromatography (silica gel) using a solution of CH₃OH in CH₂Cl₂ (80: 20 v/v) as the eluent (3.72 g, 90 %) (see

Figure 1.29). ^1H NMR (400 MHz, CDCl_3) δ 10.76 (s, 1 H, $\text{C}_2\text{-H}$), 7.45 and 7.43 (apparent triplets, $J = 2$ Hz, 1 H each; $\text{C}_4\text{-}$ and $\text{C}_5\text{-H}$), 5.57 (s, 2 H, benzylic-H), 3.87 (s, 3 H, N-CH_3); ^{13}C NMR δ 138.6 (C_2), 124.1 and 121.6 (C_4 and C_5), 40.6 (N-CH_2), 36.8 (N-CH_3); ^{19}F NMR δ -141.1 (d, $J = 13.3$ Hz o,o' -F), -150.01 (apparent t, $J = 18.4$ Hz m,m' -F), -159.8 (m, p -F); MS (EI; solids' probe): m/z (%) 263 (3.3, $\text{M}^+ - \text{Cl}$), 181 [100, $\text{M}^+ - (1\text{-methylimidazole}) - \text{Cl}$], 82 (53, $\text{M}^+ - \text{C}_6\text{F}_5\text{CH}_2 - \text{Cl}$).

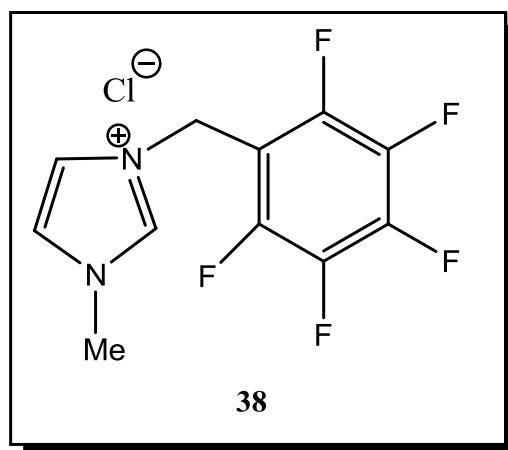


Figure 1.29 Chemical structure 1-methyl-3-(pentafluorophenyl)imidazolium chloride.

1.2.4 General Method for the Determination of CMC by UV-vis Technique.

The CMC determinations were done at 20°C as described earlier.² A $50\ \mu\text{L}$ aliquot of 8-anilino-1-naphthalenesulfonic acid **27** from the 1 mM stock solution was added to a quartz cuvette containing 3 mL of 30 mM aqueous solution of quaternary salts as a dye indicator. Series of the UV-Vis spectrum was recorded by addition of incremental amounts ($5\ \mu\text{L}$ or $10\ \mu\text{L}$) of the stock solutions using a micro syringe to the contents in the cuvette. The cuvette was inverted several times to insure mixing of the components after each incremental addition of the surfactant stock solution. The absorption spectra in

the range of 200 to 500 nm were recorded after allowing the solution to reach steady state (about 5 min). CMC values were obtained from the accumulation of 40 spectra for each quaternary salts by monitoring the absorbance values at 360 nm **37** and 320 nm **38** for different concentrations of SDS. The inflection point of the absorbance versus [SDS] plot was taken as the CMC of the SDS in the corresponding imidazolium salt solutions.

1.3 RESULTS AND DISCUSSION

1.3.1 Ionic Liquids as Modulators of the Critical Micelle Concentration of Sodium Dodecyl Sulfate. The variation of CMC of surfactants with the hydrophilic or hydrophobic nature of polymeric additives has been well established.¹²³⁻¹²⁷ RTILs, as nonvolatile and 'green' solvents, may be used as alternatives to the polymeric additives. The solvent properties of the solutions of surfactants in RTILs and supercritical CO₂ have been reviewed.¹²⁸ However, to date there have been no systematic studies on the dependence of CMC of surfactants on the nature of the additive RTILs. Recent works of Armstrong and co-workers and Fletcher and co-workers have shown that anionic and nonionic surfactants can form aggregates with selected RTILs. The solvation behavior of the surfactant-ionic liquid micellar system was also studied by inverse gas chromatography.^{100, 101} The hydrophobic-hydrophilic properties of the RTILs can be dramatically altered by the choice of the side chains. For example, the hydrophobicity would be expected to increase as the chain length is increased from methyl to octyl group due to the aggregation of the RTILs with surfactants.¹²⁷ Using SDS as the anionic surfactant and 8-anilino-1-naphthalenesulfonic acid as the dye we have measured the CMC values of various RTILs with varying side chains.

The imidazolium-based RTILs with side chains ranging from methyl to octyl groups were synthesized: Me₂IM-I **30**, BMIM-Cl **31**, BMIM-BF₄ **10**, HxMIM-Cl **32**, HxMIM-BF₄ **11**, OMIM-Cl **33**, and OMIM-BF₄ **34**.¹¹⁶⁻¹¹⁸ The ¹H NMR spectra showed distinctly different absorptions in the aromatic region for OMIM-Cl **33**, and OMIM-BF₄ **34**. The aromatic protons of the tetrafluoroborate salt **34** are significantly shielded compared to those of the chloride salt **33**. Complete exchange of the Cl⁻ with BF₄⁻ is confirmed by the absence of the corresponding ¹H NMR absorptions for the compound (**33** and **34**) (Figure 1.30).

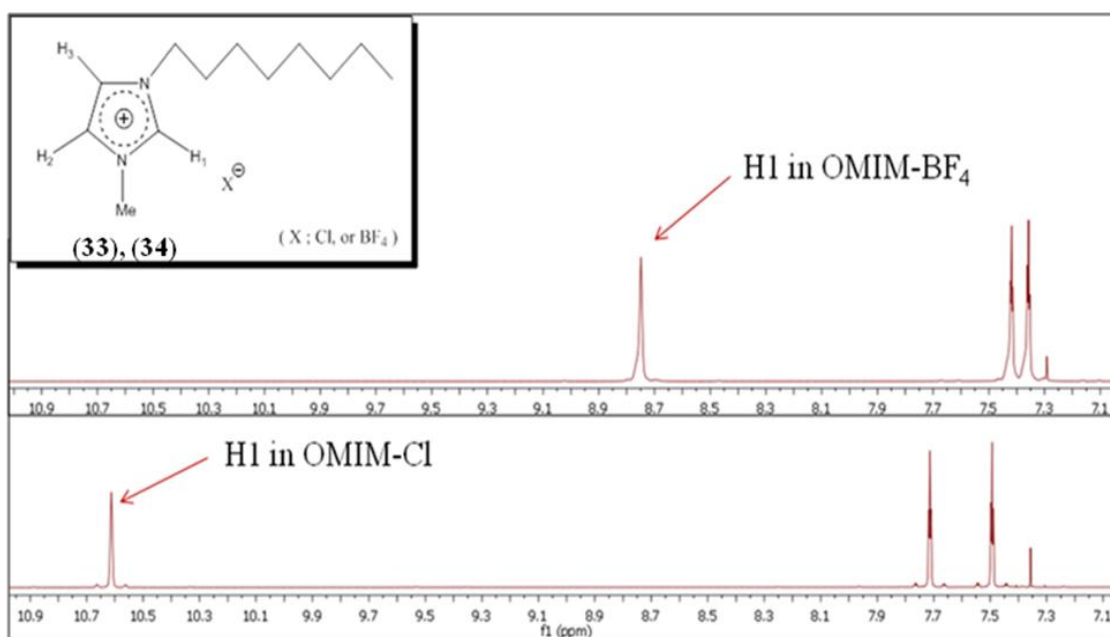


Figure 1.30 Expanded region of the 400-MHz ¹H NMR spectra for [OMIM-BF₄] and [OMIM-Cl] showing the aromatic absorptions.

CMC values of surfactants can be measured by a variety of techniques: surface tension measurements, electrochemical methods, and UV-vis spectroscopy.¹²⁹ The latter method is convenient for the CMC measurements of the solutions of SDS in RTILs. Very

small differences in the absorption maximum behavior of 8-anilino-1-naphthalenesulfonic acid were measured using the high resolution spectrophotometer. The changes in the absorbance values could be easily followed at the λ_{\max} 360 nm. Figures 1.31 to 1.35 illustrate the UV-vis technique we have used for measuring the CMC values of the aqueous SDS solutions in the presence of 30 mM RTILs. The absorbance values of the dye increase with increasing SDS concentration. This increase in absorbance values can be clearly seen at the λ_{\max} 360 nm or at λ_{\max} 270 nm. We have used the spectral region, λ_{\max} 360 nm, for CMC measurements.

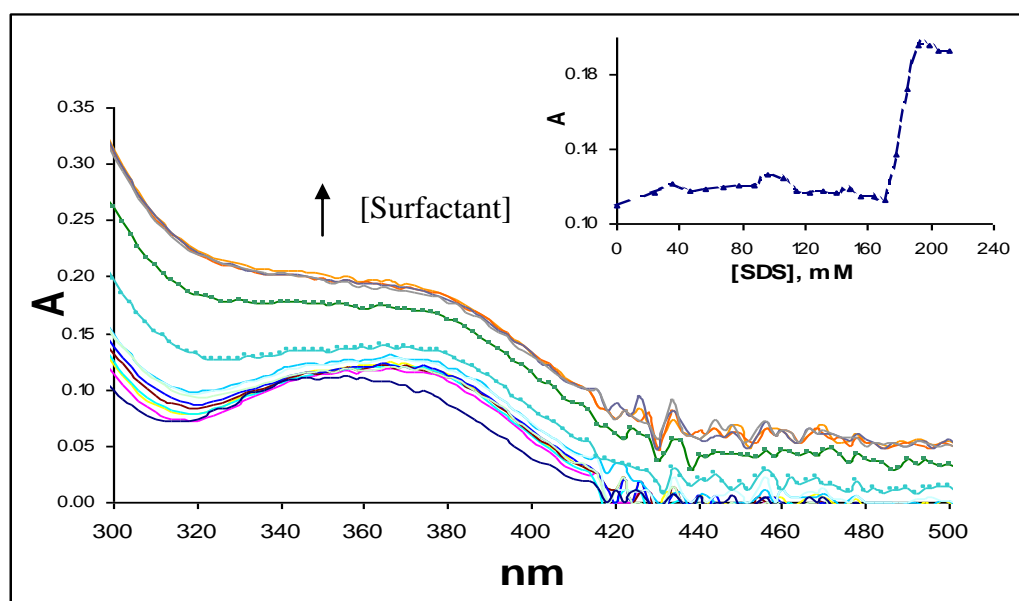


Figure 1.31 UV-vis determination of CMC of SDS using 30 mM [Me₂MIM-I] solution. Inset is the CMC fitting curve for the absorbance at 360 nm ([SDS] was increased from 23 mM to 210 mM in 5 mM increments).

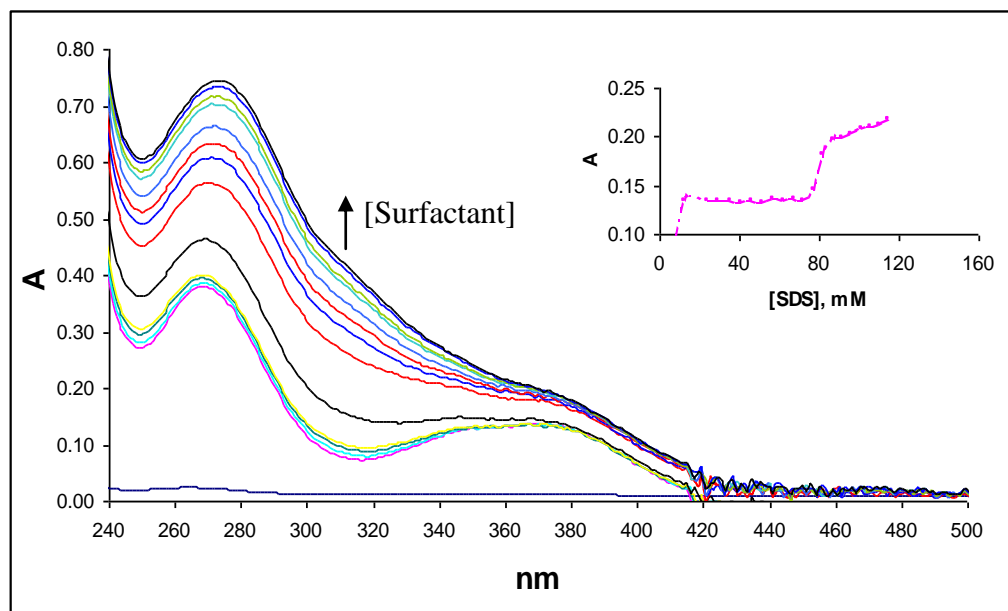


Figure 1.32 UV-vis determination of CMC of SDS using 30 mM [BMIM-Cl] solution. ([SDS] was increased from 12 mM to 115 mM in 5 mM increments). Inset is the CMC fitting curve for the absorbance at 360 nm.

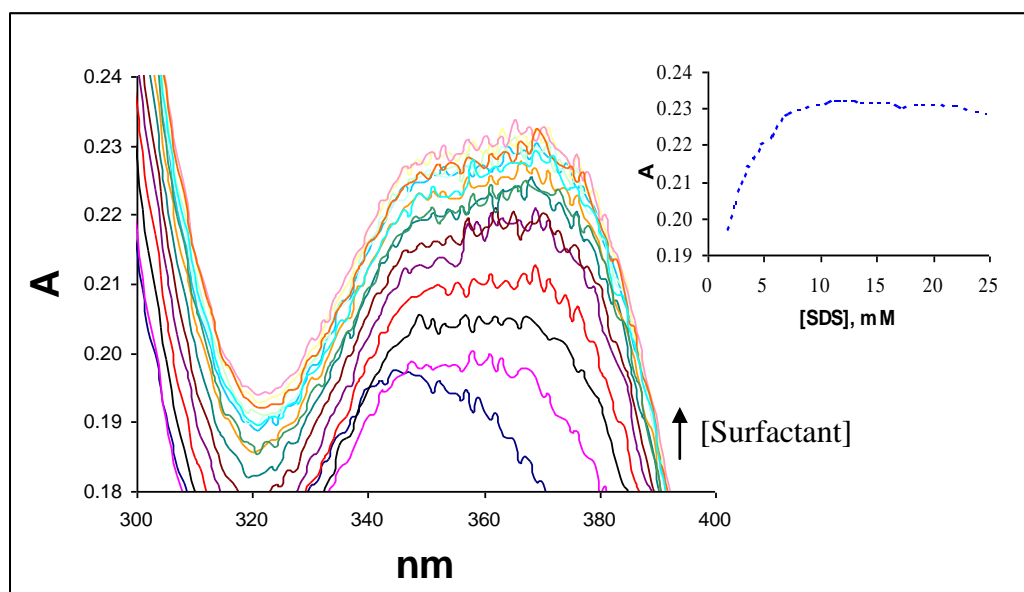


Figure 1.33 UV-vis determination of CMC of SDS using 30 mM [HxMIM-Cl] solution. Inset is the CMC fitting curve for the absorbance of HxMIM-Cl at 360 nm ([SDS] was increased from 0.8 mM to 90 mM in 1 mM increments).

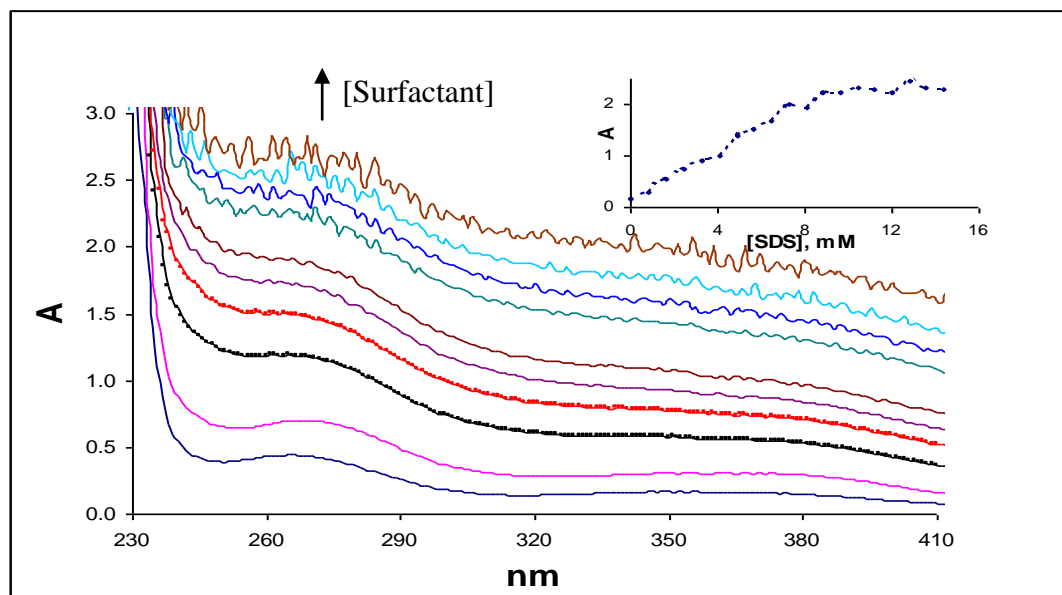


Figure 1.34 UV-vis determination of CMC of SDS using 30 mM [OMIM-Cl] solution. Inset is the CMC fitting curve for the absorbance at 360 nm ([SDS] was increased from 0.8 mM to 124 mM in 1 mM increments).

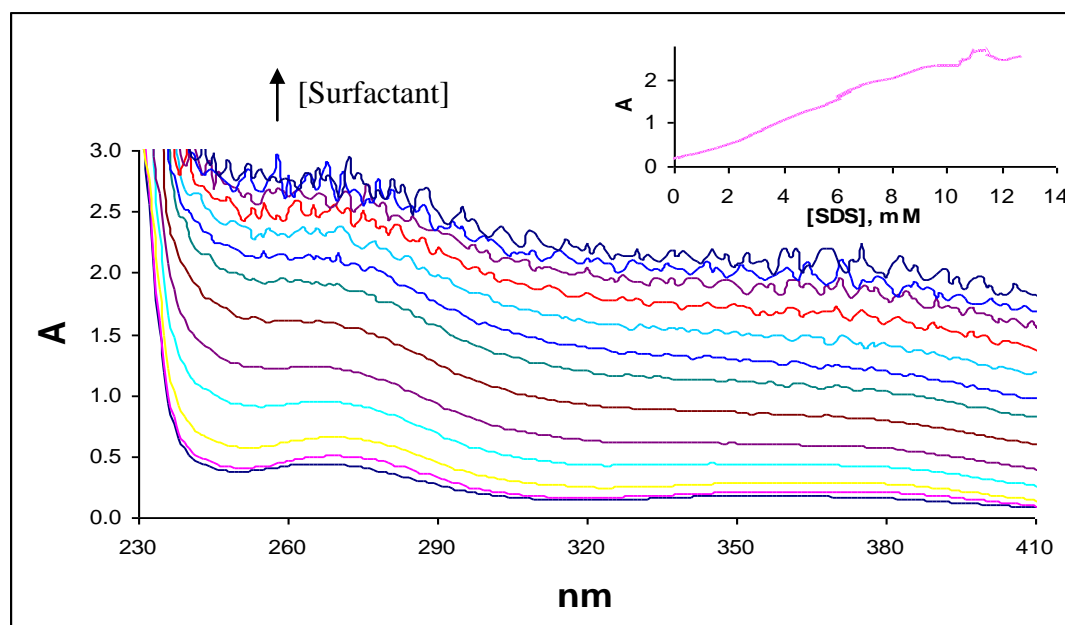


Figure 1.35 UV-vis determination of CMC of SDS using 30 mM [OMIM-BF₄] solution. Inset is the CMC fitting curve for the absorbance at 360 nm ([SDS] was increased from 0.8 mM to 124 mM in 1 mM increments).

In a typical experiment the concentration of SDS was increased from 0 mM to 210 mM with 5 mM increments (or 0 mM to 124 mM with 1mM increments depending on the concentration of the SDS stock solution). At CMC the absorbance of the dye dramatically increases. This breakpoint is clearly seen in the plots of the absorbance versus the concentrations of SDS (insets). The same results have also been obtained by monitoring the absorbance at λ_{max} 270 nm.

The CMC values obtained are summarized in Table 1.2. Of particular interest, the CMC values are independent of the gigenions for OMIM-Cl **33** and OMIM-BF₄ **34**. From these studies we can assume that the CMC values are largely influenced by the hydrocarbon unit of the RTILs.

Table 1.2 CMC of SDS in aqueous solutions of ionic liquids and water.^a

Ionic liquid (30mM)	CMC (mM)
Me ₂ IM-I 30	170
BMIM-Cl 31	70
HxMIM-Cl 32	2.8
OMIM-Cl 33	1.9
OMIM-BF ₄ 34	1.9
Water	7

^aCMC for water was measured under the same conditions for a comparison.

Table 1.2 shows a clear dependence of the CMC on the hydrophobicity of the ionic liquids. The least hydrophobic compound Me₂IM-I **30** shows a remarkably high CMC value of 170 mM. The CMC decreases with increase of the chain length on the ionic liquid. Thus, Me₂IM-I **30**, BMIM-Cl **31**, HxMIM-Cl **32**, and OMIM-Cl **33** show CMC values of 170 mM, 70 mM, 2.8 mM, and 1.9 mM, respectively.

The CMC values of Me₂IM-I **30** and BMIM-Cl **31** are significantly higher than that of RTIL-free SDS solution, 7.0 mM, whereas those of HxMIM-Cl **32** and OMIM-Cl **33** are appreciably lower. These studies thus show the modulating ability of the RTILs on the CMC of SDS: the CMC increases from 1.9 mM to 170 mM going from C₈ to C₁ side chain in the ionic liquids, by a significantly high factor of 90 (see Figure 1.36).

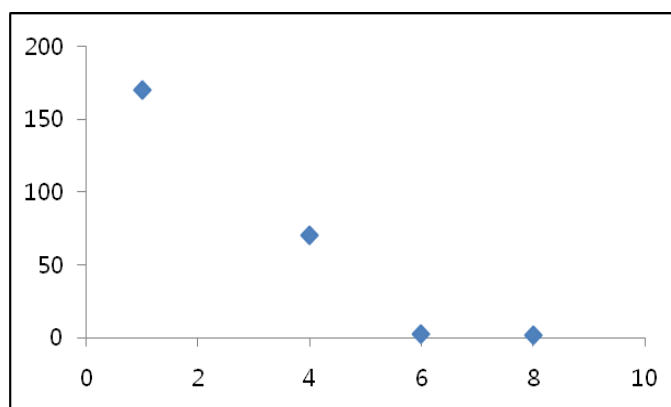


Figure 1.36 Log CMC vs number of alkane chain on Ionic Liquids.

These observations are consistent with the expected lowering of CMCs with increasing hydrophobicity of the surfactants or certain polymer additives, although relatively smaller CMC lowering was observed in the latter cases.^{130, 131} Similar observations were made for the CMCs of pure ionic liquids by Maia and coworkers. They have determined CMC of aqueous solutions of pure ionic liquids (i.e., in the

absence of SDS) HxMIM-BF₄, OMIM-BF₄ and DMIMBF₄ to be: 1.99, 0.42 and 0.11, respectively.

The CMC also was estimated by the NMR method. ¹H-NMR spectra of the surfactant solutions in the RTILs, BMIM-Cl (Figure 1.37), were recorded using a Varian INOVA 400 MHz NMR spectrometer operating at a ¹H frequency of 399.94 MHz. ¹H-NMR chemical shift reflects the molecular interaction, and therefore the aggregate formation can be detected by monitoring the chemical shift changes as a function of the surfactant concentration. The chemical shifts of protons attached to imidazolium cation (H2, H4, and H5) are deshielded with the addition of surfactant. These changes in chemical shift of imidazolium protons caused by the surfactant addition suggest that some interactions take place between the surfactant molecule and imidazolium cation. The CMC of the surfactant, in the presence of ionic liquids, is the concentration of surfactant at which there is no longer any changes in chemical shift. However, the UV-vis technique for measuring the CMC value is more convenient and sensitive method.

The decreased CMC with more hydrophobic compounds **10**, **11** or **34** can be explained as due to the solubilization of the RTILs in the micellar phase. On the other hand, the relatively hydrophilic RTILs, **30** and **31** may induce interactions with SDS in the aqueous phase resulting in the observed higher CMC values. It is clear from these studies that by careful choice of the nature of the RTILs one may be able to control the CMC values of surfactants for specific applications.

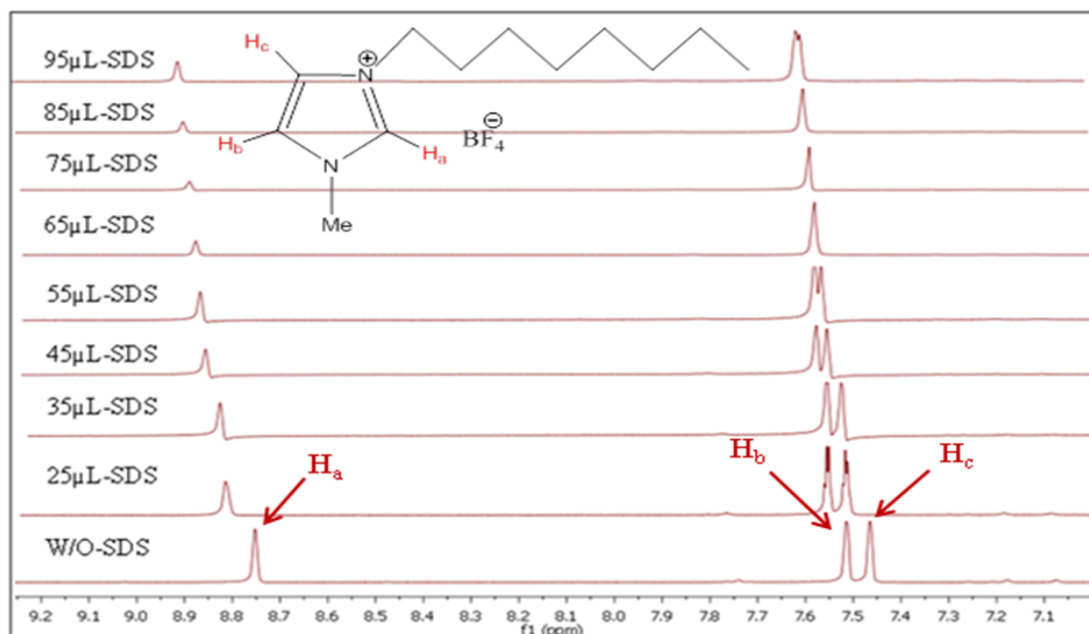


Figure 1.37 Stacked ^1H NMR spectrum (400 MHz) of 1-octyl-3-methylimidazolium tetrafluoroborate [OMIM- BF_4] with different concentration of SDS [0 to 95 μL].

1.3.2 Synthesis and CMC Studies of 1-Methyl-3-(Pentafluorophenyl)-Imidazolium Quaternary Salts. CMCs of SDS solutions in the presence of two imidazolium-based quaternary salts, **37** and **38** was investigated by using UV-Vis and ^1H NMR spectroscopic techniques. Fluorinated imidazolium based quaternary salt **38** has not been reported in the literature to our knowledge. We have synthesized compounds **37** and **38** by reacting 1-methylimidazole with benzyl chloride and 2,3,4,5,6-pentafluorobenzyl chloride, respectively.

In a control experiment, using a 1:1:1 solution of phCH_2Cl **37**, $\text{C}_6\text{F}_5\text{CH}_2\text{Cl}$ **38** and 1-methylimidazole, we have observed that the reactivity of $\text{C}_6\text{F}_5\text{CH}_2\text{Cl}$ **38** is similar that of phCH_2Cl **37**. We have found that these reactions proceed under mild conditions in the absence of any solvent. Typically the reactions were completed at room temperature in 3 h. Compounds **37** and **38** could be readily characterized by using ^1H , ^{13}C , ^{19}F NMR

spectroscopy, and EI-MS. The TGA thermograms of compounds **37** and **38** were obtained to determine the relative thermal stabilities of these compounds in air (see Figure 1.38). It can be seen from Figure 1.38 that compound **37** and **38** have similar thermal stability characteristics.

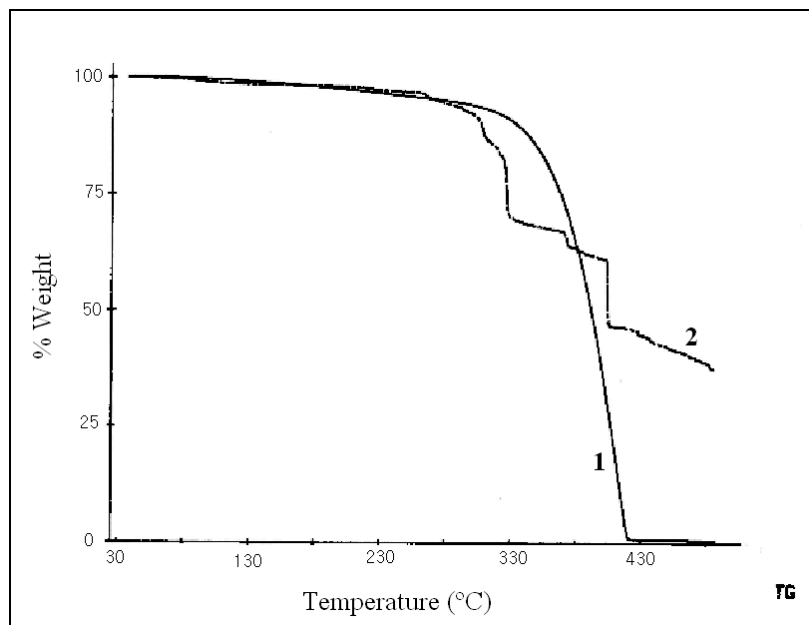


Figure 1.38 TGA weight loss of compounds [**37**, 1 in the graph] and [**38**, 2 in the graph] as a function of temperature. The scanning rate was 20 °C/min.

Compound **37** decomposes almost completely at about 420 °C; whereas compound **38** decomposes by 65 % at this temperature. Compounds **37** and **38** were found to be thermally stable up to 340 °C and 290 °C, respectively.

The CMC values of the SDS solutions have been decreased exponentially with increase in the number of carbon atoms in the side chain of the RTILs.² Fluorinated surfactants are also known to have lower CMC values than their corresponding non-fluorinated analogs.¹³² CMC studies using fluorinated imidazolium-based quaternary salts

show that the fluorinated side chains dramatically lower the CMC values (*vide infra*).

The CMCs of SDS solutions were also investigated in the presence of imidazolium-based quaternary salts, **37** and **38**, by using UV-Vis spectroscopy. The CMC measurements have been achieved using 8-anilino-1-naphthalene-sulfonic acid **27** as chromoform. The CMC fitting curves for compound **37** and **38** are derived from the data at 360 nm and 320 nm, respectively (Figures 1.39 and 1.40).

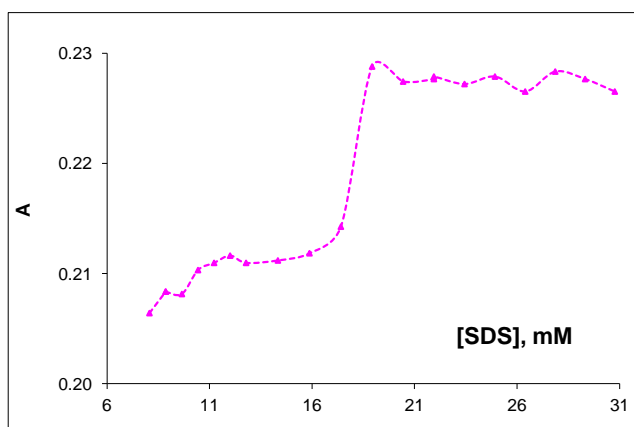


Figure 1.39 CMC fitting curve for **37** at 360 nm.

In case of compound **37** the CMC fitting curve shows a single sharp inflection point at the CMC value. On the other hand, compound **38** shows more than one inflection point. The first inflection point has been taken as the first CMC value. From these experiments, The CMC values have been obtained of 18 mM and 0.04 mM for compounds **37** and **38**, respectively (see Table 1.3).

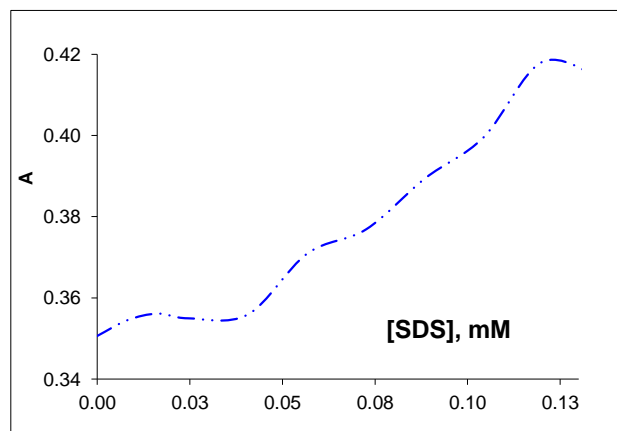


Figure 1.40 CMC fitting curve for **38** at 320 nm.

The CMC values were also measured by using ^1H and ^{19}F NMR spectroscopies. The CMC value of compound **38** is extremely low requiring the use of very dilute stock solutions of SDS. At these concentrations of SDS there was no significant shift of the ^1H and ^{19}F NMR absorptions of the quaternary salt.

Table 1.3 CMC of SDS in aqueous solutions of compounds **37**, **38** and water. ^a

Ionic liquids (30 mM)	CMC of SDS (mM)
$(\text{C}_6\text{H}_5\text{CH}_2)$ MIM-Cl 37	18
$\text{Me}(\text{C}_6\text{F}_5\text{CH}_2)$ IM-Cl 38	0.04
H_2O	7.0

^aCMC for water was measured under the same conditions for a comparison.

Compound **38** has unusually low first CMC value of 0.04 mM, indicating that it has significantly high tendency to aggregate. This value is smaller than that of the

corresponding CMC value of compound **37** by a remarkable factor of 450. This is in agreement with the increased hydrophobicity (due to the fluorine substitutions) for compound **38** as compared to that of compound **37**. These results are also in agreement with studies of Matsuoka and Moroi on the micellization of fluorinated surfactants.¹³²

The CMC values of surfactants, in general, decrease exponentially with increasing the number of carbon atoms in the nonpolar portion of the surfactants.¹³³ Similar exponential decay has been observed in case of RTILs. This exponential decrease in CMC of RTILs is due to the enhanced solubilization of the more hydrophobic RTILs in the micellar phase.² The fluorinated compound **38** is expected to be significantly more hydrophobic than that of nonfluorinated analog **37**. Thus **38** may show relatively increased solubilizations in micellar phase as compared to that of **37**, reflecting its observed lowered CMC value.¹³⁴⁻¹³⁶

1.4 CONCLUSION

Aggregation behavior of SDS, an anionic surfactant, in a range of RTILs with varied hydrophobicities was studied by using UV-vis spectroscopic methods. Derivatives of imidazolium-based room temperature ionic liquids were synthesized and characterized by ¹H NMR spectrum (see Figures 1.41 to 1.50) such as Me₂IM-I **30**, BMIM-Cl **31**, BMIM-BF₄ **10**, HxMIM-Cl **32**, HxMIM-BF₄ **11**, OMIM-Cl **33**, OMIM-BF₄ **34**, 1-benzyl-3-methylimidazolium chloride **37**, and 1-methyl-3-(pentafluorophenyl)imidazolium chloride **38** for the CMC studies. The CMC values of SDS in Me₂IM-I **30** and BMIM-Cl **31** are appreciably high as compared to those of the HxMIM-Cl **32**, OMIM-Cl **33** and RTIL-free water. The range of CMC values observed for the RTILs studied varied by a

significant factor of 90. The nature of the anions, Cl^- or BF_4^- , has no noticeable effect on the observed CMC values. ^1H NMR spectrum (400 MHz) of ILs and UV-Vis determination of CMC of SDS are also shown in Figures 1.41 to 1.51.

Micelle formation and critical micelle concentration in 1-benzyl-3-methylimidazolium chloride **37** and 1-methyl-3-(pentafluorophenyl)imidazolium chloride **38** were explored in solutions of SDS, an anionic surfactant, by using UV-Vis spectroscopic methods. The CMC value of SDS in presence of **38** is significantly lower as compared to that of **37**, by a factor of 450. It was shown by TGA that the compounds **37** and **38** have similar thermal stabilities. It is possible to modulate CMC of an anionic surfactant SDS by choice of room temperature ionic liquids [RTILs] as an additive.

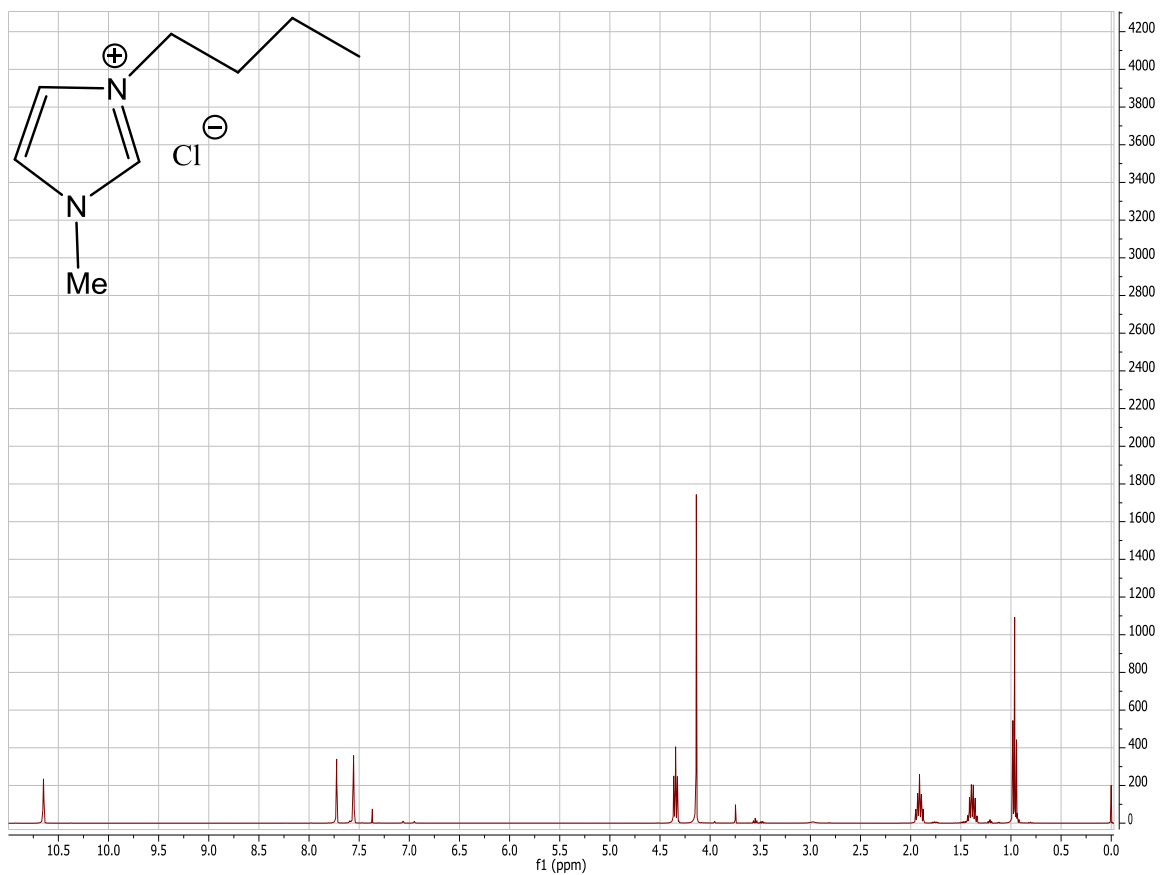


Figure 1.41 ^1H NMR spectrum (400 MHz) of 1-butyl-3-methylimidazolium chloride.

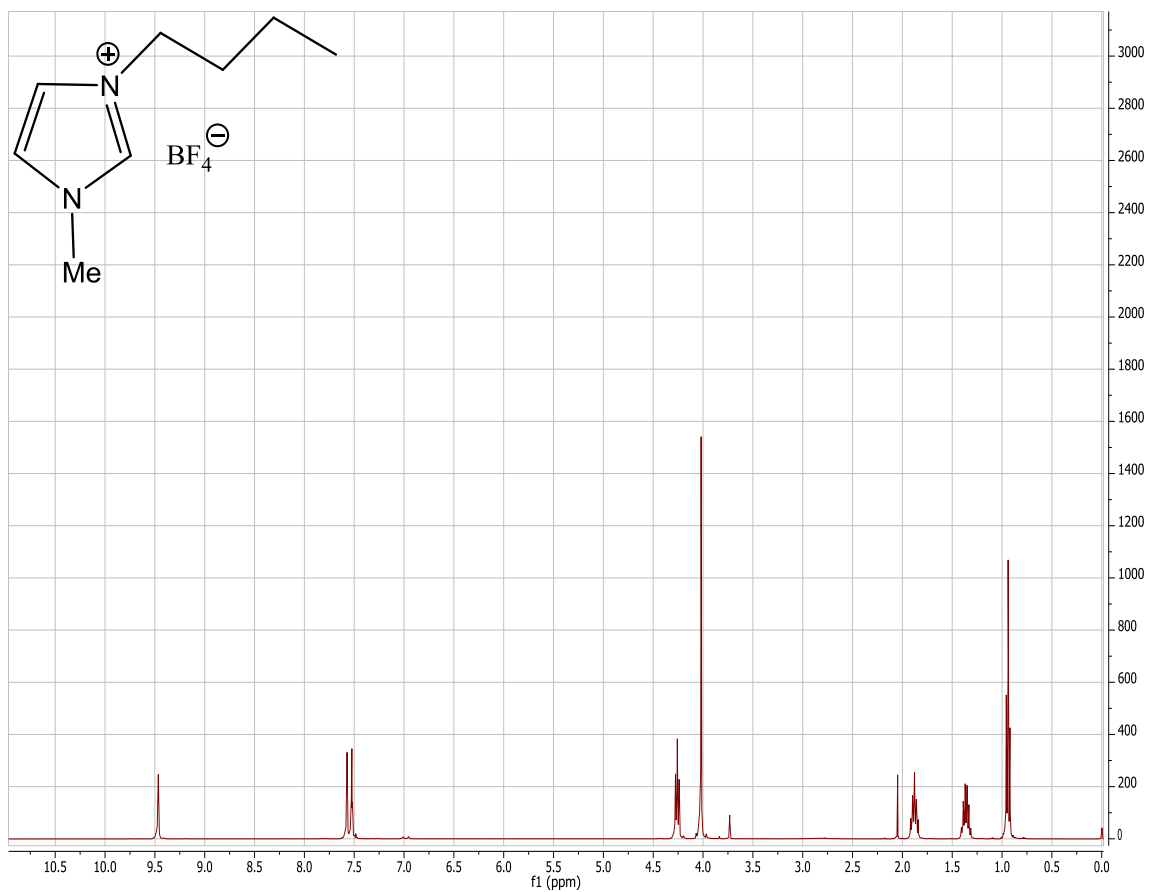


Figure 1.42 ^1H NMR spectrum (400 MHz) of 1-butyl-3-methylimidazolium tetrafluoroborate.

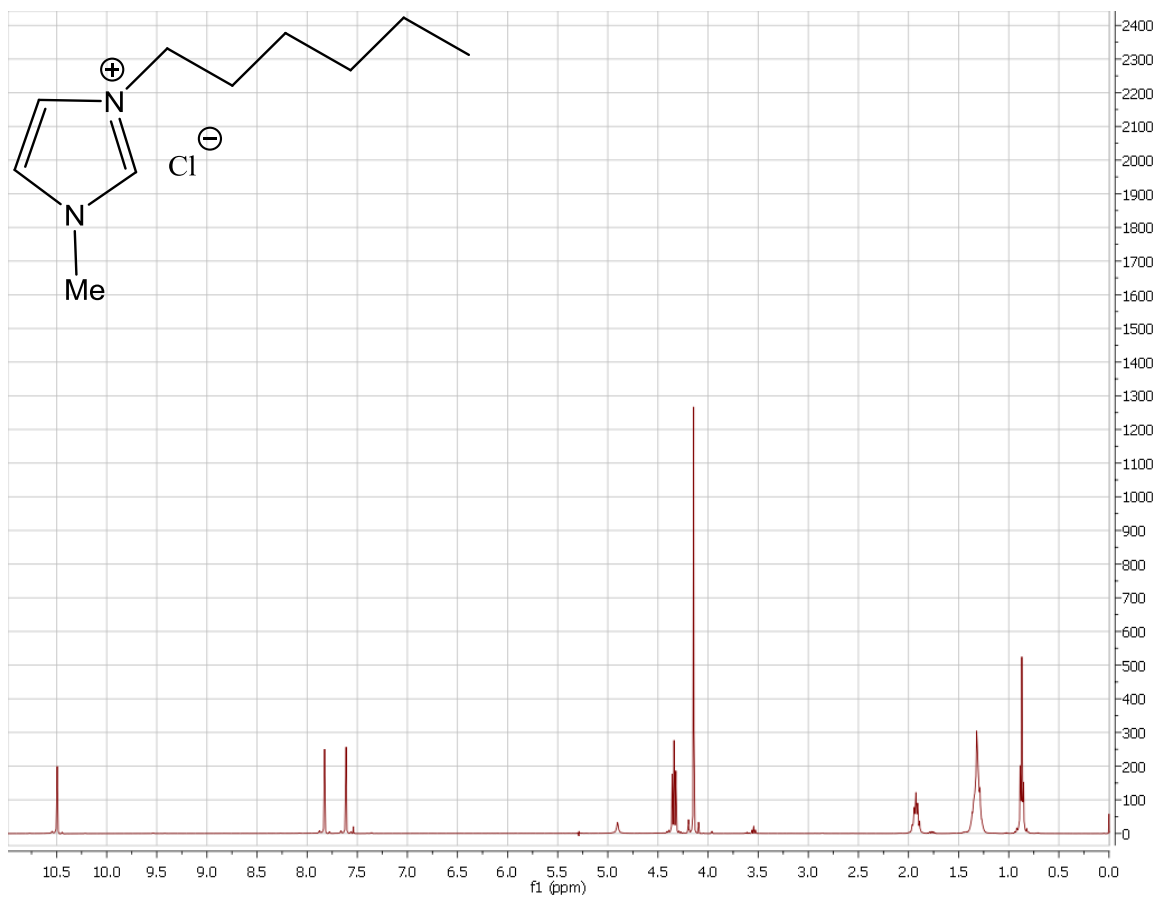


Figure 1.43 ^1H NMR spectrum (400 MHz) of 1-hexyl-3-methylimidazolium chloride.

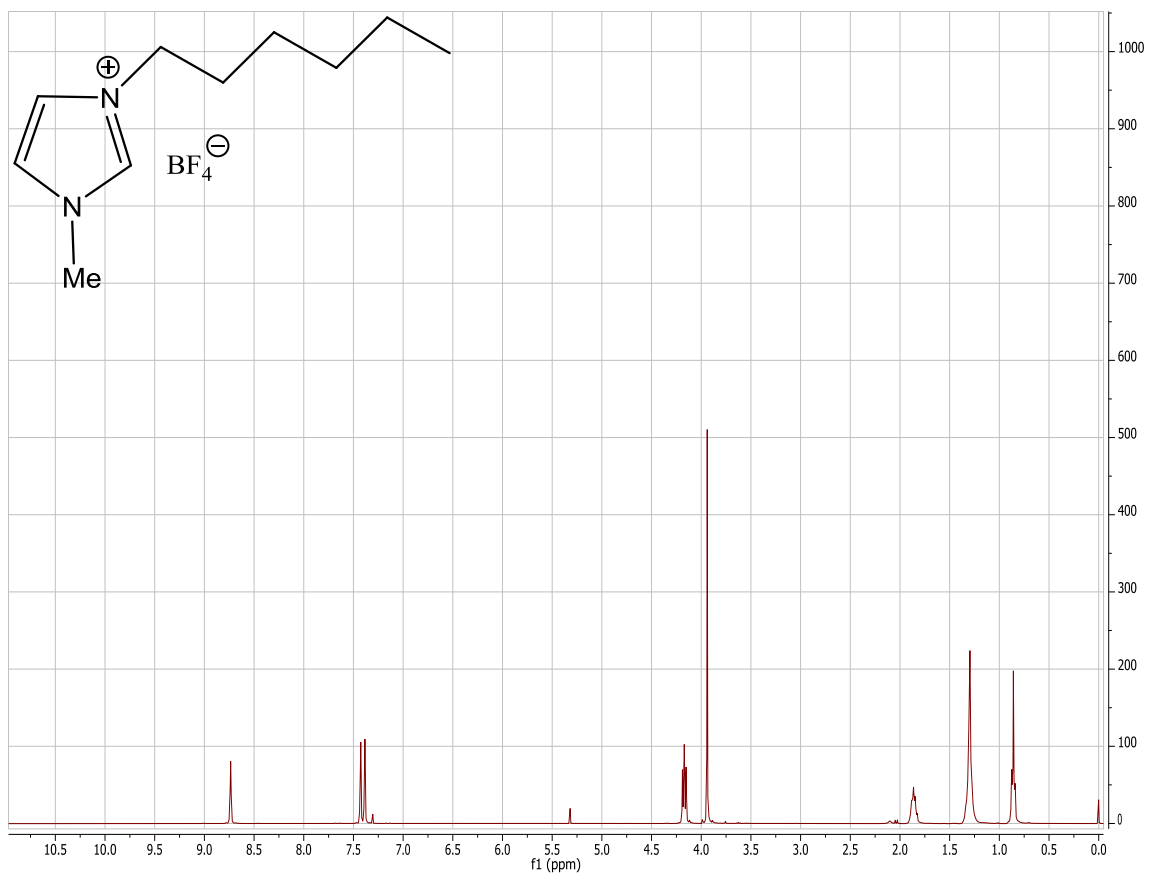


Figure 1.44 ¹H NMR spectrum (400 MHz) of 1-hexyl-3-methylimidazolium tetrafluoroborate.

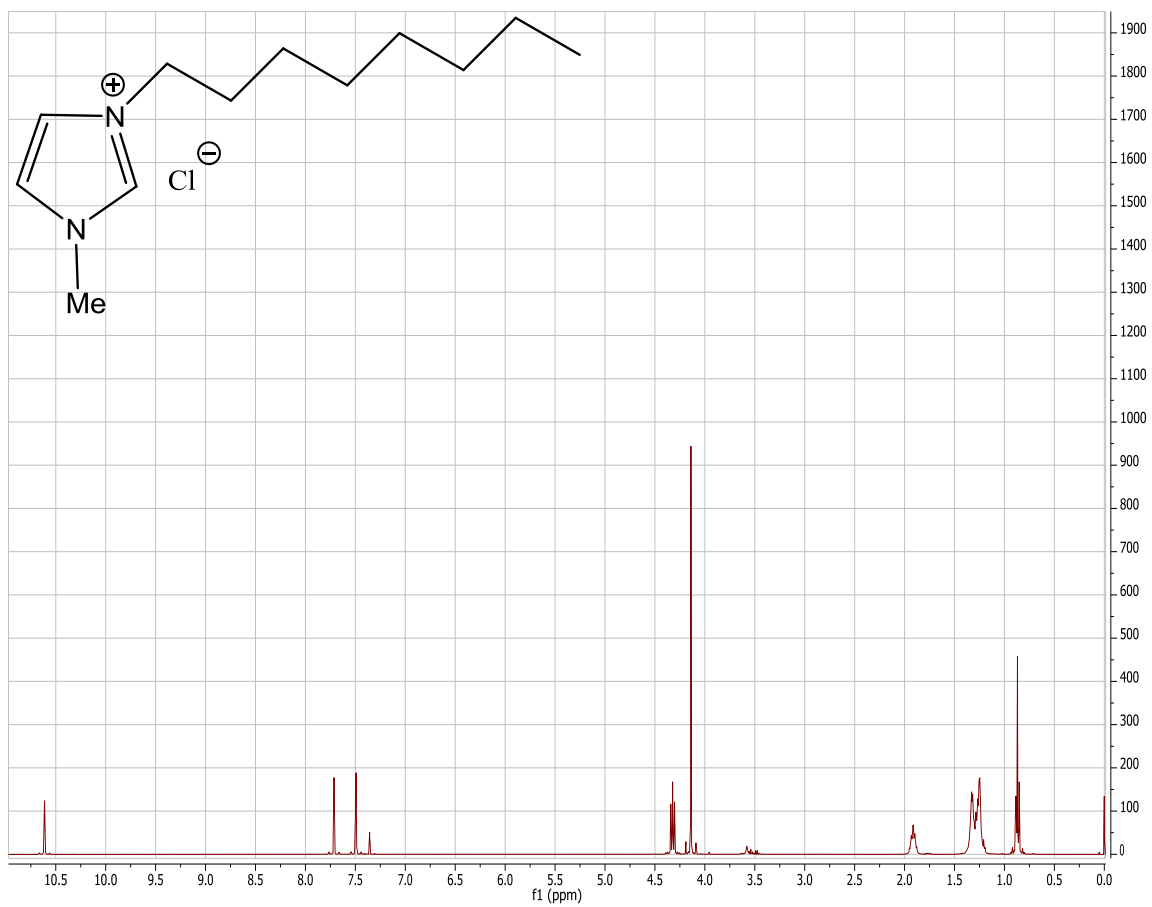


Figure 1.45 ^1H NMR spectrum (400 MHz) of 1-octyl-3-methylimidazolium chloride.

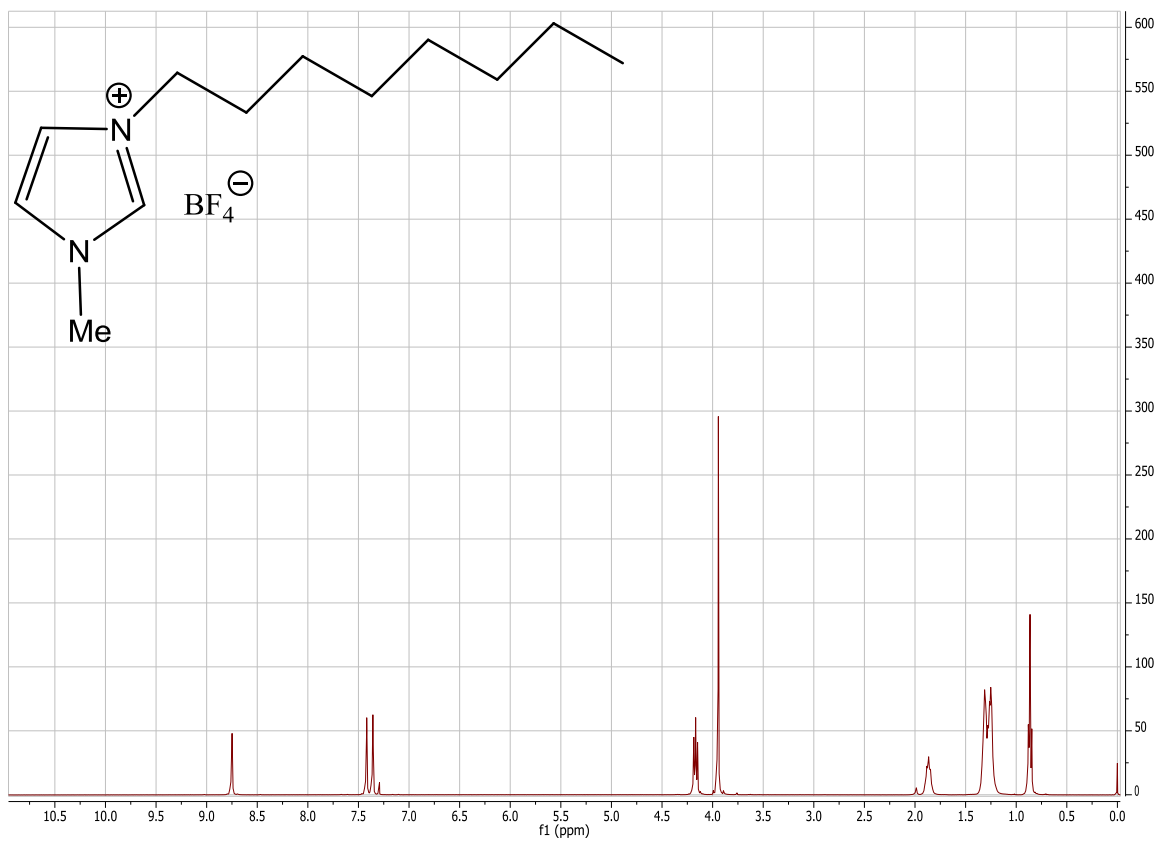


Figure 1.46 ¹H NMR spectrum (400 MHz) of 1-octyl-3-methylimidazolium tetrafluoroborate.

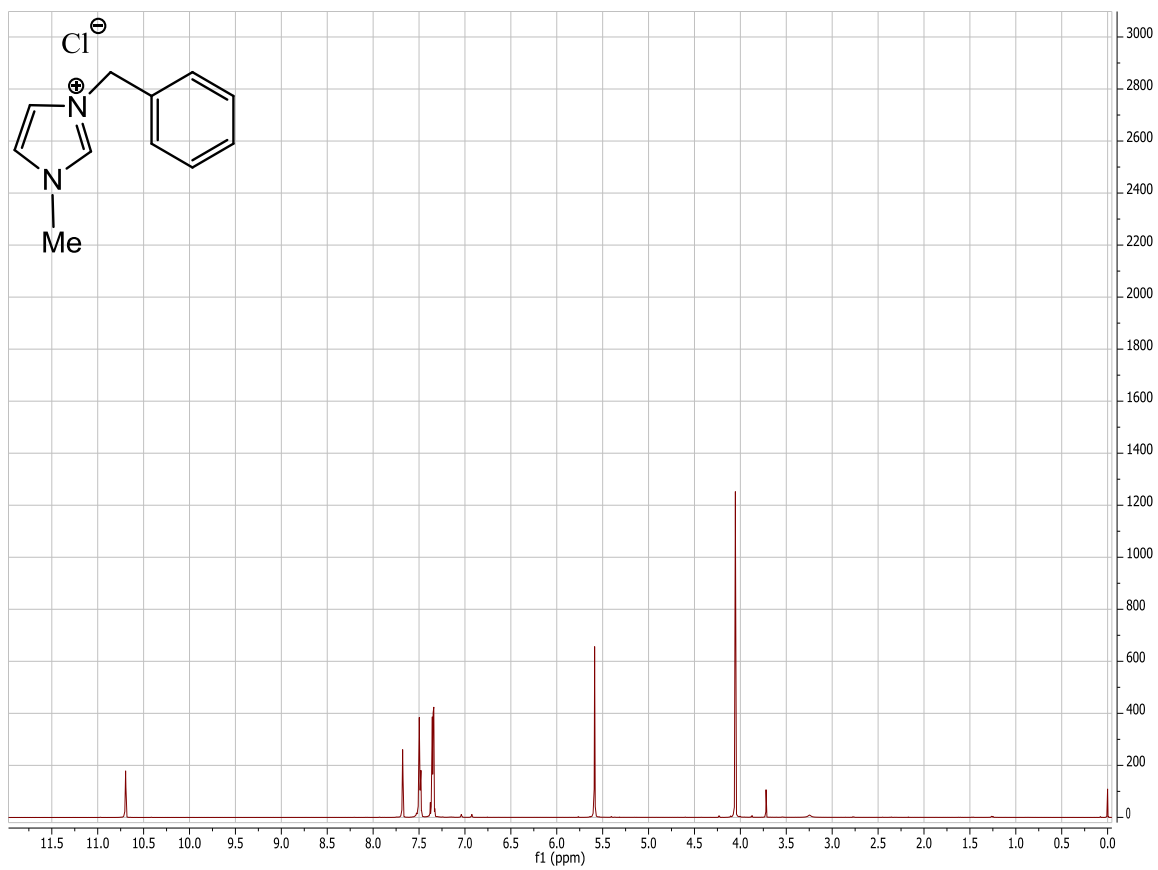


Figure 1.47 ¹H NMR spectrum (400 MHz) of 1-benzyl-3-methylimidazolium chloride.

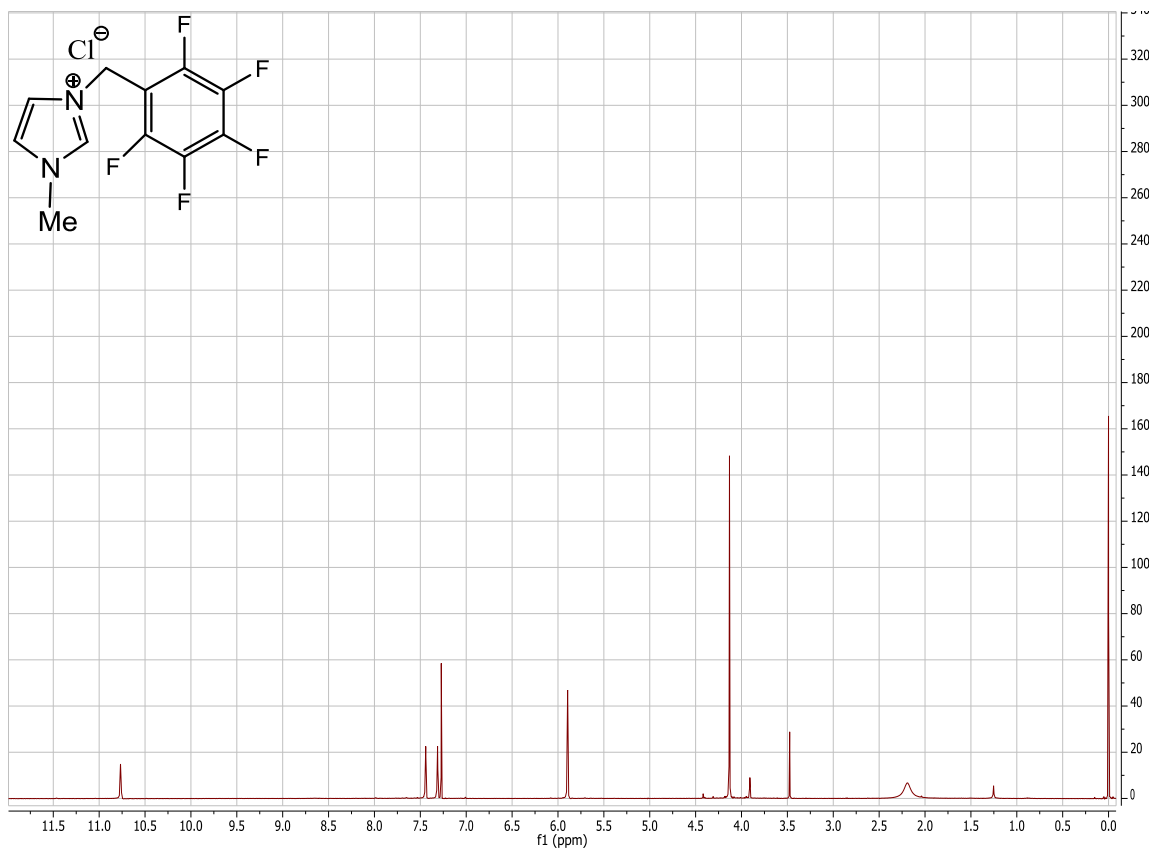


Figure 1.48 ^1H NMR spectrum (400 MHz) of 1-methyl-3-(pentafluorophenyl)imidazolium chloride.

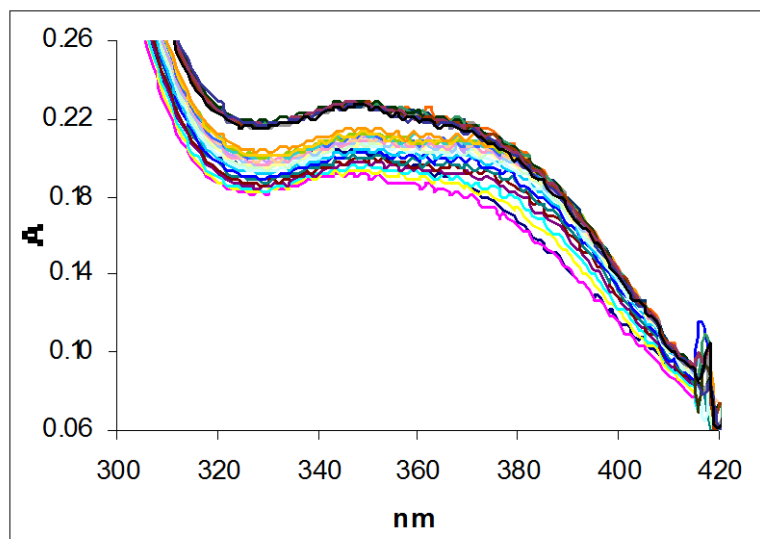


Figure 1.49 UV-Vis determination of CMC of SDS using 30 mM solution of **37**.

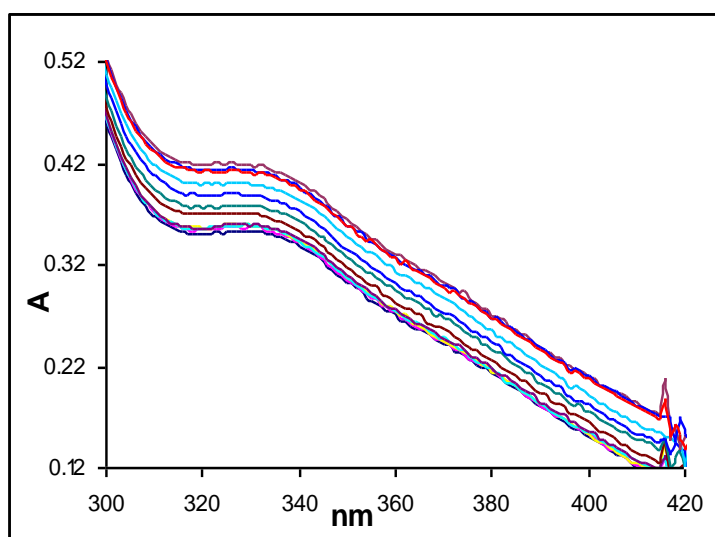


Figure 1.50 UV-Vis determination of CMC of SDS using 30 mM solution of **38**.

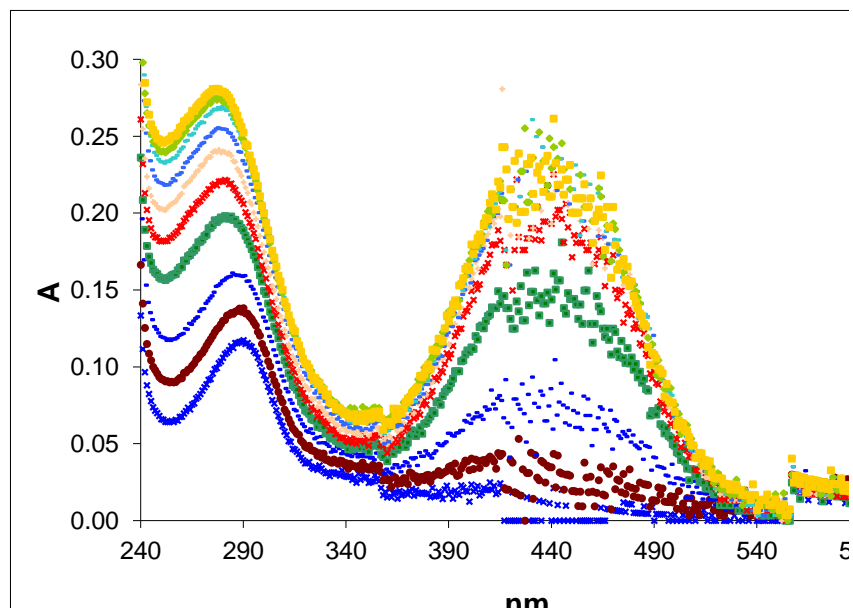


Figure 1.51 Typical UV-vis Spectrum of dye titration of surfactants; CMC of SDS using 30 mM solution [BMIM-Cl].

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2. IONIC LIQUIDS AS RECYCLEABLE CATALYSTS AND GREEN SOLVENTS.^{1,2}

2.1 INTRODUCTION

The room-temperature ionic liquid (RTILs) have been developed over the past decade as green solvents for not only academia but also for industrial applications.³⁻⁷ Environmentally-friendly reaction processes have vigorously been studied from the standpoint of green chemistry. The potential of ionic liquids to act as solvents for a broad spectrum of chemical processes is attracting increasing attention from industry because they have significant environmental benefits. Ionic liquids are salts, consisting of cations such as imidazolium, pyridinium, quaternary ammonium, and anions such as halogen, triflate, tetrafluoroborate and hexafluorophosphate, which exist in the liquid state at relatively low temperatures.^{8, 9} Their characteristic features include lack of significant vapor pressure, non-flammability, non-combustibility, high thermal stability, relatively low viscosity, wide temperature ranges for being liquids, and high ionic conductivity. Therefore, they are expected to exhibit unconventional reactivity, and their applications in a variety of organic reactions are being explored.

Ionic liquids containing chloroaluminate as the anion have been investigated for many years.¹⁰⁻²⁰ These ionic liquids are not only used as reaction solvents, but also exhibit Lewis acid or Lewis base properties, when the ratio of cations and anions is changed. However, they can only be used under an inert atmosphere or vacuum, due to their high moisture sensitivity. On the other hand, it has been found that ionic liquids containing anions such as tetrafluoroborate, and hexafluorophosphate form stable salts in air, which lead to the synthesis of numerous stable ionic liquids. Utilization of this

property enables recovery and reuse of ionic liquids, after extracting the product with an organic solvent. The RTILs have the potential to provide environmentally friendly solvents for the chemical industries. Organic reactions that have been successfully studied in ionic liquids such as Diels-Alder,²¹⁻³² Heck reaction,³³⁻⁴⁶ aldol condensation,^{4, 47-52} Suzuki-Miyaura coupling reaction,⁵³⁻⁶¹ Wittig reaction,^{62, 63} and Friedel-Crafts reaction.^{17, 64-70}

2.1.1 Biphasic Catalysis.⁷¹⁻⁸⁰ Biphasic catalysis, in which catalyst is confined to one phase and the products and reactants to another, is an ideal approach through combining the advantages of both homogeneous and heterogeneous catalysis. The catalyst phase can be recycled without treatment. As physiochemical properties of ionic liquids are easily tunable according to the requirements of catalytic system. They are attractive solvent media for biphasic catalysis. Biphasic catalysis, a method to heterogenize the catalyst and products into two separate phases without losing the selectivity and efficiency of homogeneous catalysis. In this catalysis generally reactants are confined to one phase and catalyst is in another phase before starting the reaction. During the reactions, the two phases are vigorously stirred, thus allowing the suitable interaction of catalyst and substrates. After completion of the reaction the products are confined to different phase than that of the catalyst phase, which can be separated by cation. This catalyst phase can often be recycled and reused.^{73, 77, 78, 81-85}

Water is used as solvent in biphasic catalysis as it is polar and readily available, as well as economically feasible. The main biphasic solvent system used is comprised of an aqueous-organic mixture and such processes are very effective and have been implemented in various commercial processes. While this biphasic system has many advantages, it

precludes the use of water sensitive reagents and catalysts. Many studies have focused on improving the affinities between the two liquid water-organic phases, either through increasing the lipophilic character of the catalyst phase or by immobilizing the catalyst on a support. Although all these techniques can change the solubility of organic compounds and enhances the rate of the reaction, they can also cause the leaching of the catalyst in to organic phase. The major advantage of the use of biphasic catalysis is the easy separation of the catalyst from the product phase.

There are many approaches to designing the biphasic solvents systems, and there has been a great deal of investigations to develop alternative solvents. In addition to their non-vapor pressure, non-flammability, thermal stability and their wide operating range, the key property of ionic liquids is the tunable chemical and physical properties by variation of the nature of the anions and cations. Their miscibility with different solvents depends not only on the cations' hydrophobicity, but also on the nature of anion and on the temperature.

N,N'-dialkylimidazolium cations are of particular interest because of their low melting points, more thermally stable than their tetraalkylammonium analogues, and their wide range of physiochemical properties. For the cation [BMIM]⁺, the anions [BF₄]⁻, [CF₃SO₃]⁻, [NO₃]⁻, and halide salts display partial miscibility with water at 25 °C, whereas the anions [PF₆]⁻, [SbF₆]⁻ display very low or negligible miscibility. In a similar way change of cation [BMIM]⁺ to more hydrophobic [HxMIM]⁺ cation affords a [BF₄]⁻ salt that shows low miscibility with water at room temperature. Therefore, modification of the alkyl substituents on the imidazolium ring, variable temperature, and variable anions could produce a variety of tunable ionic liquids.

2.1.2 Lewis Acid Catalysis in Organic Synthesis. Lewis acid catalyzed reactions are by far the most numerous and best studied reaction type in organic chemistry. Ionic liquids are considered as green solvents, because of their low volatility, non-flammability, and are preferred alternatives to volatile organic solvents as reaction medium.^{3, 4, 7, 73, 86-92} The most widely used ionic liquids in organic synthesis are derivatives of N,N'-dialkylimidazolium or N-alkylpyridinium with various inorganic anions (see Figure 2.1). They combine a reasonable thermal stability, tunable properties, a practically non-measurable vapor pressure, and immiscible with some of the organic solvents such as alkanes and ethers. Thus, the catalytic reactions are conducted in a single phase by adding the reagents and catalyst. After completion of the reaction, the products are extracted using selective organic solvent, while the Lewis acid catalyst is expected to remain immobilized in ionic liquid to be recovered and reused for subsequent runs.

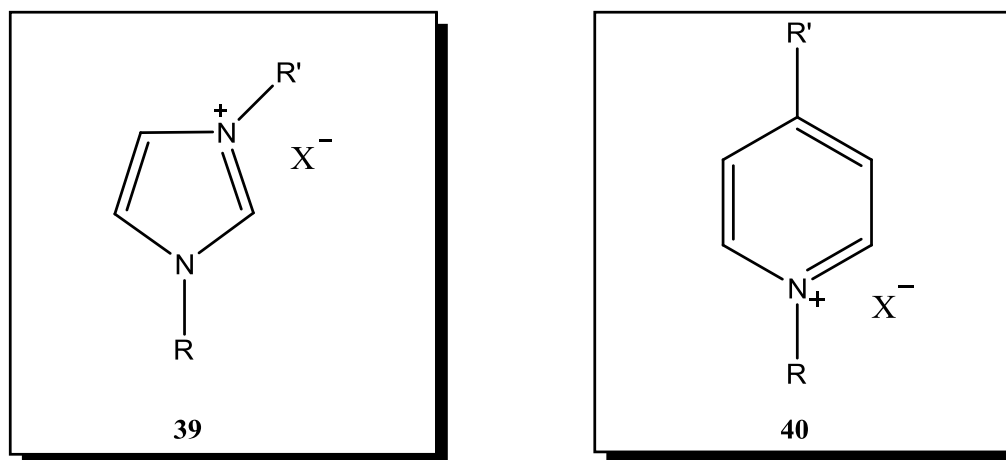


Figure 2.1 Chemical structure of imidazolium and pyridinium based ionic liquids.

2.2 EXPERIMENTAL

All reactions were carried out in air at ambient temperature in oven-dried glassware. Thin layer chromatography was carried out using silica gel coated polyester backed sheets. GC/MS spectra were recorded on Hewlett-Packard 5989A spectrometer, equipped with a Hewlett-Packard 5890 gas chromatograph. ^1H NMR and ^{13}C NMR spectra for CDCl_3 solutions were recorded on a INOVA-Varian 400 MHz spectrometer at 400 MHz and 100 MHz, respectively, and the chemical shifts are referenced with respect to internal tetramethylsilane [TMS] ($\delta = 0.0$).

2.2.1 General Synthesis of 1-Butyl-3-Methylimidazolium Salts $[\text{BMIM}]^+[\text{X}]^-$.

Room temperature ionic liquids [RTILs], $[\text{BMIM}]^+[\text{X}]^-$, were prepared by anion exchange of $[\text{BMIM}]^+[\text{Cl}]^-$ using 1mol equivalent of NaBF_4 or NaPF_6 . The RTILs were dried under vacuum for 12 h and stored under an atmosphere of dry argon.

2.2.2 General Procedure for Acetylations. A mixture of benzyl alcohol (2.00 g, 18.5 mmol) and acetic anhydride (2.26 g, 27.5 mmol) was added to $[\text{BMIM}]^+[\text{X}]^-$ (4 mL) containing $\text{Gd}(\text{OTf})_3$ (55 mg, 0.093 mmol, 0.5 mol %). The reaction mixture was stirred at room temperature and the progress of reaction monitored by TLC. Upon completion of the reaction (30 min to 2 h) diethyl ether (20 mL) was added to the contents and stirred. The supernatant ether layer containing the product was decanted, washed with water, aqueous NaHCO_3 , brine (20 mL), and dried (Na_2SO_4) and the solvent was removed on a rotary evaporator to give benzyl acetate. ^1H and ^{13}C NMR, and GC/MS of the products are in agreement with the literature data. The RTIL/ $\text{Gd}(\text{OTf})_3$ system was dried for 1 h under vacuum and recycled for subsequent runs.

2.2.3 General Procedure for Polymer. Synthesis of poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methylimidazolium) tetrafluoroborate] was shown in Figure 2.2. Co-polymer, **43**, can be synthesized by reacting styrene with 4-vinylbenzyl chloride in the presence of AIBN under nitrogen gas. Poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methyl-imidazolium) chloride] was synthesized by reacting co-polymer, **43**, with 1-methylimidazole at 120 °C for 48 h, and then poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methyl-imidazolium) tetrafluoroborate] was synthesized by exchanging anion with NaBF₄ at the room temperature.

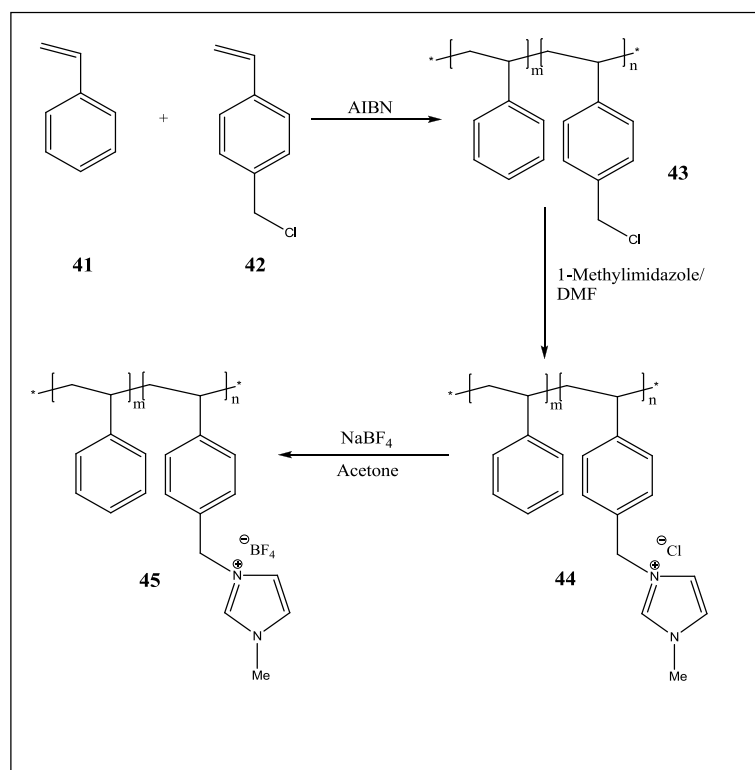


Figure 2.2 Preparation of poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methylimidazolium) tetrafluoroborate].

2.2.3.1 Synthesis of poly[styrene-co-4-chloromethylstyrene]. A solution of styrene **41** (10g, 96.0 mmol) and 4-vinylbenzyl chloride **42** (6.26 g, 41.0 mmol) in chlorobenzene (15 ml) was heated at 70°C for 12 h in the presence of AIBN (0.112g, 68 mmol) under nitrogen gas. The polymer **43** was purified by recrystallization (CH₃OH/THF) and dried under vacuum (see Figure 2.3).

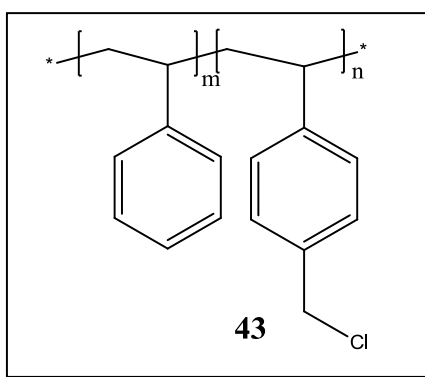


Figure 2.3 Chemical structure of poly[styrene-co-4-chloromethylstyrene].

The number-average molecular weight, M_n , and the weight-average molecular weight, M_w , of Poly[styrene-co-4chloromethylstyrene] **43** were analyzed by Gel permeation chromatography (GPC) with light scattering detector. M_n was 25,000 and M_w was 33,000. Therefore, Polydispersity(M_w/M_n) was confirmed with 1.32.

2.2.3.2 Synthesis of poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methylimidazolium) chloride]. 1-Methylimidazole **8** (2.28g, 0.028mol) was added to the solution of the polymer **43** (5g) in DMF (30mL). The mixture was stirred at room temperature for 1 h, and then heated at 120 °C for 48 h. Polymer **44** (6.6g) was obtained as a light yellowish solid after purification by precipitation into diethyl ether in Figure 2.4.

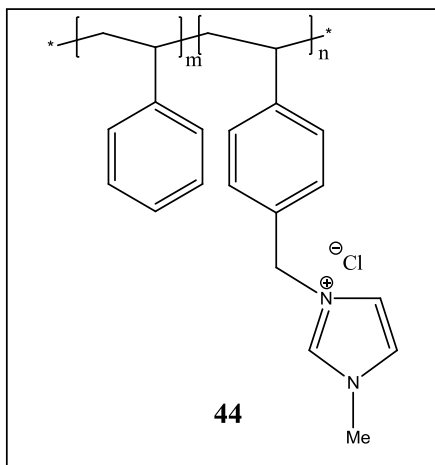


Figure 2.4 Chemical structure of poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methylimidazolium) chloride].

2.2.3.3 Synthesis of poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methylimidazolium) tetrafluoroborate]. Polymer **44** (4g) was reacted with NaBF_4 in acetone for 48 h to give the polymer **45** (see Figure 2.5).

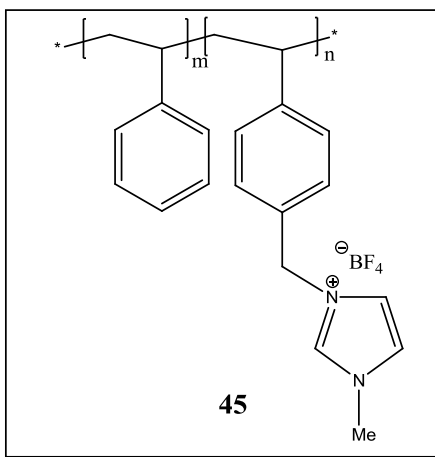


Figure 2.5 Chemical structure of poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methylimidazolium) tetrafluoroborate].

2.2.3.4 Incorporation of Gd(OTf)₃ into polymer. Acetone (40 mL) was added to the polymer **45** (1.0 g), followed by Gd(OTf)₃ (200 mg), and stirred at room temperature for 24 h. At this time, acetone was evaporated and the residue dried under vacuum for 4 h to give [**45** - Gd(OTf)₃] as a powdery material (see Figure 2.6).

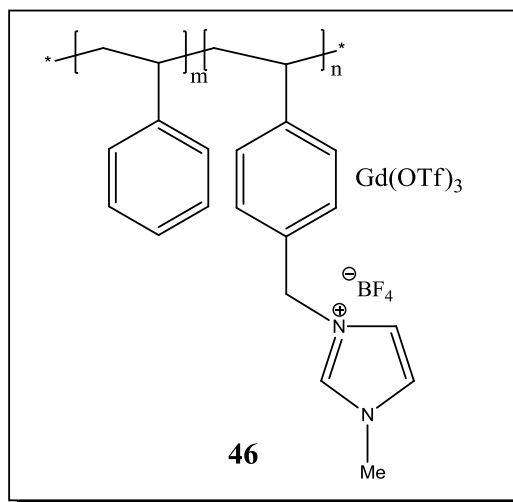


Figure 2.6 Incorporation of Gd(OTf)₃ into polymer.

2.2.4 General Procedure for Michael Additions. To a mixture of the secondary amine (5.7 mmol) and methyl acrylate (or acrylonitrile) (11.4 mmol), [**45** - Gd(OTf)₃] (0.5 mol% based on gadolinium triflate) was added at room temperature under solvent-free conditions and stirred for 1 h. (for reactions involving N-methylaniline reaction times of over 24 h are required). After completion of the reaction, ethyl acetate (10 mL) was added, filtered and the solvent evaporated under vacuum to obtain the products, essentially pure by NMR (98%). ¹H and ¹³C NMR, and GC/MS of the products are in agreement with the literature data.⁹³⁻⁹⁷

The catalytic system was dried for 3 h under vacuum and recycled for subsequent runs. Relatively high conversions could be achieved in the second and third cycles (Table 2.1, 2.2, and 2.3).

2.3 RESULTS AND DISCUSSION

2.3.1 Imidazolium-based Polymer Supported Gadolinium Triflate as a Heterogeneous Recyclable Lewis Acid Catalyst for Michael Additions. One of the main themes of contemporary synthetic organic chemistry is the development of atom-economic and environmentally benign catalytic systems.⁹⁸ In this context, the development of heterogeneous catalysis is of prime importance not only from the economic point of view, but also due to the easy workup procedures involved in the separation of products from catalyst. Imidazolium-based supported catalysis is receiving increasing attention due to the inherent advantages of the recyclability of the catalyst system from the reaction mixture.⁹⁹⁻¹⁰¹ Aluminum chloride complexes of supported ionic liquids based on silica support have been used in Friedel-Crafts alkylation and acylation reactions.¹⁰²⁻¹⁰⁴

Kobayashi and coworkers reported a polystyrene-supported Lewis acid catalyst which was useful for various organic transformations.¹⁰⁵ They also have reported Gd(OTf)₃ as a water-tolerant Lewis acid catalyst for aldol reactions of silyl enol ethers with aldehydes in aqueous media.^{106, 107} It was shown that Gd(OTf)₃ can be used as a mild and recyclable reagent for acylation of alcohols and amines.^{1, 2} As part of our ongoing research on Lewis acid catalyzed reactions, a novel heterogeneous catalytic system which involves incorporation of Gd(OTf)₃ into poly[styrene-co-(1-((4-

vinylphenyl)methyl)-3-methylimidazolium) tetrafluoroborate] [**45** - Gd(OTf)₃] was developed as an active catalyst for the Michael additions of various aliphatic and aromatic amines, and thiols to α,β -unsaturated esters and acrylonitrile.

The Michael addition products of methyl acrylate are potentially useful intermediates for the preparation of β -amino esters, which show biologically important properties and can be used as precursors for the preparation of β -lactams.^{108, 109} There are several reported examples of the preparation of β -amino esters by Lewis acid mediated Michael additions of amines to α,β -unsaturated esters. However, some of these procedures suffer from poor yields and are limited to aliphatic amines.¹¹⁰⁻¹¹³ Further, Michael addition of thiols to α,β -unsaturated esters leads to β -thio esters which have important biological applications.¹¹⁴⁻¹¹⁶

The catalytic system [**45** - Gd(OTf)₃] has been initially explored for Michael additions of amines to methyl acrylate and acrylonitrile, and compared it to that of the polystyrene-based catalytic system, PS-Gd(OTf)₃. Our control experiments revealed that under solvent-free conditions, PS-Gd(OTf)₃ and [**45** - Gd(OTf)₃] gave similar yields of the products for the Michael addition of N-methylaniline to methyl acrylate. However, whereas the former catalytic system involves a homogeneous reaction medium the latter provided a heterogeneous medium, resulting in relative ease in product separation from the catalytic system. The workup of the reaction mixture using the latter catalytic system is greatly simplified as it involves addition of the solvent ethyl acetate, followed by filtration and solvent evaporation. The catalyst system could thus be recycled conveniently. Because of the ease of separation of products from the catalyst system, and the ready recyclability of the catalyst system, this reaction has been extended to the

Michael additions of a variety of secondary amines and thiols to methyl(ethyl) acrylate, methyl methacrylate and acrylonitrile.

The [45 - Gd(OTf)₃] catalytic system was found to be convenient for the Michael additions of a variety of amines and thiols to α,β -unsaturated esters and acrylonitrile (see Figure 2.7). The reactions proceeded under mild conditions and high yields of the adducts were obtained by simple workup procedures, which involve separation of the catalyst system by filtration and solvent evaporation. Most of the reactions were complete in about 1 h at room temperature, using as low as 0.5 mol% of the catalyst based on Gd(OTf)₃.

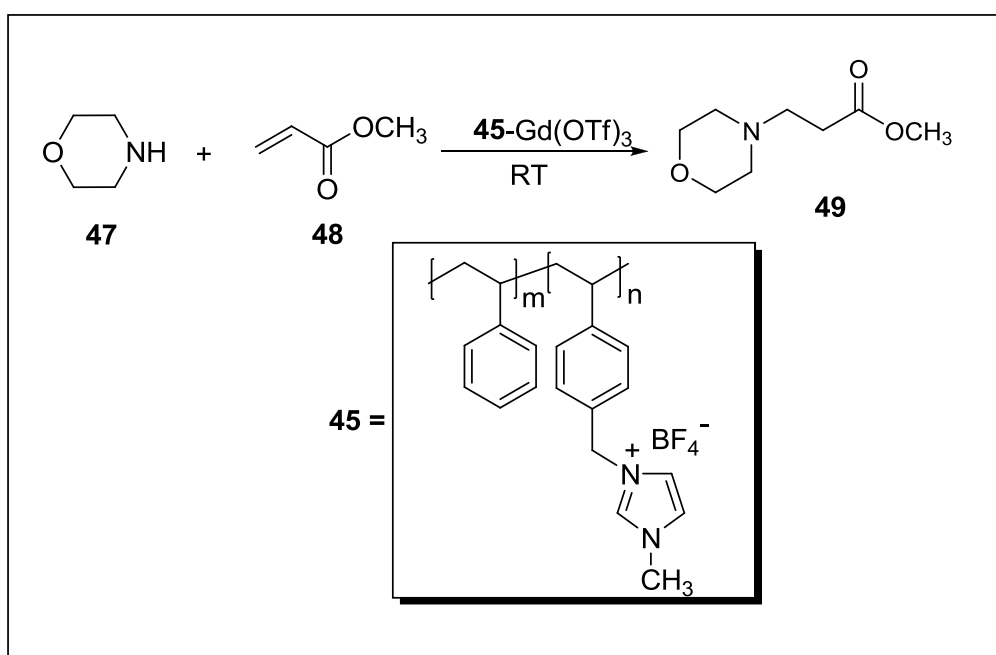


Figure 2.7 Michael addition of amines to α, β -unsaturated esters.

Relatively longer reaction times and larger amounts of catalyst (up to 3 mol%) were required for the reactions of N-methylaniline and *p*-methoxyaniline (Table 2.1,

entries 4, 8, and Table 2.2, entry 4). The catalytic system, [45 - Gd(OTf)₃], could be recycled and re-used for subsequent runs. Catalytic activity of the catalyst is maintained for at least up to 3 cycles. However, this catalytic system failed to give Michael adducts with the weakly nucleophilic benzyl carbamate, in accordance with earlier observations for related catalytic systems.¹¹⁷ In order to confirm the true heterogeneity of the catalytic system, (i. e., the absence of leaching of the Gd(OTf)₃ into the reaction mixture), we have removed the catalyst by decantation at 9% completion of the reaction, and let the reaction proceed in the absence of the catalyst for 24 h (for entry 4, Table 2.1). Analysis of the reaction mixture after 24 h by GC/MS showed 12% completion of the reaction, indicating that there was no leaching of the Gd(OTf)₃ into the reaction mixture.

The [45 - Gd(OTf)₃] catalytic system was summarized in Tables 2.1 to 2.3 for the Michael additions of a variety of amines and thiols to α,β -unsaturated esters and acrylonitrile.

Table 2.1 Solvent-free [45 - Gd(OTf)₃] catalyzed Michael addition of amines to α , β -unsaturated esters.

Entry	Amine	Substrate ^d	Product	Yield ^a %
1		3a		98 (92, 96) ^c
2		3a		95
3		3a		94 (96, 91) ^c
4		3a		63 ^b
5	Et ₂ NH 56	3a		86 (91, 89) ^c
6	Bn ₂ NH 58	3a		82 ^b
7		3b		99 ^b
8		3a		71 ^b


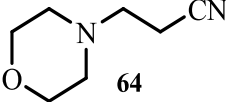

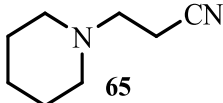
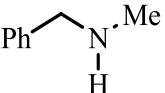
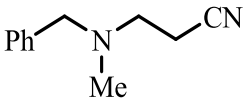
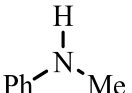
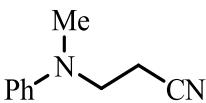
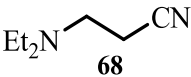
^[a] Isolated yields (0.5 mol% of the catalyst was used); reactions were carried out at room temperature for 1 h, with the exception for entries 4 and 8 (24 h and 3 mol% of the catalyst).

^[b] Yields based on GC/MS.

^[c] Yields for 2nd and 3rd cycles.

^[d] 3a = methyl acrylate; 3b = methyl methacrylate.

Table 2.2 Solvent-free [(45)-Gd(OTf)₃] catalyzed Michael addition of amines to α , β -unsaturated acrylonitrile.

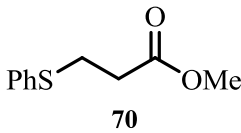
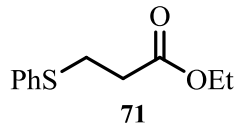
Entry	Amine	Substrate ^c	Product	Yield ^a %
1	 47	3d	 64	90
2	 50	3d	 65	90
3	 52	3d	 66	92
4	 54	3d	 67	32 ^b
5	Et ₂ NH 56	3d	 68	83

^[a] Isolated yields (0.5 mol% of the catalyst was used); reactions were carried out at room temperature for 1 h, with the exception for entry 5 (24 h and 3 mol% of the catalyst).

^[b] Yields based on GC/MS.

^[c] 3d = acrylonitrile.

Table 2.3 Solvent-free [(45)-Gd(OTf)₃] catalyzed Michael addition of thiols to α , β -unsaturated esters.

Entry	Thiols	Substrate ^c	Product	Yield ^a %
1	PhSH 69	3a	 <chem>PhS-CH2-CH2-C(=O)OMe</chem> 70	99 ^b
2	PhSH 69	3b	 <chem>PhS-CH2-CH2-C(=O)OEt</chem> 71	98 ^b

^[a] Isolated yields (0.5 mol% of the catalyst was used); reactions were carried out at room temperature for 1 h.

^[b] Yields based on GC/MS.

^[c] 3a = methyl acrylate; 3b = ethyl acrylate.

2.3.2 Gadolinium Triflate Immobilized in Imidazolium-based Ionic Liquids:

a Recyclable Catalyst and Green Solvent for Acetylation of Alcohols and Amines.

Acetylation reactions catalyzed by Lewis acids are of enormous interest and used extensively in organic synthesis.¹¹⁸ Although a number of acid- and base- catalyzed acetylation reactions are known many of them are limited in their applications either due to the instability of reactants or products under the reaction conditions or tedious workup procedures involved.¹¹⁹⁻¹²²

A variety of Lewis acid catalyzed acylations of alcohols and amines with acid anhydrides have been explored. Despite a number of methods currently available, new

and efficient methods are still in strong demand. Lewis acids such as scandium triflate ($\text{Sc}(\text{OTf})_3$),¹²³ magnesium bromide (MgBr_2),¹²⁴ tantalum chloride (TaCl_5),¹²⁵ trimethylsilyl triflate (Me_3SiOTf),¹²⁶ copper (II) triflate ($\text{Cu}(\text{OTf})_2$),¹²⁷ indium triflate ($\text{In}(\text{OTf})_3$)¹²⁸ and bismuth triflate ($\text{Bi}(\text{OTf})_3$)^{129, 130} have been used as catalysts for these transformations. Most of these metal triflates are either too expensive or water-sensitive. Further, trimethylsilyl triflate is sensitive towards moisture, and is strongly acidic and cannot be used for the acylation of acid-sensitive alcohols. In 1994, Kobayashi and co-workers used $\text{Gd}(\text{OTf})_3$ as a water-tolerant Lewis acid in the aldol reactions of silyl enol ethers with aldehydes, in aqueous media.¹³¹

From the viewpoint of today's environmental consciousness, development of environmentally benign reaction media for organic transformations is crucial. Room temperature ionic liquids (RTILs) that are air and moisture stable have recently been found to be excellent environmentally benign solvents for a variety of reactions such as esterification,¹³² Diels-Alder³², Wittig¹³³, Suzuki¹³⁴ and Heck reactions.¹³⁵ Since these RTILs have the advantage of being non-volatile, non-flammable, and recyclable they offer an alternative to conventional organic solvents. Deng and coworkers reported the application of an RTIL, 1-butylpyridinium chloride-aluminium (III) chloride, as a catalyst and reaction medium for the acylation of alcohols with acetic acid.¹³⁶ Recently imidazolium-based RTILs have been used as solvents for DCC/DMAP promoted esterification of ferrocenemonocarboxylic acid,¹³⁷ and for the acetylation of alcohols in the presence of Lewis acids, $\text{Cu}(\text{OTf})_2$, $\text{Yb}(\text{OTf})_3$, $\text{Sc}(\text{OTf})_3$, $\text{HfCl}_4(\text{THF})_2$, and InCl_3 .¹³⁸ As part of our ongoing study of Lewis-acid catalyzed reactions and ionic liquids, the recyclability of $\text{Gd}(\text{OTf})_3$ catalyst has been explored in RTILs, 1-butyl-3-

methylimidazolium tetrafluoroborate ($[\text{BMIM}]^+[\text{BF}_4]^-$) **10**, and 1-butyl-3-methylimidazolium hexafluorophosphate $[\text{BMIM}]^+[\text{PF}_6]^-$ **16** (see Figure 2.8).

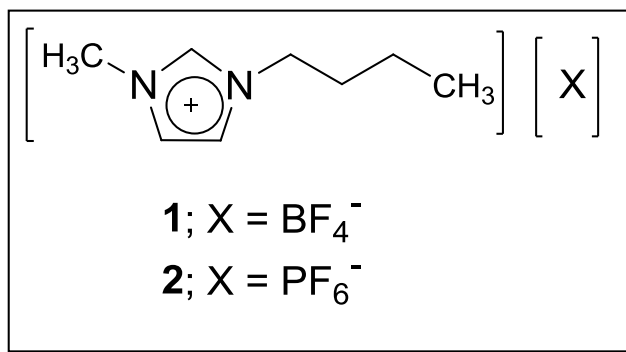


Figure 2.8 1-butyl-3-methylimidazolium $[\text{BMIM}]^+$ with different anions $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$.

$\text{Gd}(\text{OTf})_3$ is relatively more water tolerant than other lanthanide based metal triflates.¹⁴ Thus strictly anhydrous reaction conditions that have been used with other Lewis acid catalysts can be avoided in case of this catalyst. In addition, it is a relatively inexpensive reagent. We have recently used this catalyst for efficient and convenient acetylations of alcohols and amines using acetic anhydride as the reagent in conventional organic solvents. The reaction of variety of primary, secondary and tertiary alcohols proceeded at relatively high rates at ambient temperatures. $\text{Gd}(\text{OTf})_3$ has been acted as a catalyst for these reactions at as low as 0.01 mol%. $\text{Gd}(\text{OTf})_3$ catalyzed acetylation reactions also proceed in excellent yields with phenols and allylic alcohols.

As RTILs such as $[\text{BMIM}]^+[\text{BF}_4]^-$ **10** are relatively hygroscopic, we have selected $\text{Gd}(\text{OTf})_3$, a water-tolerant Lewis acid, as an immobilizable Lewis acid catalyst in these media. The combination of the environmentally benign nature of the RTILs and recyclability of the catalyst should make the present catalyst system attractive. To

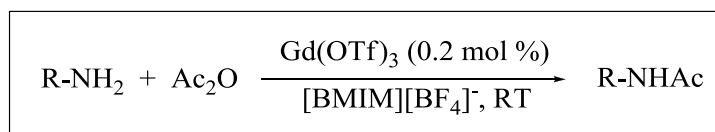
examine the catalytic activity of $\text{Gd}(\text{OTf})_3$ in RTILs, acetylation of benzyl alcohol with acetic anhydride was chosen initially as a model reaction. Benzyl alcohol reacted with acetic anhydride at room temperature in $[\text{BMIM}]^+[\text{BF}_4]^-$ **10** and $[\text{BMIM}]^+[\text{PF}_6]^-$ **16** in the presence of 0.5 mol percent of the catalyst. In $[\text{BMIM}]^+[\text{BF}_4]^-$ **10** the yields are good to excellent, whereas in $[\text{BMIM}]^+[\text{PF}_6]^-$ **16** relatively lower yields were obtained. When solvent/catalyst system is recycled and reused, the catalytic activity is slightly decreased in case of $[\text{BMIM}]^+[\text{BF}_4]^-$ **10**, whereas a drastic decrease of catalytic activity was observed in case of $[\text{BMIM}]^+[\text{PF}_6]^-$ **16** (Table 2.4).

The acetylation of amines using the $\text{Gd}(\text{OTf})_3$ have been also investigated as the catalyst in $[\text{BMIM}][\text{BF}_4]^-$ **10**. Using as low as 0.2 mol % of the catalyst we have obtained high yields of N-acetylated products (Table 2.5). $\text{Gd}(\text{OTf})_3$ catalyzed acetylation of amines proceeded in relatively shorter times as compared to acetylation alcohols as was also observed in case of CH_3CN as the solvent.¹⁵

After having optimized the reaction conditions for benzyl alcohol, acetylation of various alcohols with acetic anhydride have been carried out in $[\text{BMIM}][\text{BF}_4]^-$ in the presence of 0.5 mol % of $\text{Gd}(\text{OTf})_3$ as a catalyst at room temperature. The reactions of a variety of alcohols, phenols, diols as well as allylic alcohols proceeded in excellent yields with as low a concentration as 0.2 mol percent of $\text{Gd}(\text{OTf})_3$ (Table 2.6).

Table 2.4 Acetylation of benzyl alcohol with acetic anhydride using Gd(OTf)₃/[BMIM][X].
$$\text{PhCH}_2\text{OH} + \text{Ac}_2\text{O} \xrightarrow[\text{[BMIM][X]^-}, \text{RT}]{\text{Gd(OTf)}_3 \text{ (0.5 mol \%)}} \text{PhCH}_2\text{OAc}$$

Entry	[X]	Run	Time (h)	Yield (%) ^a
1	BF ₄	First	1	92
		Second	1	89
		Third	2	72 ^b
2	PF ₆	First	4	76
		Second	4	69 ^b
		Third	4	40 ^b

^a Isolated yields.^b Yields estimated by GC/MS.**Table 2.5** Gd(OTf)₃ catalyzed acetylation of amines in [BMIM][BF₄].

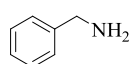
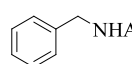
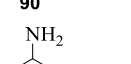
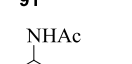
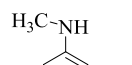
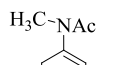
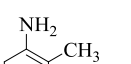
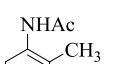
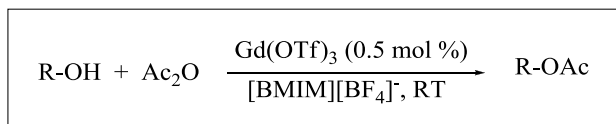
Entry	Amine	Product	Yield (%)
1			90
2			96
3			86
4			89

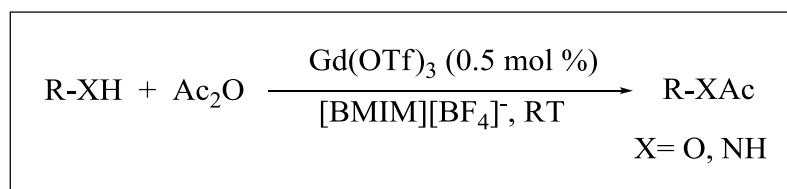
Table 2.6 Gd(OTf)₃/[BMIM][BF₄] catalyzed acetylation of alcohols.

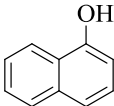
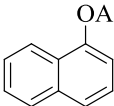
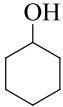
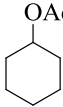
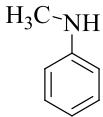
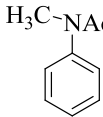
Entry	Alcohol	Product	Yield (%) ^a
1			88
2			92
3			90
4			76
5			99 ^b
6			93
7			95
8			92
9			86

^a Isolated yields.^b Yield estimated by GC/MS.^c Reactions were carried out in CH₂Cl₂ as solvent.

For selected compounds in Tables 2.5 and 2.6, recyclability and reuse of the $\text{Gd}(\text{OTf})_3/[\text{BMIM}][\text{BF}_4]^-$ catalyst system have been demonstrated (Table 2.7). Moderate to high yields of the products were obtained in second and third runs.

Table 2.7 Recyclability and reuse of $\text{Gd}(\text{OTf})_3/[\text{BMIM}][\text{BF}_4]^-$ for representative acetylation reactions.



Entry	Substrate	Product	Yield (%) ^{a,b}
1	 74	 75	92 (1st run)
			83 (2nd run)
			46 (3rd run)
2	 86	 87	92 (1st run)
			87 (2nd run)
			82 (3rd run)
3	 94	 95	86 (1st run)
			78 (2nd run)
			72 (3rd run)

^a Isolated yields.

^b 0.2 mol % of $\text{Gd}(\text{OTf})_3$ was used for entry 3.

2.4 CONCLUSION

A novel heterogeneous catalytic system was developed by incorporating the Lewis acid catalyst $\text{Gd}(\text{OTf})_3$ onto the imidazolium-based of poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methylimidazolium) tetrafluoroborate] **45**, and it was shown that it can be used as a convenient catalyst for Michael additions of a variety of secondary amines to α,β -unsaturated esters and acrylonitrile. The catalytic system could be efficiently recycled and reused. Also $\text{Gd}(\text{OTf})_3$ immobilized in RTILs is an efficient recyclable catalyst system for acetylation of aliphatic and aromatic alcohols and amines. A variety of alcohols, phenols, diols as well as allylic alcohols and amines have been acetylated using 0.01-0.2 mol percent of the catalyst in these environmentally benign solvents. Although the catalytic activity of the recovered catalyst was decreased slightly upon recycling, this method offers a good catalyst system in the context of “green” chemistry.

^1H NMR spectrums (400 MHz) of poly[styrene-co-4-chloromethylstyrene] and Poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methylimidazolium) tetrafluoroborate] are shown in Figure, 2.9 and 2.10. Schematic representation of the catalytic cycle for RTIL- $\text{Gd}(\text{OTf})_3$ catalyzed acetylations is also shown in Figure 2.11.

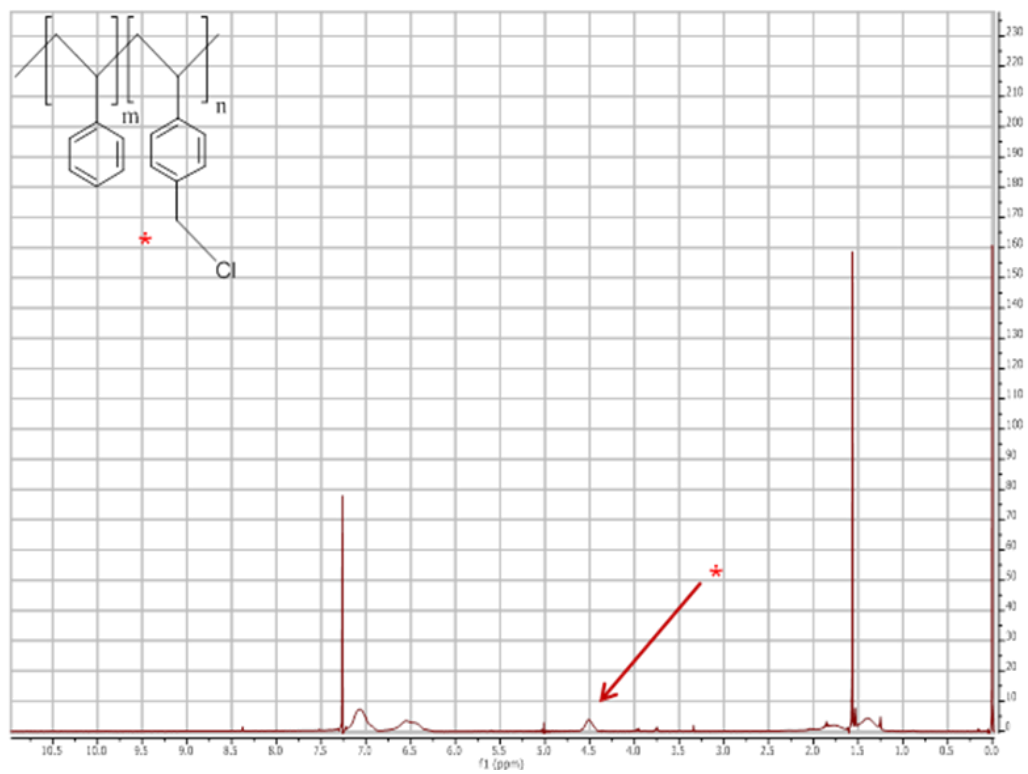


Figure 2.9 ^1H NMR spectrum (400 MHz) of poly[styrene-co-4-chloromethylstyrene].

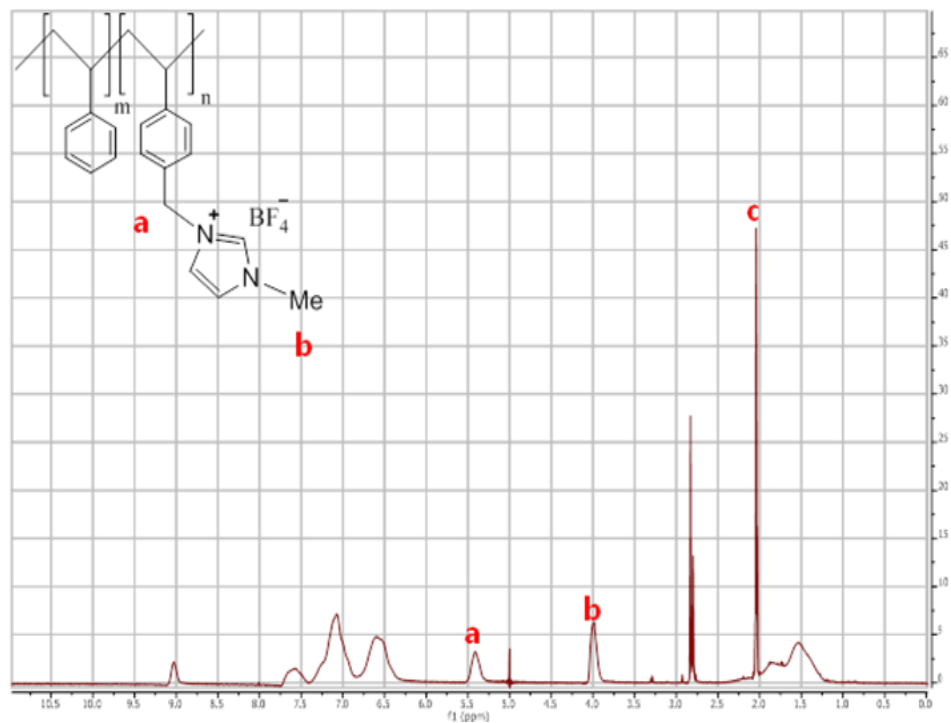


Figure 2.10 ^1H NMR spectrum (400 MHz) of poly[styrene-co-(1-((4-vinylphenyl)methyl)-3-methylimidazolium) tetrafluoroborate]. [a: $\text{N}^+\text{-CH}_2$, b: N-CH_3 , c: $\text{Acetone-}d_6$].

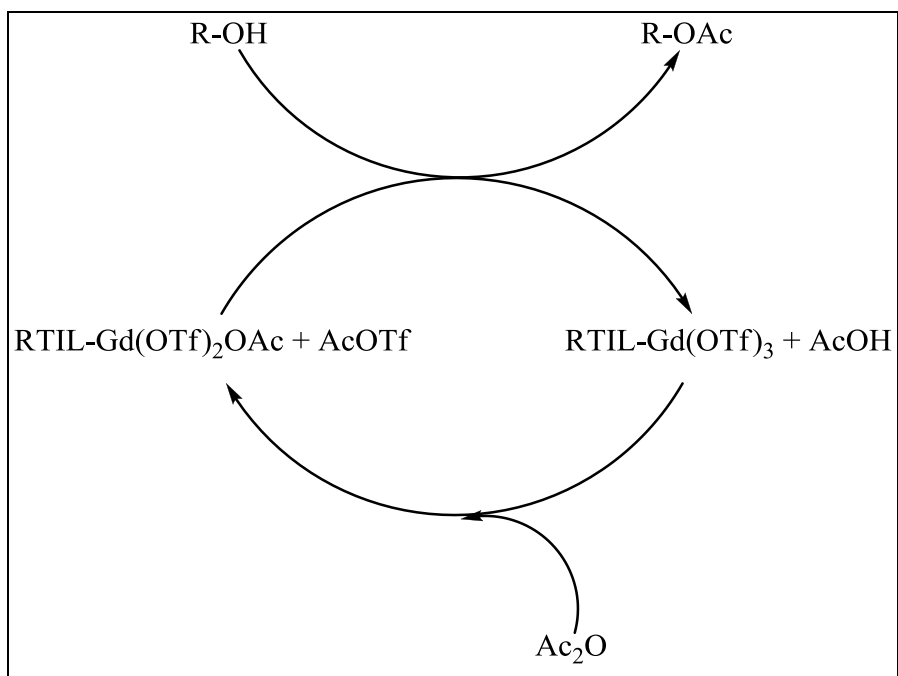


Figure 2.11 Schematic representation of the catalytic cycle for RTIL-Gd(OTf)₃ catalyzed acetylations.

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3. SYNTHESIS AND APPLICATIONS OF POLYNORBORNENE- IMIDAZOLIUM BASED IONIC LIQUIDS

3.1 INTRODUCTION

Polymeric electrolytes have received extensive attention during the last two decades. The fast development of portable electronic devices and the growing demand for improved batteries turned out to be major driving forces. The most suitable battery type is one that contains a large amount of energy in a small package, light weight and safety. Ionic liquids (ILs) are emerging as green solvents for chemical processes, because they have tunable solubility properties with negligible vapor pressure and excellent thermal and chemical stabilities.¹⁻⁵ In addition, ILs are non-corrosive and non-flammable. For example, Vygodskii and co-workers showed that the reaction rate of free radical polymerization of vinyl monomers in room temperature ionic liquids (RTILs) was much faster than that in general organic solvents, and the resulting polymers also had much higher molecular weights.⁶ On the other hand, RTILs have attractive properties for electrolytes such as high ionic content, high matrix mobility at ambient temperatures, and they have been investigated as a novel ion conductive matrices. Polymerization of acrylate monomers with imidazolium cation and organic/inorganic anion was used to prepare polymer electrolytes, since these imidazolium salts were stable toward moisture.⁷⁻¹¹ The examples of the most common ionic liquids are shown in Figure 3.1.

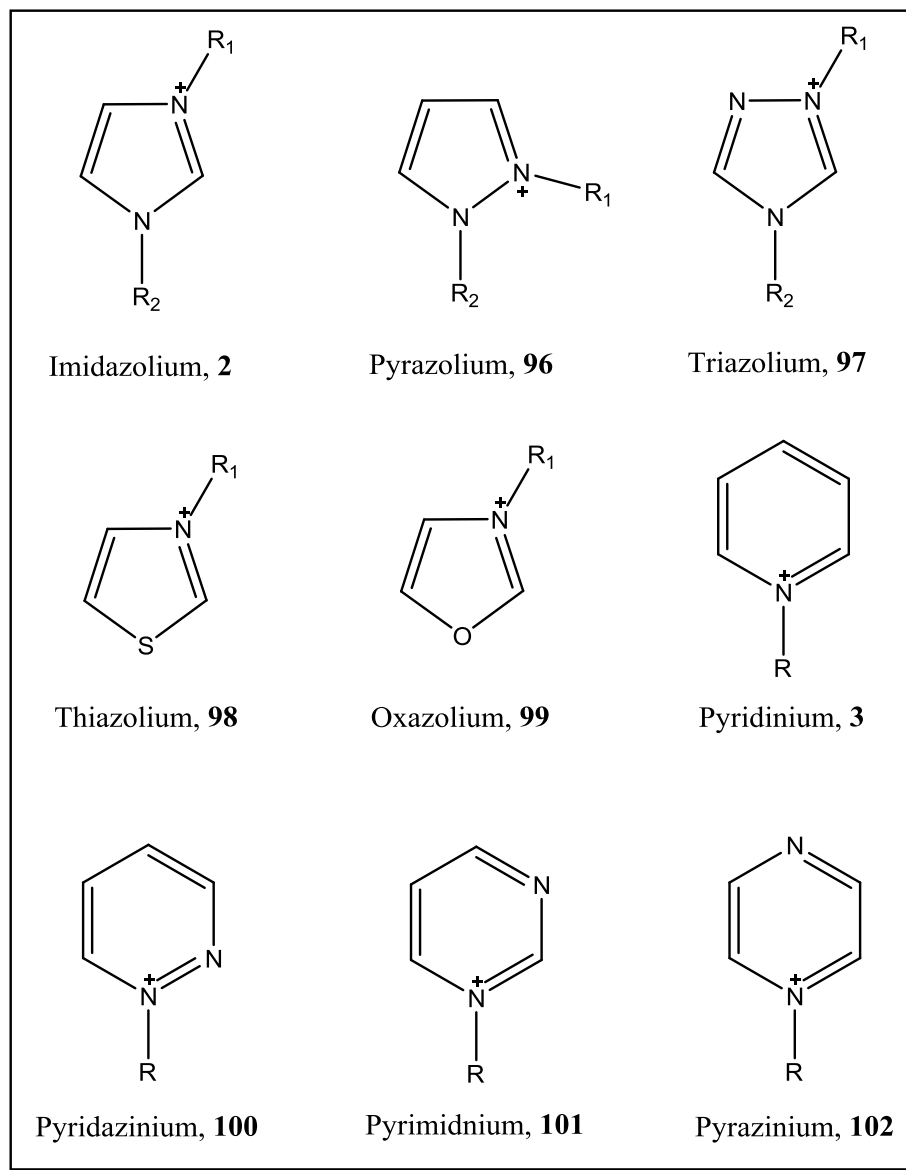


Figure 3.1 Chemical structures of delocalized heterocyclic organic cations.^{12, 13}

The battery electrolytes are generally required to have the following fundamental properties: (1) thermal and chemical stability, (2) non-toxicity and safety, (3) wide potential windows (electrochemical stability), (4) high ionic conductivity, (5) good mechanical properties, (6) low cost, and (7) low reactivity toward other components in the battery, i.e positive and negative electrodes, separators, etc.¹⁴⁻¹⁹ The development

trend in lithium ion batteries is focused on the replacement of the common liquid electrolytes with a lithium ion conducting polymer electrolyte membrane to achieve the fabrication of batteries.²⁰ Such plastic lithium ion batteries are expected to be less expensive and more easily scaled up than their liquid counterparts. In addition, the absence of free liquids allows packaging in light-weight plastic containers unlike conventional batteries which require metallic casing.²¹⁻²⁵ The plastic battery can be fabricated in any desired shape or size, a target difficult to be achieved with liquid electrolyte cells.

Historically, the first type of ionically conducting membranes to be considered for battery applications were those formed by blending high molecular weight poly(ethylene oxide) PEO with a lithium salt, LiX and most of the ionic conductive polymers have been developed as the mixture of inorganic salts and PEO derivatives.²⁶ Solvent-free, flexible, and highly conducting polyelectrolyte films containing lithium ion batteries have Li ion conductivities greater than $10^{-3} \times \text{S} \cdot \text{cm}^{-1}$.²⁷ Recently, Ohno and co-worker reported the synthesis of both imidazolium-based polymerizable monomers and the corresponding polycations.²⁸

In the case of ILs based battery electrolytes, film-like ion conductive materials are generally preferred than liquid type materials from the view point of processing, treatment, and packaging. To prepare ion conductive film materials based upon ILs, polymerization of ILs is one of powerful strategy that expands application. The solid polymer electrolyte can show good ionic conductivity without liquid components reflecting their low glass transition temperature. Their properties are good for some applications of ion conducting materials. In addition, these polymerized ILs have a

variety of structures and potential to show specific functions such as transport of target ions, polar environment and mechanical strength.

Ionic conductivity generally depends on the number of dissociated ions and their mobility within the polymer. Despite the fact that monomers derived from imidazole possess rather high ionic conductivity, their polymerization leads to a decrease in conductivity by several orders of magnitude. Possible solutions for overcoming this problem entail the increase of mobility of the fixed imidazolium cations and a reduction of the polymer's glass transition temperature (T_g).²⁸⁻³¹ Simple polymerization of ILs monomers gave very poor ionic conductivity due to both considerable elevation of glass transition temperature (T_g) and reduced number of mobile ions after covalent bonding of the component ions.²⁸ About 10^4 times lower ionic conductivity was found after polymerization. For the case of ion conductive polymers, both high ion density and low T_g are required for better performance.³⁰

ROMP has been proven to be successful method to synthesize various polymers of complicated structures, and has been widely applied in structure design, and synthesis of novel polymers, such as norbornenyl telechelic polyphosphazenes polymer electrolytes,³² norbornene bipyridine polymers,³³ and *n*-cyclo-alkyl-7-oxanorbornene dicarboximides polymers.³⁴

Grubbs' catalysts are a series of transition metal carbene complexes.³⁴⁻³⁶ The first and second generations of the catalyst are shown in the Figures 3.2 and 3.3. Grubbs' catalysts tolerate various functional groups in the alkene, are air-tolerant and are compatible with a wide range of solvents. Functional poly(norbornene) is of particular interest because of its unique physical and optoelectronic properties, such as high glass

transition temperature (T_g), optical transparency and low birefringence.^{37, 38} Ring opening metathesis polymerization (ROMP) is nowadays a well-established polymerization technique.³⁹ Grubbs' catalysts are well suited for these purposes and allow for polymerizations in a truly living manner.

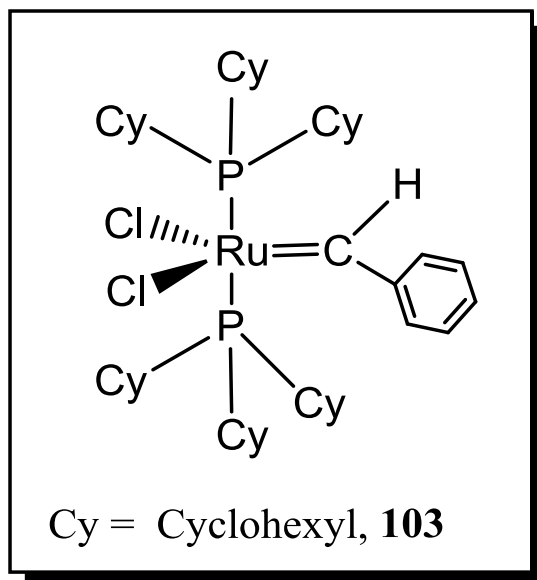


Figure 3.2 Chemical structure of benzylidenebis(tricyclohexylphosphine)dichlororuthenium (1st generation Grubbs catalyst).

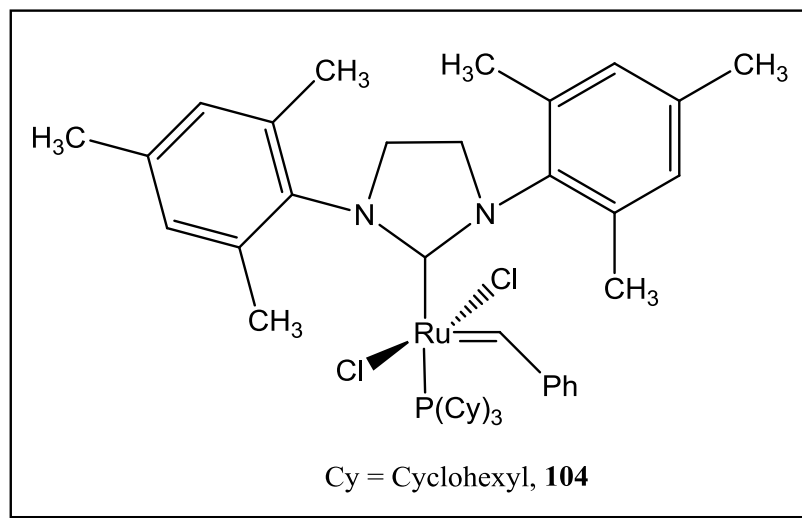


Figure 3.3 Chemical structure of [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium (2nd generation Grubbs catalyst).

3.2 EXPERIMENTAL

Dicyclopentadiene, 1-allylimidazole, 1-butylchloride, sodium tetrafluoroborate, 1-vinylimidazole, and Grubbs' catalysts were purchased from the Sigma-Aldrich Co., or Lancaster and used as received. All solvents were also purchased from Sigma-Aldrich Co., and purified over drying agents under nitrogen prior to use. All the reactions were carried out under an atmosphere of dry nitrogen.

¹H NMR spectra were obtained at 400 MHz using a Varian INOVA 400 MHz NMR spectrometer and are referenced to internal tetramethylsilane (TMS). Molecular weight of compound **110** was also obtained by matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry.

3.2.1 General Procedure for Imidazolium Functionalized Norbornene Monomer and Polynorbornene. A flame-dried round flask was charged with the desired amount of 1st generation Grubbs' catalyst **103**, appropriate amount of CH₂Cl₂, and

monomer **109**. The reaction mixture was stirred under an atmosphere of dry nitrogen. The ROMP polymerization mixture was quenched with excess of ethyl vinyl ether. The resulting polymer was isolated by removal of the solvent in vacuum. Preparation of imidazolium-base ILs on polynorbornene was shown in Figure 3.4.

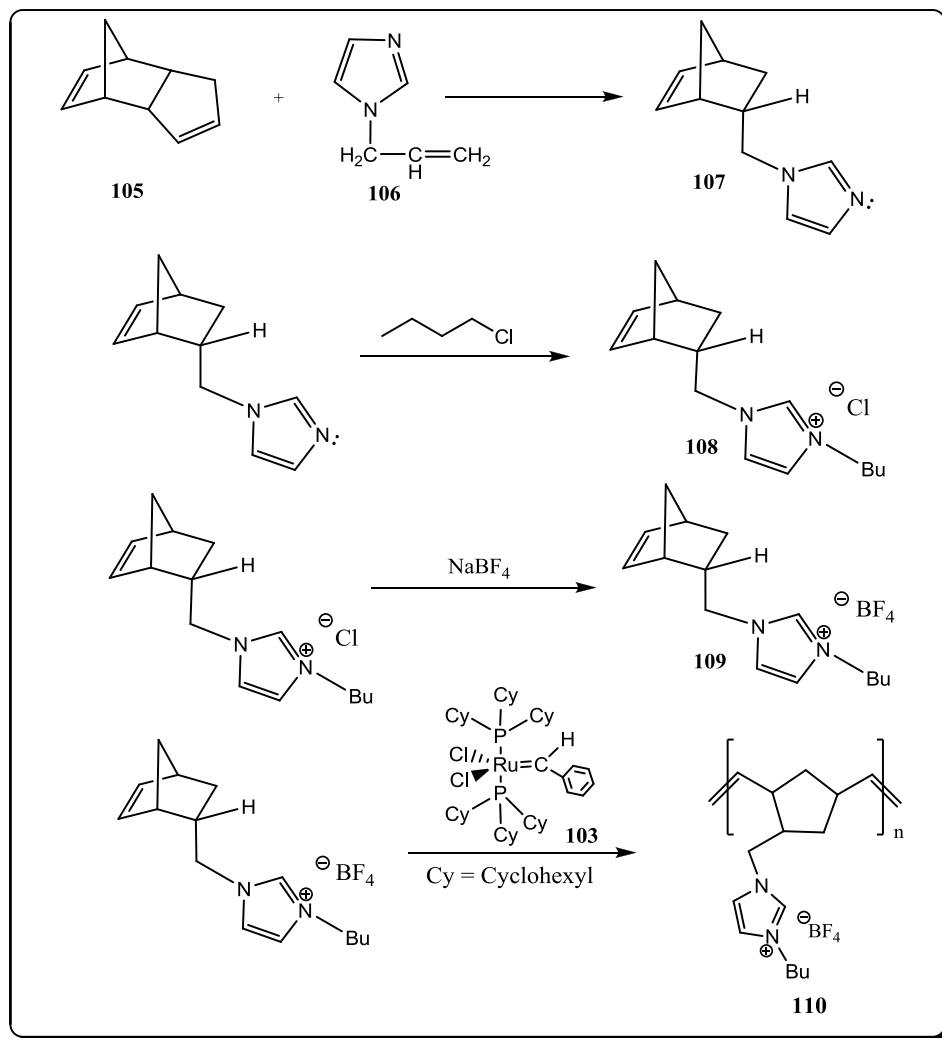


Figure 3.4 Preparation of imidazolium-base ILs on polynorbornene.

3.2.2 Synthesis of 1-(Bicyclo[2.2.1]hept-5-en-2-ylmethyl)-Imidazole.

Dicyclopentadiene (5 g, 0.0378 mol) and 1-allylimidazole (8.18 g, 0.0756 mol) were stirred at 170 °C for 18h under an atmosphere of dry nitrogen. The reaction was monitored by TLC and excess 1-allylimidazole was removed from the reaction mixture via vacuum distillation (0.5 torr, 50 °C). Compound **107** was isolated as a brown oil (7.97 g, 80 %) (see Figure 3.5). ¹H NMR (400 MHz, CDCl₃): δ 7.48 (s, 1 H), 7.10 (t, 1 H), 6.93 (t, 1 H), 6.26 (d, 1 H), 6.12 (d, 1 H), 3.75–3.51 (m, 2 H), 2.82 (br, 1 H), 2.71 (br, 1 H), 2.0-1.75 (m, 2 H), 1.51-1.22 (m, 3 H).

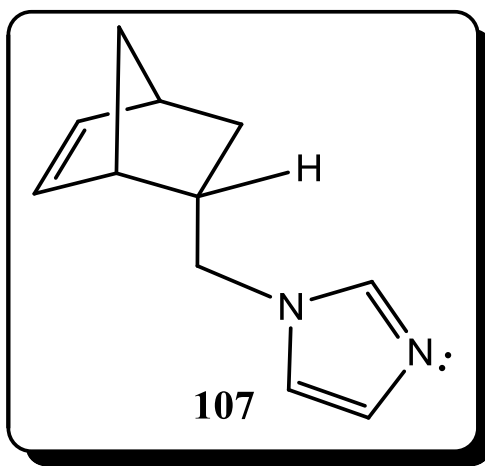


Figure 3.5 Chemical structure of 1-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-imidazole.

3.2.3 Synthesis of 1-(Bicyclo[2.2.1]hept-5-en-2-ylmethyl)-3-Butylimidazolium

Chloride. 1-chlorobutane (2.31 g, 0.025 mol) and 1-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1*H*-imidazole **107** (2.9 g, 0.016 mol) was refluxed for 24h. Viscous yellowish oil was obtained after reaction (2.50 g, 90 %) (see Figure 3.6). ¹H NMR (400MHz, CDCl₃): δ 10.76 (s, 1 H), 7.71 (t, 1 H), 7.61 (t, 1 H), 6.26 (d, 1 H), 6.21 (d, 1 H), 4.45 (t,

2 H), 4.11–3.90 (m, 2 H), 2.83 (br, 1 H), 2.74 (br, 1 H), 2.01–1.80 (m, 5 H), 1.51–1.25 (m, 4 H), 0.9 (t, 3 H).

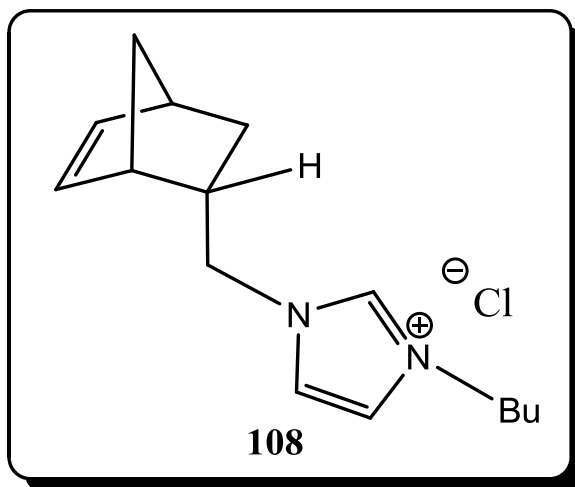


Figure 3.6 Chemical structure of 1-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-3-butylimidazolium chloride.

3.2.4 Synthesis of 1-(Bicyclo[2.2.1]hept-5-en-2-ylmethyl)-3-Butylimidazolium Tetrafluoroborate. 1-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-butyl-3*H*-imidazolium chloride **108** (2 g, 0.0075 mol) was stirred with a saturated aqueous solution of sodium tetrafluoroborate (0.82 g, 0.0075 mol) for 24 h at room temperature. Compound **109** was obtained by extracting with dichloromethane, washed with water, dried (MgSO₄), and removed the solvent by rotary evaporation (see Figure 3.7). ¹H NMR (400 MHz, CDCl₃): δ 8.79 (s, 1 H), 7.49 (t, 1 H), 7.40 (t, 1 H), 6.26 (d, 1 H), 6.21 (d, 1 H), 4.25 (t, 2 H), 3.95–3.81 (m, 2 H), 2.83 (br, 1 H), 2.74 (br, 1 H), 2.0–1.80 (m, 5 H), 1.51–1.25 (m, 4 H), 0.9 (t, 3 H).

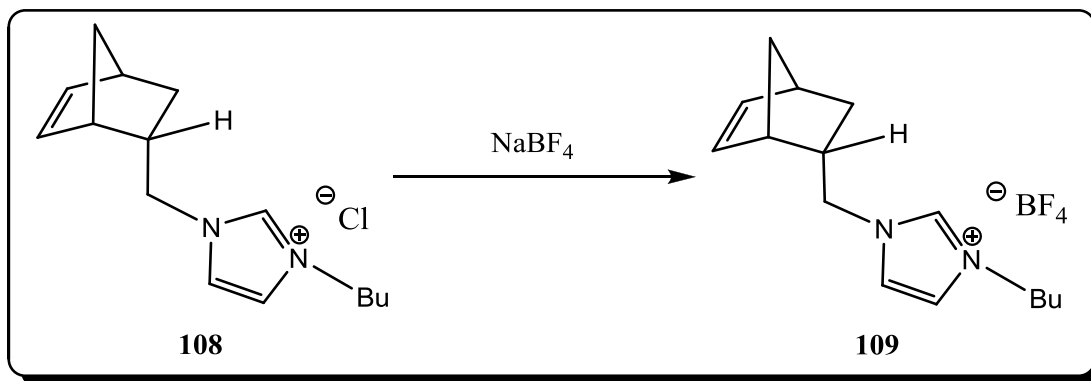


Figure 3.7 Preparation of 1-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-3-butyl-imidazolium tetrafluoroborate.

3.2.5 Synthesis of Imidazolium-Functionalized Polynorbornene. Under an atmosphere of dry nitrogen, Grubbs' 1st generation catalyst (20.0 mg, 2.44×10^{-5} mol), and compound **109** (2.9 g, 9.15×10^{-3} mol) were dissolved in CH_2Cl_2 (20 ml) (see Figure 3.8). Mixture was stirred at room temperature for 16 h. After completion of the reaction, the ROMP polymerization reaction was quenched by adding ethyl vinyl ether (3ml). The resulting imidazolium-functionalized polynorbornene **110** was isolated by removal of the solvent and other volatile compounds in vacuum.

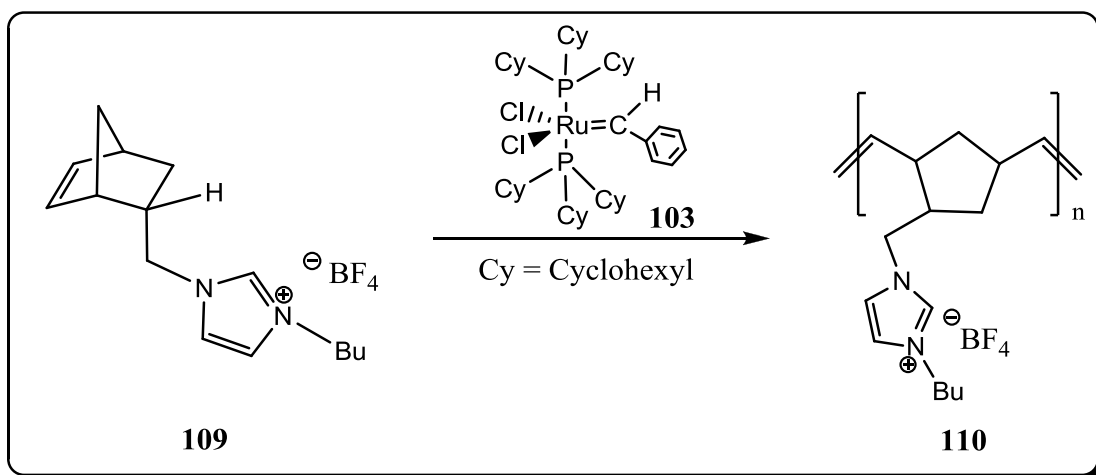


Figure 3.8 Preparation of imidazolium-functionalized polynorbornene.

3.3 RESULTS AND DISCUSSION

Norbornene-derived imidazolium ionic liquids were synthesized from commercially available dicyclopentadiene and 1-allyl chloride followed by quaternization of the imidazole moiety with 1-butyl chloride. Subsequent exchange of the imidazolium chloride by other anions such as BF_4^- yielded the desired compounds as yellowish viscous oil in high purity. Figure 3.9 shows dicyclopentadiene reversibly decomposes to 1,3-cyclopentadiene at 170°C .

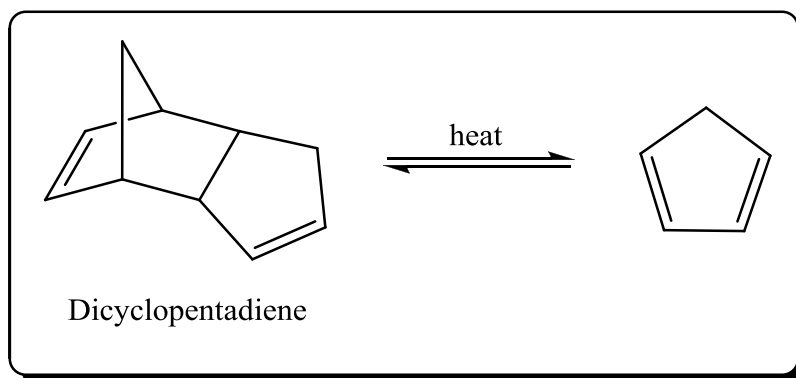


Figure 3.9 Dicyclopentadiene reversibly decomposes to 1,3-cyclopentadiene at 170°C .

The polymerizations were carried out at room temperature in methylene chloride solvent by the addition of a solution of the ruthenium-based initiator, 1st Grubbs catalyst, to monomer **109**. The ruthenium initiator was chosen because of its high tolerance to polar functional groups.³⁹ ¹H NMR spectra Compound **110** were obtained at 400 MHz using a Varian INOVA 400 MHz NMR spectrometer, and molecular weight of compound **110** was also obtained by MALDI-TOF. Unfortunately, oligomeric compound **110** was obtained instead of the expected high molecular weight polymer due to either low concentration of Grubbs' catalyst or due to its low reactivity. Similar phenomenon was reported by Yakov, S., and co-workers previous work.³⁹ The molecular mass of compound **110** was also determined by MALDI-TOF as 894. Use of second generation Grubbs' catalyst may solve these problems, and further modifications of the reaction conditions are in progress in laboratory.

3.4 CONCLUSION

Imidazolium-functionalized polynorbornene, compound **110**, was synthesized and analyzed by ¹H NMR spectra at 400 MHz using a Varian INOVA 400 MHz NMR spectrometer. Molecular weight of compound **110** was also measured by MALDI-TOF. Polymerization of 1-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-3-butyl-imidazolium tetrafluoroborate **109** was initiated with a solution of 1st generation Grubbs' catalyst. Disappointingly, oligomer (molecular weight 894) was formed. Polymerization of ILs is one of the important methods to prepare ion conductive polymer films. Further modification of the reaction conditions, e.g. change of solvents, reaction temperature, or 2nd generation Grubbs' catalyst, are currently in progress in our laboratory.

Application of the imidazolium salts and the polynorbornene based imidazolium salts for the preparation of carbon nanotubes (CNTs) and Ag nanowires are also in progress. Ionic liquids lower the CMCs of surfactants and our preliminary studies confirmed the convenient preparation of these nano materials in the presence of ILs.⁴⁰

¹H NMR spectra (400 MHz) of 1-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-3-butylimidazolium chloride, and 1-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-3-butylimidazolium tetrafluoroborate are shown in Figures 3.10 and 3.11.

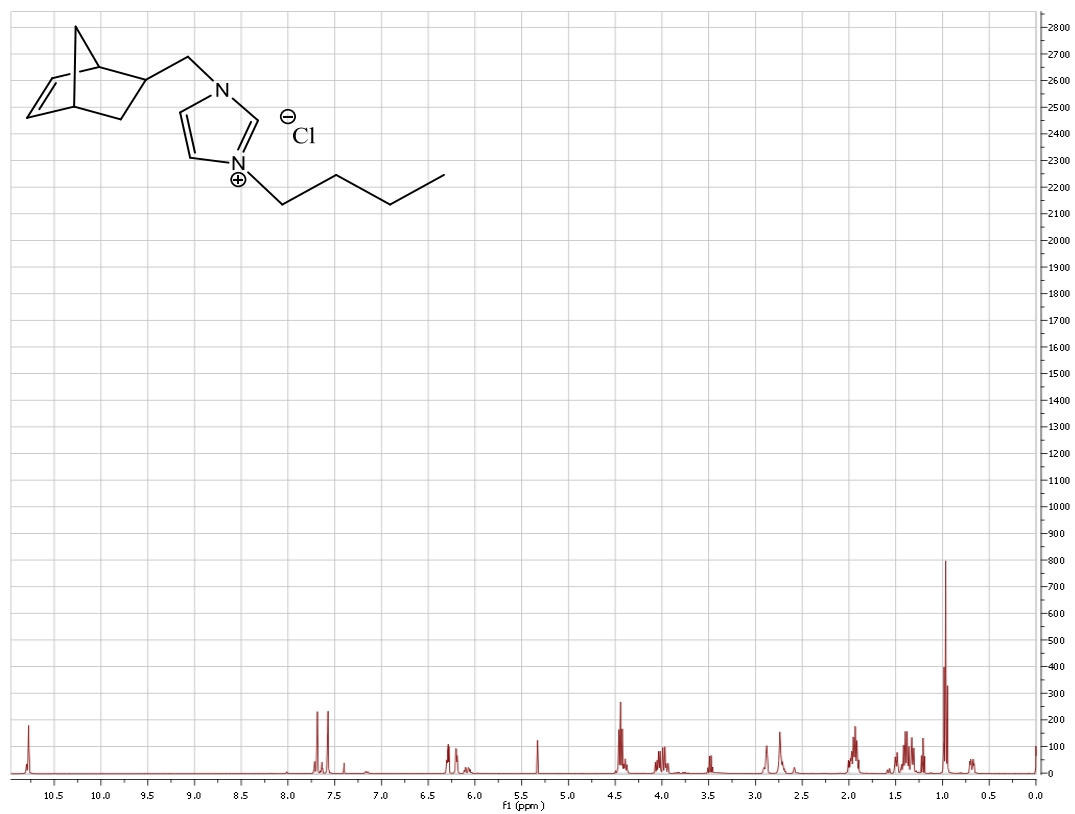


Figure 3.10 ¹H NMR spectrum (400 MHz) of 1-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-3-butylimidazolium chloride.

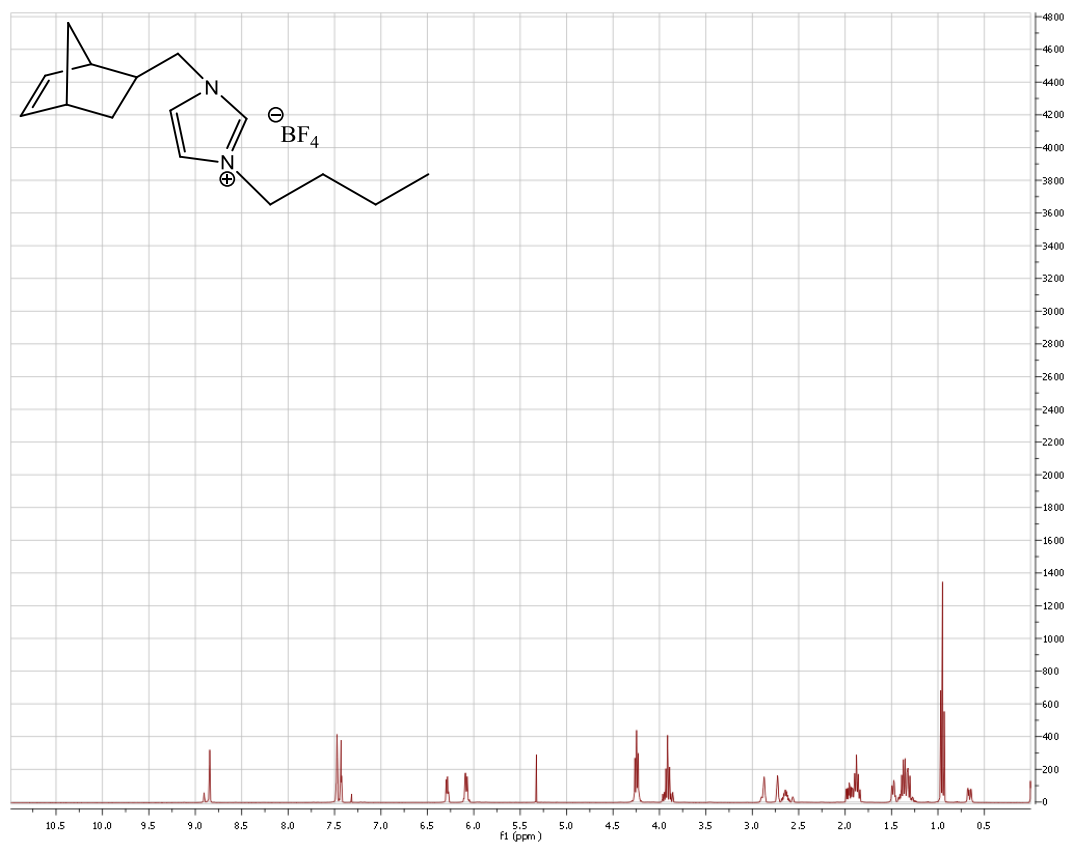


Figure 3.11 ¹H NMR spectrum (400 MHz) of 1-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-3-butylimidazolium tetrafluoroborate.

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VITA

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