



# IONIC LIQUIDS AND PHOTOELECTRON SPECTROSCOPY

离子液体与光电子能谱  
(英文版)

Liu Yanhui Men Shuang Gao JingLong

刘艳辉 门爽 高景龙 © 著



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## 内容简介

本书从光电子能谱的角度,以揭示结构与性能间相互关系为目标,对离子液体进行了系统详细的阐述。同时对离子液体中的催化剂体系进行了初步介绍。

本书共6章,介绍了离子液体主要物理化学性质、离子液体合成、X射线光电子能谱,还从光电子能谱角度研究了离子液体体系和离子液体中催化剂体系等。

本书根据高等学校工科学科发展的需要,注重理论知识的传授,同时强调实际应用。本书可供高等学校材料类、化学类或其他相关专业使用,也可作为有关技术人员的参考用书。

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## Preface

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This book is written based upon the research work being conducted by Dr. Yanhui Liu, Prof. Jinglong Gao and myself (all from Shenyang Ligong University). The commencement of this project dates back to the year of 2008, when I firstly joined the Nottingham Ionic Liquids group. Throughout the whole of my Ph.D study, many attempts had been made with the view of demonstrating the electronic environment of ionic liquids by the state-of-the-art ultra high vacuum technique, X-ray photoelectron spectroscopy. I was a bit of luck to have finally systematically investigated three families of ionic liquids, including imidazolium, pyrrolidinium and pyridinium, as well as directly probed the interaction of solute-solvent and solute-ligand in ionic liquids. I was delighted to see these studies had made this field expanded and matured.

It was in the year of 2012, when Dr. Liu and I founded the Ionic Liquid Group at Shenyang Ligong University. I am fortunate to have collaborated with Dr. Liu, who has shown strong background in theory and great intelligence in doing research. With her tremendous helps, I am flattered to see we could add something to this research area. The recent publishing of the paper about the impact of the cation acidity on the cation-anion interaction in ionic liquids inspires us to finish this book, which summarily describes all aspects of our research with reference to ionic liquids.

Herein, we bring all results together in a coherent and smooth account of the field in simple words. *Chapter 1* and *Chapter 2*, which briefly introduce the basic aspects of ionic liquids and the XPS technique respectively, were written by Dr. Liu. One of the results chapters, *Chapter 5*, was also written by Dr. Liu. I wrote two of the results chapters, *Chapter 3* and *Chapter 4*. The

*Appendix* chapter, which demonstrates XP spectra for all ionic liquids studied in this book was written by Prof. Gao. We hope some may read this book for basic understanding, some for further improvement and some for enjoyment.

So many people helped me in this project, whom if I do not show my appreciation, I will be failing in my duty. To Prof. Peter Licence who is my academic Ph.D supervisor and the person I respect the most, I owe my biggest debt grateful. His wisdom and encouragement is always a constant source of motivation throughout the whole of my research life. Furthermore, I am on behalf of Dr. Liu to acknowledge the International Cooperation Project (F16-214-6-00) from the Department of Science and Technology of City of Shenyang for financial support. Last but not least, I must thank Dr. Liu and Prof. Gao once again, for spending several months with me in front of the laptop preparing this book.

Shuang Men

November 19<sup>th</sup> 2017

## 前言

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离子液体主要是指完全由有机阳离子,以及无机或有机阴离子组成的,在室温或接近室温下呈现出液体状态的熔融盐类。离子液体具有不易挥发、无污染、不易燃、易与产物分离、易回收、可循环使用以及使用方便等优点,是传统有机溶剂的理想替代品。它有效地避免了传统有机溶剂造成的环境污染、健康受损、安全隐患以及设备腐蚀等问题,是名副其实的、环境友好的“绿色溶剂”,适应清洁技术和可持续发展的要求。

近年来,离子液体的应用已经处于工业试验阶段,即将进入工业应用;另一方面因为离子液体种类繁多,每一种化学反应在离子液体中进行都有可能取得与传统方法不同的、令人惊异的结果,这一巨大的化学新宝藏有待我们去开发。

笔者所在课题组近几年来以咪唑类离子液体为突破口,一直从事离子液体的合成、提纯、表征及应用研究。本书不仅介绍了课题组成员的大量研究结果,也介绍了相关基本的知识。这包括从光电子能谱角度,揭示了离子液体结构与性能间的关系;在对离子液体进行系统详细阐述的同时,也对离子液体中的催化剂体系进行了初步介绍。

本书分为6章,第1章、第2章和第5章由沈阳理工大学刘艳辉博士编写,第3章和第4章由沈阳理工大学门爽博士编写,附录由沈阳理工大学高景龙教授及高级实验师编写。本书的出版得到了沈阳理工大学学科发展规划处学术专著基金和沈阳市科技局国际合作处国际合作项目(F16-214-6-00)的共同资助。在本书的编写过程中,英国诺丁汉大学 Peter Licence 教授给予了指导和支持,电子工业出版社有关同志为本书的顺利出版付出了辛勤的劳动,在此一并表示诚挚的谢意!

由于离子液体领域的研究正在蓬勃发展,知识体系更新迅速,而且以X射线光电子能谱手段研究离子液体的结构性能是一种崭新的技术,加上笔者所在的课题组成员水平所限,成书难免会有不足之处,敬请广大读者批评指正。

刘艳辉

2017年12月

于沈阳理工大学

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# Chapter 1

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## Ionic Liquids

Over the past decade, ionic liquids have attracted an expanding interest from not only academic but also industrial sources.<sup>[1, 2]</sup> The widespread investigation of ionic liquids now provides opportunities to understand in more depth, many processes, *e.g.* catalysis. The ultra high vacuum (UHV) technique, *i.e.* X-ray photoelectron spectroscopy (XPS), is now accepted as a reliable method for the study of ionic liquid-based systems.<sup>[3]</sup> This method, based upon offering information on the electronic environment of metal catalysts, allows further design of catalytic systems with the aim to enhance catalytic reactions. It is the primary goal of this research.

To allow design of catalytic systems, a key consideration is the tuning of the metal centre to achieve the desired reaction performance. Varying the electronic environment at the metal centre appears to be the general idea of such topic. However, there is relatively little experimental data about how the electronic environment of the metal centre is influenced by either the solvent or the ligand. In principle, the necessary information can be derived from XPS such that a valid comparison and correlation can be made between the XPS data and the reaction performance. Unfortunately, common molecular solvents used in catalysis suffer rapid evaporation under UHV conditions. As ionic liquids have negligible volatility, they can offer the opportunity to explore this correlation in a new approach. However, such a correlation between XPS data and the reaction performance is actually difficult to obtain due to reasons such as the low solubility of the metal catalyst in ionic liquids and difficult identification of subtle electronic changes at the metal centre. Moreover, even after a proper understanding of such a correlation, to finally design a metal catalytic system with the aim to enhance a catalytic reaction is also not trivial.

What makes this book a significant improvement upon the previous work is that the influence of both the ligand and the solvent on the electronic environment of the metal centre is investigated systematically. The correlation between XPS data and the reaction performance is also made for two such systems. This correlation is then used to design a metal catalytic system to enhance a selected reaction. To the best of our knowledge, it is the first time that XPS has been applied as a tool to enhance a catalytic reaction conducted in ionic liquids.<sup>[4]</sup>

*Chapter 1* introduces the basic aspects of ionic liquids. The XPS technique employed is presented in *Chapter 2*. *Chapter 3* describes the use of XPS to study a range of pure ionic liquids and some simple ionic liquid mixtures, employing imidazolium-, pyrrolidinium- and pyridinium-based cations with common anions. These investigations are used to define a series of robust C 1s fitting models and therefore to identify the aliphatic carbon component ( $C_{\text{aliphatic}}$  1s) which is used as a common charge reference point. Moreover, charge correction methods are discussed in detail for different cation-based ionic liquids, to allow accurate measurement of reliable binding energies for solutes in ionic liquid-based solutions. In *Chapters 4* and *5*, XPS is used to probe the electronic environment of a solute metal centre. *Chapter 4* focuses on interactions between solute and solvent; *Chapter 5* illustrates the investigation of metal-ligand interactions.

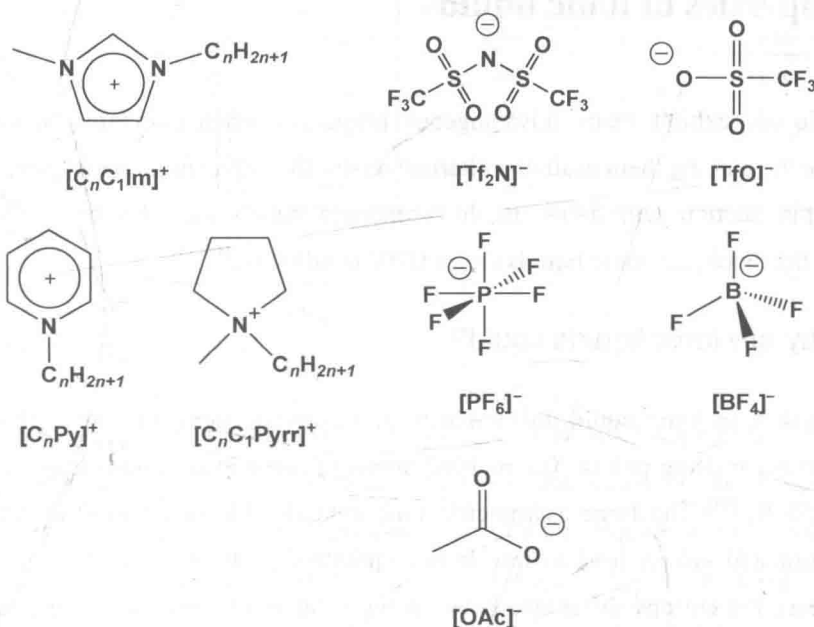
This Chapter reports the basic structure and properties of ionic liquids, reviews the application of ionic liquids to catalysis and briefly introduces the synthesis of ionic liquids. A more thorough introduction of each part of this work is presented in the subsequent results Chapters (3, 4 and 5).

## 1.1 Ionic liquids

### 1.1.1 Definition

Ionic liquids are salts with melting points below 100°C. They are generally composed of large and asymmetric cations and simple anions.<sup>[5]</sup> To date, a large range of cation and anion combinations have been used to generate ionic liquids. However, the main stream of research has focused upon combinations of imidazolium-, pyrrolidinium- and pyridinium-based cations with

inorganic anions, see Figure 1.1. Ionic liquids that are liquid at room temperature or below are also commonly referred to as room temperature ionic liquids (RTILs).



**Figure 1.1** Commonly used cations and anions of ionic liquids. There are a vast number of cation-anion combinations which can form over  $10^6$  possible primary ionic liquids and at least  $10^{12}$  binary and  $10^{18}$  ternary ionic liquids respectively<sup>[2]</sup>

### 1.1.2 A brief history of ionic liquids

The investigation of ionic liquids dates back to at least the year of 1914, when Walden studied ethylammonium nitrate.<sup>[1]</sup> However, the first boom in ionic liquid research was stimulated by the development of chloroaluminate-based ionic liquids in the 1960s.<sup>[6, 7]</sup> These ionic liquids are both air and water sensitive and thus were found to have restricted applications.

At the end of the 20<sup>th</sup> century, the second boom in ionic liquid research occurred, with the development of air- and water-stable ionic liquids.<sup>[2, 8, 9]</sup> Due to their negligible volatility and non-flammability, ionic liquids were employed as potential alternatives for the replacement of organic solvents.<sup>[10]</sup> More recently, by varying the functionality of either the cation or the anion, the potential to tune physico-chemical properties of ionic liquids was realised, which consequently, led to the development of functionalised ionic liquids or “task-specific” ionic liquids.<sup>[11]</sup>

## 1.2 Properties of ionic liquids

Ionic liquids exhibit many advantageous properties when compared to commonly used organic solvents, making them desirable alternatives for the application in a large range of research areas.<sup>[1, 2]</sup> This Section will focus on the properties which are relevant to the investigation presented in this book, *i.e.* ionic liquids under UHV conditions.<sup>[12, 13]</sup>

### 1.2.1 Why are ionic liquids liquid?

What makes an ionic liquid distinctive from a common inorganic salt is that, ionic liquids have much lower melting points. The melting points of some ionic liquids have been found to be as low as 255 K.<sup>[14]</sup> The large asymmetric ions with flexible non-charge carrying groups and weakly coordinated anions lead to low lattice enthalpies; whilst the highly charge delocalised cations increase the entropy difference between the solid and liquid state. These two factors give rise to negative Gibbs free energies of fusion under ambient conditions, which results in the liquid state of ionic liquids to be thermodynamically favoured.<sup>[15]</sup>

### 1.2.2 Viscosity

In general, ionic liquids are more viscous than water (1 cP) and other commonly used organic solvents, with their viscosities ranging from 10 cP to more than 2000 cP at room temperature.<sup>[1]</sup> The choice of the anion can significantly influence the viscosity of ionic liquids; however, the alkyl chain length of the cation can also be used to more finely tune the viscosity. It has been shown that the viscosities of ionic liquids increase with the increasing of the alkyl chain length.<sup>[1]</sup> The viscosities of representative ionic liquids can be found in Table 1.1.

**Table 1.1** Available melting point/glass transition, viscosity and conductivity values for the ionic liquids used to prepare metal catalyst-containing solutions in this book

Ionic liquids	Melting point/glass transition/K	Viscosity/cP(298 K)	Conductivity/ms. cm <sup>-1</sup> (298 K)
[C <sub>8</sub> C <sub>1</sub> Im][OAc]	200.1 <sup>①②</sup>	701 <sup>①</sup>	
[C <sub>8</sub> C <sub>1</sub> Im]Cl	186.1 <sup>[16]②</sup>	2087 <sup>[17]</sup>	
[C <sub>8</sub> C <sub>1</sub> Im][BF <sub>4</sub> ]	194.7 <sup>[18]②</sup>	220 <sup>[19]</sup>	0.58 <sup>[20]</sup>

(To be continued)

Continued Table

Ionic liquids	Melting point/glass transition/K	Viscosity/cP(298 K)	Conductivity/ms. cm <sup>-1</sup> (298 K)
[C <sub>8</sub> C <sub>1</sub> Im][TfO]	268.1 <sup>[21]</sup>	390 <sup>①</sup>	*
[C <sub>8</sub> C <sub>1</sub> Im][PF <sub>6</sub> ]	203.2 <sup>[22]②</sup>	690 <sup>[23]</sup>	0.26 <sup>[20]</sup>
[C <sub>8</sub> C <sub>1</sub> Im][Tf <sub>2</sub> N]	193.1 <sup>[24]②</sup>	90 <sup>[24]</sup>	1.30 <sup>[24]</sup>
[C <sub>8</sub> C <sub>1</sub> Pyrr][Tf <sub>2</sub> N]	258.5 <sup>[25]</sup>	128 <sup>①</sup>	
[C <sub>8</sub> C <sub>1</sub> Pyrr][BF <sub>4</sub> ]	302.9 <sup>①</sup>		
[C <sub>8</sub> Py][BF <sub>4</sub> ]	248.0 <sup>[26]</sup>	721 <sup>①</sup>	

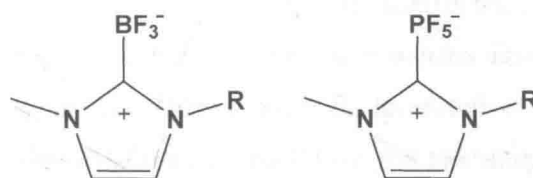
① data measured in this book

② glass transition

### 1.2.3 Low volatility

Initially, ionic liquids were considered to have no detectable vapour pressure although theoretical simulations and estimations had been conducted with regards to the vapour pressure of ionic liquids.<sup>[27]</sup> It was thought that the decomposition of ionic liquids would occur before the temperature of evaporation was achieved.<sup>[28]</sup> However, more recently, it has been indicated that several ionic liquids have appreciable volatility, specifically under reduced pressure and high temperature.<sup>[29]</sup>

To date, a wide range of ionic liquids have been vaporised<sup>[27, 30]</sup> and even distilled. A large amount of work conducted in this field at the University of Nottingham was shown that spectroscopically pure distillates can be produced especially in the case of [Tf<sub>2</sub>N]<sup>-</sup>-based ionic liquids, where the  $\Delta_{\text{vap}}H$  is the smallest. Where  $\Delta_{\text{vap}}H$  is large, sometimes competing reaction can occur. An excellent example has been found in both [BF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup>-based ionic liquids, where at high temperature, a carbene-based product can be yielded, see Figure 1.2.<sup>[31, 32]</sup>



**Figure 1.2** Structures of borate- and phosphonate-based carbene adducts according to ref [32]

Above all, ionic liquids possess very low vapour pressures at room temperature and therefore can be transferred into a UHV chamber, *i.e.* XPS chamber, without leading to a noticeable increase in instrument-base pressure.<sup>[33]</sup> It allows the analysis of ionic liquids at room temperature by XPS, and thus the commencement of this work.

### 1.2.4 Conductivity

Ionic liquids conduct *via* ion mobility. Typical conductivity values for ionic liquids are between  $0.1$  and  $3 \text{ ms}\cdot\text{cm}^{-1}$ ,<sup>[34]</sup> although some ionic liquids with conductivities up to  $110 \text{ ms}\cdot\text{cm}^{-1}$  have also been prepared.<sup>[35]</sup> However, ionic liquids are not as conducting as one might expect.<sup>[36]</sup> The conductivities of ionic liquids are similar to the non-aqueous electrolytes but are considerably lower than those of concentrated aqueous electrolytes.<sup>[37]</sup>

Moreover, it has been reported that conductivity and viscosity can be correlated with each other. The relatively high viscosity<sup>[38]</sup> causes the lower conductivities observed for pure ionic liquids.

In general, an increase in the alkyl chain length of the cation usually results in a large decrease in conductivity.<sup>[39]</sup>

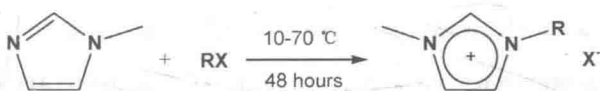
### 1.2.5 Solvation properties

There are a huge number of different ionic liquids, each with their own solvation properties. They can dissolve a variety of materials, *e.g.* aromatic and aliphatic organic compounds,<sup>[40]</sup> inorganic compounds,<sup>[41]</sup> transition metal catalysts,<sup>[42]</sup> nanoparticles,<sup>[43]</sup> polymers,<sup>[44]</sup> biomaterials<sup>[45]</sup> and enzymes.<sup>[46]</sup> By modifying their chemical structures, the solvation properties of ionic liquids can be altered.<sup>[47]</sup> Generally, ionic liquids are immiscible with commonly used non-polar solvents, *e.g.* toluene; whilst miscible with polar or protic solvents, *e.g.* acetonitrile and methanol.<sup>[48]</sup> Consequently, ionic liquids can find application in biphasic systems such as solvent-solvent separations and extractions.<sup>[49]</sup>

The solubility of a metal catalyst in an ionic liquid depends upon the nature of ionic liquid and the solute-solvent interaction involved. Neutral metal compounds are generally found to be poorly soluble in ionic liquids and therefore leach out of catalytic systems. This problem can be overcome by either employing charged metal complexes or by adding functional ligands to enhance the solubility of neutral metal compounds.<sup>[50]</sup>

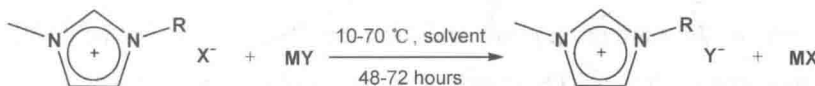
## 1.3 Synthesis of ionic liquids

Ionic liquids used for the analysis discussed in this book were all prepared using a variety of methods. The experiments presented in the following sections are based upon literature methods. Ionic liquids can be synthesised in two steps from simple organic starting materials. The first step is N-Alkylation to make several types of basic ionic liquids, for example imidazolium-based ionic liquids, *i.e.*  $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}$ , see Scheme 1.1.



**Scheme 1.1** Alkylation of 1-methylimidazole with an alkylation agent; R = ethyl, butyl, hexyl, octyl, decyl or dodecyl; X = Cl, Br or I.

The second step is the salt metathesis of the basic ionic liquids to yield the desired ionic liquid containing commonly used anions, *i.e.*  $[\text{Tf}_2\text{N}]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{TfO}]^-$ ,  $[\text{BF}_4]^-$  and  $[\text{OAc}]^-$ , see scheme 1, 2.



**Scheme 1.2** Salt metathesis reaction for the preparation of ionic liquids; M =  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{Ag}^+$ ; Y =  $[\text{PF}_6]^-$ ,  $[\text{BF}_4]^-$ ,  $[\text{Tf}_2\text{N}]^-$ ,  $[\text{TfO}]^-$  and  $[\text{OAc}]^-$ . The reaction solvent is  $\text{H}_2\text{O}$ .

### 1.3.1 Materials

1-Methylimidazole was distilled over calcium hydride prior to use. 1-Methylpyrrolidine, pyridine and all other chemicals were obtained from Sigma-Aldrich or Alfa Aesar and were used as received. Lithium bis[(trifluoromethane)sulfonyl]imide was obtained from 3M and also used as received.

### 1.3.2 Instrumentation

The purity of ionic liquids can influence their properties or even reactivity for catalysis.<sup>[13, 51]</sup> Consequently, the characterisation of the locally prepared ionic liquids became curial. In this book,



all ionic liquids were characterised by ESI-MS using Bruker MicroTOF, as well as  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra recorded using a Bruker DPX-300 spectrometer at 300 and 75MHz respectively as solutions in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$  and  $\text{DMSO}-d_6$ . Thermal data was determined by DSC (Q2000 V24.4 Build 116).

Ionic liquids are hygroscopic and thus able to absorb moisture from the atmosphere.<sup>[52, 53]</sup> In this work, water was removed under high vacuum at  $60^\circ\text{C}$  for at least 12h for all ionic liquids samples. However, even by this treatment, water is still present at ppm level. Karl Fischer analysis (Mitsubishi CA-100 Moisturemeter) was used to determine the water concentrations and they were all found to be approximately 40 ppm. Moreover, as has been found by the Nottingham Ionic Liquids group, no water presents in  $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$  at  $\sim 10^{-9}$  mbar above  $\sim 245\text{K}$ .<sup>[54]</sup> Since the pressure in the main XPS chamber remained  $\leq 1 \times 10^{-8}$  mbar during all XPS measurements, it suggests that all volatile impurities, *i.e.* water, are removed, leading to high purity samples.<sup>[31, 54]</sup>

Anion chromatography (Dionex, ICS-3000, IonPack AS15,  $4\text{mm} \times 250\text{mm}$  analytical column) was used to determine the halide concentration when salt metathesis was one of the synthetic steps. The eluent is a mixture of Millipore Milli-Q  $18\text{ M}\Omega$  ultrapure water, 100mm NaOH aqueous solution and acetonitrile in a 60:15:25 volume ratio and the flow rate is 0.2 ml/min. Specifically for acetate-based ionic liquids, halide concentrations were found to be between 36 and 1010 ppm due to the difficult post reaction separations of the starting materials and the products. However, it should be noted that no halide signal was observed during XPS analysis for any acetate-based samples, *i.e.* the concentration was below the limit of detection in all cases. For other cases, the halide concentrations were all below 10 ppm. Anion retention times associated with the anion chromatography experiment are shown in Table 1.2.

**Table 1.2** Standard retention times for different anions during anion chromatography measurements

Anion	Time/min	Anion	Time/min	Anion	Time/min
$[\text{OAc}]^-$	4.5	$[\text{TfO}]^-$	8.5	$[\text{PF}_6]^-$	22.5
$\text{Cl}^-$	5.1	$[\text{BF}_4]^-$	9.1	$[\text{Tf}_2\text{N}]^-$	30.9
$\text{Br}^-$	6.5	$\text{I}^-$	10.5		

### 1.3.3 Imidazolium-based ionic liquids

#### 1.3.3.1 $[\text{C}_2\text{C}_1\text{Im}]\text{Br}$

1-Methylimidazole (20g, 0.24mol) was placed in a round-bottomed flask fitted with a water