Quantification of chlorine impurities in water immiscible ionic liquids using ICP-MS

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A Thesis submitted to the Chemistry Department and the Faculty of Graduate Studies in partial fulfillment of the requirements for a Master of Science degree in Applied Science

Aug 17, 2006

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Certification

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Abstract:

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A methodology for quantification of chloride in water immiscible ionic liquids has been developed using ICP-MS with organic accessory. Solvent mixtures using various ratios of organic solvent relative to water were studied for their ability to dissolve water immiscible ionic liquids and were used to examine the effect on detection limits. Two processes to reduce the content of chlorine in water immiscible ionic liquids were compared as was the effect of different synthetic routes for the same ionic liquid. The effect of instrumental parameters such as auxiliary gas, aspiration rate of sample, reflected power and forward power on system stability and signal enhancement were also examined. The quantitative relationship between the water content and halide content as well as other experimental issues will be discussed.

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List of Abbreviations

NTf$_2$	bis(trifluoromethylsulfonyl)imide
Mim	Methylimidazole
IC	Ion Chromatography
LOD	Limit of Detection
LOQ	Limit of Quantification
CV	Cyclic Voltammetry
LSV	Linear Sweep Voltammetry
SWV	Square Wave Voltammetry
CSV	Cathodic Stripping Voltammetry
Me	Methyl
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
RSD	Relative Standard Deviation
X	Halide
Co	Cobalt
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]
Et	Ethyl
Hmim	1-hexyl-3-methylimidazolium
[N(CN)$_2$]	Dicyanamide
C$_4$dmim	1-butyl-2,3-dimethyl-imidazolium
C$_4$Py	1-butyl pyridinium
OTf	Triflic
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
rf	radio frequency
FT-IR	Fourier Transform Infrared
LC	Liquid Chromatography
NMR	Nuclear Magnetic Resonance
ppm	Part-Per-Million
ppb	Part-Per-Billion
THF	Tetrahydrofuran
DMSO	Dimethyl sulfoxide

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1.0 Introduction

1.1 Ionic Liquids

1.1.1 Definition of Ionic liquids

The term "ionic liquid" refers to a compound that it is a liquid that consists only of ions. It is a type of salt that remains in the liquid state at room temperature and possesses properties which are different from typical metallic salts such as sodium chloride. Also, an ionic liquid is differentiated from the classical definition of a molten salt. [2] A molten salt is usually considered as high-melting, highly viscous and very corrosive medium, but an ionic liquid remains in the liquid state at low temperatures (usually ≤ 100 °C).

1.1.2 Development of ionic liquids

The first report of an ionic liquid in 1914 described the synthesis of ethylammonium nitrate that is liquid at room temperature but usually contains a small amount of water (200-600ppm).[1] In 1948, the first ionic liquids with chloroaluminate ions were developed by Hurley and Wier at Rice Institute in Texas. However, these systems were not studied further until the late 1970s when the groups of Osteryoung and Wilkes studied the synthesis of room-temperature liquid chloroaluminate melts.[4] The object of this research was focused on electroplating aluminum from bath solutions.[3] At the beginning of the 1980's, chloroaluminate melts were applied as non-aqueous polar solvents to study transition metal complexes by the groups of Seddon and Hussey, during which the initial research was focused on the

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electrochemical aspects of the related transition metal complexes. [5] This work was followed by spectroscopic and complex chemistry experiments. [6] Since then, ionic liquids have become more widely known to the broader scientific community. It was not until the end of the 1980's that the first reports about the study on which ionic liquids were described as new reaction media and catalysts for organic synthesis were published. These reports indicated that Lewis acidic ionic liquids with chloroaluminate ions are effective as Friedel-Crafts catalysts [7] and that phosphonium halide melts could be successfully applied in nucleophilic aromatic substitution reactions. [8] Chauvin et al [9] and Wilkes et al [10] first reported the role of ionic liquids in homogeneous catalysis in 1991. The extension of the concept of ionic liquids to more types of cationic and anionic species rather than only to chloroaluminate ions was contributed by the work of Wilke's group, who revealed that low melting tetrafluoroborate melts possess significantly enhanced stability against hydrolysis. These new systems widened the range of applications for ionic liquids especially for transitional metal catalysed reactions due to their higher tolerance of functional groups compared to chloroaluminate based ionic liquids. In 1992, ionic liquids research progressed greatly due to the efforts of Wilke's group, who illustrated the synthesis of ionic liquids with significantly improved stability against hydrolysis such as low melting tetraflouroborate melts. [11] Wilkes's work clearly showed that ionic liquids were by no means confined within chloroaluminate melts, but a whole range of cation/anion combinations can form low-melting salts.

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1.2 Ionic liquids synthesis

Quaternization of an amine or phosphine to form the cation [12, 13] is usually the

initial step in the synthesis of ionic liquids. Several typical component cations of ionic

liquids, are shown in Figure 1.1.

| Imidazolium ion | Pyridinlium ion | Ammonium ion | Phosphonium ion |
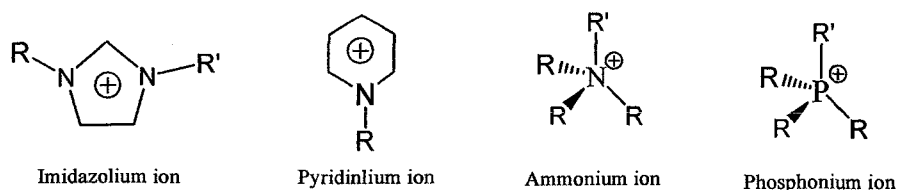
Figure 1.1. Common cations in ionic liquids

The different anions contained in these salts can be obtained through quaternization

reactions, depending on the nature of various alkylation reagents. It is interesting that

ionic liquids with melting points lower than 100°C can be obtained *via* direct

quanternization (Table 1.1).

Table 1.1. Examples of ionic liquids formed by direct quaternization

Ionic liquid	Alkylation reagent	M.p.[°C]
[Emim] CF_3SO_3 [a]	Methyl triflate	-9
[Bmim] CF_3SO_3 [b]	Methyl triflate	16
[Ph3POc]OTs[c]	OcOTs	70-71
[Bu3NMe]OTs	MeOTs	62
[Bmim]Cl	chlorobutane	65-69

[a] Emim= 1-ethyl-3-methylimidazolium; CF_3SO_3= triflate anion.
[b] Bmim= 1-butyl-3-methylimidazolium.
[c] Oc= octyl; Ts= $H_3CC_6H_4SO_2$ (tosyl)

Some anions can be formed by the direct quaterization reaction, while others need

extra steps to be synthesized (i.e. steps IIa or IIb in Figure 1.2.).

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$$NR_3$$

Step I

$$+ R'X$$

$$[R'R_3N]^+X^-$$

Step IIa

$$+ \text{Lewis acid } MX_y$$

Step IIb

1. + Metal salt $M^+[A]^-$

   − MX (precipitation)

2. + Bronsted acid $H^+ [A]^-$

   − HX (evaporation)

3. Ion exchange resin

$$[R'R_3N]^+[MX_{y+1}]^-$$

$$[R'R_3N]^+[A]^-$$
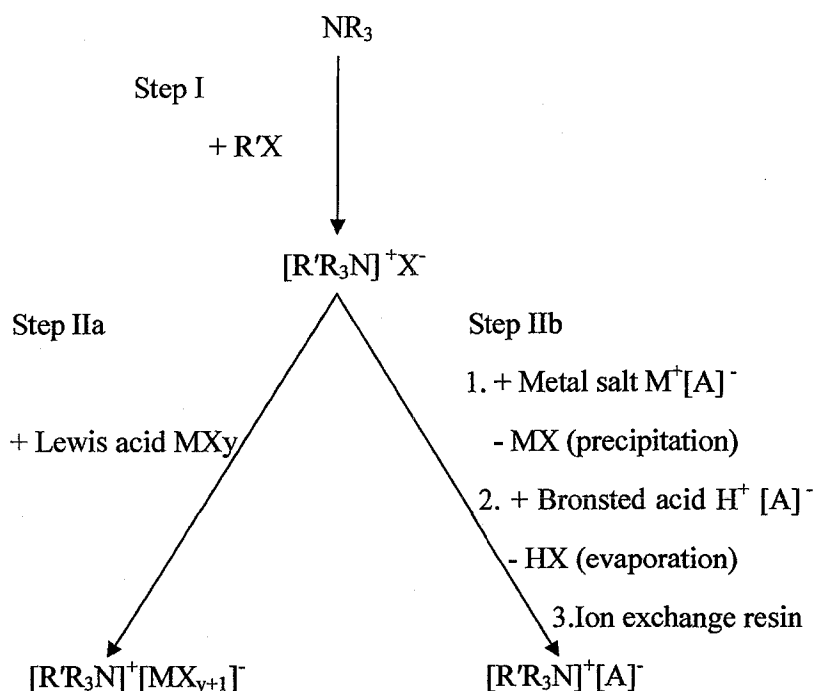
Figure 1.2. Synthesis paths for preparation of ionic liquids

As shown in Figure 1.2, the whole process of synthesis of amine based ionic liquids consists of two main steps. In Step I, the quanternization reaction of a selected amine, NR_3, with an alkyl halide, $R'X$, generates an ammonium halide, $[NR'R_3]^+X^-$, The desired anion of ionic liquid is obtained *via* the second step (IIa or IIb). As shown in Step IIa, an ammonium halide $[NR'R_3]^+X^-$ can undergo an addition reaction with Lewis acids MX_y to produce ionic liquids of type $[NR'R_3]^+ MX_{y+1}^-$, examples of which are shown in Table 1.2. In this case, reaction shown in Eq-1.1 is equilibrated by two components $[NR'R_3]^+X^-$ and MX_y.

$$[NR'R_3]^+X^- + MX_y. \longrightarrow [NR'R_3]^+ MX_{y+1}^- \quad \text{Eq-1.1}$$
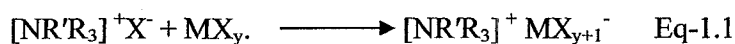
Chloroaluminate melts utilize the following synthetic route:

$$[NR'R_3]^+AlCl_4^- + AlCl_3 \longrightarrow [NR'R_3]^+ Al_2Cl_7^- \quad \text{Eq-1.2}$$
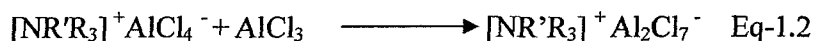
It has been reported [31] that the anionic species generated in this example vary with the

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ratio of chloride to $AlCl_3$. Different anionic species such as $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, can be obtained by selecting the specific mole ratio of Cl^- to $AlCl_3$. As shown in Step IIb in Figure 1.2, three alternative routes to synthesize ionic liquids adopt the same type of metathesis reaction. In the first case, an ammonium halide reacts with a metal salt and the liquid product is isolated by filtration of the precipitate. In the second case, an ammonium halide is treated with Brönsted acids containing the desired anion and the product is subjected to vacuum to remove hydrogen halide by-product. In the last case, an anion exchange resin is used to exchange the anion of ammonium halide with the anion of choice. The properties of ionic liquids can be tuned by varying the types of cations and anions.

Table 1.2. Ionic liquids that can be generated by reaction of a halide salt and a Lewis acid

Ionic liquids[a]	Established anion
[cation]Cl/AlCl$_3$	Cl-, AlCl$_4$-, Al$_2$Cl$_7$-, Al$_3$Cl$_{10}$-
[cation]Cl/AlEtCl$_2$	AlEtCl$_3$-, Al$_2$Et$_2$Cl$_5$-
[cation]Cl/BCl$_3$	Cl-, BCl$_4$-
[cation]Cl/CuCl	CuCl$_2$-, CuCl$_3$-, Cu$_3$Cl$_4$-
[cation]Cl/SnCl$_2$	SnCl$_3$-, Sn$_2$Cl$_5$-

[a] = cation, pyridinlium, imidazolium ion
(This table is adapted from Peter Wasserscheid Wilhelm Keim Angew. Chem. Int. Ed. 2000, 39, 3772)

This thesis will focus on the synthesis of water immiscible ionic liquids. There are a number of papers that describe the synthesis of this type of ionic liquid. [33, 31, 88]

1.3. Applications of ionic liquids

The special chemical structures of ionic liquids provide some unique physical properties, especially where ionic liquids are used as solvents for synthesis. These

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attractive properties include: 1) dissolve a wide variety of solutes; 2) generally highly polar but non- or poorly- coordinating; 3) immiscibility with some organic solvent and/or water hence allowing biphasic applications; 4) low melting points; and 5) lack of volatility at room temperature.

These characteristics of ionic liquids enhance their potential applications in a wide range of chemical reactions. The quality of a synthetic path is not only determined by whether the desired product can be produced, but also whether high selectivity and high yield can be obtained. To understand the importance of ionic liquids to chemical industry deeply, it is necessary to know about their applications in the following classical chemical reactions:

1.3.1 Diels-Alder reaction:

The Diels-Alder reaction has been studied for a long time for its utility in cycloaddition reactions[14] such as is shown in Figure 1.3.
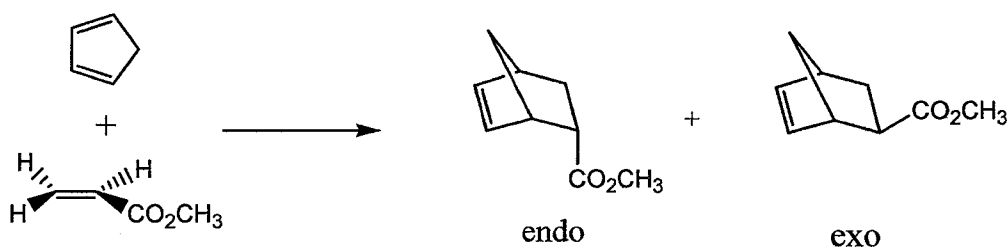
Figure 1.3. Diels-Alder cycloaddition of cyclopentadiene and methyl acrylate

In this type of reaction, a mixture of exo and endo products is produced. It is well known that the endo/exo selectivity is determined by the polarity of solvent. More polar solvents result in higher exo vs. endo selectivity in the products. Compared with water, the ionic liquid has the advantage in the application of the moisture-sensitive

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reagents.

For Diels-Alder reactions, a series of ionic liquids that have been applied and have shown that the reactions prefer for the *endo* productcompared with nonpolar organic solvents include: $[EtNH_3][NO_3]$,[15] $[Emim][BF_4]$, $[Emim][ClO_4]$, $[Emim][CF_3SO_3]$, $[Emim][NO_3]$, and $Emim][PF_6]$.[16]

1.3.2 Alkylation of Sodium β-Naphthoxide

Ionic liquids based on phosphonium and ammonium halides as solvents involved in the reaction of C vs O alkylation of sodium 2-naphthoxide have been studied to compare their performances on regio- selectivity of C vs O alkylation with respect to conventional solvents.[17] The study showed that it is much more likely to produce the O-alkylation product than C-alkylation in dipolar aprotic solvents. Hence, a series of aprotic ionic liquids such as n-Bu$_4$PBr, n-Bu$_4$NBr, [Emim]Br, and n-Bu$_4$PCl as solvents can lead to the high regioselectivity of the O-alkylation product in every case (between 93% and 97%). Other research indicated that indole showed almost exclusive N-alkylation in the same solvent conditions as mentioned above.[18]

1.3.3 Hydrogenation reactions

The hydrogenation reaction of C=C bonds catalyzed by transition-metal complexes has been widely studied. A lot of research effort searching for good solvents that could serve as media in this reaction demonstrated that some ionic liquids can increase the reaction rate and yield. It was found that the hydrogenation

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rate proceeds much faster in ionic liquids containing [SbF$_6$]⁻ or [PF$_6$]⁻ than in acetone with the same catalysts. This increase in rate has been attributed to catalyst stability when dissolved in the ionic liquids. [19]

Rh catalyzed hydrogenation of cyclohexene [20] showed that the use of [Rh(cod)$_2$] [BF$_4$] (where cod =cyclooctadiene) as catalyst and [BF$_4$] based ionic liquids can result in higher overall conversion of cyclohexene to cyclohexane than can the use of RhCl(PPh$_3$)$_3$. It should be highlighted that [Rh(cod)$_2$][BF$_4$] has greater solubility in the ionic liquid than does RhCl(PPh$_3$)$_3$.

1,3-butadiene can be reduced to produce a mixture of but-1-ene, but-2-enes, and n-butane. [21] By dissolving a Co catalyst in [Bmim]+ containing ionic liquids to form complex of [Bmim]$_3$[Co(CN)$_5$], it is possible for hydrogenation of 1,3-butadiene to achieve 100% selectivity to but-1-ene. In addition, the chiral catalyst [RuCl$_2$-(S)-BINAP]$_2$NEt$_3$ dissolved in the ionic liquids has been used to asymmetrically hydrogenate 2-phenylacrylic acid and 2-(6-methoxy- 2-naphthyl) acrylic acid [22] (Figure 1.4).
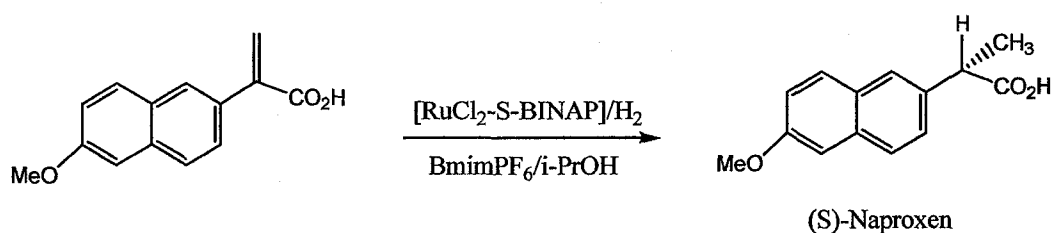
Figure1.4. Formation of (s)-naproxen in a [Bmim][BF$_4$] ionic liquid

1.3.4 Dimerization of butadiene

The hydrodimerization of butadiene can lead to octa-2,7-dien-1-ol as the major

product and 1,3,6- octatriene as the minor product [23] in a of mixture of palladium

dichloride, acetate, and acetylacetonate dissolved in the [Bmim][BF4] or [Bmim][PF6]

ionic liquids. Interestingly, this system containing ionic liquids can work efficiently

without aid of CO_2. However, the addition of CO_2 into the reaction mixture is

necessary, if the solvents are replaced by conventional molecular solvents.

1.3.5 Heck reaction

The reaction of bromobenzene with *n*-butyl acrylate catalyzed by

dichlorobis(triphenylphosphine) palladium(II) and palladium(II) acetate formed by

palladium complex with ionic liquids of phosphonium salts in the presence of

triethylamine at 100 °C result in *trans*-cinnamic *n*-butyl ester in good yields; 5% of the

cis-isomer can be synthesized if sodium acetate is added to the reaction mixture [24]

(Figure 1.5.). This catalyst system can produce high conversation levels and the

palladium(II) catalysts could be reused in this system after the reaction without loss of

catalytic activity for at least two further runs.

Where R=H, OCH3, NO2 and X=Br, Cl
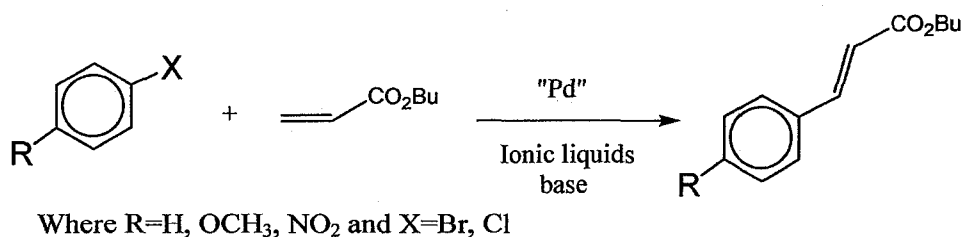
Figure 1.5. Heck coupling reactions in tetraalkylammonium and phosphonium
bromide salts

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1.3.6 Oxidization reaction

The application of ionic liquids in selective oxidation reactions were published by Song and Roh [25] In their investigation of the epoxidation of, for example, 2,2-dimethylchlomene with chiral $Mn^{III}(salen)$ complex ([N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclo-hexane-diamine] manganese(III) chloride) in a solvent mixture of [Bmim] PF_6 and CH_2Cl_2 (1:4 v/v) (Figure 1.6), it is shown that an 86% conversion of 2,2-dimethlychromene was obtained after 2 hours. But without the ionic liquids under the same conditions the same conversion was observed after 6h.

yield: 86%, ee: 96%
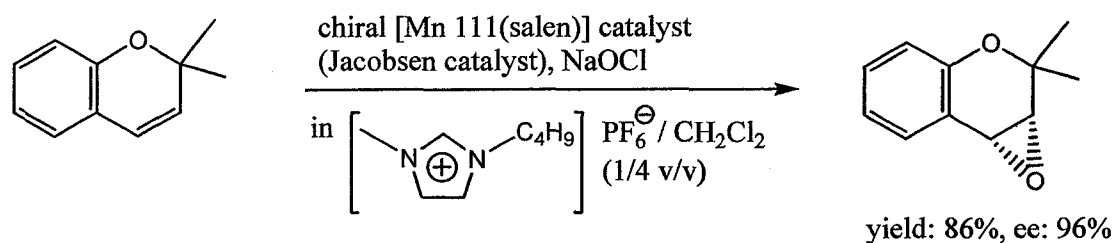
Figure 1.6. Epoxidation of, for example, 2,2-dimethylchlomene with chiral $Mn^{III}(salen)$ complex

1.3.7 Catalyst recycling and product separation.

As mentioned previously, the properties of ionic liquids such as nonvolatility at room temperature and wide range of solvent properties endow ionic liquids with good performance on aspects of environmental protection such as limiting air pollution, reusing the catalysts, separation of products from reaction mixtures easily and facilitating purification of products. The following five examples of chemical reactions explain these concepts explicitly.

In the alkylation of sodium β-naphthoxide, characterization by ^1H and ^{31}P NMR

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indicated that the ionic liquids remained unchangeable by the reaction and could be recycled to achieve the same results.[17]

The highly efficient catalyst performance in hydrogenation reactions was attributed to the homogeneous catalysis system, but the poor separation of catalyst complex from reaction solution has been problematic for a long time until the discovery of new application of ionic liquids as solvent. For example, ionic liquids were found to be capable of extracting the catalyst of [Rh(nbd)PPh$_3$][PF$_6$] (nbd =norbornadiene) from the substrate. [27]

Butadiene can undergo hydrodimerization smoothly and efficiently with the catalyst of mixture of palladium dichloride, acetate, and acetylacetonate, all of which were dissolved in the [Bmim][BF$_4$] or [Bmim][PF$_6$] ionic liquids to become homogenous solutions at 70 °C, but the product can be isolated easily after the reaction media cools down to 5 °C. [28]

Regarding the Heck reaction, the product could be obtained from the solution mixture by means of distillation because of nonvolatile property of the catalysts complex formed by catalyst dissolved in ionic liquids. [29]

In the epoxidation of 2,2-dimethylchromene with a chiral MnIII(salen) complex in the mixture of [Bmim]PF$_6$ and CH$_2$Cl$_2$ (1:4 v/v), [25] ionic liquids can facilitate catalyst recycling without special modification of catalyst, with only a simple wash of the organic phase with water and then by extraction of the product with hexane.

These examples mentioned above point out the valuable applications of ionic liquids in the process of separation and purification, intending to make great

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contributions in the development of "Green Chemistry".

1.4 Halide ions in ionic liquids

1.4.1 Sources of halide ions in ionic liquids

As mentioned earlier one of the specific approaches to the synthesis of ionic

liquids is the methathesis of an quarternary ammonium halide with a metal salt or a

Brönsted acid, both of which may contain the desired anionic group. In these

synthetic routes, halogen ions cannot be removed completely from the final salt

product. Halide containing by-product, such as halide salts, can normally be removed

via precipitation or the halide acid can be eliminated under vacuum. In the preparation

of water immiscible ionic liquids, water is most frequently used as a reaction medium.

Although some ionic liquids become immiscible with water, there remains trace water

in the ionic liquids. It is this trace water that might be responsible for *"trapping"* the

halide ions in ionic liquids. It was reported [30] that BmimBF$_4$ and HmimBF$_4$ are better

alternative solvents than EmimBF$_4$, because EmimBF$_4$ is more difficult to purify than

BmimBF$_4$ (especially in the process of removing halide impurities). BmimBF$_4$ and

HmimBF$_4$ have longer alkyl chains on the imidazole ring than EmimBF$_4$, so they are

less hydrophilic (and more hydrophobic) than EmimBF$_4$. This higher hydrophilic

property leads to a lower amount of water content, resulting in lower amount of halide

ion content. This assumption is supported by the result of the previous research by

Singer *et al.* [32] In this report, it was found that the "wet" reagent grade acetone used in

the synthesis of BmimBF$_4$ increased the residual chloride content in the final product.

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1.4.2 Halide ion effects on ionic liquids

Since many applications of ionic liquids in chemical reactions have been reported, their chemical and physical properties have been increasingly more studied to disclose their role in reaction mechanisms and new applications. The results of this research show that the halide ion and water remaining in the ionic liquids may jeopardize their performance in these applications. The following examples show how halogen ions and water impurities limit the applications of ionic liquids.

Halide ions impurities in ionic liquids cause discrepancies in melting points and increases of viscosity. Ionic liquids have low melting points, in part, because of their non-symmetric cations. Their non-symmetric structure make it difficult to form crystals, therefore they are liquids at room temperature compared with similar metallic salts. [31] Constant melting points of ionic liquids are crucial for the selection of ionic liquids in specific reaction systems. However, the impurities such as halogen ions and water impurities, even present in trace amounts, account for discrepancies observed in literature melting points. [32]

Many papers have reported [26, 27, 31] that the viscosity of ionic liquids is higher than that of traditional organic solvents. It has been suggested that the comparatively high viscosity is caused by the longer alkyl substituents on the imidazolium ring. Hence, this property can be controlled within a certain tolerance. However, chloride impurity can also increase the viscosity of ionic liquids. For example, the viscosity of [Bmim][BF$_4$] that is 0.01 molal (denoted as the number of moles of a given substance per kilogram of solvent) Cl$^-$ can be increased to 47 mPa s^{-1} (this unit means 1 N·s/m^2

by increasing to 0.5 molal Cl⁻). [28, 31] The melting point of BmimCl is 70°C. Increases of viscosities of this magnitude will critically lower the efficiency of mass transfer and increase the energy requirements for mixing in liquid reaction systems. This effect of chloride ions on viscosity might be attributed to an increase in van der Waals forces relative to hydrogen bonding.[29] The viscosity of ionic liquids such as $BmimPF_6$ is also dependent on water content. The viscosity of dry ionic liquids is much higher than that of ionic liquids saturated with water.[31] Therefore, when the ionic liquids are washed by water, the lower viscosity can facilitate the chloride ions migrating from $BmimPF_6$ to water. However, if ionic liquids are dried under vacuum, the viscosities increase as the water is removed from $BmimPF_6$.

It has been demonstrated that halide ion impurities could diminish the thermal stability of ionic liquids. One of reasons why the ionic liquids are referred to as "green" solvents is because they have high thermal stability.[33, 34, 35, 36, 37] For example, [Bmim][BF_4] and BMIM bis(triflate)amide were reported to start to decompose at 300°C and 400°C. [33, 36] The nature of both ions play a critically role in the thermal stability of ionic liquid. For example, imidazolium salts are more stable than tetralkyl ammonium salts and the relative order of decreasing anion stabilities is: [33] BF_4^- and bis(triflate)amide⁻ > tris(triflate)methyl⁻, PF_6^- and AsF_6^- > I⁻, Br⁻ and Cl⁻. Recently, studies showed that the chloride ions residual in the ionic liquids decrease thermal stability of ionic liquids. [33] Therefore, the ionic liquids with a trace amount of chlorine ions have potential to decompose during some stage of reaction or drying under heating process.

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Halide ions can also poison catalysts. It is well known that the effectiveness of transition-metal catalysis is determined by the active metal center. During the reaction involving metal catalysis, the reaction of the metal center in the catalyst with starting materials generates intermediates with lower free energy than that of intermediate without the aid of the catalyst. This is usually a rate-determine step in a multiple-step reaction. Hence, the reaction may not go smoothly, or even not occur, without the active metal center. Some catalytic processes can be limited by chloride impurities that deactivate the metal center of a catalyst through coordination of the chloride ion with the metal center of the catalyst. For example, in the reaction of Ir(I)-catalyzed hydrogen isotope exchange labeling of substrate [38] ionic liquids, such as BmimPF$_6$, as a solvent, become ideal alternative to dichloromethane that limits dissolution of substrate molecules. This reaction was found to yield more efficient deuterium and tritium exchange of N-(4-methoxyphenyl)-N-methyl benzamide (Figure 1.7) under standard conditions in BmimPF$_6$ than that in dichloromethane. Surprisingly, the water miscible ionic liquids BmimBF$_4$ failed to mediate this catalytic exchange. Since BmimBF$_4$ is more difficult to purify than is BmimPF$_6$, the presence of trace amount of highly coordinative chloride ions might be responsible for deactivation of the Crabtree catalyst by irreversibly binding to the iridium metal center.
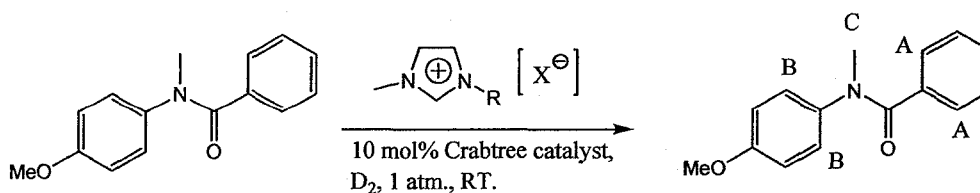
Figure 1.7. One step deuteration of N-(4-methoxyphenyl)-N-methyl benzamide

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Halide ions may narrow the electrochemical window of ionic liquids. The electrochemical window, denoting electrochemical stability, is determined by cyclovoltammetry (CV). [39] The wider the electrochemical window an electrolyte has, the more stable it is against oxidation or reduction processes. Ionic liquids can be applied as electrolytes in electrochemical applications due to their attractive performance on dissolving a broad range of chemical substances and general lack of volatility. However, chloride ions can narrow the electrochemical window of ionic liquids. In this sense, chloride ions can be oxidized easier rather than other anions such as fluoride, leading to significantly lower electrochemical stabilities of ionic liquids in the process of electrochemical reactions. In addition, these chloride ion impurities can interfere with the metal deposition process.

1.5 The purpose of this project:

As mentioned above, halogen ions can not be eliminated from ionic liquids completely and may cause a lot of problems during their application as solvents. Therefore, chemists continue to search for alternative syntheses or other methods to reduce the amount of halogen ions remaining in the ionic liquids. Before the strategy to reduce the amount of residual chloride ions is found, it is necessary to develop a method to quantify its amount. So this project is intended to develop a method for quantification of very low levels of halogen ions, specifically chlorine, in ionic liquids.

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1.5.1 Previous work

Singer *et al*, [32] succeeded in quantification of chlorine in BmimBF$_4$, a water soluble ionic liquid, by means of ICP-MS. Five different reaction conditions were studied to find which resulted in the least amount of chlorine in final product. These five reaction conditions are shown in Figure 1.8.
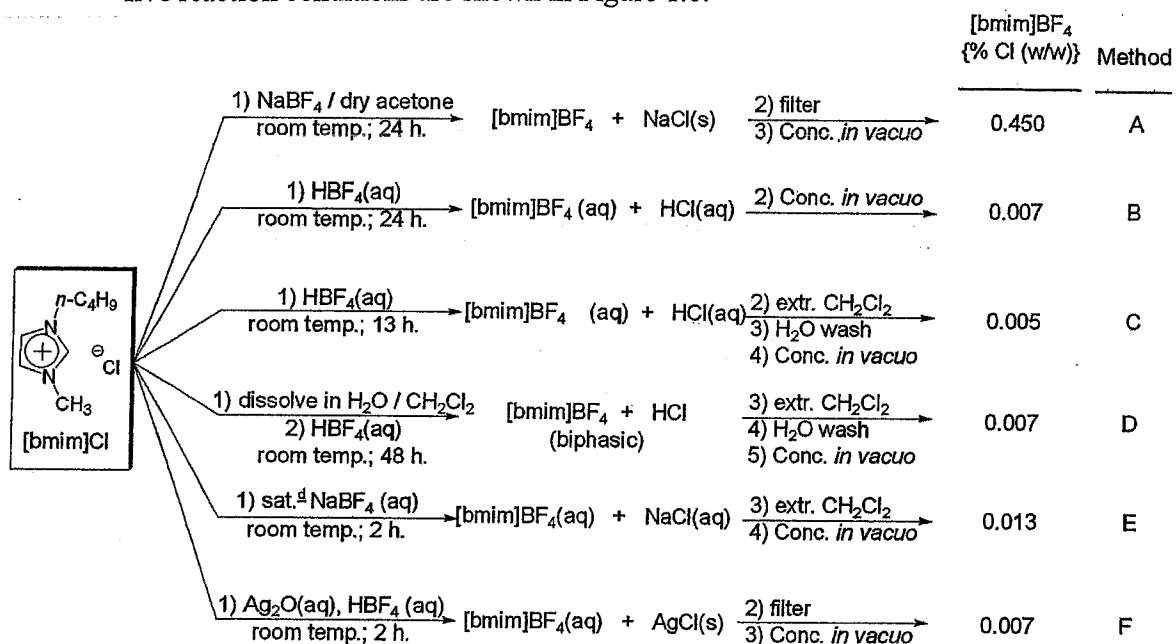
Figure 1.8. Methods for the preparation of 1-butyl-3-methylimidazolium tetrafluoroborate, Reproduced with permission from Dr. Robert Singer

Based on the data presented in this study, it is clearly indicated that the lowest amount of residual chlorine content can be obtained *via* a metathesis reaction between [Bmim]Cl and HBF$_4$(aq) in which the by-product of HCl can be removed under vacuum. Chlorine is efficiently minimized via the reaction F, in which a highly insoluble AgCl(s) precipitate was formed and could be efficiently removed from the reaction mixture *via* straight forward filtration through a celite bed. The ^{35}Cl isotope was selected for analysis using ICP-MS rather than the ^{37}Cl isotope that experiences interference by the polyatomic ion ^{36}Ar^{1}H. During the course of reproducibility studies

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of the results, it was found that the use of "wet" acetone in the metathesis reaction between [Bmim]Cl and NaBF$_4$ resulted in consistently high residual chlorine content. It was suspected from these observations shown in Figure 1.8 that the solubility of NaCl(s) in [Bmim]BF$_4$ itself may be responsible for, at least in part, the high residual chlorine content in those methods in which NaCl is a by-product. This report showed that the ICP-MS method of analysis is easily applied to any water soluble ionic liquid. However, the difficulties in getting reliable results were encountered when the water insoluble ionic liquids were analyzed using ICP-MS.

1.5.2 Current work.

In this project, the main purpose is quantitative analysis of halogens residual in water immiscible ionic liquids, BmimPF$_6$, Bmim[NTf$_2$], Bmim[N(CN)$_2$]. This analysis will be performed using ICP-MS equipped with an oxygen gas delivery system connected to the Ar nebulizer gas supply.

1.6 Previous relevant research

To date research of ionic liquids has been focused mainly on reactions conducted using them as solvents and the physical characterization of ionic liquids themselves. However, there are not many publications concerning the purity of the ionic liquids. Although the negative impacts of halide impurities on the usefulness of ionic liquids has been generally known, few methods on quantification of halogen ions and other impurities in ionic liquids have been reported. These methods include Singer *et al* [32]

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ICP-MS, Holbrey *et al* [40] colorimetric method, Constanza Villagra'n *et al* ion chromatography (IC), [41] Compton *et al* electroanalytical, [42] and use of a chloride - selective electrode. [43]

1.6.1 Holbrey *et al* colorimetric method

Holbrey *et al* developed a simple colorimetric method to monitor the end-point of the alkylation reaction and determine the levels of unreacted 1-methylimidazole contamination. This was based on the complexation of 1-methylimidazole with copper(II) chloride in ethanol to form the $[Cu(Mim)_4]^{2+}$ ion that has an intense blue color, while the interaction of copper(II) chloride with [Emim]Cl in ethanolic solution gives a yellow solution in the absence of 1-methylimidazole. This spectral shift with different amount of Mim residue allows a colorimetric determination based on the position of λ_{max} of the absorption band in the electronic absorption spectrum.

1.6.2 Constanza, Villagra'n *et al* ion chromatography (IC)

Constanza, Villagra'n *et al*, published a paper on quantification of halogen ions in ionic liquids using IC. [32]

To examine the cation effect on the detection of chloride ion in ionic liquids, four types of chloride salts with different cations containing 0.4 ppm chloride were measured. The chloride salts [C$_4$dmim]Cl, [C$_4$Py]Cl, [Bmim]Cl and choline chloride were compared with an aqueous solution containing 5.1 ppm NaCl. These salts were adopted to compare their individual chloride retention time. The results showed that

the relative standard deviations (RSD) of the chloride retention time for these four compounds were determined as 0.3, reflecting an acceptable cation effect on chloride retention among these four compounds.

In this paper, different anions, such as carbonate dip from the eluent, anion of ionic liquids and fluoride from the hydrolysis of fluorinated anions of ionic liquids interfered with chloride on the ion chromatogram. This interfered peak could be resolved by selecting appropriate eluent of the mixture of 3.2 mM Na_2CO_3 with 1.0mM $NaHCO_3$ and by regulating flow rate at 1mL/min during first 10 min followed by raising flow rate to 1.6 mL/min.

In the examination of matrix effects on chloride retention, the chloride ions in sodium chloride were added into water and chloride free [Emim][EtSO$_4$] that was prepared by direct alkylation of 1-methylimidazole with diethyl sulfate. The water and [Emim][EtSO$_4$] solutions with a known added concentration of sodium chloride were analyzed with IC and checked for the recoveries of chloride ions. The results showed that the recoveries were within the acceptable limit. The method of IC can offer limit of detection (LOD) for chloride at 10ppb.

There are still some disadvantages on the IC application for quantification of chloride in ionic liquids. Although the problems associated with interference of high concentration of other anion, such as [PF$_6$] anion and [NTf$_2$] anion, can be relieved by using pre-concentration columns to make these ions retained on the column to remove these ions from sample before analysis, operation using this method become still time consuming. For example, the [PF$_6$] anion takes 2 hours to begin to elute, while [NTf$_2$]

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anion does not elute.

1.6.3 Compton *et al* electroanalytical

Compton *et al.* [42] determined chloride ion impurities in BmimBF$_4$, Bmim[NTf$_2$] and BmimPF$_6$ ionic liquids using electro analytical methods including Linear Sweep Voltammetry (LSV), Square Wave Voltammetry (SWV), and Cathodic Stripping Voltammetry(CSV). In this report, the LOD and LOQ between these three methods were explored and compared to each other, which are shown in Table 1.3.

Table 1.3. Comparison of LOD and LOQ for BmimBF$_4$, Bmim [NTf$_2$], and BmimPF$_6$ using the LSV, SWV and CSV [48]

Methods / LOQ and LOD / Ionic Liquids	LSV		SWV		CSV	
	LOD/ppm	LOQ/ppm	LOD/ppm	LOQ/ppm	LOD/ppm	LOQ/ppm
BmimBF$_4$	3.50	14.50	2.70	6.20	0.16	0.31
Bmim[NTf$_2$]	4.20	25.60	4.30	6.80	0.09	0.30
BmimPF$_6$	7.20	28.60	9.30	28.60	0.16	0.25

The voltammagram obtained from CV is one full cycle. For reversible reaction, the concentration of analyte (here is referred to chlorine ions) is related to peak current (i_p) based on the Randles-Sevcik [45] expression at Eq-1.3 [48]

$$i_p = 2.686 \times 10^5 \, n^{3/2} A c_0 D^{1/2} v^{1/2} \qquad \text{Eq-1.3}$$

where i_p is the peak current in amps, A is the electrode area (cm^2), D is the diffusion coefficient (cm^2 s^{-1}), c_0 is the concentration in mol cm^{-3}, and v is the scan rate in V s^{-1}, n is the number of electrons transferred.

The fact that LOD and LOQ value of BmimPF$_6$ are higher using SWV than using LSV could be attributed partly to the higher viscosity of BmimPF$_6$. The application of

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LSV proved most sensitive in chloride detection of all three methods. It was described that the operation of CSV experiences two steps. The first step is to concentrate analytes species; the second step is to measure pre-concentrated analytes by the means of a potential scan. These electroanalytic methods have the common limitation such as offering very little or no information on identities of the species, and requiring that substance must be oxidizable or reducible in the range and the solvent and electrode are electrochemically inert.[48]

1.6.4 Chloride ion-selective electrode [41],[43]

A chloride ion-selective electrode is selective and more sensitive to the relevant ion than to foreign species. The concentration of chloride ion can be determined based on the Nernst equation Eq-1.4:

$$E = E_o + (RT) / (zF) \ln a_x \qquad \text{Eq-1.4}$$

$$a_x = f_x * c_x$$

where E is electrode potential of the half-cell, E_o is standard electrode potential for the half-cell (a=1), R is gas constant, T is absolute temperature, F is Faraday's constant, z is charge number of the ionic species, and a_x=the activity of the ion species X

Seddon et al. [41] measured the chloride content of ionic liquids containing the [Bmim] cation using a chloride-selective electrode. They found an effect of the type of cation on the intercept and the slope of the calibration curve for analysis of chloride ion. This effect was attributed to the different polarities of the various ionic liquids studied and to the cation-dependent degree of hydrogen bonding.

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1.7 ICP-MS

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) combines the two advantages of the rapid multielement capabilities of ICP-OES and the superb detection limits of GFAA to become the best option for trace element analysis. Only modern ICP-OES with 2D solid state detector (such as CCD or CID detector have rapid multi-element detection capabilities and ICP-MS LODs is not equal to those of GFAAS but rather exceeds the LOD of GFAAS for most elements. In the following introduction to this analytical tachnique, the features and basic principles of ICP-MS will be presented. ICP-MS consists of a nebulizer, spray chamber, plasma torch, interface, quardrupole mass analyzer and detector.

1.7.1 Fundamental Principle of ICP-MS

The following sections will provide a brief description of the fundamental and operating principles of ICP-MS and its various instrumental components. A more detailed description of ICP-MS and its components can be found in Reference No. 49 to 55. Proper operation of ICP-MS requires that the sample, which must be in a liquid form (i.e. in aqueous solution), be pumped into a nebulizer, where sample is turned into a fine aerosol with argon gas. The fine droplets of the aerosol, which are separated from larger droplets using a spray chamber, are evacuated from the exit tube of the spray chamber and are delivered into the plasma torch through a sample injector. In the plasma torch, the sample droplets experience drying, vaporization, atomization, and ionization as they travel through the different heating zones. The heat is generated

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via collision between argon ions under an intense magnetic field produced by radio frequency [rf] generator. Once the ions are produced in the plasma, they are directed into the quadrupole mass separation device *via* the interface region and through ion optics, in which photons formed in plasma torch are eliminated. Only ions of a selected mass are allowed to pass through the quadrupole mass separation device, while the others are ejected from the quadrupole. Finally, the sample ions hit the detector to generate a signal, establishing plot of signal counts to standard concentration of sample.

1.7.2 The sample introduction system

The application of ICP-MS typically involves the analysis of liquid samples. The basic components of this system compromise nebulizer and spray chamber. The former fulfills the task of aerosol generation and the latter performs droplet selection.[50]

In the nebulizer, the sample is normally pumped at about 1 mL/min *via* a peristaltic pump into the spray chamber, ensuring a constant flow of liquid, irrespective of differences in viscosity between samples, standards, and blanks.

After the sample enters the spray chamber as shown in Figure 1.9, it is broken up into a fine aerosol by the pneumatic action of gas flow (~1 L/min) that smashes the liquid into tiny droplets. The problem that the plasma discharge is inefficient at dissociating large droplets can be solved by the spray chamber, whose primary function is to allow only the small droplets (~5–10 μm in diameter) to enter the

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μm in diameter) fall out by gravity and exit through the drain tube at the end of the spray chamber. Its secondary purpose is to smooth out pulses that occur during the nebulization process, due mainly to the peristaltic pump. In this process, the aerosol droplets emerge from the nebulizer and are directed into a central tube from the bottom of the chamber. While traveling the length of this tube, the large droplets (greater than ~10 μm in diameter) fall out by gravity and exit through the drain tube at the end of the spray chamber. Finally the fine droplets (~5–10 μm in diameter) pass between the outer wall and the central tube and eventually emerge from the spray chamber and are transported into the sample injector of the plasma torch. In addition, some spray chambers are externally cooled to 2–5 °C in order to minimize the amount of solvent going into the plasma and reduce the generation of oxide species, otherwise the leakage of these impurities would result in great matrix noise.

1.7.3 The plasma source

A plasma discharge is formed in the plasma torch and is used to convert the sample aerosol into a stream of positively charged ions. The components within the plasma source include a plasma torch, a radio frequency (rf) coil, and rf power supply. [51] Three tubes including the outer tube, middle tube and sample injector, are assembled into a plasma torch. The gas (usually argon), passing between the outer and middle tubes at a flow rate of 12–17 L/min, is used to form the plasma (plasma gas) and the auxiliary gas flowing between the middle tube and the sample injector at 1 L/min is to change the position of the base of the plasma relative to the tube and the injector. The nebulizer gas carrying the sample at 1 L/min from the sample introduction system goes through sample injector and then into the electromagnetic field generated by rf oscillation of the current in the coils, when the rf power (typically 750-1500W) is applied to the coils. Under this intense electromagnetic field, the ions of argon, electrons of which are stripped away from their atom as the argon gas is subject to a high-voltage spark, collide with each other. This collision breaks down the gas into argon atoms, atom ions and electrons in a chain reaction and is known as the inductively coupled plasma. This effect can produce a temperature zone at more than 6000 °C in the plasma. The sample experiences the various stages from desolvation to ionization into positively singly charged ions, which is illustrated in Figure 1.10. Usually, the sample can be ionized into positively charged ions at temperature of 6000°C -- 6800°C. Higher temperatures than that would result in excessively oxidized species (i.e. multiple charged species), while lower temperatures

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would lead to inefficient ionization.

Droplet	Solid	Gas	Atom	Ion
$M(H_2O)^+X^-$ $\xrightarrow{\text{(Desolvation)}}$ $(MX)n$ $\xrightarrow{\text{(Vaporization)}}$ MX $\xrightarrow{\text{(Atomization)}}$ M $\xrightarrow{\text{(Ionization)}}$ M^+				
From sample injector $\xrightarrow{\hspace{5cm}}$ To mass spectrometer				
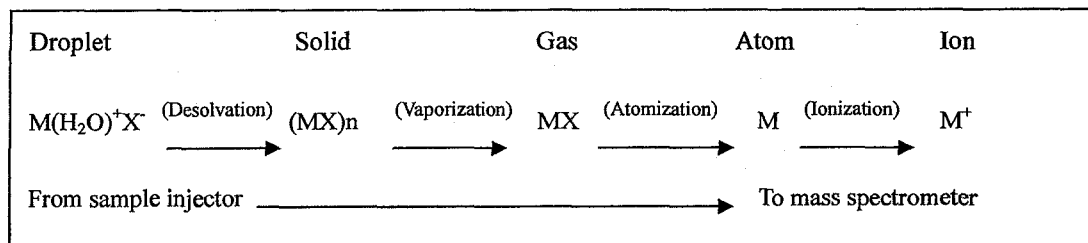
Figure 1.10. Mechanism of conversion of a droplet to a positive ion in the ICP

1.7.4 The interface region

The interface region plays an important role in transportation of the ions from the plasma, which is at atmospheric pressure (760 Torr), to the mass spectrometer analyzer region, where the pressure is at approximately 10^{-6} Torr. The interface is composed of two metallic cones (generally made of Ni) including a sampler cone and a skimmer cone, both of which are maintained at a vacuum of 2 Torr with a mechanical roughing pump.[52] Once the ions emerge from the plasma torch, they pass through the sampler cone with an orifice diameter of 0.8-1.2 mm and then travel a short distance to the skimmer cone that has a much smaller orifice diameter of 0.4-0.8 mm. The interface housing is cooled by water and made from a material such as copper or aluminum that dissipates heat easily, in order to reduce the damage to the cone from high-temperature plasma. Also this cool plasma would reduce argon-based polyatomic interferences such as $^{40}Ar^{16}O$, $^{38}Ar^{1}H$.

1.7.5 The ion focusing system

The ion optics are assembled by one or more electrostatically controlled lens

components to focus ions by taking ions from the plasma at atmospheric pressure *via* the interface cones and steering them into the mass analyzer under high vacuum. [53] The other function of the ion optics is to prevent particulates, neutral species, and photons from going through to the mass analyzer and detector. Otherwise, these species would lead to high level of signal instability and background noise and degrade the detector capacity further. In this region, the pressure is maintained at approximate 10^{-3} to 10^{-4} Torr with a turbomolecular pump.

1.7.6 The mass analyzer

A variety of mass analyzers have been adopted in the ICP-MS, such as quadrupole mass filters, double focusing magnetic sectors, time-of-flight, and collision-reaction cell technology. In this thesis, the most common of the mass separation devices used in ICP-MS, the quadrupole mass filter, will be utilized. A quadrupole consists of four cylindrical or hyperbolic metallic rods of the same length and diameter and is maintained at a vacuum of approximately 10^{-6} Torr with a second turbo-molecular pump. [54] The process that ions of a selected mass are allowed to pass through the rods to the detector, while the others are ejected from the quadrupole, is achieved by regulating a direct current (dc) field applied on one pair of rods and a radio frequency (rf) field on the opposite pair. Resolution power (R) is an important performance specification of a mass analyzer to govern its ability to separate an analyte peak from a spectral interference. In theory, the resolution of a quadrupole mass filter can be changed between 0.3 and 3.0 amu. Improving resolution is always

accompanied by a sacrifice in sensitivity. In practice, the quadrupole is normally operated at a resolution of 0.7–1.0 amu for most applications.

1.7.7 Detector

The detector system counts the number of ions emerging from the mass analyzer and then converts the ions into electrical pulses that are processed by computer. [55] Therefore, the quantification of trace elements in an unknown sample is then implemented by matching the ion signal with known calibration or reference standards.

1.8 Application of ICP-MS

ICP-MS has been commercially available for about 20 years. The applications of ICP-MS in the quantitative analysis include natural materials such as rocks, minerals, soil, sediment air, water, and plant and animal tissue; environmental sciences food industry, including purificationand distribution of water the analysis of elements not readily identified by AAS such as Sulfur, Boron, Phosphorus, Titanium, and Zirconium.

Due to its easy operation and fast analysis, more and more fields are applying ICP-MS for quantification of trace elements. For example: R. B. Philp, F. Y. Leung, and C. Bradley compared the metal content of some benthic species from coastal waters of the Florida Panhandle using ICP-MS; [44] Oleg V. Borisov *et al* determined Palladium, Rhodium and Titanium in automotive catalytic converters using ICP-MS; [45] S.

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Rattanachongkiat, *et al* determination of arsenic species in fish, crustacean and sediment samples from Thailand using high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS); [46] Zhensheng Chen *et al* analyzed of calcium isotopes in Human Serum using Inductively Coupled Plasma Mass Spectrometric, [47] etc.

2.0 Results and Discussion

2.1 Selection of ionic liquids samples and purification

BmimPF$_6$ and BmimNTf$_2$ were selected as representative ionic liquids in this research due to their ease of synthesis, water immiscibility, water-stability, non-coordinating ability, and other typical ionic liquids properties. Both of them are categorized as imidazolium based ionic liquids and have dominated the area over last twenty years. It has been reported that the imidazolium based ionic liquids possess higher negative reduction potential than Al(III) so that they are expected to be very stable in reduction-oxidation reactions when acting as solvents. It was discovered that imidazolium based salts displayed lower melting points than the 1-alkylpyridium salts. The imidazolium based cation can be synthesized *via* an extremely simple quaternization reaction, in which the amine was mixed with a wide range of cheap haloalkanes at a reasonable temperature. Water-stable anions of PF$_6^-$ and NTf$_2^-$ aid the application of these ionic liquids in synthesis and purification in biphasic applications. BmimPF$_6$ and BmimNTf$_2$ are water immiscible due to the difficulties in salvation by water that results from large molecular size and a shortage of hydrogen-bonding. These ionic liquids can be applied as a solvent in water sensitive reactions. The properties of BmimPF$_6$ and BmimNTf$_2$ present interesting possibilities for synthetic and electrochemical applications.

It was reported [56, 57, 58, 59, 60] that water and Et$_2$O can be used as the solvents to wash BmimPF$_6$ and BmimNTf$_2$ for purifying or recycling product. In this research, water was selected as the solvent to wash the water immiscible ionic liquids as many

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inorganic impurities contained within them are water soluble. The process of the purification of water immiscible ionic liquids with pure water can be regarded as Liquid-liquid extraction that is a method to separate compounds based on their preferences of solubility for two different immiscible liquids, water and water immiscible ionic liquids. It is an extraction of a substance from one liquid phase into another liquid phase. Compared with Et_2O, water is a more polar solvent and more environmentally friendly. Et_2O is usually used to extract the product residual amount of starting material, and catalyst from the reaction mixture in which ionic liquids were used as solvent. For example: Hisahiro Hagiwara et al. [61] reported that the product synthesized from the heterogeneous Heck reaction catalyzed by Pd/C in an ionic liquid of BmimPF$_6$ was extracted from the ionic liquid with diethyl ether. In this report, the product isolated from the ionic liquid using the diethyl ether had a strong affinity to the organic non-polar phase containing ether, since it was an organic and low polarity compound. However, the impurity that was intended to be removed in our research was ionic by-product; namely, chloride ions. Chloride ion is highly polar and has lone pairs that are solvated by water. Hence, water has the ability to readily dissolve this ionic species and extract it from the water immiscible ionic liquids. Therefore, water was an ideal solvent to wash BmimPF$_6$ and BmimNTf$_2$. It has also been previously reported that the water was used to purify these water immiscible ionic liquids. [61, 62]

2.2. Solubility

The chemistry term *immiscibility* refers to the property of various substances, particularly liquids, that disable them to be mixed together and form a heterogeneous phase. For example, oil and water. Solubility is designated as the amount of a solute that can be dissolved in a specific solvent under given conditions. In this research, the ionic liquids that were analyzed for the quantification of chlorine are water immiscible, which means that these ionic liquids can not mixed with water to form a biphasic liquids system, instead of the homogeneous solution. The factors that determine the ability of a ionic liquid to be miscible with water and be dissolved in water will be discussed in the followings. In addition, the water content remaining in some water immiscible ionic liquids will be mentioned in Section 2.6.

In the process of dissolving the ionic compound in a certain solvent, two major forms of solute species exist in the solution: one is the ion pair, the other is the dissociated ions. In the former case, each ion is closely bonded to the other by the force caused by opposite charge – electrostatic attractions. In the latter case, dissociated ions exist independently in the solution and are surrounded by a number of solvent molecules, the process of which is called solvation. In the process of solvation, the solvent molecules surrounding the dissociated ions are called the solvation shell. It is clear that the ability for an ionic compound to be dissolved in a certain solvent requires that ions can be well separated and solvated by solvent molecules.

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It is well known that the ability of a solvent to separate ions is measured by its dielectric constant ε that is expressed in Eq-2.1

$$E = k (q_1 q_2) / (\varepsilon r) \hspace{2cm} \text{Eq-2.1}$$

Where E is the interaction energy of two ions, q_1 and q_2 are charges of two ions of solute, r is the distance between these two charged ions of solute, k is the proportionality constant and ε is dielectric constant. According to Eq-2.1, the higher dielectric constant a solvent possesses, the lower energy a solvent requires to separate two ions with the opposite charges. Therefore, the solvent with higher dielectric constant is easer to dissolve the ionic compounds than that with lower dielectric constant. Besides the effect of the dielectric constant, the protic nature and electron-donating ability of a solvent also contribute to the stabilization of ions in solution. Solvent molecules can solvate anions by these factors through hydrogen-bond donor – acceptor interactions and solvate cations by through Lewis-base and ion-dipole interaction. Based on the description above, water is the ideal solvent for ionic compounds, because it has a high dielectric constant, about 78, compared with many other common organic solvents, to separate the ions of opposite charge effectively. Besides, water is able to solvate anions and cations readily since it is a donor solvent, a good Lewis-base and a protic, hydrogen-bond donor. However, it is reported that the imidazolium-based ionic liquids with long alkyl chains have limited water solubility; some of them are, in fact, immiscible with water completely. Ionic liquids with long alkyl chain have great tendency to be dissolved in organic solvents mainly *via* attractive van der Waals forces, reflecting organic characteristic

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features of ionic liquids. Therefore, it can be predicted that organic solvents with high dielectric constant are able to dissolve the water immiscible ionic liquids.

2.2.1 Immiscibility of Bmim [NTf₂] with water

It was reported[29] that all the bis(triflyl)amide based ionic liquids are immiscible with water due to the absence of H-bonding ability of the anion. Such anions as bis(triflyl)amides with perfluorinated species possess strong delocalization of the negative charge, weakening the hydrogen bonding with the cation. This assertion was confirmed by Holbrey and Seddon [30] who found that in the ^{1}H NMR analysis of [Cn-mim][BF$_4$] (n = 2–8), both in solution in propanone-d6 and neat, that the chemical shift of the C(2)–H protons of the tetrafluoroborate salts are all remarkably similar and do not show the large downfield shift related to hydrogen bonding observed for the chloride salts [30, 63]. Bonhote et al [29] found that the saturating water content is the same for EmimNTf$_2$ and for BmimNTf$_2$, while it is slightly higher for the ionic liquid containing the MeOC$_2$H$_4$MeIm$^+$ cation, in which an oxygen atom in the side chain acts as donor enabling H-bonding with water. These results show that unlike the immiscibility of ionic liquids without bis(triflyl)amides anion with water, the immiscibility of bis(triflyl)amides based ionic liquids with water increases not with lengthening the alkyl-chain in the cation but with decreasing the possibility of H-bonding between bis(triflyl)amides anion and water.

In this work, it was found that BmimNTf$_2$ still contained a certain amount of water after being washed with water. [29, 30] For instance, Pierre Bonhote et al [29]

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reported that the water content of saturated BmimNTf$_2$ is 2 wt% water. This water residual may contribute to retention of chloride ions in BmimNTf$_2$.

2.2.2 Immiscibility of Bmim PF$_6$ with water

The water content of saturated BmimPF$_6$ has been reported in the literature ranging from 1.2 to 2.3 wt%, [31, 64, 65, 66, 86] reflecting its relatively hydrophobic property. However, it was discovered that the water immiscible ionic liquid 1-butyl-3-methyl-imidazolium hexafluorophosphate can be totally miscible with aqueous ethanol between 0.5 and 0.9 mol [86] fraction ethanol. The extensive study [66, 86] on the liquid structure and association in ethanol/water compositions indicated that when X_{EtOH} < 0.2, ethanol molecules cluster with the ethyl chains forming a hydrophobic core surrounded by water molecules and at 0.2 < X_{EtOH} < 0.8, a sandwich-type cluster containing extended chains of hydrogen-bonded ethanol and water occurs. The interactions, occurring between the water/ethanol clusters and the IL to lead to the total miscibility region, have not been yet clear. Free-volume cavities or void space within the IL matrix [65, 86] may allow ethanol and water to be dissolved together. In addition, the bulk ethanol/water hydrogen-bonding structure with the only weak interaction between the alkyl-groups of the IL and the hydrophobic ethyl-substituents of the water/ethanol chains would help to improve the miscibility of BmimPF$_6$ with mixture of water and ethanol. Based on these results, it was surmised that mixtures of methanol and water, containing as a low amount of methanol as possible, should dissolve the BmimPF$_6$. Hence, solubility tests (Table 2.1) revealed

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the lowest amount of methanol required in the aqueous mixtures required to dissolve

BmimPF$_6$.

2.2.3 Miscibility of BmimNTf$_2$ and BmimPF$_6$ with other solvents

Since the ionic liquids selected in this research are water immiscible, it was

necessary to find other organic solvents in which they were soluble in order to

perform ICP-MS analysis. It has been reported [29] that ionic liquids are miscible with

solvents of medium and high dielectric constant ε; for example low molecular weight

alcohols and ketones, dichloromethane (ε 8.93), and THF (ε 7.58). They are

immiscible with alkanes, dioxane (ε 2.01), toluene (ε 2.38), and diethyl ether (ε 4.33).

Based on these data, several organic solvents and water/organic mixtures were

selected for dissolvability test, which is shown in Table 2.1.

Table 2.1 Solubility test for water immiscible ionic liquids:

Ionic Liquids Solvent(v/v)	BmimPF$_6$	BmimNTf$_2$	Bmim[N(CN)$_2$]
Methanol	S	S	NS
Methanol:H$_2$O= 1:99	S	NS	NS
Methanol:H$_2$O= 5:95	S	NS	NS
Methanol:H$_2$O= 10:90	S	NS	NS
Ethanol	S	S	NS
Ethanol:H$_2$O= 1:3	S	NS	NS
Ethanol:H$_2$O= 1:1	S	S	NS
Isopropanol	-------	S	NS
Isopropanol : H2O = 3:1	-------	S	NS
Isopropanol : H2O = 1:1	-------	S	NS
DMSO	S	S	S
S: Soluble ; NS: Not soluble			

2.3 Aqueous solvent operation

2.3.1 Interference of doubly charged and oxide species

In the stage of signal optimization of ICP-MS, the element Cerium , Ce, was selected to check the formation doubly charged species and oxide. It is well known that the energy in the plasma should be enough to ionize the analytes of interest, while excessive energy imposed on them would cause them to be ionized into doubly charged species and form oxides. Consequently, the excessive energy would reduce the number of singly charged species of the analyte detected and depress the analyte signal. Hence, it is necessary to design a method to monitor the ratio of doubly charged species to singly charged species and of oxide to single charged species. Based on previous research, [67] elements such as Ce are ionized into doubly charged ions and oxides at the significant expense of the population of singly charged analyte ions, as their second ionization potentials are lower than the first ionization potential of argon. Therefore, it can be concluded that the control of doubly charged species and oxide of Ce element under certain instrumental conditions suggests that other analytes of interest are limited to undergo second ionization and oxidation.

2.3.2 Factors affecting precision of data acquisition

Precision is defined as the measure of the reproducibility of the replicate analyses by Morrison and Skogerboe and can be expressed by the standard deviation. [68] The relative standard deviation (%RSD) shown in Eq-2.2 is applied to normalize the standard deviation for the comparison between different magnitudes of measurements.

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$$\% \text{ RSD} = 100 \, (s \, / \, x) \qquad\qquad \text{Eq-2.2}$$

where s is the measured standard deviation of replicates and x is the mean of the replicates.

The precision encountered in ICP-MS analysis include short-term precision and long-term precision. The former one is considered as the reproducibility of the measurement of consecutive determinations. The latter one is regarded as the reproducibility measured over a period of several hours, but within the domain of a single analysis session. Compared with short-term precision, long-term precision has instability caused by instrument drift and thus is poorer than the corresponding short-term precision, after the ICP-MS has been operated for a long time.

Measurement of precision is dependent on several factors related to equipment conditions, such as the stability of the detector, stability of the control electronics, the thermal stability of the operating environment, the stability of the ICP (including the regulation of gas flow rates), and the stability of the sample introduction system. Usually, variability in the plasma ionization process can be regulated by controlling gas flow rates, especially the nebulizer gas flow. Besides the instrument conditions, the concentration of the analyte can also influence the precision. The higher concentration of analyte, the lower % RSD (relative standard deviation) becomes. An example of the way the data should be reported is as $1250 \pm 10 \mu g/g$, where 1250 is the mean concentration of the analyte in the sample in units of $\mu g/g$, and 10 is the standard deviation in the same concentration units.

To obtain the relative precision, replicate analysis should be performed at least 3

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times. Running more replicate measurements can improve the accuracy of the mean

value and lower the magnitude of the standard deviation. The precision and accuracy

of measurements improve to a limited degree beyond 10 replicates because of

counting statistics which indicate that S/N improves by the square root (n), n is the

number of replicates

In this project, the parameter of the number of sweeps was examined to find out

how these parameters influence % RSD of data acquisition. Based on the data in Table

2.2, it shows that the precision of acquisition data can be tuned by adjusting the

number of sweeps.

Table 2.2 Acquisition conditions *vs.* quality of data

Matrix (Methanol : water) (v/v)	Sweeps	Dwell time (ms)			% RSD of the *signal of ^{35}Cl analyte in blank
		^{8}Be	^{35}Cl	^{115}In	
1:99	100	10	30	10	2.490
5:95	200	60	60	60	0.868
Remark: * Signal is collected at 30 runs and each run has the number of sweeps shown in the column of Sweeps.					

With the other constant parameters, the increase of the number of sweeps can improve

the precision of acquisition data. This result is consistent to the method of ensemble

averaging. [69, 70] The method of ensemble averaging relates the signal-to-noise ratio to

the number of times for which the data points are collected and averaged, shown in

Eq-2.3.

$$S / N = n^{1/2} (S_x / N_x) \qquad Eq\text{-}2.3$$

Where S is signal, N is noise, S_x is signal at one of the data points x, N_x is noise at one

of the data points x, n is the number of times the data points are collected and

averaged. Here the frequency variable, n, is equal to the sweep parameter. Based on this classic equation, it is easy to relate the RSD to the number of sweeps and the number of separate replicate. The method of ensemble averaging is effective in improving the RSD and is illustrated by Douglas A. Skoog and James J. Leary.[69] Therefore, it is easy to understand why increasing the number the sweeps and/or number of replicates can improve the precision of data acquisition. Moreover, it was found from Table 2.3 that shorter uptake time of 120 second can result in the lower signal to an extent at the first run than that at the second and third run for each sample, compared with longer uptake time of 180 second, so that the mean of signal under the operation at the uptake time of 120 second become less reliable than that at the uptake time of 120 second. Therefore, under the operation with uptake time of 120 second, the signal data at the first run for each standard sample should be removed from the data used for the calculation of standard deviation and detection.

Table 2.3: Signal of external calibration standards of BmimCl with addition of the internal standard ^{115}In in the aqueous operation

| | | Uptake time is set 120 second | | | | | Uptake time is set 180 second | | |
| | | ^{9}Be | ^{35}Cl | ^{115}In | | | ^{9}Be | ^{35}Cl | ^{115}In |
Run	Sample	signal(CPS)	signal(CPS)	signal(CPS)	Run	Sample	signal(CPS)	signal(CPS)	signal(CPS)
1	blank	252.002	44305.100	34682.550	1	blank	112.334	39226.531	22757.863
2	blank	249.169	65081.830	34184.020	2	blank	114.334	38867.469	21869.644
3	blank	233.919	65507.940	34231.710	3	blank	115.250	39178.483	21418.127
1	0.1 ppm	230.919	52735.570	35094.640	1	0.1 ppm	117.000	41092.516	21890.008
2	0.1 ppm	220.168	70988.690	34756.480	2	0.1 ppm	117.250	40545.790	21230.597
3	0.1 ppm	218.835	69991.040	34567.440	3	0.1 ppm	117.667	39821.925	22005.101
1	0.5 ppm	213.835	58675.420	34934.330	1	0.5 ppm	115.834	53275.405	22004.601
2	0.5 ppm	213.668	87211.140	34709.950	2	0.5 ppm	115.250	51745.212	22219.266
3	0.5 ppm	203.835	83846.840	35727.200	3	0.5 ppm	119.667	51047.793	21724.589
1	1 ppm	195.585	74126.070	35701.640	1	1 ppm	118.167	70337.231	22252.484
2	1 ppm	198.751	110626.100	36248.430	2	1 ppm	120.001	66650.284	22261.081
3	1 ppm	203.251	106835.800	35964.880	3	1 ppm	113.417	66480.579	21229.846
1	5 ppm	196.168	192042.900	36637.920	1	5 ppm	114.750	213358.200	24956.28
2	5 ppm	204.668	331291.700	39001.830	2	5 ppm	118.917	207027.660	24401.906
3	5 ppm	190.335	318732.700	38793.690	3	5 ppm	114.334	206454.870	23572.682
1	10 ppm	189.418	399726.200	39202.720	1	10 ppm	117.000	371740.480	25321.839
2	10 ppm	180.584	689302.500	39598.310	2	10 ppm	115.584	378270.670	25269.162
3	10 ppm	179.001	668935.400	40556.910	3	10 ppm	111.250	387398.360	24624.371
1	20 ppm	187.835	690102.000	39705.100	1	20 ppm	113.167	767709.450	26386.847
2	20 ppm	173.084	1234988.000	40951.950	2	20 ppm	114.834	758313.430	25318.416
3	20 ppm	175.584	1217463.000	40371.550	3	20 ppm	114.834	746280.530	25657.687

2.3.3 Effect of methanol content on the signal and the sensitivity

In the situation of quantitative analysis, the sensitivity [68] is regarded as the ability

to measure small differences in the concentration of analyte species. Usually,

sensitivity is a function of the slope of the analytical calibration curve divided by the

precision (expressed as standard deviation of ion current) of an intermediate

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concentration calibration standard. The equation for calculating the sensitivity is shown in Eq-2.4:

$$\gamma = (dI/dC) / s = m / s \qquad \text{Eq-2.4}$$

where, γ is the sensitivity, I is ion current, C is concentration of the analyte, m is the slope of the calibration curve, and s is the experimentally measured standard deviation of the ion current of an intermediate concentration standard.

For an element with several different isotopes, the isotope with the highest abundance among these different isotopes has highest sensitivity. The measurement of the analyte sensitivity is also influenced by the ionization degree. Most elements are ionized greater than 90% in the ICP, resulting in similar sensitivity. But some elements, such as Hg or Se, have lower sensitivity due to their lower degree of ionization.

Sensitivity is also dependent on the transmission of ions into the mass spectrometer, such as the total number of ions reaching the detector of the spectrometer per unit of concentration, which in turn is associated with the resolution setting of the instrument. Generally, sensitivity can be lower with the higher resolving power and lower transmission. Hence, it is usual to regulate resolution at a minimum level to achieve as high a sensitivity as possible. Other factors influencing the sensitivity are quite complex and originate from many sources and thus the determination of sensitivity will be empirical.

The detection limit [68] is defined as "smallest concentration of a given analyte for which a reliable measurement can be made to determine whether this analyte is

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absence or presence". Two types of detection limits are essentially equivalent: one is the absolute limit that is expressed as weight and has units such as nanograms or picograms; the other is the relative limit that is expressed as concentration units in the total sample and has units such as nanogram/gram or microgram/liter. The choice between these two approaches is dependent on the details of a particular methodology used for a particular application. The detection limit has been used to select and evaluate instrumentation and methodology and it can be computed by the following equation in Eq-2.5a:

$$C_{DL} = 3 \, s_b \, / \, m \qquad\qquad Eq\text{-}2.5a$$

where is C_{DL} detection limit, 3 is used for the proportionality constant, m is the slop of the analytical calibration curve, and s_b is the standard deviation of analyte signal in the blank. The detection limit can change with different manufacturer's instrumentation and are susceptible to the different modes of the sample introduction. In addition, the detection limits are dependent on the operating parameters. Therefore, frequent computations of detection limit with each batch of samples analyzed are good to reliably report ultra-trace concentration levels. Comparatively, the term of Limit of Quantification is defined as "smallest concentration of a given analyte for which a reliable measurement can be made to determine the specific quantity of this analyte" Limit of Quantification can be computed by the following equation in Eq-2.5b:

$$C_{LOQ} = 10 \, s_b \, / \, m \qquad\qquad Eq\text{-}2.5b$$

where is C_{LOQ} detection limit, 10 is used for the proportionality constant, m is the slop

of the analytical calibration curve, and s_b is the standard deviation of analyte signal in the blank.

It is true that BmimPF$_6$ can not be dissolved in pure water. However, it was found in this research that BmimPF$_6$ can be dissolved in aqueous methanol. This discovery makes it possible to analyze the chloride ion in BmimPF$_6$ using ICP-MS without the organic kit that involves the introduction of oxygen. The reason why the pure methanol solution can not be applied in ICP-MS operation easily is because the operation is very unstable and the plasma will be shut off in a short time in the presence of methanol after instrument starts running. This unstable operation involving the pure methanol might be caused by the high evaporation factor of the methanol. Large amounts of methanol vapor leaking into plasma are burned with oxygen, producing excessive heat; hence, the whole instrument system could be shut off by self-protection system under the rapidly increased temperature. Therefore, aqueous methanol was adopted to dissolve BmimPF$_6$, minimizing the amount of methanol leaking into plasma.

It was found that different amounts of methanol in the aqueous methanol solution may cause various sensitivities (Table 2.4).

Table 2.4 Results of calibration under the solvents with various methanol percentage in mixture of water methanol

Solvent (Percentage of methanol in water-methanol mixture (v/v))	Sensitivity (CPS/ppb)	SD* (Standard Deviation) (ppm)	Detection Limit (ppm)	Limit of Quantification (ppm)	Signal (CPS) of 20ppm chloride in the mixture of methanol water
1	48.68	0.038	0.11	0.38	1226225.2
5	30.30	0.030	0.09	0.30	757434.47
15	12.79	0.022	0.07	0.22	269833.48
Remark: SD* is calculated from the expression that s_b (the standard deviation of analyte signal in the blank) is divided by m (the slop of the analytical calibration curve)					

The detection limit was calculated from the Eq 2.5 (Section 2.3.3). Based on the chart above, both the sensitivity and the signal of 20 ppm chloride are decreased with the increase of methanol content, reflecting that even a small amount of methanol leaking into the plasma can suppress the signal of analyte, which in turn can depress the sensitivity. One of the root causes of signal suppression by the presence of methanol in aqueous solution might be energy reduction, because the methanol leaking into plasma could consume some energy in this process. It is noticed from Table 2.4 that the detection limit dose not change significantly with the amounts of the methanol content in water methanol mixture.

2.3.4 Method to purify BmimPF$_6$

Two purification methods were adopted in this research: one is to wash the sample with a certain amount of water; the other is to remove chlorine impurities in the sample under vacuum. The former method is intended to extract the chlorine impurities from ionic liquids with pure water and the latter one is to remove volatile

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impurities (i.e. HCl(g)), because the vapor pressure of Hydrochloric acid is 3.23 psi (21.1

°C). Under the high pressure of vacuum suction, the low pressure inside the vial,

containing the mixture of ionic liquids and the impurities of water and Hydrochloric

acid, enhances the evaporation of the Hydrochloric acid. The amount of chloride content

decreases with increase of the numbers of water washes, whch is shown in Figure 2.1a

and 2.1b and the data shown in Figure 2.1a and 2.1b is mass percentage with unit of

gram/gram.

Figure 2.1a Removal of chloride from BmimPF₆ whereBmimPF₆ is synthesized by
metathesis of BmimCl with HPF₆ and is dissolved in the mixture of methanol and
water (10:90) (v/v)

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Table 2.5: Reproducibility of Cl percentage in BmimPF$_6$ that was synthesized from BimCl and KPF$_6$

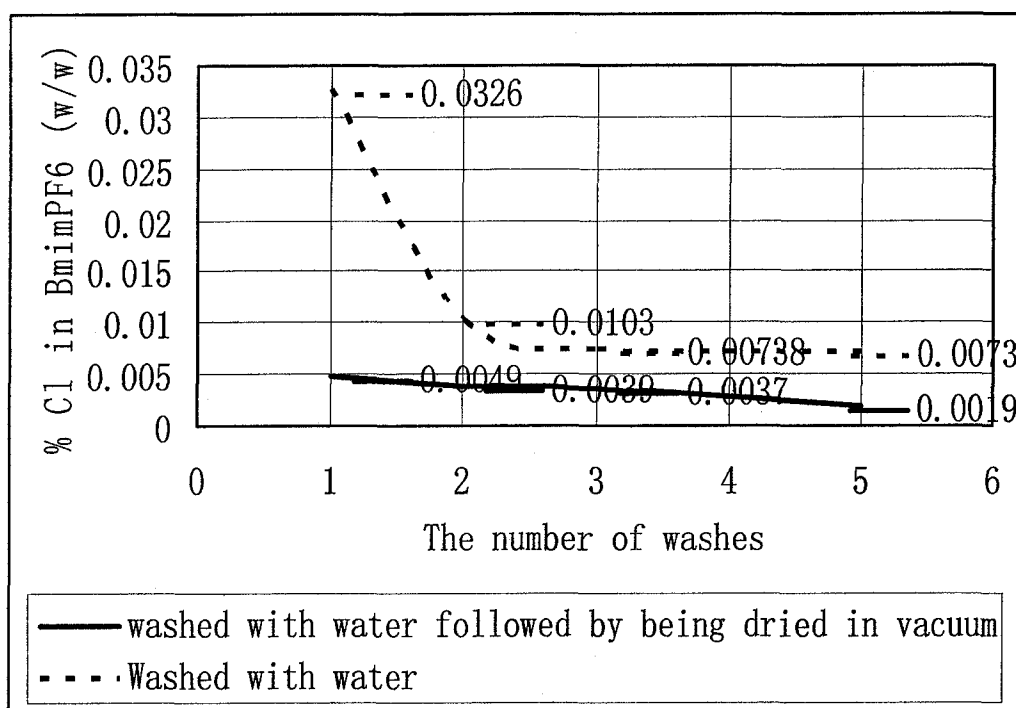| Purification methods	RUN Cl % Washes	First	Second	Third	Mean	Standard deviation
Purification of BmimPF$_6$ with pure water followed by vacuum	1 Time	0.8471	0.7821	0.9328	0.854	0.075
	2 Times	0.4285	0.3943	0.4937	0.438	0.050
	3 Times	0.3638	0.3285	0.4184	0.37	0.045
	4 Times	0.3149	0.2795	0.3941	0.329	0.058
	5 Times	0.3365	0.2683	0.3864	0.33	0.059
Purification of BmimPF$_6$ with pure water but without vacuum	1 Time	0.3894	0.3007	0.4572	0.382	0.078
	2 Times	0.1284	0.0997	0.2143	0.147	0.059
	3 Times	0.0978	0.0863	0.1002	0.094	0.007
	4 Times	0.0926	0.0802	0.0983	0.09	0.009
	5 Times	0.0853	0.0721	0.0904	0.082	0.009
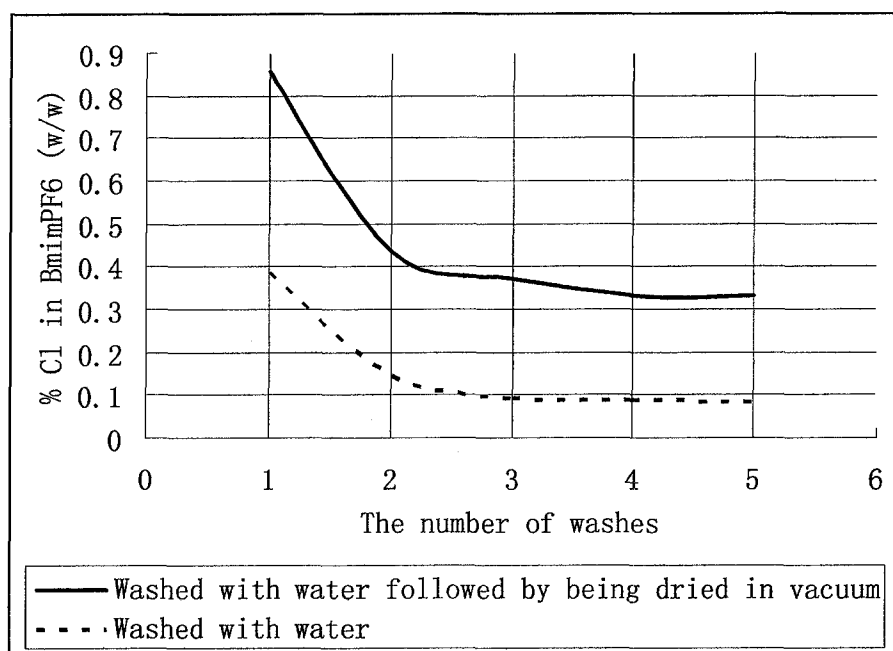
Figure 2.1b Removal of chloride from BmimPF$_6$ BmimPF$_6$is synthesized by metathesis of BmimCl with KPF$_6$ and is dissolved in the mixture of methanol and water (10:90) (v/v)

Two synthetic routes were adopted to synthesize the BmimPF$_6$: one involves the

metathesis between BmimCl and HPF$_6$, generating HCl by-product; the other is to

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exchange anion by dissolving two salts of BmimCl and KPF$_6$ in water, producing KCl as a by-product. Both by-products from these two synthetic routes can be reduced by washing with water, while HCl by-product, instead of KCl, can be removed *in vacuo* because Hydrochloric acid can evaporate under the lower pressure generated by the vacuum. Therefore, the curves in Figure 2.1a show that the method of water washing combined with being dried under vacuum can easily remove the HCl resulting in a low level of chlorine content, compared with the method involving only water washing. However, the curves shown in Figure 2.1b reflect a different tendency from that in Figure 2.1a. In Figure 2.1b, the chlorine impuritites are in form of KCl and can not be removed *in vacuo* as it is not volatile. However, residual water in BmimPF$_6$ can be removed *in vacuo*. Therefore, in this case, the percentage of chlorine in form of KCl in the BmimPF$_6$ is higher when water washing is followed by being dried *in vacuo* than that when only washing with water is adopted to purify the BmimPF$_6$. By comparing the curves shown in Figure 2.1a with that in Figure 2.1b, it is noticed that the HCl by-product is much easier to remove than KCl by-product. For the KCl by-product, however, the only way to remove the KCl is by being washed with water, while drying in vacuum can make the concentration of KCl increase.

2.4 Different operation conditions between aqueous and organic solution

In this research, the ICP-MS was also operated using organic solutions with oxygen introduction. Here, the following topics will be discussed: 1/ examination of how organic solvents affect the plasma and the sample introduction system; 2/

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determine optimal conditions to stabilize the plasma and minimize the interference caused by organic species; 3/ compare the operating conditions using organic solution samples with those using aqueous solution samples.

There are a few reviews and articles related to the study of ICP-MS operation with aqueous solution samples. However, there are comparatively very few publications about analysis of organic solutions using ICP-MS coupled with organic accessory kits. Since ICP-MS is being more frequently applied for quantitative analysis, it would be extremely useful to transfer knowledge obtained using ICP-AES to ICP-MS as far as possible.[71] Gray [72] and Browner and Zhu [73] have discussed fundamental distinctions between the two techniques And thereby provided a basis for experimental conditions for running organic solvents in ICP-MS. Some details are discussed in the following.

2.4.1 Cone selection

While analyzing aqueous solutions a nickel cone was selected from among a variety of metals including aluminum, copper, nickel and platinum. This was because the nickel cone is usually found to give the best general compromise between cost and durability. For example, it has been reported that the life of nickel cones may be many months of all-day use, when the system is run in the solution of 1% nitric acid. Before the cone is installed in place, it is necessary to check its tip since surface pitting and roughness on the tip may result in lower stability of the ions transferred into the mass separation device. This could cause unstable data and high relative standard deviation. While analyzing organic solutions, the nickel cone should be replaced with a platinum

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cone, because the more durable platinum cone can resist oxidation better and hence give a more stable operation.

2.4.2 Temperature of spray chamber

Solvent vapor loading (i.e. the amount of solvent evaporating from spray chamber into the plasma) is the major factor reducing the plasma stability with the introduction of organic solutions. Highly volatile solvents, such as n-heptane, cyclohexane, methanol, diethyl ether, require a reduction in the plasma solvent loading at room temperature. Therefore, it is necessary to find an approach to decrease the solvent vapor loading. In this research, a cold spray chamber was adopted to limit the solvent vapor loading, while the temperature could be controlled according to the nature of the solvent. For example, in the analysis of an aqueous solution, the temperature of the spray chamber was controlled within 4 °C, while temperatures lower than this setting might cause water to freeze preventing waste drainage from the spray chamber. When analyzing organic solutions the temperature of the spray chamber was set at -4 °C. This sub-zero temperature could be used since organic solvents have lower freezing and boiling points and higher evaporation factors that those of water. Another research group adopted an alternative method to decrease the solvent vapor loading. Wiederin et al [74] used ultrasonic nebulization with cryogenic desolvation to reduce the solvent load on the argon inductively coupled plasma. In this process, the aerosol was first heated above the boiling point of the solvent; subsequently, the solvent was removed in two condensers kept at -10 °C and -80 °C.

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Using ICP-AES, Hausler and Taylor [75] observed that the detection limit was improved

by a factor rising from 15 to 1000 on cooling from room temperature to 0°C. By

analyzing the distinctions between the two techniques, [72, 76] it can be concluded that

cooling the spray chamber is also advantageous in ICP-MS. In addition, Maessen [77]

fitted a condenser after the spray chamber, rather than on the spray chamber, and the

same effect was obtained.

2.4.3 Forward power

It can be seen from Figure 2.2 that the chloride signal increases with the increase

of forward power in analysis of aqueous solutions. This tendency is consistent with

the Saha equation (Eq-2.6)

$$\frac{n_e^2}{n - n_e} = \frac{2}{\Lambda^3} \frac{g_1}{g_0} \exp\left[\frac{-\varepsilon}{k_B T}\right] \qquad \text{Eq-2.6}$$

Where n_e is the density of atoms in the first state of ionization, that is with *one*

electrons removed, n is defined as the total density including n_e and non-ionized atom,

g_1 and g_0 is the degeneracy of states for the singly charged ion and non-ionized atom,

ε is the energy of ionization, T is the temperature of the gas, k_B is the Boltzmann

constant, Λ is the thermal de Broglie wavelength of an electron and is expressed in

Eq-2.7

$$\Lambda \equiv \sqrt{\frac{h^2}{2\pi m_e k_B T}} \qquad \text{Eq-2.7}$$

Where m_e is the mass of an electron, T is the temperature of the gas, k_B is the

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Boltzmann constant, h is Planck's constant. When analyzing aqueous solutions the forward power is usually set at 1350W, while ICP-MS operation using the organic accessory and analyzing organic solutions requires higher forward power to ionize the analytes so that the sensitivity and detection limit can be enhanced. This increased power while analyzing organic solutions, compared to that in aqueous solution, is caused by the carbon contain species that also consume part of forward power to be burned out. Based on the result in Figure 2.2, it is clear that increasing of forward power can enhance the signal of chloride ions with high ionization energy [79] (13eV-14eV) significantly. This finding is consistent with the previous report, [78] which demonstrated that increasing power can help to improve the signal of the analytes with high ionization energy (13 eV and higher), while there is little variation between the intensities of analytes with lower ionization energy.
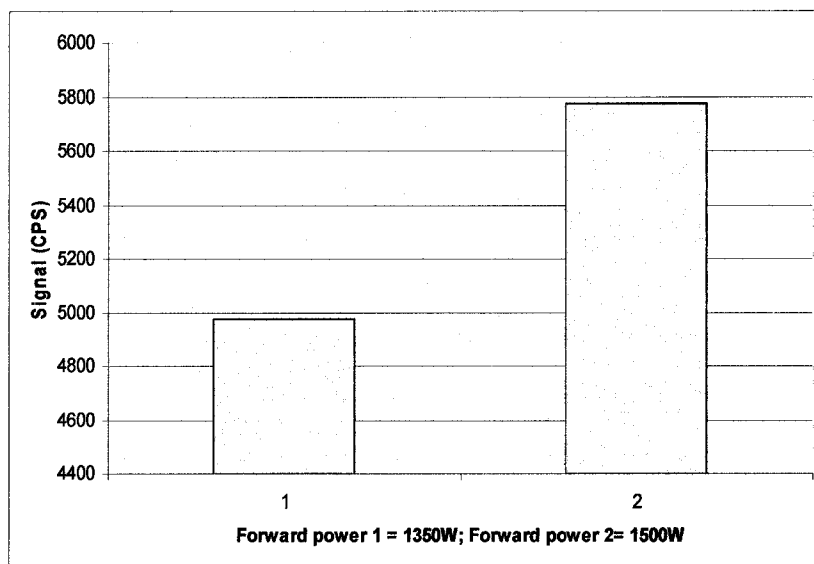
Figure 2.2 Effect of forward power on signal of 1ppm chlorine in isopropanol

Other research groups also examined the effect of the forward power on the

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metallic analyte signals,[78] while the chloride ion, instead of metallic elements, was selected as the target to be discussed in this project. For example, Hutton[78] found that a maximum in the intensity of the ^{63}Cu signal at a power of 1.8kW applied for organic solution analysis compared with at that of 1.3kW generally applied for aqueous solution analysis. After several experiments conducted at 1500W of forward power while analyzing isopropanol solutions, we found that the plasma was unstable and shut off in 2 hours after the plasma ignited. This unstable operation under the higher forward power may result from the auto protection system of ICP-MS through which the higher temperature caused by higher forward power can shut off the plasma to protect the instrument. Resetting the power setting at 1350W resulted in a system capable of running stable for about 8 hours or more. This allowed quantitative analysis for a whole range of the samples at this power setting at expense of lower signal.

2.4.4 Oxygen introduction

A small amount of oxygen was "leaked" into the gas stream to oxidize and volatilize the carbon containing species in the organic solutions in order to prevent sooting and blocking of the extraction aperture caused by deposition of carbon from the organic solvent. An additional mass-flow controller parallel with the nebulizer controller or a modified spray-chamber-to-torch transfer tube was designed to add the auxiliary gas containing oxygen and argon to the carrier gas after the nebulizer. Addition of oxygen to the carrier gas can reduce the background emission and then

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increase the sensitivity through the combustion of carbon contained molecular species.

The amount of oxygen added into system can be regulated by the visual inspection of the plasma. Organic compounds introduced into the plasma can result in a green C_2 emission band that can be observed at the base, the sides, and in the central sample injection region of the plasma. If this green emission was observed at the base and not in the inner region then the amount of oxygen was sufficient. The green emission at the sides could not be eliminated completely. The data in Table 2.6 shows that for the same operational conditions with different concentrations of organic solvent in sample solution, the amount of oxygen in the auxiliary gas must be increased as the relative amount of organic solvent increases.

Additionally, the amount of oxygen transferred into plasma with argon is not only determined by the relative concentration of the organic solvent in sample, but is also dependent upon the type of organic solvent, the type of oxygen introduction system, and other instrument parameters. For example, Hausler [79] reported that the 2 : 98 oxygen : argon was added into the carrier gas after nebulizer. By comparing the amount of the oxygen introduction in various solvents, we found that the operation using aquoues solutions of organic solvents did not require oxygen introduction. It was found that the oxygen introduction method was adopted in the cases of methanol and isopropanol solutions where the amount of oxygen introduction to burn the methanol vapor with higher vapor pressure was higher than that to burn the isopropanol vapor with lower vapor pressure, which shows that the vapor pressure

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also determine the amount of oxygen introduction. This finding is corresponds to the previous report in which Barrett and Pruszkowska [82] designed a method to figure out that when the xylene was adopted as solvent in the operation of ICP-MS, approximately oxygen amount with 14% of the aspirated xylene that possesses a lower vapor pressure than chloroform was required, but in the case of chloroform, oxygen amount with with 35% of chloroform that was required. Here, the higher vapor pressure of the methanol than that of the isopropanol results in a higher amount of solvent load into plasma, which in turn requires more oxygen introduction. The amount of oxygen introduction is critical to the operation and maintenance of ICP-MS. Too little oxygen can result in sooting and block of extraction aperture (Figure 2.3), while excessive oxygen may cause rapid deterioration of the orifice of the sample cone.
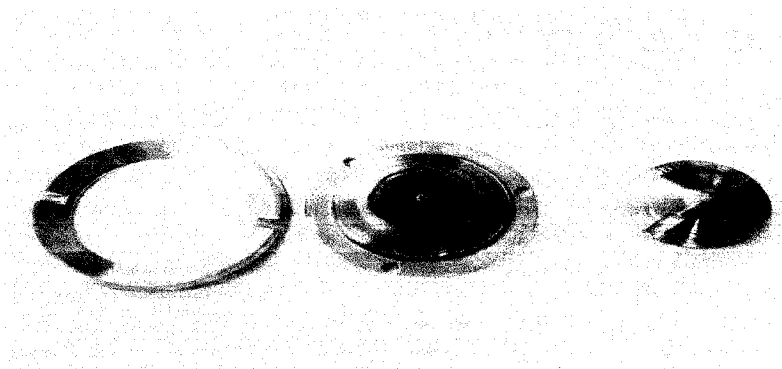
Figure 2.3. Sooting and blocked cone caused by less oxygen introduction

To avoid the problem of adding excessive oxygen, some research groups [79] have adopted the method that utilizes nitrogen instead of the oxygen being introduced into the system with the argon. However, this approach failed to give good sensitivity and stable plasma. Therefore, the introduction of oxygen is regarded as a good approach

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to minimize the problem of sooting, blocking of the extraction aperture, and reduction of noise caused by carbon contained species.

2.4.5 Other factors to improve operation

It was found that the sample uptake rate is lower when analyzing organic solutions at 10% than that when analyzing aqueous solutions: the sample uptake rate in the organic solvent operation is 10% of the total while that in the aqueous operation is 20% of the total. The study on the effect of uptake rate on the stability showed that slower uptake rate resulted in higher plasma stability but lower signal, demonstrating that a lowering of sample uptake rate is another factor on reducing plasma solvent loading. Andrew W. Boorn' and Richard F. Browner [80] studied the uptake rate for various organic solvents. Kreuning [77] established the solvent plasma load (Q_{SPL}) of water, methanol and chloroform as a function of the liquid uptake rate (Q_L) by using a continuous weighing method for recording the rate differences between the relevant liquid streams. Hutton [78] improved the plasma stability in the organic solvent operation by reducing the sample uptake rate to 0.5 mL/min that is less 2 times than the rate in standard aqueous solvents operation. Besides the approach of lowering sample uptake rate, Hausler [81] succeeded in increasing plasma stability by reducing the carrier-gas flow rate. This case can be explained by realizing that a reduction in the carrier-gas flow rate can lower the speed by which the sample is transferred into the plasma and thus the residence time of the sample in the plasma will be extended. Regarding the effects of other instrument conditions on the signal intensity and

stability of plasma, Shuler et al reported that a smaller diameter of injector tube improved the stability of the plasma while running volatile organic solvents. However, Barrett and Pruszkowska [82] found that reduction in the diameter of an injector tube decreased the analyte signal.

2.4.6 Internal standardization

The ICP-MS signal can fluctuate with power variation, the changes in the conditions of nebulization and the fluctuation in the pressure within the spray chamber. The interference caused by these instrument drift can be corrected by adding appropriate concomitant elements to the test solution and measuring the intensity ratio, which is called internal standardization and these appropriate concomitant elements are called internal standards. [67]

Several criteria for the selection of the elements as internal standards include: 1) the internal standard elements should not be present or at an insignificantly low concentration in the samples; or if present, the potential internal standard element should be at a constant concentration in all blanks, standards and unknowns before a known amount of the element of interest is added to the test standards and unknowns 2) the internal standard elements should be as pure as possible, otherwise any trace impurities should be reported on the certificate of analysis; 3) it should be necessary to maintain the concentration of internal standards that were added precisely into all calibration standards, blanks, and samples; 4) the concentration of the internal standard elements should be sufficient so as to give a good signal to noise ratio; 5) the

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internal standard elements can not interact with matrix or analyte elements from sample; 6) if the plasma temperature were to go up or down, it should be necessary to check whether the internal standard likely to follow the same pattern of intensity change as the analyte

In the aqueous operation of this research, the internal standards were prepared to contain 1 ppb ^{7}Li, ^{45}Sc, ^{89}Y, ^{115}In, ^{140}Ce, ^{9}Be, in 2% HNO_3(aq) and ^{115}In was selected as the elements used for internal standards. Based on the data shown in Table 2.3, the signal of ^{9}Be is much lower than that of ^{115}In at the concentration of 1ppb. The low signal of ^{9}Be is due to Be's high ionization energy (9ev-10ev) [67] which causes a smaller fraction of Be to be ionized compared to ^{115}In, which has a lower ionization energy (less than 7ev). [67] In this case, ^{9}Be is giving such a low signal that it cannot be used for the calculation of the analyte to internal standard ratio. The reason why ^{115}In was selected as internal standard is not only because it is giving a signal that is strong enough to correct the interference but also because it is absent in the blank, the standards and the unknown samples. Comparatively, in the organic operation of this research, the internal standards were prepared from 1ppb ^{115}In and ^{9}Be and ^{9}Be was selected as internal standard element. It is shown in Table 2.6 that the signal of ^{9}Be is much higher than that of ^{115}In in the organic operation, unlike what was observed when aqueous solution of ionic liquids was analyzed (see Table 2.3).

Table 2.6: Signal of external calibration standards of BmimCl with addition of the internal standard ^{9}Be in the organic operation

Run	Label	^{9}Be signal (CPS)	^{35}Cl signal (CPS)	^{115}In signal (CPS)
1	blank	5153.096	6436.283	771.690
2	blank	5696.052	6973.452	780.520
3	blank	5820.352	7041.735	783.36
1	1 ppm	5649.200	7626.452	805.690
2	1 ppm	6336.738	8270.560	882.030
3	1 ppm	6219.187	8010.829	899.360
1	5 ppm	5326.243	7726.506	928.610
2	5 ppm	5883.295	8187.596	948.530
3	5 ppm	6023.186	8413.644	962.780
1	10 ppm	5319.490	7708.996	907.030
2	10 ppm	5911.390	8411.392	919.610
3	10 ppm	6061.452	8509.450	955.700
1	50 ppm	5288.145	13227.370	898.280
2	50 ppm	5962.327	14345.780	928.450
3	50 ppm	6153.408	14634.330	942.950
1	100 ppm	5304.318	20501.030	873.690
2	100 ppm	5865.954	21784.100	897.280
3	100 ppm	5972.248	22341.870	906.780
1	200 ppm	5314.822	35930.210	919.530
2	200 ppm	5877.125	38023.290	924.530
3	200 ppm	6077.209	39414.800	934.110

The higher signal of ^{9}Be could be because of higher temperature in the torch caused by combustion of organic contents with oxygen than that in aqueous operation. Meanwhile, the signal of ^{115}In in the organic operation shows lower than that in aqueous operation. This phenomenon could be because the organic operation can give an excessive energy in the plasma caused by high temperature so that the ^{115}In could experience over-ionized into doubly charged ions and decrease the effectiveness of

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generating singly charged ions, unlike aqueous operation. Like the internal standards in the aqueous operation, the internal standards in the organic operation was absent in the sample.

2.5 Analysis in isopropanol

2.5.1 Linearity of calibration curve and effect of solvent on analysis

The calibration range established in the analysis of the isopropanol solution was: blank, 1ppm, 5 ppm, 10 ppm, 50 ppm, 100 ppm, 200 ppm, which was over one order of magnitude compared with the calibration range set in case of aqueous solutions. In the quantitative analysis of the chlorine residual in the isopropanol solutions, the linearity of calibration curve should be regarded as an index determining the reliability of the data collected from this analysis. It is well known that the signal output is directly proportional to the concentration of an element over several orders of magnitude. Hence, a good method to reach good linear calibration will make quantitative analysis reliable. There are few publications on how to correct the linearity of calibration curve in ICP-MS analysis. Fernando [87] studied the effects of the instrument parameters on the curvature of the calibration line and found that correction of settings, especially the nebulizer gas flow, contribute to the maintenance of a linear calibration curve. Based on our experience optimal linear calibration curves can be obtained by enlarging the calibration range. By comparing two calibration curves shown in Figure 2.4a and in Figure 2.4b (calibration curve in two concentration range), it is clear that the calibration curve established in higher concentration standards is more linear than that in lower concentration standards.

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Intercept CPS=6821.752611 Intercept Conc=46601.439102
Sensitivity=0.146385 Correlation Coeff=1.000000
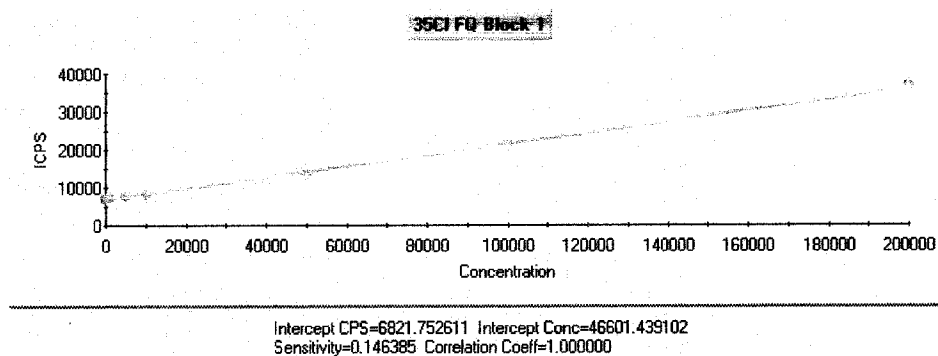
Figure 2.4a. Calibration curve in wider concentration range in the isopropanol solvent

Intercept CPS=1003.770034 Intercept Conc=77211.194821
Sensitivity=0.013000 Correlation Coeff=0.648501
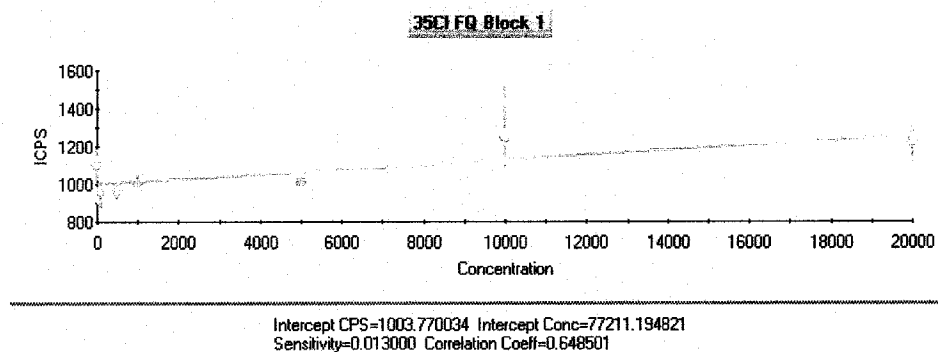
Figure 2.4b.Calibration curve in narrower concentration range in the isopropanol solvent

As mentioned before, excessive organic vapor leaking into plasma results in significant background that requires higher concentration standards in order to show greater signal differentiation than those with less significant background. We assumed that this higher concentration of calibration standards could generate optimum calibration linearity by compensating the background from a high amount of organic vapor leakage.

The data shown in Table 2.7 indicate that detection limit increases with the decrease of the amount of the isopropanol content in water isopropanol and lowest detection in this case shows under the operation using pure isoprpopanol as solvent. At the same time reflected power increases significantly with an increased proportion

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of isopropanol, which indicates that the isopropanol can generate pronounced heat by burning with the oxygen.

Table 2.7 Results of calibration under the solvents with various isopropanol percentage in mixture of water ispropanol

Solvent (Percentage of methanol in water-methanol mixture (v/v))	Sensitivity (CPS/ppb)	SD (standard deviation) (CPS)	Detection limit (ppm)	Limit of quantification (ppm)	Reflect power (W)	Nebulizer pressure (bar)	Oxygen amount (bleed unit)
100	0.109	0.343	1.03	3.43	8.2	3.23	370
75	0.146	0.752	2.26	7.52	3.6	3.13	210
50	0.284	1.619	4.86	16.19	3	3.08	130
Remark: SD* is calculated from the expression that s_b (the standard deviation of analyte signal in the blank) is divided by m (the slop of the analytical calibration curve)							

It is shown that the average detection limit in the analysis undertaken in aqueous solution is much lower than that undertaken in isopropanol with higher evaporation factor, since the solvent loading into plasma can generate great background. Due to this high background, the signal of analytes can be suppressed, causing high detection limit and low sensitivity.

2.5.2 Quantitative relationship between the number of washes and chlorine content in BmimNTf₂

According to the instrumental conditions mentioned above, the quantification of residual chlorine in BmimNTf$_2$ was undertaken in pure isopropanol with oxygen introduction. Based on our experience comparing the effects of two solvents (methanol and isopropanol) on ICP-MS operation stability, we found that the plasma involving the methanol will shut off in one or two hours after the plasma is turned on, while the operation involving the isopropanol can sustain a plasma for at least 6 hours.

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This allowed quantitative analyses in isopropanol solutions. From the data shown in Figure 2.5, and again not surprisingly, the residual chlorine decreases with the increase of the number of water washes.

Table 2.8: Reproducibility of Cl percentage in BmimNTf₂ purified with pure water

Washes \ Cl(%) \ RUN	First	Second	Third	Mean	Standard deviation
1 Time	0.197	0.152	0.119	0.156	0.039
2 Times	0.109	0.063	0.045	0.072	0.033
3 Times	0.042	0.034	0.031	0.035	0.005
4 Times	0.03	0.026	0.024	0.026	0.003
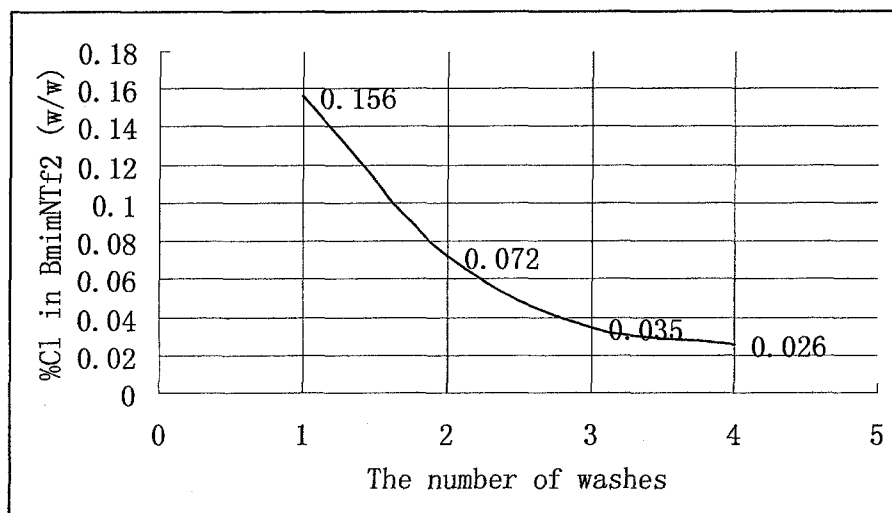
Figure 2.5. The change of residual chlorine with increase of the number of washes and BmimNTf₂ was synthesized by metathesis of BmimCl with LiNTf₂ and dissolved in pure isopropanol

In these experiments the method of water washing, instead of drying *in vacuo*, to purify the water immiscible ionic liquid BmimNTf₂ was adopted. This ensured the lowest amounts of residual chlorine in the samples of BmimNTf₂. It has been shown that the purification method of water washing followed by drying *in vacuo* can

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increase the percentage of chlorine impurities in $BmimPF_6$, the synthesis of which involves metathesis between BmimCl and KPF_6 and generate non-volatile compound KCl. Similarly, this purification method can also increase the percentage of residual chlorine in $BmimNTf_2$ that is synthesized from BmimCl and $LiNTf_2$ and generate the LiCl by-product

2.6 Comparison of chlorine impurities content in $BmimPF_6$ with that in$BmimNTf_2$

By converting the mass concentration of chlorine impurities in $BmimPF_6$ (Figure 2.1b) and in $BmimNTf_2$ (Figure 2.5) into molar percentage (molar/molar), the molar percentage of chlorine in $BmimPF_6$ (M=284.18 gram/mole) is 0.76% and that in $BmimNTf_2$ (M=419.36 gram/mole) is 0.35%. It is shown that the chlorine content in $BmimNTf_2$ is much less than in BmimPF6 that is synthesized from BmimCl and KPF_6, after both ionic liquids undergo thorough purification by being washed with water. In the process of the purification of water immiscible ionic liquids, the deionized water was transferred into the vial containing the ionic liquids followed by shaking to mix the water with ionic liquids. During this mixing stage, the water acted as an extractant to extract the chloride ion from the ionic liquids phase. Regarding the chlorine content in $BmimPF_6$ and in $BmimNTf_2$, two factors influence the chlorine concentration in both ionic liquids: one is the viscosities of both ionic liquids; the other is the water content in both ionic liquids.

Highly viscous ionic liquids can impede the chlorine impurities migrating from

ionic liquid phase to water phase (i.e. a mass transfer effect). According the previous report, the viscosity of BmimPF$_6$[83] is 285 cp at the temperature 293 K. and that of BmimNTf$_2$[29] is 52 cp at the same temperature as BmimPF$_6$. It is known that similar viscosity of two liquids can help mix these two liquids, causing a good interaction between these two liquids, which in turn enhance the migration of chlorine impurities into water phase. Therefore, viscosity is one of the factors that explain higher chlorine content in BmimPF$_6$ compared to that in BmmNTf$_2$.

The higher water content in water immiscible ionic liquids is another factor affecting chlorine content. Although both BmimPF$_6$ and BmimNTf$_2$ are considered as water immiscible ionic liquids, both of them still contain finite amounts of water. The water dissolved in water immiscible ionic liquids can compete with the water phase to trap the chlorine impurities in the ionic liquids. Hence, higher water content can result in more chlorine impurities content in water immiscible ionic liquids. Jonathan G. Huddleston [31] reported the water content of BmimPF$_6$ about 11700ppm and BmimNTf$_6$ about 3280ppm at 25°C. From the perspective of the water content effect, the chlorine impurities content in BmimPF$_6$ is expected to be higher than that in BmimNTf$_2$. This conclusion can also be deduced from other reports. For example: John D. Holbrey and Kenneth R. Seddon [30] found that the EmimBF$_4$ is more difficult to purify than BmimBF$_4$ is (especially removing halide impurities), because BmimBF$_4$ is less hydrophilic than EmimBF$_4$. Singer et al found that the "wet" reagent acetone used in the synthesis of BmimBF$_4$ can increase the chlorine impurities impurity content.

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3.0 Conclusions

This work has shown that ICP-MS can be adjusted to analyze the chlorine content in water immiscible ionic liquids. Although $BmimPF_6$ and $BmimNTf_2$ cannot be dissolved in water, $BmimPF_6$ can be dissolved in aqueous methanol and $BmimNTf_6$ can be dissolved in water/isopropanol mixture. Less methanol than ethanol is required to enable water/alcohol mixture to dissolve $BmimPF_6$. Experiments showed that the lowest ratio of methanol to water in water/methanol mixture that is able to dissolve $BmimPF_6$ is 1:99 (v/v). It has been shown that the higher the proportion of organic solvent in the sample solution results in higher interference and the lower the analyte signal. Such low methanol content in the water/methanol mixture makes it possible to analyze the residual chlorine impurity in $BmimPF_6$ using ICP-MS under standard aqueous conditions instead of using the organic accessory. However, $BmimNTf_2$ can not be dissolved in the aqueous methanol solvent, but is soluble in water/isopropanol mixtures. The solubility tests shows that the lowest proportion of isopropanol in this mixture that is cable of dissolving $BmimNTf_2$ is 50% v/v. Therefore, the ICP-MS analysis involving such a high organic solvent content requires the employment of the organic accessory with the oxygen introduction. The trial of three different solvents---water, methanol, and isopropanol in ICP-MS operation individually shows that the operation involving pure methanol is not stable and the plasma shuts off automatically in one or two hours after the plasma ignites, the operation using isopropanol as a solvent sustains a plasma on for at least 6 hours, while the water is ideal solvent for ICP-MS operation in terms of the operation stability and the

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interference from matrix.

When experiments are run on a daily basis the data acquisition can be stabilized by adjusting the instrument parameters of sweep, dwell time and uptake, besides some other factors related to equipment conditions, such as the stability of the detector, stability of the control electronics, the thermal stability of the operating environment, and the stability of the ICP (including the regulation of gas flow rates).

ICP-MS operation involving pure methanol is so unstable that the plasma usually shut off in one or two hours after the instrument is turned on, causing an analysis experiment finished incompletely. The sample solution prepared using aqueous methanol is capable of sustaining a plasma on for at least 6 hours allowing quantitative analysis. In the operation involving the aqueous methanol, both the sensitivity and the signal of 20 ppm chlorine impurities are decreased with the increase of methanol content and the detection limit dose not change significantly with the amounts of the methanol content in water methanol mixture

The chlorine content can be reduced by washing $BmimPF_6$ with the water. For the purification of the $BmimPF_6$ synthesized from $BmimCl$ and HPF_6, the chloride ions, in the form of HCl, remaining in $BmimPF_6$ can be further reduced by being dried *in vacuo*. However, in the case of the $BmimPF_6$ synthesized from $BmimCl$ and KPF_6, the chlorine impurities, in the form of KCl, can not be removed under vacuum, while the removal of water *in vacuo* increases the concentration of chloride ions in $BmimPF_6$ by reducing the total volume of the solution while the amount of impurity remains constant. Therefore, the purification method involving water washing

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followed by being drying in vacuo can reduce the concentration chloride ions in BmimPF$_6$ that is synthesized from BmimCl and HPF$_6$, but not for BmimPF$_6$ from BmimCl and KPF$_6$. In addition, the residual chlorine content obtained *via* a metathesis reaction between BmimCl and HPF$_6$(aq), in which chlorine becomes contained within the HCl by-product, is lower than that obtained *via* a metathesis reaction between BmimCl and KPF$_6$(aq), in which chlorine becomes contained within the KCl by-product.

Compared with the ICP-MS analysis of aqueous solutions, the analysis of organic solutions requires higher forward power to compensate for the energy lost in burning organic solvent.

Linear calibration curves for isopropanol solutions can be obtained by increasing the calibration range by a factor of 10, compared with linear calibration curves for aqueous methanol. Since the chlorine signal can be suppressed by organic solvents, increasing the concentrations of standards increases the signal sensitivity, which in turn makes calibration curve linear. The reflected power increases with the isopropanol introduction. Excessive increase of reflected power can result in system over heating, which in turn causes the system to automatically shut off. Also, higher isopropanol content results in higher detection limits, while it influences the reflected power markedly.

As in the case of BmimPF$_6$, the residual chlorine in BmimNTf$_2$ can be reduced by washing with water. For the BmimNTf$_2$ synthesized from BmimCl and LiNTf$_2$, the purification involving drying in vacuo increases the chlorine concentration as it did in

the case of BmimPF$_6$.

The chlorine content in BmimNTf$_2$ is much less than in BmimPF$_6$, after both of ionic liquids undergo thorough purification by being washed with water. The factors of viscosity and water content of both of ionic liquids influence the chlorine content. The higher viscosity and more water content in water immiscible ionic liquids results in higher chloride content.

4.0 Future direction:

In case of the analysis of chlorine impurities in BmimPF6 and in BmimNTf2, the isopropanol will be adopted to dissolve BmimPF6 and the methanol water mixture will be used to dissolve BmimNTf2 to study the operational parameter and LOQ.

To broaden the application of ICP-MS on the quantitative analysis of halide ion in water immiscible ionic liquids, other organic solvent could be tried to obtain the stable operation of ICP-MS. In the future research, acetonitrile and DMSO will be selected to dissolve water immiscible ionic liquids to study the operation behavior of ICP-MS and detection limit, because it is shown that DMSO can dissolve wider range of water immiscible ionic liquids.

To check the reliability of data collected from ICP-MS operation further, the interference in the ICP-MS operation will be examined where DMSO is selected to dissolve water immiscible ionic liquids

Based on the previous two result, the Quantitative analysis of chloride ion in Bmim[N(CN)$_2$] will be undertaken, because Bmim[N(CN)$_2$] becomes more and more important in modern chemical industrial.

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5.0 Experimental

General

All ionic liquids used in this research were synthesized in oven-dried glassware. The toluene used for the synthesis of BmimCl was dried and distilled over $CaSO_4$ for 5 hours and freshly distilled immediately prior to use. The acetonitrile used for recrystallization of BmimCl was distilled and refluxed from CaH_2 for 6 hours and freshly distilled immediately prior to use. The diethyl ether that was used for adjusting solubility of BmimCl in acetonitrile in recrystallization stage was dried and distilled over the sodium - benzophenone and freshly distilled immediately prior to use. All other reactants and reagents used for the synthesis of ionic liquids were purchased from Sigma-Aldrich Inc. and used as received. Volatile organic solvents were removed from products after reaction by rotary evaporation (Buchi Vac V-513). The hygroscopic ionic liquids were dried *in vacuo* and were weighed in a glove box. All the products were characterised using nuclear magnetic resonance spectrometer, FT-IR spectrometer (Brucker Vector 22) and LC-MS, Ion trap mass spectrometer (Agilent 1100) with direct injection. The NMR analysis was performed on a Bruker 250 MHz spectrometer at Atlantic Regional Magnetic Resonance Center; BmimCl was dissolved in D_2O for ^1H NMR analysis and in the Methanol-d4 for ^{13}C NMR analysis, $BmimPF_6$ was dissolved in the Methanol-d4 for ^1H, ^{13}C, ^{19}F NMR analysis, $BmimNTf_2$ was dissolved in the Methanol-d4 for ^1H, ^{13}C, ^{19}F NMR analysis, and BmimBr was dissolved in the Methanol-d4 for ^1H and ^{13}C NMR analysis. $Bmim[N(CN)_2]$ was dissolved in the Acetone-d6 for ^1H, ^{13}C NMR analysis. The solid

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sample of BmimCl for FT-IR analysis was prepared with a KBr pellet and the liquids samples of $BmimPF_6$, $BmimNTf_2$, and $Bmim[N(CN)_2]$ were recorded as neat films. The water used for synthesis and making solutions was purified through reverse osmosis (Milli-R012Plus, Millipore water purification system) followed by water deionization (Sybron / Barnstead filtration unit). The balance (Mettler PC400) that was used to weigh reactants and reagents for synthesis was reported mass value limit at 0.01 grams and that was used for preparation of standards and unknown sample was a TR-104 Balance (Denver Instrument Company), readability 0.1 mg, maximum weight capacity 110 g, linearity 0.2 mg, repeatability ±0.1 mg. All standards and unknown samples were prepared as mass concentrations by transferring a known amount of material to a volumetric flask followed by dilution to the specified volume with corresponding solvents. The pipettes used for making standards were purchased from Fischer Scientific.

General procedure for ICP-MS analysis

Trace amounts of chlorine contained within the ionic liquids studied were determined using a Thermo VG PQ Excell Inductively Coupled Plasma Mass Spectrometer. This ICP-MS system was assembled with an auto-sampler system, and was equipped with a quadrupole mass separation device. Prior to daily operation of the ICP-MS, the gas system was checked by monitoring argon gas pressure. The tubing system was then set up to connect rinse solution and waste drainage to the spray chamber system. The whole system was initiated by clicking the standby button,

while the peristaltic pump was switched on automatically. After plasma in the torch was on, the system was kept running for 20 minutes to warm and initialize the instrument. During the initialization of ICP-MS operation, it was necessary to check whether the tubing is working properly. If the liquids did not flow smoothly through the tubing, the screw on the clamp of peristaltic pump could be adjusted by releasing or tightening the screw to loosen or pressurize the tubing. If it was found that the tubing became white and lost elasticity after prolonged use. This stretched tubing was replaced with a new tubing when necessary. After the tubing was checked and the instrument was initialized for 20 minutes, the tubing was transferred from the rinse bottle to another bottle containing the tuning solution and the detection system was turned on by clicking the operation button in the instrument menu. After the system was tuned to get the highest signal, and the appropriate ratio of oxide species to the mono charged species and the appropriate ratio of double charged species to the mono charged species, the short term stability was ran. As long as the %RSD value was less than 5% during the short term stability test, the calibration standards and unknown sample to detect the chloride ions quantitatively could be analyzed.

5.1 Synthesis of ionic liquids

5.1.2 1-n-Butyl-3-methylimidazolium chloride

Freshly dried and distilled 1-methylimidazole (40 mL, 0.50mol) and 1-chlorobutane (90 mL, 0.86mol) were injected *via* syringe and septum into dry toluene (50 mL) in an oven dried – nitrogen cooled round-bottomed Schlenk flask.

The mixture was refluxed at 70°C under inert atmosphere after which two layers had formed. The upper layer containing toluene and excess 1-chlorobutane was decanted. The flask was allowed to cool to room temperature and was then cooled to -10 degree overnight, during which time a white solid of BmimCl was formed. If necessary, seed crystals of previously prepared BmimCl were added to induce crystallization.

BmimCl was recrystallized by dissolution in a minimum amount of dry acetonitrile (i.e. 30 mL) followed by the addition of dry diethyl ether (i.e. 10 mL). The resulting white precipitates were washed with a cold mixture of acetonitrile and diethyl ether and then dried *in vacuo* for 1 h to remove the trace solvent. Yield: 54%.

^{1}H NMR (250 MHz): δ 0.95 (t, 3H, N-CH$_2$CH$_2$CH$_2$CH$_3$, ^{3}J=7.3Hz), 1.33 (sextet, 2H, N-CH$_2$CH$_2$CH$_2$CH$_3$, ^{3}J=7.3Hz), 1.88 (quintet, 2H, N-CH$_2$CH$_2$CH$_2$CH$_3$, ^{3}J=7.3Hz), 3.92 (s, 3H N-CH$_3$), 4.19 (t, 2H, N-CH$_2$CH$_2$CH$_2$CH$_3$, ^{3}J=7.3Hz), 7.45 (br s, 1H, H4/H5), 7.50 (br s, 1H, H4/H5), 8.73 (s, 1H, H2). ^{13}C NMR (250 MHz): δ 16.61, 23.25, 35.95, 39.41, 52.84, 126.48, 127.75, 140.68.

FTIR (KBr pellets): 3083cm^{-1} (M) (C-H) aromatic ring; 2869 cm^{-1} (C-H) aliphatic; 2963 cm^{-1} (M) (C-H), Aromatic-N-CH$_3$.

Ion trap mass spectrum: *m/z* 139 [bmim]$^+$

5.1.2 1-butyl-3-methylimidazolium hexafluorophosphate

Approximately 43.97 g (0.25mol) of the solidified BmimCl salt was melted (mp 65 °C) in a 1-L round-bottom flask and allowed to cool at room temperature. It was then dissolved in water (75 mL). Aqueous hexafluorophosphoric acid (37.2 mL, 60%,

0.26 mol) was added dropwise over 2 h (CAUTION: the addition of HPF_6 should be done slowly to minimize the amount of heat generated). The mixture was vigorously stirred for 1 h in the ice bath during which time two phases formed. The lower very pale yellow organic phase was $BmimPF_6$, which is not soluble in water while the upper phase was a very acidic aqueous solution containing the excess hexafluorophosphoric acid and hydrochloric acid. The aqueous phase was decanted away using separation funnel and the $BmimPF_6$ was washed by pure water followed by being dried in vacuo.

^1H NMR (250 MHz): δ 0.94 (t, 3H, $N-CH_2CH_2CH_2CH_3$, $^3J=7.3Hz$), 1.38 (sextet, 2H, $N-CH_2CH_2CH_2CH_3$, $^3J=7.3Hz$), 1.86 (quintet, 2H, $N-CH_2CH_2CH_2CH_3$, $^3J=7.3Hz$), 3.90 (s, 3H $N-CH_3$), 4.19 (t, 2H, $N-CH_2CH_2CH_2CH_3$, $^3J=7.3Hz$), 7.51 (br s, 1H, H4/H5), 7.57 (br s, 1H, H4/H5), 8.77 (s, 1H, H2). ^{13}C NMR (250 MHz): δ 16.49, 23.17, 35.79, 39.17, 51.12, 126.32, 127.63, 140.37. ^{19}F NMR (250 MHz): δ 66.71 (doublet, PF_6). ^{31}PNMR (250 MHz): δ 138.47 (septate, PF_6)

FTIR [84, 85] (neat): 3126, 3172cm^{-1} (M) (C-H) aromatic ring; 2878 cm^{-1} (C-H) aliphatic; 2966 cm^{-1} (M) (C-H), Aromatic-N-CH$_3$; 838 cm^{-1} (P-H).

Ion trap mass spectrum: m/z 139 [bmim]$^+$

5.1.3 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

Approximately 10 g (57.2mmol) of BmimCl was transferred to a 25 mL round bottom flask and a 1.1 molar equivalents of Li[NTf$_2$] (18.1g, 62.9mmol) were added, followed by 25 mL of deionized water. After mixing, two phases formed where the

bottom phase was Bmim[NTf$_2$] and the top phase was aqueous LiCl. Both phases were colorless. The aqueous phase was decanted away using separation funnel and the Bmim[NTf$_2$] was washed by pure water followed by being dried in vacuo. The yield is 80%.

^{1}H NMR (250 MHz): δ 1.00 (t, 3H, N-CH$_2$CH$_2$CH$_2$CH$_3$, 3J=7.3Hz), 1.38 (sextet, 2H, N-CH$_2$CH$_2$CH$_2$CH$_3$, 3J=7.3Hz), 1.90 (quintet, 2H, N-CH$_2$CH$_2$CH$_2$CH$_3$, 3J=7.3Hz), 3.93 (s, 3H N-CH$_3$), 4.22 (t, 2H, N-CH$_2$CH$_2$CH$_2$CH$_3$, 3J=7.3Hz), 7.56 (br s, 1H, H4/H5), 7.62 (br s, 1H, H4/H5), 8.88 (s, 1H, H2). ^{13}C NMR (250MHz): δ 13.7, 19.9, 32.7, 36.6, 50.2, 116.91, 123.4, 124.8, 137.3. ^{19}F NMR (250 MHz): δ 74.88 (s, CF$_3$).

FT-IR [84, 85] (neat): 3160, 3122cm^{-1} (M) (C-H) aromatic ring; 2878 cm^{-1} (C-H) aliphatic; 2969 cm^{-1} (M) (C-H), Aromatic-N-CH$_3$; 1194, 1139 cm^{-1}, (CF$_3$); 1352 cm^{-1}, (C-SO$_2$-N).

Ion trap mass spectrum: m/z 139 [bmim]

5.1.4 1-butyl-3-methylimidazolium bromide

Freshly dried and distilled 1-methylimidazole (40 mL, 0.50 mol) and 1-bromobutane (92 mL, 0.86 mol) were dissolved in dry toluene (50 mL) in an oven dried – nitrogen cooled round-bottomed Schlenk flask. The mixture was refluxed at 70°C under inert atmosphere for 24 hours upon which two layers had formed. The setup for this reaction was the same as that used for synthesis of BmimCl. The upper layer containing toluene and excess 1-bromobutane was decanted. The flask was

allowed to cool to room temperature and was then cooled to -10 °C overnight, during which a yellow solid of BmimBr was formed. The yellow product was recrystallized by addition of dry diethyl ether to a saturated acetonitilre solution of BmimBr. The resulting white precipitate was washed by a cold mixture of acetonitrile and diethyl ether and then was dried *in vacuo* for 1 h to remove trace solvent.

^{1}H NMR(250MHz):   δ 1.00 (t, 3H, N-CH$_2$CH$_2$CH$_2$CH$_3$, 3J=7.3Hz), 1.41 (sextet, 2H, N-CH$_2$CH$_2$CH$_2$CH$_3$, 3J=7.3Hz), 1.89 (quintet, 2H, N-CH$_2$CH$_2$CH$_2$CH$_3$, 3J=7.3Hz), 3.95 (s, 3H N-CH$_3$), 4.21 (t, 2H, N-CH$_2$CH$_2$CH$_2$CH$_3$, 3J=7.3Hz), 7.60 (br s, 1H, H4/H5), 7.66 (br s, 1H, H4/H5), 8.98 (s, 1H, H2). ^{13}C NMR (250MHz): δ 16.58, 23.24, 35.93, 39.45, 52.83, 126.46, 127.73, 140.63.

FTIR [84, 85] (KBr pellets): 3078cm^{-1} (M) (C-H) aromatic ring; 2868 (C-H) aliphatic; 2960cm (M) (C-H), Aromatic-N-CH3.

Ion trap mass spectrum: *m/z* 139 [bmim]$^+$

5.1.5 1-butyl-3-methylimidazolium dicyanamide

Eqimolar amounts of sodium dicyanamide(0.50mol, 44.5g) and silver nitrate(0.50mol, 84.5g) were mixed in water (50g) to make aqueous solution that was covered by aluminum foil to protect the reaction from light. After the mixture was stirred for 15 minutes, solid silver dicyanamide precipitated from the solution. The solid precipitate was filtered and washed with water to remove any residual sodium nitrate. Excess silver dicyanamide (0.55mol, 95.7g) was then reacted with 1-butyl-3-methylimidazolium bromide (0.5mol, 109.5g) in acetone (250g) for 48

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hours to produce the ionic liquid of Bmim[N(CN)₂]. All solid precipitates (silver bromide and excess silver dicyanamide) were filtered and the homogeneous acetone solution containing Bmim[N(CN)$_2$] was kept. The ionic liquid of Bmim[N(CN)$_2$] was obtained by removing acetone under the rotary vapor followed by being dried *in vacuo* for 1 h. The aqueous phase was decanted away using separation funnel and the Bmim[C(CN)$_2$] was washed by pure water followed by being dried in vacuo. The yield is 70%.

^{1}H NMR(250MHz): δ 0.95 (t, 3H, N-CH2CH2CH2CH3, 3J=7.3Hz), 1.37 (sextet, 2H, N-CH2CH2CH2CH3, 3J=7.3Hz), 1.94 (quintet, 2H, N-CH2CH2CH2CH3, 3J=7.3Hz), 4.07 (s, 3H N-CH3), 4.38 (t, 2H, N-CH2CH2CH2CH3, 3J=7.3Hz), 7.74 (br s, 1H, H4/H5), 7.79 (br s, 1H, H4/H5), 9.13 (s, 1H, H2). ^{13}C NMR(250MHz): δ 13.79, 20.03, 32.76, 36.66, 50.17, 123.39, 124.70, 137.62, 206.85.

FTIR [84, 85] (neat): 3149, 3102cm^{-1} (M) (C-H) aromatic ring; 2872 (C-H) aliphatic; 2962cm (M) (C-H), Aromatic-N-CH3; 2233cm, (N-CN)

Ion trap mass spectrum: *m/z* 139 [bmim]$^+$

5.2 Solubility tests

Since the unknown samples were diluted with a solvent before analysis by ICP-MS, the mass concentration of all ionic liquids used for solubility tests (BmimPF$_6$, BmimNTf$_2$ and Bmim[N(CN)$_2$]) in solvent was set at approximately 100g/L (i.e. 100,000ppm).

2 mL of a selected solvent was introduced in a vial, followed by addition 200 mg

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of an ionic liquid into this solvent. The vial was sealed with a cap and was shook by hand to mix the sample with solvents. The solubility is determined by checking whether the sample was precipitated from solution or not. A homogeneous and clear solution indicated that this solvent is able to dissolve this solute at or lower than this concentration of 100 g/L or 100,000ppm.

5.3 Sample purification

All water immiscible ionic liquids were washed several times by ultrapure water, followed by being dried *in vacuo*(optional) before analysis using ICP-MS. In each run of purification processes, an equal volume of ionic liquid and water was mixed in a vial and the mixture was shaked vigorously manually and then was set on bench to separate two phases for 24 hours. After purification with water, the lower layer of ionic liquid was decanted and was dried *in vacuo* for 8 hours (optional).

5.4 Solution preparation

The volumetric flasks used to make calibration standards and unknown samples were pre-rinsed with 10% aqueous nitric acids followed by rinsing 5 times with ultrapure water. All organic solvents used for preparing calibration standards, tuning solution, internal standards, unknown samples and rinse solutions were of HPLC grade. Ultrapure water (resistivity of 18 MW) that was used during all stages of synthesis and analysis was obtained by reverse osmosis (Milli-RO 12 Plus, Millipore water purification system) followed by water deionization (Sybron/ Barnstead

filtration unit). In the analysis of chloride ion in $BmimPF_6$ where aqueous methanol was used as a solvent, a series of concentrations for BmimCl standards as calibration standards were: Blank, 0.1, 0.5, 1.0, 5.0, 10.0 and 20.0 ppm; the tuning solution was made to contain 1 ppb Li, Be, Ba, Co, In, U, Ce in 2% HNO_3 that was of trace metal grade; the internal standards were prepared to contain 1 ppb ^7Li, ^{45}Sc, ^{89}Y, ^{115}In, ^{140}Ce, ^9Be, in 2% $HNO_3(aq)$ and ^{115}In was selected as the elements used for internal standards. For the analysis of chlorine in $BmimNTf_2$ where the isopropanol and aqueous isopropanol were used as solvents, a series of concentrations for BmimCl standards as calibration standards were: Blank, 1, 5, 10, 50, 100 and 200 ppm; the tuning solution was made from 50 ppb Li, Be, Ba, Co, In, U, Ce in pure isopropanol. The internal standards were prepared to contain 1ppb ^{115}In and ^9Be and ^9Be was selected as internal standard element. In the stage of preparing unknown samples, each ionic liquid sample was accurately weighed on a balance with a readability of 0.0001 gram, followed by dilution in corresponding solvent in a 10 mL volumetric flask according to the result of solubility test.

5.5 Operation of ICP-MS

5.5.1 Instrumentation

The Thermo Elemental VG PQ ExCell (Thermo Electron) ICP-MS was employed to analyze the chlorine content. Glassware used for the ICP-MS analysis was pre-rinsed 3 times with 10% HNO_3 (Trace Metal Grade, Fisher Scientific) followed by washing 3 times with ultrapure water.

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5.5.2 ICP-MS setup with organic accessory

The Tygon pump tubing was replaced with Black Viton (isoversic) pump tubing as recommended in the SPC Science Book. The oxygen supply was connected to the oxygen inlet in the instrument and the oxygen pressure was set at no less than 3 bars. Before the instrument was switched on, oxygen bleed valve was set at zero and the power was adjusted to 0 W. Once the instrument was on, the oxygen function was switched on by clicking MFC button in the instrument control menu. In order to make sure that oxygen supply worked smoothly, the oxygen bleed valve could be gradually opened by monitoring the change of the nebulizer pressure. If the nebulizer pressure increased with increase of the oxygen amount, it showed that the oxygen supply was able to work; otherwise, the plasma was shut off and the connection of oxygen had to be checked. The Peltier chiller temperature was then adjusted to -5°C so that the low temperature of the spray chamber could limit the amount of organic solvent evaporating into plasma. Then the power was increased to 1500-1600 W. The amount of oxygen was determined by whether the green color that was caused by burning carbon from the organic solvent was eliminated.

5.5.3 ICP-MS acquisition parameters

The acquisition parameters for operation of ICP-MS with aqueous solutions are shown in Table 4.1 and those with organic solvent and organic accessory are shown in Table 4.2. In addition, the typical instrumental conditions are shown in Appendix A and the associated data and results are shown in Appendix B.

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Table 5.1 ICP-MS acquisition parameters for aqueous solutions

Instrument detector	simultaneous
Dynamic range for chloride	0.1-20 ppm
Acquisition mode	continuous, peak jumping
No. sweeps	200
Dwell time	30 ms
Channels per mass	1
Acquisition duration	15 s
Channel spacing	0.02 amu
Main scan region	^{35}Cl (34.96 amu)
Sampler cone	Nickel

Table 5.2 ICP-MS acquisition parameters for organic solutions

Instrument detector	simultaneous
Dynamic range for chloride	1-200 ppm
Acquisition mode	continuous, peak jumping
No. sweeps	200
Dwell time	60 ms
Channels per mass	1
Acquisition duration	38 s
Channel spacing	0.02 amu
Main scan region	^{35}Cl (34.96 amu)
Sampler cone	Platinum

5.5.4 Optimization of signal

For ICP-MS analysis of aqueous solutions, the ICP-MS was tuned with a standard solution containing 1 ppb Li, Be, Ba, Co, In, U, Ce, in 2% HNO_3 aqueous solution and the tuning parameters were optimized to get signal of ^{115}In more than 90,000 and maintained the ratio of Ce^{++}/Ce^+ and CeO^+/Ce^+ to less than 5%. For ICP-MS analysis organic solutions using the organic accessory, the tuning solution was made from 50 ppb Li, Be, Ba, Co, In, U and Ce in pure isopropanol and the tuning parameters were adjusted to get signal of ^{115}In more than 40,000 and maintained the ratio of Ce^{++}/Ce^+ and CeO^+/Ce^+ to less than 5%. The procedure of adjusting the parameters to optimize

the signal was divided into two steps as described as follows:

Firstly, the optic settings were adjusted by starting with D1, followed by Extraction, Lens 1, Lens 2, Lens 3 and Focus, then Pole bias. The parameter of Focus can be adjusted to focus the sample ions and the adjustment of parameters of Lenses can select and reject the intense photons that are generated in the plasma. This was done to avoid the leakage of these photons into the detector which can increase the noise.

Secondly, the ICP settings were tuned by adjusting the torch position and gas flow. It should be noted that the torch should not be too close to the cone by regulating the parameter of sampling depth, otherwise the torch might be melted in the high temperature of plasma.

5.5.5 Short term stability

Two modes of short term stability were utilized in this research: one was for aqueous solutions, the other was for organic solutions. For the analysis of aqueous solutions a standard solution of [bmim]Cl containing 0.05 ppm Cl⁻ was used and the internal standard was made from 1 ppb Li, Sc, Y, In, Ce, Be in 2% HNO_3 and In, Be were selected as internal standards elements. For the analysis of organic solutions a standard solution of [bmim]Cl containing 1 ppm Cl⁻ was used and the internal standard was made from 0.1 ppm Y, Mn, Li. The percentage relative standard deviation (%RSD) for BmimCl standard was less than five percent.

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